Evolution of Surface Texture in Thermal Chlorine Etching and Molecular Beam Epitaxy of Gallium Arsenide

by

Jens H. Schmid


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Abstract

Many fabrication processes for semiconductor nanostructures rely on the understanding of surface pattern evolution during crystal growth and etching. In this thesis, the morphological evolution of GaAs surfaces during thermal chlorine etching and molecular beam epitaxial growth is investigated by atomic force microscopy and light scattering. The experimental results are compared to numerical simulations based on continuum models. For both etching and growth, the evolution of flat surfaces and small amplitude (<30 nm) random surface patterns can be modeled with excellent accuracy with stochastic differential equations for the surface height as predicted by kinetic roughening theory. For MBE growth this equation is the Kardar-Parisi-Zhang (KPZ) equation while etching requires the extension of the KPZ model with a fourth-order linear term. Anisotropic etch rates with respect to crystal orientation are found to be a major consideration for surface pattern transfer by thermal chlorine etching. It is shown how pattern transfer of one- and two-dimensional gratings can be predicted and optimized by varying the orientation of the pattern and by the use of a directional molecular beam to supply the chlorine. To describe the complex shapes evolving from etching and growth on microfabricated gratings, models based on two coupled differential equations for the surface concentration of etchant or adatoms and the surface height are developed. Excellent fits to the experimental shapes observed over a wide range of etching and growth conditions can be obtained with these models and they emerge as a powerful tool to understand the pattern evolution in terms of the underlying microscopic physics such as surface diffusion, spatial flux inhomogeneity, sticking coefficients, step edge incorporation and diffusion bias.
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Chapter 1

Introduction

1.1 In-situ Etching and MBE Regrowth as a Method for Fabricating Semiconductor Nanostructures

The invention of semiconductor heterostructures is one of the groundbreaking successes of science and technology in the 20th century. By making modern optical and wireless communication technology possible these structures have had a huge impact on society. Heterostructure devices are used in semiconductor lasers, light emitting diodes, photodetectors and high performance transistors. Naturally, these applications and their underlying physics have stimulated an enormous amount of basic and applied research. The significance of this field is reflected in the Nobel Prizes awarded to Z. Alferov and H. Kroemer in 2000 for the invention and development of semiconductor heterostructures.

Historically the development of heterostructures has progressed from classical thin film structures to quantum wells and superlattices and most recently to two- or three-dimensional quantum confined nanostructures, such as quantum wires and dots. A review of this history and its implications in terms of physics and devices is given in Ref. [2]. Semiconductor multilayer structures can be fabricated with very high quality by epitaxial growth techniques such as molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) with monolayer thickness control. The synthesis of laterally confined semiconductor nanostructures is significantly more difficult. This problem is expected to be one of the dominant research topics in thin film crystal growth for the foreseeable future [42].

The most common methods for fabricating two- or three dimensional nanostructures are either self-assembly (see [70] for a review) or etching of patterns into the surface of a layered structure and possibly regrowth of additional layers on top of the patterned substrate. The two main issues that
arise in any fabrication process are: first, the achievable structural quality of the heterostructure, which is limited by the introduction of defects and contamination into the crystal and second, the control that one can achieve over size and shape of the structures to be fabricated. The self-assembly approach has produced heterostructures of a very high quality; however, due to the inherent randomness of the process, size and shape control remains a critical issue in spite of the intense efforts in this field over the last few years. The approach is also limited to only a few material systems, such as the prototypical InGaAs-GaAs and SiGe-Si systems.

In general, etching and regrowth appear to be more controlled and versatile processes than self-assembly. In this approach, interface contamination and defects can be caused either by the processing or by exposure to air between processing steps. A promising strategy to avoid this problem is to carry out at least the last etching step prior to regrowth in-situ, i.e. in the same vacuum system that contains the chamber where film growth takes place. Several such integrated etching and growth systems have been described in the literature for the technologically important GaAs/AlGaAs material system. Layer-by-layer etching inside the growth chamber has been demonstrated using beams of AsCl$_3$ [79] or AsBr$_3$ [36] incident on the sample, and several groups have reported separate processing chambers attached to an MBE system for either plasma etching [14], chemically assisted ion beam etching [16, 75, 77], or thermal etching [25, 46]. In-situ etching has also become an enabling technique to obtain epitaxial regrowth on highly reactive AlAs surfaces [14]. Regrowth on AlAs is not possible after exposing the surface to air. Thermal Cl$_2$ etching has been found to be an especially effective process to obtain high quality regrowth interfaces. It has been shown that it can be used to remove a layer from the surface that has been damaged by exposure to energetic ions during a preceding plasma process, leading to large improvements in the interface quality [16, 75, 39] and high electron mobilities have been achieved at etched and regrown GaAs/AlGaAs interfaces [8]. A combined crystal growth and thermal Cl$_2$ etching system was set up for this thesis work by extending an existing MBE system with an etch chamber which was designed and built at UBC.

The second important fabrication issue, size and shape control, has so far not been investigated thoroughly for thermal Cl$_2$ etching. A better understanding of the evolution of both surface roughness and surface patterns during etching is an important prerequisite to using thermal Cl$_2$ etching in a nanofabrication process. From an experimental point of view, thermal Cl$_2$
etching is an ideal process to study the evolution of surface morphology during a complex etching process since the number of parameters that have to be controlled in the process, namely the gas pressure and the substrate temperature, is much smaller than for example in a plasma etch process. On the other hand, many of the factors that determine morphology evolution during thermal Cl₂ etching, such as anisotropic etch rates with respect to crystal orientation, surface diffusion, spatial inhomogeneity of etchant supply, shadowing effects and re-emission of etchant molecules from the surface, are generic issues relevant to many etching processes.

Regrowth of multilayer structures on patterned substrates can by itself be a nanostructure fabrication method that relies on one's ability to predict the shape evolution during growth [41, 9]. In spite of a large body of theoretical literature, which is partly reviewed in Chapter 2, the evolution of surface roughness and patterns during epitaxial growth is at present not well understood even for homoepitaxy of the most common materials. The comparison of experimentally observed surface morphology with models of surface evolution can be a powerful tool to gain a better understanding of the underlying atomistic surface processes and thus the growth process in general.

This thesis is organized as follows: The following introductory section describes in more detail how interesting heterostructures can be fabricated by in-situ etching and MBE regrowth. Chapter 2 is a review of the theoretical concepts used to describe surface morphology evolution as they relate to the experimental results presented in this thesis. The combined crystal growth and etching apparatus used for the experiments is described in Chapter 3. This chapter also contains brief reviews of the chemistry of the thermal Cl₂ etching process, surface morphology measurements and sample preparation. Experimental results on surface roughness evolution during etching and growth are presented in Chapter 4, while Chapter 5 contains the experimental results on the evolution of patterned surfaces.
1.2 Buried Oxide Gratings and Low-Dimensional Quantum Confined Structures

The possibility of fabricating GaAs/aluminum oxide (AlO\textsubscript{x}) gratings buried in GaAs/AlGaAs structures was the original motivation for the setup of the in-situ etch chamber. The basic fabrication steps are shown schematically in Fig. 1.1. First a multilayer structure is grown by MBE with a thin high aluminum content Al\textsubscript{x}Ga\textsubscript{1-x}As (x > 0.96) layer (typically 50 nm thick) and a GaAs cap with a thickness of approximately 150 nm. The surface of this structure is then patterned with a grating by standard lithographic and etching techniques, without exposing the buried AlGaAs layer, as shown in Fig. 1.1 a). This is important since the aluminum contained in the AlGaAs is extremely reactive with oxygen and exposure of the AlGaAs layer to air would therefore cause the formation of a surface oxide which cannot be removed. The sample is then introduced into the combined crystal growth and etching system. An etch is performed to transfer the grating into the AlGaAs layer, as shown in Fig. 1.1 b). The sample is then transferred in vacuum to the growth chamber of the MBE where regrowth of additional layers is performed, resulting in a structure that is penetrated by AlGaAs “fingers” as depicted in Fig. 1.1 c). The high aluminum content AlGaAs can subsequently be oxidized laterally by exposure to hot water vapor at 400°C, a process known as “selective wet oxidation” (a review is given in [13]). The resulting GaAs/AlO\textsubscript{x} grating is interesting from an optical point of view because its near infrared index of refraction contrast (n(AlO\textsubscript{x})\approx 1.6 compared to n(GaAs)= 3.5 at \lambda = 1 \mu m) is much higher than achievable with combinations of different semiconductor alloys. The same process can be carried out with two dimensional gratings as they are used for planar photonic crystals, the only restriction being that the AlGaAs layer has to remain continuous after patterning to enable successive wet oxidation.

Thin optical gratings buried in semiconductor slab waveguides form the basis of distributed feedback (DFB) lasers, one of the most important components in optical communication systems. One of the important design parameters of a DFB laser is the coupling constant \( \kappa \) that describes the coupling between forward and backward travelling modes in the waveguide introduced by the presence of the grating. This coupling constant can easily be calculated within the framework of coupled-mode theory [40] and is found
Figure 1.1: Fabrication of buried oxide gratings. See text for explanation of the steps.
to be proportional to the index contrast $\Delta n$ of the grating and the overlap of the optical mode with grating layer $\Gamma$:

$$\kappa \propto \Delta n \Gamma$$

Both parameters depend on the indices of refraction of the materials used for the grating layer. The mode overlap with the grating layer can be estimated by calculating the overlap of the grating layer with the unperturbed mode profile of the multilayer waveguide in the absence of the grating layer; however, in the case of the GaAs/AlO$_x$ gratings, the low index of the oxide introduces a significant perturbation of the mode profile. A simple way of approximating this perturbation is by calculating the unperturbed mode profile for a waveguide in which the grating layer is replaced by a continuous layer with an average index corresponding to the two grating constituents, i.e. $n = \frac{1}{2}(n(GaAs) + n(AlO_x))$ for the GaAs/AlO$_x$ gratings. An example is shown in Fig. 1.2. On the left side the GaAs/AlGaAs waveguide structure is shown. It consists of a 250 nm thick GaAs core embedded in Al$_{0.6}$Ga$_{0.4}$As. Centered in the core is a 50 nm thick GaAs/AlO$_x$ grating layer. Except for the active region which could consist of InGaAs or InGaNAs quantum wells inside the GaAs core, this is a basic DFB laser structure. For the purpose of calculating the unperturbed mode profile, this layer is considered a 50 nm thick layer with an index of 2.55, the average of the GaAs and AlO$_x$ indices. By design, this is a single-mode waveguide for light with a wavelength of 1 $\mu$m and the calculated intensity profile is shown on the right side of Fig. 1.2 (solid line). For comparison the dashed line shows the profile of the same waveguide in which the grating layer is replaced with GaAs, i.e. a simple trilayer waveguide. The profiles were calculated using the characteristic matrix method [81]. The low average index of the grating layer pushes the mode out of the center of the waveguide, leading to a reduced overlap of the mode and the grating layer. From this calculated mode profile the overlap integral $\Gamma$ and thus $\kappa$ can be calculated. In spite of the reduced intensity in the grating region, coupling constants $\kappa$ as large as 4000 cm$^{-1}$ can be achieved using oxide gratings, a factor of ten larger than for typical DFB lasers. It should be noted that such large coupling constants are not desirable for conventionally designed DFB laser since they cause a highly non-uniform intensity profile along the laser cavity which in turn leads to a nonlinear optical output due to spatial hole burning [60]; however, large coupling constants may be desirable in novel designs such as microlasers [30].
Figure 1.2: Left: GaAs/AlGaAs multilayer waveguide structure with a 50 nm thick buried AlO$_x$ grating embedded in the GaAs core. Right: Calculated optical mode intensity profile for this waveguide with (solid line) and without (dashed line) buried grating. For the calculation the grating layer is replaced by a continuous layer with the average index of refraction of GaAs and AlO$_x$.

Fig. 1.3 shows a side view of a AlO$_x$ grating buried in GaAs fabricated as explained above and shown in Fig. 1.1 taken with a scanning electron microscope (SEM). The pitch of the grating is 3 $\mu$m which is approximately ten times larger than the optical gratings used inside a typical DFB laser. Fabrication of these smaller gratings according to the procedure above is significantly more difficult since it requires good pattern replication after etching, as in Fig. 1.1 b), which is more easily achieved for larger patterns. One of the important conclusions of the study of pattern evolution during thermal Cl$_2$ etching presented in Chapter 5 is that gratings have to be oriented along the [100] crystal direction for optimized pattern transfer.

Another application of in-situ etching and regrowth is the fabrication of quantum wires or dots as proposed by Heyn et al. [29]. A fabrication procedure is shown schematically in Fig. 1.4. The steps are very similar to the ones used to make buried gratings. Again, the second etching step
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(a→b in Fig. 1.4) has to be carried out in-situ to avoid oxidation of the AlGaAs. For the fabrication of a quantum wire the initial pattern is a one-dimensional ridge whereas the fabrication of a quantum dot proceeds from a two-dimensional surface pattern. The evolution of both one- and two-dimensional surface patterns is investigated in detail in Chapter 5. To observe quantum confinement effects in these structures, the length scale of the patterns has to be on the order of 10 nm, significantly smaller than the optical gratings discussed above. At these short length scales one may also expect that the surface roughness that develops during the processing may cause significant random size fluctuations.

Surface roughness is also an important issue for photonic devices, in particular in the field of microphotonicics. This is because the fabrication of microcavities and miniaturized waveguides relies on the use of materials with a high index contrast which increases scattering losses due to surface or interface imperfections [47, 65]. Experimental results on the evolution of surface roughness during growth and etching are presented in Chapter 4.

Finally, it should be noted that surface morphology evolution can also be an important consideration in the fabrication of nanostructures by self-assembly. Fig. 1.5 shows an atomic force microscopy image of self-assembled InAs quantum dots on GaAs\(^1\). In this case the GaAs film was grown with an atypically small arsenic overpressure. This results in a surface with a “ripple morphology’. The subsequent deposition of approximately two monolayers

\(^1\)This growth was carried out as part of the Engineering Physics Project Lab of R. Kumaran, E. Lai and B. Lau “Use of bismuth surfactants to modify and control size and position of InAs quantum dots on GaAs”, Fall 2003
Figure 1.4: Fabrication of GaAs/AlGaAs quantum dots or wires. The etching and regrowth steps are analogous to the fabrication of buried gratings but with a different multilayer structure and shorter length scale.
of InAs leads to the formation of the quantum dots which appear to nucleate preferentially in the valleys of the surface texture. A self-alignment of dots in valleys has also been observed for growth on substrates which were patterned by lithography [52]. This example shows how the understanding and control of surface morphology during growth can be used to manipulate the random nucleation process of the quantum dots.
Chapter 2

Continuum Models for Surface Evolution

Continuum equations are commonly used to model surface evolution on length scales that are much larger than the atomic spacing of the substrate. The surface that in reality consists of discrete in-plane positions and heights corresponding to the surface atoms is coarse-grained and described by a continuous height function $h(\vec{x}, t)$. The models then consist of differential equations for $h$. From a practical point of view the main advantage of this approach lies in faster computational speed compared to discrete Monte-Carlo methods. Continuum equations make it possible to simulate surface morphology on length scales between tens and millions of atomic lattice spacings and for growth of films which are several microns thick, whereas Monte-Carlo methods are typically restricted to length scales smaller than approximately a thousand lattice spacings and growths of a few hundred nanometers. On a more fundamental level, the advantage of continuum models is that they can be studied analytically and the resulting analytical expressions can at least in principle facilitate comparisons with experiments in a more straightforward and possibly more convincing way than the trial and error approach of discrete modeling. Of course, the best way to gain insight into the physics of surface evolution of a system may often be a combination of continuum and discrete models.

Two types of continuum models are used to model etched and grown surfaces in this thesis. The first one consists of single stochastic equations for $h$ which describe the evolution of surface roughness. These models have been described in detail in several review papers and textbooks such as [63, 7, 43]. The important results as they relate to the experimental work described in this thesis are summarized in section 2.2. The second type of continuum model consists of two coupled differential equations for the surface concentration of etchant or adatoms $n$ and the surface height $h$. These models are found to be much more successful at describing the shape evolution of micro-
fabricated gratings during etching and growth. They will be introduced in section 2.3. In the first section a review of the concepts and quantities that are used to describe randomly rough surfaces is given (more extensive reviews of these statistical concepts can be found in many textbooks, e.g. [83, 27, 23]).

2.1 Statistical Description of Rough Surfaces

Power spectral density, autocorrelation function and RMS-roughness

Both deposition and etching processes have a random component and therefore they lead to the formation of randomly rough surfaces. A particular rough surface \( h(\vec{x}) \) that is observed in an experiment or as the result of a numerical simulation is a specific realization of an ensemble of possible surfaces with the same statistical properties. Therefore, the surface height \( h \) itself is not a good quantity to describe the properties of a randomly rough surface, and statistical quantities are needed instead. The most important such quantity used in this thesis is the power spectral density (PSD) of the surface from which most other statistical quantities of interest can be derived, as will be shown in this section. The PSD of a surface of area \( A \), denoted by \( P \), is defined as the square of the Fourier transform of the surface height \( h \):

\[
P(\vec{q}) = \frac{1}{(2\pi)^2 A} \left| \int_A h(\vec{x}) e^{i\vec{q}\cdot\vec{x}} \, d^2x \right|^2
\]  

(2.1)

Since \( h \) is a real function in units of [nm], the PSD is symmetric, \( P(\vec{q}) = P(-\vec{q}) \), and it has units of [nm\(^4\)]. The finite area of the surface leads to a lower cutoff for the spatial frequencies \( q \) over which the PSD is defined: \(|q_{\text{min}}| = 2\pi/L\), where \( L \) is the linear dimension in the direction of \( \vec{q}_{\text{min}} \). Both experimental AFM images and numerical simulations are discrete representations of the surface height on a grid of \( N \times N \) points and in this case there is also an upper frequency cutoff for the PSD of \(|q_{\text{max}}| = 2\pi N/L\).

The most basic quantity of interest for a rough surface is the root-mean-
square or RMS roughness $\sigma$. It is defined by

$$\sigma^2 = \frac{1}{A} \int_A [h(\vec{x})]^2 \, d^2 x$$

(2.2)

It is easy to show by direct integration that this is equal to the integral of the PSD over all wavevectors $\vec{q}$:

$$\sigma^2 = \int P(\vec{q}) \, d^2 q$$

(2.3)

This shows that the PSD is a measure of the surface roughness at a length scale of $2\pi/q$. The PSD forms a Fourier pair with the autocorrelation function $\gamma$ of the surface:

$$\gamma(\Delta \vec{x}) = \frac{1}{2\pi} \int P(\vec{q}) e^{-i\vec{q} \cdot \Delta \vec{x}} \, d^2 q = \frac{1}{2\pi A} \int h(\vec{x}) h(\vec{x} + \Delta \vec{x}) \, d^2 x$$

(2.4)

This can be verified using the convolution theorem for Fourier transforms and the definition of the PSD (2.1). Equation (2.4) is called the Wiener-Khinchin theorem. The form of the autocorrelation function makes it clear that it is a spatially averaged quantity and therefore the same is true for the PSD as its Fourier transform. An implicit assumption in using the autocorrelation function or the PSD of a particular surface to represent properties of an ensemble of surfaces is therefore that the spatial averaging is equivalent to taking an ensemble average, i.e. $h$ is ergodic. Instead of the PSD, some authors are using the structure factor $S = \langle h(\vec{q}) h(-\vec{q}) \rangle$ to discuss statistical properties of surfaces. This structure factor is an ensemble average of the PSD.

**Self-affine surfaces, dynamic scaling and universality classes**

Many growth models lead to the formation of a self-affine surface morphology. Self-affinity means that statistical properties of the surface remain unchanged if one changes the scale by different factors along the surface and perpendicular to the surface, i.e. in a statistical sense

$$h(b \vec{x}) = b^\alpha h(\vec{x})$$

(2.5)

 Unless otherwise noted, the average surface height is set to zero, i.e. $h$ is defined as the difference between the actual surface height and the average height.
The exponent $\alpha$ is called the roughness exponent. In the case that $\alpha = 1$, the surface is called self-similar. This behavior leads to a power law scaling of the RMS roughness as a function of the system size:

$$\sigma(L) \propto L^\alpha,$$

where $L$ is the linear size of the surface. The power law behavior of the RMS roughness translates into a power law for the PSD. According to (2.3) and (2.6):

$$\sigma^2(L) = \int_{2\pi/L}^{\infty} P(\tilde{q}) \, d^d q \propto L^{2\alpha}$$

(2.7)

where $d$ indicates the dimensionality of the surface, i.e. either $d = 1$ or $d = 2$. This results in:

$$P(|q|) \propto |q|^{-2\alpha - d}$$

(2.8)

The roughness exponent $\alpha$ can therefore be obtained directly from the slope of the PSD on a log-log plot. Obviously, both (2.6) and (2.8) break down for large length scales or low $|q|$. Typically the PSD will approach a constant value at low $|q|$ and the crossover length scale between the two regimes is called the correlation length $\xi$ of the surface. It is related to the decay of the autocorrelation function. In fact, a model autocorrelation function that is sometimes used to describe self-affine surfaces is given by [72]:

$$\gamma(|\Delta x|) = \frac{\sigma^2}{2\pi} \exp \left[-\left(\frac{|\Delta x|}{\xi}\right)^{2\alpha}\right], \quad 0 < \alpha \leq 1$$

(2.9)

To illustrate how the PSD can be used to extract the quantities described above, Fig. 2.1 shows a model power spectral density function of a self-affine surface plotted on a log-log scale. From the plot the roughness exponent can be obtained from the slope of the PSD at high $q$ values and the correlation length from the position of the knee. The graph is a plot of the function

$$P(q) = \left(1 + \frac{q^2 \xi^2}{(2\pi)^2}\right)^{-\alpha-1}$$

(2.10)

which has the appropriate behavior of a self-affine PSD. This function is, however, not the Fourier transform of $\gamma$ in Eq. (2.9) which does not have an analytical Fourier transform for all values of $\alpha$. On the other hand an alternate expression for the self-affine autocorrelation function involving Bessel functions can be calculated by Fourier transforming Eq. (2.10) [61].
During growth or etching the correlation length $\xi$ increases as a function of time according to

$$\xi \propto t^{1/z}$$

(2.11)

which defines the dynamic scaling exponent $z$. In a finite size system of length $L$, once $\xi$ reaches the system size, the power law scaling extends over the entire range of length scales and the roughness parameters saturate:

$$\xi = L$$

(2.12)

$$\sigma = \text{const}$$

(2.13)

Before the system saturates the RMS roughness also increases as a function of time according to a power law with the growth exponent $\beta$:

$$\sigma \propto t^\beta$$

(2.14)

The above scaling properties can be summarized in the so called Family-Vicsek scaling relation:

$$\sigma(L,t) \propto L^\alpha f \left( \frac{t}{L^z} \right)$$

(2.15)
with a scaling \( f(x) \) which has the properties \( f(x) \propto x^\beta \) for \( x < 1 \) and \( f(x) = \text{const} \) for \( x > 1 \). For the PSD this translates into:

\[
P(q, t) \propto q^{-2\alpha-d} g \left( \frac{t}{q^{-z}} \right)
\]  

(2.16)

with \( g(x) \propto x^{(2\alpha+d)/z} \) for \( x < 1 \) and \( g(x) = \text{const} \) for \( x > 1 \). The three scaling exponents are linked by the relation:

\[
z = \frac{\alpha}{\beta}
\]  

(2.17)

The three exponents \( \alpha, \beta \) and \( z \) are universal in the sense that different physical mechanisms or models can lead to the same values for the exponents. Systems or models that produce the same values for the exponents are said to belong to the same universality class.

From the point of view of an experimentalist, the concepts of self-affinity, scaling and universality introduced in this section can be useful tools in describing and fitting experimental data by giving an indication which model may reproduce the observed morphology; however, it will be shown in the next section that even simple models can lead to a very complex scaling behavior. Therefore, one has to be careful about deducing scaling exponents and universality classes from measurements over a limited range of times and length scales. One might also have the opinion that it is in general more interesting to understand the dominant physical mechanisms that determine surface morphology in a given system than to just categorize its universality class.

### 2.2 Stochastic Differential Equation Models for Kinetic Roughening

The starting point for the derivation of the conventional stochastic continuum equations for kinetic roughening is the contribution of a surface to the free energy of a system:

\[
\mathcal{F} = \int_A \sigma \sqrt{1 + (\nabla h)^2} d^2x
\]  

(2.18)

where \( \sigma \) is the surface tension, i.e. the free energy per unit area, which is assumed to be independent of the surface orientation. Strictly speaking,
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this expression for the surface free energy is not applicable to the case of a single crystal. A relatively smooth surface of a single crystal which is close to a low-index plane consists of terraces and atomic steps. In this case, the atoms on the terraces are in their minimal energy configuration and each atomic step contributes an additional amount of energy due to its dangling chemical bonds. In a first approximation the excess surface energy is then proportional to the density of steps and therefore:

$$J \propto \gamma \int_A |\nabla h| d^2x$$

where $\gamma$ is the line tension of an atomic step. Higher order terms have to be added to Eq. (2.19) at finite temperatures to account for the entropy of the atomic steps and step-step interactions as discussed in a recent review article by H.-C. Jeong and E. D. Williams [31]. Due to the discontinuous derivative of the integrand in Eq. (2.19) at $\nabla h = 0$, this expression cannot be used to derive continuum equations in the same way as Eq. (2.18). It is commonly assumed that expression (2.18) is applicable to the surface of a single crystal on large length scales if the surface is microscopically rough. This is the case during growth or etching. When no growth is taking place this approach is clearly invalid since the free energy (2.18) is minimized by a perfectly flat surface $h = 0$; however, at finite temperatures the equilibrium surface morphology is not perfectly smooth. For GaAs, the material under consideration in this thesis, recent experimental results show that surface roughness is present in thermal equilibrium at typical growth temperatures [19].

To derive an equation for the evolution of the surface height function $h$, the free energy in (2.18) is then interpreted as a functional of $h$, rather than a function of the temperature and surface area as in conventional thermodynamics. The driving force for mass transport on the surface is the gradient of the surface chemical potential $\mu$. From Eq. (2.18) the chemical potential can be calculated as a variational derivative ($f$ denotes the integrand in (2.18) and $v$ is the molecular volume$^2$):

$$\mu = v \frac{\delta F}{\delta h} = v \left( \frac{\partial f}{\partial h} - \nabla \cdot \frac{\partial f}{\partial (\nabla h)} \right) = -v\sigma \frac{\nabla^2 h}{(1 + (\nabla h)^2)^{3/2}} \approx -v\sigma \nabla^2 h$$  

(2.20)

$^2$In this chapter the crystal structure is for simplicity assumed to be simple cubic with a lattice constant $a_0$ and $v = a_0^3$
In a first order approximation the chemical potential is proportional to the curvature of the surface. This result is called the Henry-Mullins formula. A linear surface evolution equation can be derived from this chemical potential by considering the effects of evaporation and condensation on the one hand and surface diffusion on the other. For the first case of evaporation-condensation dynamics the differential rate of change of the surface height is assumed to be proportional to the surface chemical potential (2.20):

$$\frac{\partial h}{\partial t} \propto -\mu = \nu \nabla^2 h$$  \hspace{1cm} (2.21)

This means that surface atoms in regions with a positive curvature (valleys) have a lower rate of evaporation and a higher rate of condensation than surface atoms in a region with negative curvature (peaks). For the case of mass transport along the surface by diffusion, the gradient of the chemical potential acts as a driving force on the adatom current density $j$ and therefore $j \propto -\nabla \mu$. Together with the continuity equation $dh/dt = -a_0^4 \nabla \cdot j$ this yields:

$$\frac{\partial h}{\partial t} \propto \nabla \cdot \nabla \mu = -K \nabla^4 h$$  \hspace{1cm} (2.22)

The sign is negative by convention, so that positive values for both $\nu$ and $K$ lead to a smoothing effect. In Appendix A a more detailed derivation of (2.21) and (2.22) is given which yields explicit expressions for $\nu$ and $K$. It shows that, if the desorbing and the diffusing species are the same, the ratio of the two coefficients $\nu$ and $K$ is related to the activation energies for desorption $E_{des}$ and diffusion $E_{diff}$ by the following relation:

$$\frac{K}{\nu} = a_0^2 \exp \left( \frac{E_{des} - E_{diff}}{kT} \right)$$  \hspace{1cm} (2.23)

where $k$ is the Boltzmann constant and $T$ is the substrate temperature. This relation has so far not been discussed in the literature.

Another mechanism leading to the expression (2.21) is a diffusion bias of adatoms or Schwoebel effect. This bias is due to an asymmetric step-edge potential that causes atoms to drift preferentially uphill or downhill. Therefore the adatom current density is proportional to the step density $j \propto \nabla h$. Applying the continuity equation $dh/dt = -a_0^4 \nabla \cdot j$ one arrives at expression (2.21). In this case, $\nu$ is negative for an uphill bias in diffusion and positive for a downhill bias. A negative $\nu$ causes a surface instability. In
general both desorption and diffusion bias may contribute to $\nu$ and the two effects cannot be distinguished.

The complete linear evolution equation is obtained by combining (2.21) and (2.22) and adding a flux term $F$ which is the growth or etch rate in nm/s, as well as a noise term $\eta$ that takes into account the random fluctuations in the deposition or etch process:

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h - K \nabla^4 h + F + \eta$$  \hspace{1cm} (2.24)

For $\nu \neq 0$ and $K = 0$, (2.24) is called the Edwards-Wilkinson equation (originally derived in [22]) and for $\nu = 0$ and $K \neq 0$ it is called the noisy Mullins equation (the diffusion term was originally derived in [53]). The addition of the flux term $F$ simply leads to a monotonic change $h = Ft$ that does not affect the surface morphology. It can therefore be ignored. The noise $\eta$ is typically assumed to be Gaussian white noise with zero mean and no correlations:

$$\langle \eta(\vec{x},t) \rangle = 0$$  \hspace{1cm} (2.25)

$$\langle \eta(\vec{x},t)\eta(\vec{x}',t') \rangle = \tilde{D} \delta(\vec{x} - \vec{x}') \delta(t - t')$$  \hspace{1cm} (2.26)

If the dominant noise source is the shot noise of the flux then

$$\tilde{D} = Fa_0^3$$  \hspace{1cm} (2.27)

in Eq. (2.26) for a 2-dimensional surface$^3$.

Kinetic roughening is the result of a competition between the noise input $\eta$ and the smoothing terms (2.21) and (2.22) which are derived from the free energy (2.18) that tries to minimize surface roughness. Due to (2.26) the noise term causes equal roughening of the surface at all length scales, leading to an increasing, uniform PSD. The smoothing terms, on the other hand, act most efficiently at short length scales. The competition between the two therefore leads to a PSD that decays for large values of the wavevector $q$.

$^3$If the noise term is the only non-zero term in Eq. (2.24) then $h(\vec{x},t) = \int_0^t \eta(\vec{x},t')dt'$. Relation (2.27) ensures that in this case the mean square deviation of the surface height $\langle h(x_N, t)^2 \rangle = \int_0^t \int_0^t \langle \eta(x_N, t') \eta(x_N, t'') \rangle dt' dt''$ is given by $\langle h(x_N, t)^2 \rangle = Fa_0 t$, where $h(x_N)$ is the height at lattice site $x_N$, averaged over a surface unit cell $A_N$, i.e. $h(x_N) = \frac{1}{a^2} \int_{A_N} h(\vec{x}, t) d^2x$. This corresponds to a fluctuation of $\sqrt{n}$ monolayers after deposition or etching of $n$ monolayers.
Due to the random noise input, Eq. (2.24) does not have a deterministic solution; however, the PSD of a surface evolving according to this equation can be calculated exactly. Spatial Fourier transformation of Eq. (2.24) yields:

$$\frac{\partial h(\vec{q}, t)}{\partial t} = -(\nu q^2 + K q^4) h(\vec{q}, t) + \eta(\vec{q}, t)$$  

(2.28)

This is an ordinary first order linear differential equation which can be solved by using an integrating factor of $e^{-(\nu q^2 + K q^4) t}$. The solution is:

$$h(\vec{q}, t) = h(\vec{q}, 0) e^{-(\nu q^2 + K q^4) t} + e^{-(\nu q^2 + K q^4) t} \int_{0}^{t} \eta(\vec{q}, t') e^{(\nu q^2 + K q^4) t'} dt'$$  

(2.29)

If $h(\vec{q}, 0) = 0$ the PSD can be calculated from Eq. (2.29) using Eq. (2.26) and (2.27) with the result:

$$P(q, t) = \langle h(\vec{q}, t) h(-\vec{q}, t) \rangle = F a_0^3 \frac{1 - e^{-2(\nu q^2 + K q^4) t}}{\nu q^2 + K q^4}$$  

(2.30)

The PSD decays exponentially with a $q$-dependent rate towards the saturated value of

$$P_{sat} = \frac{F a_0^3}{\nu q^2 + K q^4}$$  

(2.31)

If either $\nu$ or $K$ is zero, the PSD exhibits the simple power law behavior expected for a self-affine surface as described in the previous section. If both coefficients are non-zero, then there is a cross-over length scale corresponding to a wavevector $q_c = \sqrt{\nu/ K}$ which separates two different scaling regimes of the PSD. For $q > q_c$ the PSD decays as $P \propto q^{-4}$ and for $q < q_c$ as $P \propto q^{-2}$. A second important length scale is the correlation length $\xi$ corresponding to the wavevector $q_\xi$. For $q > q_\xi$ the PSD has reached its equilibrium value (2.31) whereas for $q < q_\xi$ the PSD is constant in $q$. From Eq. (2.30), $(\nu q_\xi^2 + K q_\xi^4) = 1/(2t)$. This behavior of the PSD is shown in Fig. 2.2 in which the PSD of Eq. (2.30) is plotted on a log-log scale for three different times. As a function of time the correlation length moves to longer length scales or smaller wavevectors. At short times when $q_\xi > q_c$ the behavior of the PSD is the same

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4The power law exponent is independent of the dimensionality $d$ for both the Edward-Wilkinson (EW) and the noisy Mullins (NM) equation. According to Eq. (2.8) this means that the roughness coefficient $\alpha$ depends on $d$. In fact, for the EW equation $\alpha = 1 - d/2$ and for the NM equation $\alpha = 2 - d/2$. 

as that of the noisy Mullins equation and $q_c$ is irrelevant. At intermediate times when $q_\xi < q_c$ but larger than the cutoff wavelength $q_L = 2\pi / L$ due to the system size, both $q_c$ and $q_\xi$ are important. At long times when $q_\xi < q_L$ the PSD is saturated. The scaling behavior of the RMS roughness as a function of time and system size can therefore be very complex depending on the values of the coefficients $\nu$ and $K$. Experiments that attempt to measure the scaling properties of a surface evolving according to Eq. (2.24) conclusively require an unrealistically wide range of time and length scales, e.g. five orders of magnitude in interface width and twenty orders of magnitude in time according to the plots in Ref. [49]. This problem can be avoided by comparing PSDs of experimental data with the result of numerical simulations instead of only trying to determine the scaling coefficients $\alpha$, $\beta$ and $z$.

![Figure 2.2: PSD of a surface according to Eq. (2.30) for three different times. The wavevector $q_{\xi,1}$ corresponds to the 1 s long growth and $q_{\xi,2}$ to the $10^4$ s long growth. The significance of the various crossover length scales is explained in the text.](image)

In 1986, an additional nonlinear term for the growth equation (2.24) was introduced by M. Kardar, G. Parisi and Y.-C. Zhang to describe growth that occurs in a direction locally normal to the surface [37]. This lateral growth had been observed in discrete growth models such as the Eden model [21].
Locally normal growth with a growth rate $F$ is described by:

$$\frac{\partial h}{\partial t} = F\sqrt{1 + (\nabla h)^2} \approx F + \frac{F}{2} (\nabla h)^2$$  \hspace{1cm} (2.32)

The last expression is an expansion of the square root for small slopes and the nonlinear term is often referred to as the *KPZ term*. Adding this term to Eq.(2.24) results in:

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h + \frac{\lambda}{2} (\nabla h)^2 - K \nabla^4 h + F + \eta$$  \hspace{1cm} (2.33)

which, in the case that $K = 0$, is called the *KPZ equation*. According to the lateral growth assumption (2.32), $\lambda$ in Eq. (2.33) should be equal to $F$; however, this is not necessarily the case. An obvious example where $\lambda \neq F$ is an anisotropic growth or etch rate $F = F(\nabla h)$ as is the case for thermal Cl$_2$ etching. In general this leads to a term different from the KPZ term; however, if one considers as a particular slope dependence $F(\nabla h) = F_0 \sqrt{1 + (\nabla h)^2}$ in Eq. (2.32) then $\lambda = 2F_0$. Similarly, if $F(\nabla h) = F_0 / \sqrt{1 + (\nabla h)^2}$ then $\lambda = 0$. Although these examples use a particular functional form for the slope dependent etch or growth rate, for small slopes, a KPZ term with a coefficient $\lambda \neq F$ may also imitate other functional forms of $F(\nabla h)$. Other, more general interpretations of the KPZ term than the normal growth argument, are also possible. In fact, the terms in Eq. (2.33) can be more generally regarded as a low order expansion of a series with the symmetry required to describe surface evolution:

$$\frac{\partial h}{\partial t} = F + \eta + \sum_{n,k} A_{nk} (\nabla^{2n} h)(\nabla h)^{2k}$$  \hspace{1cm} (2.34)

It can be shown that higher order terms become irrelevant for the evolution on long length scales (the so-called *hydrodynamic limit*) and after long times. This has already been discussed for the special case of the linear equation (2.24); however, since the length and time scale required to neglect certain terms in Eq. (2.34) depend on the unknown coefficients $A_{nk}$, this observation is not very useful in practice. Nevertheless, in this very general approach, the KPZ equation is the simplest possible surface evolution.

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5Following the symmetry arguments given by Barabási [7] it would be perfectly reasonably to include terms proportional to $|\nabla h|$ and it’s odd powers in (2.34) as well; however, these are typically omitted. Presumably this is due to the singularity at $|\nabla h| = 0$ which causes mathematical difficulties in analytical treatments.
The effect of the KPZ term on surface evolution is illustrated in Fig. 2.3. An initially sinusoidal profile that evolves according to $dh/dt = \lambda/2(\nabla h)^2$ develops mounds and sharp valleys if $\lambda > 0$ and an inverted profile if $\lambda < 0$. This can be easily understood within the normal growth picture. On the contrary, both of the linear terms in Eq. (2.33) acting on a sinusoidal profile

Figure 2.3: Effect of KPZ term on surface evolution: The plot shows numerical integrations of $dh/dt = \lambda/2(\nabla h)^2$ with an initially sinusoidal surface. For $\lambda > 0$ the surface develops mounds and valleys with cusps due to the outward growth, for negative $\lambda$ the situation is inverted.

equation and the coefficients $A_{nk}$ have no physical meaning a priori. Very commonly the linear terms are still interpreted in terms of desorption or Schwoebel barriers and surface diffusion. For the KPZ coefficient $\lambda$, on the other hand, interpretations different from the lateral growth argument are also used. For example, J. Villain has derived an explicit expression for $\lambda$ for the special case of growth on a stepped vicinal crystal surface which is proportional but not equal to the growth rate $F$ if desorption also occurs but zero if there is no desorption [80]. While the approach of Eq. (2.34) may appear very general, it should be mentioned that the equation is still local, i.e. the rate of change of $h$ at the point $x$ depends only on the various derivatives of $h$ at $x$ and not other locations $x'$. The equation therefore neglects any nonlocal effects such as shadowing [38, 20].
Table 2.1: Scaling coefficients for the continuum equations described in this section.

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edwards-Wilkinson</td>
<td>$dh/dt = \nu \nabla^2 h + \eta$</td>
<td>$2-\frac{d}{2}$</td>
<td>$\frac{2-d}{4}$</td>
<td>2</td>
</tr>
<tr>
<td>Noisy Mullins</td>
<td>$dh/dt = -K \nabla^4 h + \eta$</td>
<td>$\frac{4-d}{2}$</td>
<td>$\frac{4-d}{8}$</td>
<td>4</td>
</tr>
<tr>
<td>Kardar-Parisi-Zhang</td>
<td>$dh/dt = \nu \nabla^2 h$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{3}{2}$ (1D)</td>
</tr>
<tr>
<td></td>
<td>$+\frac{\lambda}{2} (\nabla h)^2 + \eta$</td>
<td>0.38</td>
<td>0.24</td>
<td>1.58 (2D)</td>
</tr>
</tbody>
</table>

Figure 2.4: Surface morphology created by the Kuramoto-Sivashinsky equation in a 3D view obtained from a numerical simulation starting with a flat surface.

will simply smooth it out by reducing its amplitude. The reason for this is that in Fourier space, the linear terms will lead to a separate equation for each wavevector $q$, as seen in Eq. (2.28), whereas the nonlinear term, which is a product in real space, becomes a convolution that causes coupling of the waves with different wavevectors. Obviously, the addition of the KPZ term also changes the behavior of the PSD and the scaling coefficients. These are summarized in Table 2.1 for the models described in this section. The scaling coefficients for the KPZ equation can be obtained by a renormalization group treatment in 1D and by numerical simulations in 2D.

If the parameter $\nu$ is negative, Eq. (2.33) is called the Kuramoto-Sivashinsky equation. The result of a numerical simulation of this equation using a flat initial condition is shown Fig. 2.4 in a 3D view. Some more details on the
numerical simulations will be given in Chapter 4. The resulting morphology is reminiscent of a snowfield covered with sun cups. This can be understood from the preceding discussion of the various terms in the equation: Ignoring the nonlinear term at first, from the deterministic part of Eq. (2.28) one can see that, because of the negative value of $\nu$, the solution is exponentially increasing with $t \cdot q^2$ for small $q$. For large $q$ the fourth order term is dominant and stabilizes the solution. The combined effect of these two terms and the white noise input on the PSD at finite times is a pronounced peak at the crossover length wavevector $q_c$. In real space the surface develops a preferred length scale which is clearly visible in Fig. 2.4 as the size of the "sun cups". The addition of the KPZ term then causes cuspy ridges and the rounded bottoms of the valleys as in Fig. 2.3. The coefficient $\lambda$ was negative for the simulation shown in (2.4). The Kuramoto-Sivashinsky equation has been used to describe ripple formation in ion-sputtering experiments [17].

### 2.3 Coupled Equations Models for Shape Evolution

In a nanofabrication process, the understanding of the evolution of patterned surfaces is as important as the understanding of the surface roughness. In principle, the equations discussed in the previous section are suitable to describe shape evolution as well. In this case, one could use only the deterministic part of the equations. In chapter 5 of this thesis it will be shown that these equations, which describe the evolution of surface roughness extremely well, fail to reproduce key features of the experimentally observed shape evolution for etching or growth on microfabricated gratings. One obvious reason for this failure is that the average surface slope and curvature are significantly larger on the patterned samples. Coming back to Eq. (2.34) this means that higher order terms, in particular nonlinear ones, become more important and may not be negligible any more at the time and length scales of interest; however, it is highly undesirable to add more terms to the evolution equations with parameters that are not only unknown but also have no physical interpretation. Expressions (A.5) and (A.11) which are derived in Appendix A can be used as a starting point for a new approach. Both coefficients $\nu$ and $K$ are proportional to the surface concentration of adatoms $n$. Assuming constant coefficients is therefore equivalent to assuming a uniform
concentration $n$. It is easy to imagine that this assumption will break down for patterned surfaces and it seems very natural to write separate equations for a time- and space-dependent concentration $n(x, t)$ which then couples to an equation for the surface height $h$. If the adatoms or etchant molecules diffuse on the surface, $n(x, t)$ obeys a diffusion equation with additional terms for the addition of atoms from the flux, and loss by incorporation. The use of a diffusion equation for $n$ goes back to a classic paper by Burton, Cabrera and Frank [12] and coupled equations have been used by Hata et al. [28] and recently by Braun et al. [11]. In their simplest form these equations are:

$$\frac{\partial n}{\partial t} = F + D \frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau}$$ (2.35a)

$$\frac{\partial h}{\partial t} = -a^2 \frac{n}{\tau}$$ (2.35b)

The minus sign in the second equation is valid for etching and has to be replaced with a positive sign for the case of growth. As the equations (2.35) will mainly be used to describe grating evolution during thermal $\text{Cl}_2$ etching in this thesis, the terms will be discussed for this case: The concentration $n$ then refers to the chlorine on the surface. The first term in Eq. (2.35a) is the addition of chlorine to the surface from the incident flux. This flux is uniform across the surface if the chlorine is supplied to the surface from a low pressure background gas phase. If it is supplied as a directional molecular beam, due to the smaller projected area of the sloped sidewalls of the grating, the flux is inhomogeneous according to

$$F(\theta, \theta_0) = F_0 \cos(\theta - \theta_0)$$ (2.36)

where $\theta$ is the angle of the surface with respect to the plane of the substrate $\theta = \arctan(\nabla h)$ and $\theta_0$ is the angle of the incident beam of $\text{Cl}_2$ with respect to the substrate normal. The second term in (2.35a) accounts for surface diffusion with a diffusion constant $D$. This is undirected diffusion, i.e. it is not driven by the gradient of the chemical potential. The last term corresponds to the loss of chlorine from the surface through the etching reaction and subsequent desorption which leads to a finite lifetime $\tau$ of chlorine on the surface.

---

6The flux term $F$ has different units here than in the previous section. The coupled equations are only applied to one-dimensional profiles in this thesis and in this case the concentration $n$ has units of [nm$^{-1}$]. The factor $a_0^2$ in (2.35b) converts this to [nm] for the surface height.
surface. Since this etching and desorption rate removes atoms from the surface, the same term appears in Eq. (2.35b). The discussion of the terms for the case of MBE growth is completely analogous if the etch and desorption rate is replaced by an incorporation rate.

For thermal Cl\textsubscript{2} etching the etch rate is dependent on the crystal orientation. This means that a given flux of Cl\textsubscript{2} will cause different etch rates \( R \) for different substrate orientations. For a grating structure this means that for a constant flux, the sidewalls of the ridges etch at a different rate than the flat sections, \( R = R(\theta) \). There are two obvious ways of incorporating the crystal anisotropy of the etch rate into coupled equations. The first one is through a surface orientation dependent sticking coefficient for the Cl\textsubscript{2} molecules \( S(\theta) \). This coefficient then enters the equations as a multiplier to the flux term, i.e. \( F(\theta, \theta_0) \rightarrow S(\theta) \cdot F(\theta, \theta_0) \) in Eq. (2.35a). In this case the steady state solution of Eq. (2.35a) in the absence of surface diffusion for non-directional flux is \( n_{ss}=\frac{\tau S(\theta)F_0}{\tau_d} \) and with this Eq. (2.35b) becomes \( \frac{dh}{dt}=a_0^2 S(\theta)F_0 \). This shows that the angle dependence of the etch rate is given directly by \( S(\theta) \). The second way is the addition of a desorption term \( -\frac{n}{\tau_d(\theta)} \) to Eq. (2.35a), corresponding to chlorine that desorbs from the surface without reacting chemically\textsuperscript{7}. This reduces the lifetime of the chlorine on the surface depending on its orientation from \( \tau_0=\tau \) to \( \tau_0=\tau\tau_d/(\tau + \tau_d) \).

Results of numerical simulations of the equations are very similar for the two described implementations of crystal anisotropy as long as the diffusion length \( l=\sqrt{D\tau_0} \) is kept the same.

In Fig. 2.5 the results of example numerical solutions obtained by discretizing and solving the coupled equations (2.35) starting with a trapezoidal surface, plotted at the top, are shown. In these examples, no anisotropic etch rates are used and \( S(\theta) = 1 \). Rather they illustrate the combined effects of the spatial inhomogeneity of the flux and surface diffusion. The parameters used are \( a_0^2F_0 = 0.33 \text{ nm/s}, \ D = 6000 \text{ nm}^2/\text{s} \) and \( \tau = 0.5 \text{ s} \). In the middle panel the solution to Eq. (2.35a) for the surface concentration is shown after an etch time of 5 seconds. At this time the surface profile is still almost identical to the starting condition shown above. In the case of non-directional exposure from a background gas, the flux \( F = F_0 \) is uniform leading to a constant concentration \( n \) across the surface (heavy line in Fig. 2.5).

\textsuperscript{7}Note that simply replacing \( \tau \rightarrow \tau(\theta) \) does not lead to an angle dependent etch rate: A higher desorption rate from an inclined surface leads to a lower concentration on this surface and the increase in the etch rate due to the higher desorption rate exactly cancels with the decrease due to the lower concentration.
Chapter 2. Continuum Models for Surface Evolution

Figure 2.5: Numerical solution of Eq. (2.35) on a trapezoidal starting surface (top) for three cases: Cl₂ molecular beam incident at 40° off normal, at normal incidence and Cl₂ supplied non-directionally. The middle panel shows the solution of (2.35a) for the concentration after 5 seconds of etching. The lower panel shows the resulting surface profiles after 750 seconds of etching, corresponding to an etch depth of 250 nm.
normally incident directional flux, \( F = F_0 \cos \theta \). The concentration on both of the sidewalls is reduced by a factor of \( \cos \theta \). The concentration profile is smoothed out by the diffusion leading to a reduced concentration on the flat sections next to the sidewalls within a diffusion length of \( \sqrt{D} \tau = 55 \text{ nm} \) (semi-heavy line). For a directional beam incident at an angle of 40° to the substrate normal, the incident flux on the sidewall facing the incident beam (left) is higher than on the flat sections and it is reduced on the sidewall facing away from the beam (right). This leads to a concentration profile with a smoothed out maximum on the left sidewall and a smoothed out minimum on the right (thin line).

The effect on the shape evolution is shown in the lower panel in which the solution to (2.35b) is shown after 750 seconds of etching. In the first case the shape of the grating is unchanged\(^8\). For normally incident flux the surface profile develops little peaks on the upper flat section next to the sidewalls due to the reduced etch rate that results from the depletion of the chlorine concentration. For the same reason the lower corners are rounded off, as the etch rate is reduced on the flat section next to the sidewalls. Finally, in the case of the off-normal beam, a characteristic shape distortion is observed: A peak forms on the top, next to the right sidewall whereas the left top corner becomes rounded as does the bottom right corner. A trench develops at the foot of the left sidewall. Again all these features can be understood from the etch rate which is proportional to the concentration profile plotted in the middle panel. Another interesting effect observed with the off-normal beam is that the entire elevated surface feature moves to the right, i.e. away from the incident beam. This is due to the higher etch rate of the left sidewall compared to the right one.

From this discussion it is clear that the etch rate at a point \( x \) on the surface in this model depends on the slope of the surface within a diffusion length of point \( x \), not only on the derivatives of \( h \) at the point \( x \). The slope dependent spatial inhomogeneity of the flux is spread out by surface diffusion and therefore the model becomes non-local.

Other physically sensible terms can be included in the coupled equations (2.35). The Schwoebel effect, as discussed in the previous section, leads to a surface current of \( j \propto Dn\nabla h \). This, together with the continuity equation
\[ \frac{\partial h}{\partial t} = \frac{1}{\rho} \nabla \cdot j \]

\(^8\)A slight rounding of the corners is visible in the simulation. This is due to the addition of a small \( \nu \)-term to Eq. (2.35b), i.e. a term \( \nu \cdot d^2 h/dx^2 \) with \( \nu = 0.5 \text{ nm}^2/s \). This helps to keep the simulations numerically stable but has no effect on the shape evolution other than the rounding of the corners.
tion for $n$ (i.e. $dn/dt = -a_0 \nabla \cdot j$) leads to a term:

$$\frac{\partial n}{\partial t} = \eta D \nabla (n \nabla h)$$

(2.37)

where $\eta$ is a constant. During growth adatoms are incorporated into the crystal either at step edges or by formation of new islands. The first contribution to the incorporation rate is proportional to the step density $S$ and the diffusion constant, $\tau^{-1} \propto DS$ and the latter is proportional to the density of adatoms and the diffusion constant, $\tau^{-1} \propto Dn$. Conversely, steps may also reemit incorporated atoms back into the adatom phase at a rate $\kappa$, leading to a term:

$$\frac{\partial n}{\partial t} = \kappa S$$

(2.38)

Putting together all of these effects one arrives at the following growth equations:

$$\frac{\partial n}{\partial t} = F + D \frac{\partial^2 n}{\partial x^2} + (\kappa - aDn)S - bDn^2 + \eta D \nabla (n \nabla h)$$

(2.39a)

$$\frac{\partial h}{\partial t} = a_0^2 (aDn - \kappa)S + bDn^2$$

(2.39b)

where $a$ and $b$ are constants.

An approximate analytical expression for the step density can be derived by observing that during growth or etching the surface is rough on atomic length scales with a steady state density of atomic steps $S_0$ which have a random orientation. This steady state density depends on the growth conditions in a non-trivial way and is used as an adjustable parameter of the model. Adding this randomly oriented step density to the step density $\nabla h$ which is due to the surface slope on a larger length scale and averaging over the random orientation one arrives at the following expression:

$$S = \sqrt{S_0^2 + (\nabla h)^2}$$

(2.40)

Equations (2.39) in combination with (2.40) can be used with good success to model shape evolution of gratings during growth as will be shown in Chapter 5.
Chapter 3

Experimental Method

This chapter gives a description of the experimental apparatus that was used to obtain the results that will be discussed in the following two chapters. The central part of this apparatus is a combined vacuum system for crystal growth and etching. The system is a III-V solid source molecular beam epitaxy system (VG V80H) that was extended to include an etch chamber which was designed and built at UBC for this thesis work. This chamber is described in detail in the second section. The first section gives an overview of the experimental conditions and some general properties of the thermal chlorine etch. The chapter is concluded with a review of surface morphology measurements by atomic force microscopy and elastic light scattering and a description of the various sample preparation procedures.

3.1 Thermal Chlorine Etching

Thermal chlorine etching of GaAs is accomplished by exposing the GaAs surface to a low pressure atmosphere of Cl$_2$ gas at an elevated substrate temperature. An etch rate of approximately one monolayer per second can be achieved at 200°C at a pressure of 10$^{-4}$ mbar. The adsorption and reaction of Cl$_2$ with GaAs has been studied extensively (see [71] for a review) and a brief summary is given here.

The Cl$_2$ molecules are first physisorbed and then cracked on the surface into chemisorbed atomic Cl [18]. This two-step adsorption process is referred to as a precursor-mediated dissociative chemisorption. The atomic chlorine reacts chemically with the Ga and As surface atoms in a multi-step reaction.
to form trichlorides:

\[
\begin{align*}
\text{GaAs} + 2\text{Cl} & \rightarrow \text{GaCl} + \text{AsCl} \\
\text{GaCl} + \text{Cl} & \rightarrow \text{GaCl}_2 \\
\text{AsCl} + \text{Cl} & \rightarrow \text{AsCl}_2 \\
\text{GaCl}_2 + \text{Cl} & \rightarrow \text{GaCl}_3 \\
\text{AsCl}_2 + \text{Cl} & \rightarrow \text{AsCl}_3
\end{align*}
\]

(3.1a) (3.1b) (3.1c) (3.1d) (3.1e)

The various chlorinated products on the right hand side of Eqs. (3.1) as well as molecular arsenic can then desorb from the surface into the gas phase thus removing material from the substrate. The product distribution depends on the substrate temperature as does the etch rate. This is shown in Fig. 3.1 which is taken from a paper by C. Su et al. [76]. At temperatures below \(\approx 350^\circ\text{C}\) (regions I and II in Fig. 3.1) the main reaction products that are found desorbing from the surface are GaCl₃, As₄ and AsCl₃. Above \(350^\circ\text{C}\) Ga desorbs mainly as a monochloride. The etch rate increases with temperature according to an Arrhenius law \(R \propto \exp(-E_a/kT)\) below \(\approx 200^\circ\text{C}\) (region I) and is constant above (region II) until it starts increasing again above \(350^\circ\text{C}\) where monochloride desorption becomes dominant (region III). It becomes constant again at temperatures above \(\approx 400^\circ\text{C}\) (region IV). At very high temperatures above \(650^\circ\text{C}\) Ga desorption sets in and the etch rate increases again with temperature. In the region between \(200^\circ\text{C}\) and \(350^\circ\text{C}\) (region II) where the etch rate is independent of temperature, it is linear in Cl₂ pressure [25].

The simplest explanation for this behavior of the etch rate, that is consistent with the observed etch products, is that the etch rate is limited by desorption of the etch products below \(200^\circ\text{C}\) and limited by the supply of Cl₂ to the surface, proportional to the pressure, between \(200^\circ\text{C}\) and \(350^\circ\text{C}\). Above, it becomes limited by desorption of the (different) etch products and by the Cl₂ supply, again above \(400^\circ\text{C}\). At these high temperatures Ga is desorbed as the monochloride and therefore the limit set to the etch rate by the Cl₂ supply is higher than at lower temperatures where Ga is desorbed as the trichloride. While this explanation is simple and elegant, it cannot be the full truth, as the etch rate is also found to be pressure dependent in the temperature region below \(200^\circ\text{C}\), where desorption was presumed to be rate limiting. In this region the pressure dependence is sub-linear (see [24] and Fig. 22 in Ref. [76]). In view of the complexity of the described multi-step
surfaces it is not surprising that the etch rate cannot be explained
that simply.

The etch rate is not only dependent on the pressure and the substrate
temperature but also on the crystallographic orientation of the substrate. All
low-index planes except for the \{111\}A plane show the same general behavior
as a function of temperature as the \{001\} plane shown in Fig. 3.1, i.e. two
Arrhenius and two plateau regions. The \{111\}A plane, in contrast, only has
one plateau at high temperatures above 400°C (corresponding to region IV
in Fig. 3.1) and an Arrhenius behavior at lower temperatures, i.e. region III
is extended all the way down to room temperature. For the practically most
important temperature region between 200°C and 350°C, the following etch
rate sequence has been found by Furuhata et al. [24]: \{111\}B > \{011\} =
\{001\} > \{111\}A. From the chemistry described in the previous paragraphs
one can get an intuitive understanding of this etch rate sequence. In Fig. 3.2
a projected view along the [110] direction of the GaAs crystal structure is
shown with three of the low-index surfaces: \{001\}, \{111\}A, and \{111\}B. All
of these surfaces are polar surfaces, with alternating layers of Ga atoms and
As atoms. Since As and the As-containing products are more volatile, the
surface is Ga-terminated during etching. The atoms on the Ga-terminated
{001} surface have two dangling bonds and are back-bonded to the crystal with two bonds. On the \{111\}A surface the Ga atom only has a single dangling bond and three back-bonds, and on the \{111\}B surface it has three dangling bonds (only two are visible in the projected view of Fig. 3.2) and one back-bond. It is then easy to imagine that GaCl$_3$, the main reaction product at the intermediate temperatures, is very readily formed on the \{111\}B surface, whereas the Ga on the \{111\}A surface preferentially forms GaCl which can only be desorbed at high temperatures. The picture for the \{001\} surface and the non-polar \{011\} surface which has both Ga and As atoms in each layer, is less clear; however, the fact that their etch rates are intermediate between the two \{111\} planes seems intuitively reasonable.

### 3.2 In-situ Etch Chamber

#### 3.2.1 Design and operation

A UHV vacuum chamber for thermal chlorine etching that is compatible with the existing MBE growth system was designed and built for this project. A schematic of the combined system with its interconnected vacuum chambers is shown in Fig. 3.3. After samples are loaded into the preparation chamber of the MBE system through the load lock, the sample transport mechanism can be used to transfer them back and forth between the growth and etch.
chambers without breaking the vacuum.

The etch chamber is attached to the preparation chamber through a gate valve on an 8 inch diameter Conflat flange. The existing sample transport mechanism of the V80H MBE system is designed to work with a dual growth chamber system, i.e. a system that has a second growth chamber in lieu of the etch chamber in Fig. 3.3. It could therefore be used without modifications, although an adjustment of the alignment was necessary. The etch chamber has a cylindrical stainless steel body with a diameter of 12 inches, identical to the preparation chamber, and a length of 8 inches. The base of the cylinder that faces the preparation chamber has an off-center, 1.5 inch long, 6 inch diameter port with the 8 inch flange that is connected to the gate valve. This side of the chamber is a mirror image of the corresponding face of the preparation chamber. In Fig. 3.4 a drawing of the etch chamber is shown. On the top of the chamber is a 6 inch flange on which the sample heater is mounted. It has electrical feedthroughs for a type C thermocouple and the two heater wires. At 45° is a 6 inch viewport that allows one to see both the sample heater and the transport trolley when it is inside the etch chamber. The wobblestick is needed to pick up the sample from the trolley and insert it into the heater. The latter two ports are in identical geometry as corresponding ports on the preparation chamber. On the bottom of the chamber are four 2.75 inch viewports, labelled A to D in Fig. 3.4 with line of sight to the sample surface. These ports are used for optical measurements as described in the following section. Finally a port with a 6 inch diameter flange on the side is connected to the pumping tee (a T-shaped stainless
Figure 3.4: Schematic side view of the etch chamber as seen from the preparation chamber showing the position of the sample inside the chamber and the various ports. This figure is drawn to scale.

The sample is in the position indicated in Fig. 3.4 with the surface pointing down. This position is dictated by the necessary compatibility with the sample transport system. Another 4.5 inch viewport is on the opposite base of the chamber (facing away from the preparation chamber, not visible in Fig. 3.4) approximately centered at the sample position.

During idle periods the etch chamber is pumped by a 60 L/s ion pump (Varian 911-5034) and during etching it is pumped by a 115 L/s turbomolecular pump (Leybold Turbvac 150) backed by a standard mechanical pump (Alcatel 2012A). Due to the extreme corrosivity of the chlorine gas it is essential to use inert Fomblin oil in the mechanical pump. Even with Fomblin oil the pump needed two rebuilds during the course of this work due to the
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damage to the shaft and the seals caused by the chlorine gas. The bearings of the turbomolecular pump are purged by nitrogen gas during etching. This is supposed to prevent the chlorine gas from reaching the bearings; however, failure of the turbo pump due to corroded bearings was still the main cause of down time for the system. Eleven bake heaters are permanently attached to the outside of the chamber. These heaters and heating tape wrapped around the pumping tee are used to bring the entire system to a temperature of approximately 100°C during bake-out. Higher temperatures can be reached easily; however, a much hotter bake-out (≈ 200°C) that was done at an early time during the project caused visible damage to the stainless steel walls of the chamber, presumably due to the desorption of chlorinated steel from the chamber walls. During bake-out, the sample heater is kept at ≈ 150°C to prevent adsorption of the gases desorbing from the hot walls on the heater. The typical base pressure reached after a two day bake-out is $5 \times 10^{-9}$ mbar. The pressure is measured with a hot filament ion gauge with a range between $10^{-4}$ and $10^{-6}$ mbar and a cold cathode gauge with a range between $10^{-3}$ and $10^{-6}$ mbar, both mounted on the pumping tee. During etching the hot filament gauge was usually turned off since chlorine exposure causes premature failure of the filaments.

The sample heater is based on an earlier design by Jim Mackenzie for the sample heater inside the MBE growth chamber. It is designed to hold the standard 3 inch diameter MBE sample holders used in the lab (details and drawings of the holders can be found in the Ph.D. thesis of Shane Johnson [33]). They are heated radiatively from the back side by a 3 inch diameter resistive pyrolytic graphite heating element encapsulated in pyrolytic boron nitride (Advanced Ceramics HT-63) at a distance of approximately 1.5 cm. The boron nitride is chemically inert and no degradation of the heater due to the chlorine exposure was found during this project. The electrical feed wires for the heater are tantalum wires which are attached to the heater by carbon screws and washers. Carbon screws are used to avoid failure of the contacts due to the larger thermal expansion of a metal screw. The heating element is mounted in a housing made from refractory metals. This housing is attached to an aluminum plate with three molybdenum threaded rods and the aluminum plate is attached to the 6 inch diameter heater flange by three stainless steel threaded rods bolted into the flange. To measure the temperature of the heater, a type C (tungsten-rhenium) thermocouple is mounted inside the housing without touching the heating element. The heater is powered by a Variac power supply.
Chlorine gas is supplied to the sample either with no directionality from a low pressure gas phase, or as a directional molecular beam. In the first case, Cl₂ is brought into the chamber through a leak valve on a vacuum port on the pumping tee with no direct line of sight to the sample. To create a directional molecular beam on the surface, a stainless steel tube with an inner diameter of 1 mm is brought into proximity to the sample surface at a distance of approximately 2 cm. The tube is welded to a 2.75 inch flange that can be attached either on port B (in Fig. 3.4) for off-normal incidence or on port C for normal incidence. Chlorine gas is fed into the tube through a leak valve.

The geometry of the molecular beam etching setup is shown in Fig. 3.5. The directionality of the etch depends on the ratio of the flux of Cl₂ to the surface from the beam (with a corresponding pressure \( P_B \)) and from the background pressure \( P_C \) in the chamber. A rough estimate of this ratio can be obtained by the following consideration: If the Cl₂ flux from the tube follows a \((\cos \phi / r^2)\)-distribution, where \( \phi \) is the angle with respect to the axis of the tube and \( r \) is the distance from the end of the tube, then the footprint of the beam on the sample can be calculated to be approximately 1 inch FWHM. By approximation, the entire flux has to pass through this area, so that it can be regarded as an entrance orifice to the chamber. The throughput through this orifice is equal to the conductivity \( C_O \) of the orifice and the pressure difference \( P_B - P_C \) [56]. Since all Cl₂ is pumped by the turbo pump, the throughput from the chamber to the pump must be the same. This throughput is proportional to the conductivity of the 4 inch
diameter and 20 inch long tube to the pump $C_P$ and the chamber pressure $P_C$ (assuming the pressure at the pump is zero). Therefore,

$$C_O(P_B - P_C) = C_P P_C$$  \hspace{1cm} (3.2)$$

The conductivities for an orifice and a tube with the given geometry are given by $\nu A_O/4$ and $0.2\nu A_T/4$ respectively, where $A_O$ is the area of the orifice, $A_T$ is the area of the tube and $\nu$ is the average velocity of the molecules. Using these expressions in Eq. (3.2), the pressure ratio $P_B/P_C$ can be calculated to be approximately 4. In practice, the non-directional exposure is found to be suppressed by more than a factor of ten, as explained below.

The Cl$_2$ gas is stored in a bottle in a vented cabinet. The purity of the gas is certified by the supplier (Scott Specialty Gases) to be better than 10 ppm. To minimize contaminants from outgassing of the stainless steel tubes to the chamber and from the pressure regulator, the entire gas lines including the regulator are pumped out and refilled with fresh etch gas before etch experiments are carried out.

### 3.2.2 Characterization

**Sample temperature**

Since the thermocouple gauge is mounted inside the housing of the sample heater, it is expected that the actual sample temperature can be quite different from the temperature read by the thermocouple. An initial calibration was carried out to find the correction factors to convert the thermocouple reading to the real sample temperature. This was done by using diffuse reflectance spectrometry (DRS), the same method used to measure the sample temperature during MBE growth. The required instrumentation was moved from the growth to the etch chamber for this calibration. A detailed description of the method is given in the Ph.D. thesis and related publications by Shane Johnson [33, 34, 35]. A tungsten halogen lamp was mounted on port C of the chamber (see Fig. 3.4) and the filament was focussed on the sample with a lens. Since the surface of the sample is very smooth, its contribution to the diffusely reflected light is negligible. The diffusely reflected light from the sample back side and the boron nitride heating element behind the sample was collected with a lens on port B and focussed onto the pick-up fiber bundle of a monochromator. By scanning the monochromator, transmission spectra of the sample were obtained and the sample temperature was deduced from
Table 3.1: Temperature calibration by diffuse reflectance spectroscopy. The first column lists the voltage of the Variac power supply to the heater, the second column is the voltage of the thermocouple inside the heater, the third is the thermocouple voltage converted to a temperature in °C and the last column is the actual sample temperature obtained from the DRS measurement.

<table>
<thead>
<tr>
<th>Variac Voltage (V)</th>
<th>TC (mV)</th>
<th>TC (°C)</th>
<th>Sample Temp.(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.2</td>
<td>85</td>
<td>115</td>
</tr>
<tr>
<td>15</td>
<td>2.4</td>
<td>160</td>
<td>175</td>
</tr>
<tr>
<td>17.5</td>
<td>3.3</td>
<td>215</td>
<td>210</td>
</tr>
<tr>
<td>20</td>
<td>4.4</td>
<td>275</td>
<td>240</td>
</tr>
<tr>
<td>22.5</td>
<td>5.2</td>
<td>320</td>
<td>260</td>
</tr>
<tr>
<td>25</td>
<td>6.0</td>
<td>360</td>
<td>290</td>
</tr>
<tr>
<td>27.5</td>
<td>6.9</td>
<td>410</td>
<td>320</td>
</tr>
<tr>
<td>30</td>
<td>7.4</td>
<td>435</td>
<td>335</td>
</tr>
<tr>
<td>32.5</td>
<td>8.2</td>
<td>480</td>
<td>365</td>
</tr>
<tr>
<td>35</td>
<td>9.0</td>
<td>520</td>
<td>400</td>
</tr>
<tr>
<td>37.5</td>
<td>9.5</td>
<td>545</td>
<td>420</td>
</tr>
<tr>
<td>40</td>
<td>10.1</td>
<td>575</td>
<td>445</td>
</tr>
<tr>
<td>42.5</td>
<td>10.6</td>
<td>600</td>
<td>470</td>
</tr>
<tr>
<td>45</td>
<td>11.1</td>
<td>625</td>
<td>500</td>
</tr>
<tr>
<td>47.5</td>
<td>11.7</td>
<td>660</td>
<td>535</td>
</tr>
<tr>
<td>50</td>
<td>12.3</td>
<td>690</td>
<td>565</td>
</tr>
</tbody>
</table>

A fit to the absorption edge. The result is listed in Table 3.1. It shows that the difference between the thermocouple reading and the actual sample temperature can be significant, especially at high temperatures. The calibration was found to be reproducible to within ±20° C and Table 3.1 was used as a look-up table to convert thermocouple voltages to sample temperatures.

**Etch rate**

Laser reflectometry on GaAs/AlAs multilayer structures was used as a way to measure the etch rate in real time during etching. The principle of the method is shown in Fig. 3.6: Due to the different indices of refraction of GaAs (n=3.856+0.196i at λ=633 nm) and AlAs (n=3.13 at λ=633 nm) an
Figure 3.6: Specular reflectivity measurement on a GaAs/AlAs/GaAs multilayer structure. The multiple internal reflections lead to interference effects. There are also multiple reflections inside the AlAs layer which are not drawn. They lead to a modification of the Fresnel reflection coefficient of the GaAs/AlAs interface.

infinite series of reflections inside the multilayer structure contributes to the specular reflectivity. Depending on the thickness of the layers this can lead to destructive or constructive interference and as the layers are etched, interference fringes appear in the reflectivity as a function of time.

For the measurements the beam from a He:Ne laser at $\lambda = 633$ nm was incident on the sample through port B and the specular reflection was measured with a Si photodiode on port D. The photodiode signal during etch of a GaAs/AlAs/GaAs layer structure identical to the one in Fig. 3.6 is shown in Fig. 3.7 a). The sample was grown in the MBE chamber and then moved directly into the etch chamber. The thickness of the GaAs cap layer was 250 nm and that of the AlAs layer was 330 nm. The interference fringes are clearly visible as a function of time as the etch proceeds through the layers. A code was written that calculates the reflectivity of the multilayer structure as a function of the etch depth by summing up all contributions from the internal reflections. The calculation is done using the Fresnel reflection coefficients for s-polarized light whereas the laser beam in the experiment does not have a well defined polarization; however, the polarization does not affect the phase of the interference fringes. The result of the calculation for the described structure is shown in Fig. 3.7 b) as a function of the etch depth. The correspondence of the calculated and the measured fringes is very clear. The GaAs/AlAs interface is indicated in the figure. Obviously, by comparing
Chapter 3. Experimental Method

Figure 3.7: a) Measured interference fringes in the reflectivity of a GaAs/-AlAs/GaAs multilayer structure as a function of etch time. b) Calculated reflectivity as a function of etch depth for the same structure.

Fig. 3.7 a) which has a time axis with Fig. 3.7 b) which has a depth axis, the etch rate can be obtained. The conditions were kept constant during the etch (substrate temperature = 200°C, Cl₂ pressure = 10⁻⁴ mbar) and one can see that the etch rate for AlAs \( R_{AlAs} \) is slightly higher than the etch rate for GaAs \( R_{GaAs} \). In fact, from Fig. 3.7, \( R_{GaAs} = 11 \) nm/min and \( R_{AlAs} = 16 \) nm/min.

Measurements of the etch rate by laser reflectometry have been found to be an invaluable tool as a real-time monitor of the etch progress during fabrication and to re-calibrate the etch rates regularly. The latter is important as the cold cathode gauge, which is used to measure the Cl₂ pressure during etching, is affected by the Cl₂ exposure so that its pressure calibration changes over time.

For etches with a directional molecular beam, the non-uniformity of the etch rate across the sample causes an additional complication. A map of the etch rate on the sample surface was obtained by the following method: A sample was grown by MBE containing a 50 nm thick AlAs layer and a 400
nm thick GaAs cap. This sample was then transferred into the etch chamber and Cl₂ etching was performed at a substrate temperature of 200°C. During the etch the specular reflection was recorded as described above with a well known position of the He:Ne laser beam on the sample. The total etch depth at the position of the spot was inferred from the number of interference fringes in the reflectivity as a function of etch time. After the etch was finished the sample was removed from the vacuum system. Due to the non-uniformity of the GaAs cap layer after etching, colored interference rings around the spot with the maximum etch rate (the point closest to the tube) were clearly visible on the sample. Figure 3.8 shows a black and white contrast-enhanced photo of such a sample. The sample is a quarter of a 2 inch diameter wafer, which is the sample size used for most of the experiments described in this thesis. Together with the etch rate at the position of the laser spot during the in-situ measurement, the rings allow one to map out the etch rate as a function of position on the sample. In this case the maximum etch rate was found to be 41 nm/min at the center of the rings and 18 nm/min at the center of the round edge of the sample. To obtain the above etch rates, the chamber pressure had to be kept at 8×10⁻⁶ mbar, compared to ≈20 nm/min at 10⁻⁴ mbar for etches using non-directional gas injection. Since the etch rate is linear in pressure at this temperature, this shows that with the directional gas injection the non-directional Cl₂ gas from the background pressure
Chapter 3. Experimental Method

Figure 3.9: Shape of an AFM tip. The tip radius $r$ of approximately 10 nm limits the lateral resolution and the cone angle $\Phi \approx 10^\circ$ limits the maximum surface slope that can be measured.

is reduced by a factor of 10 to 20 compared to the total flux, somewhat more than the factor of 4 estimated in the previous section based on the geometry.

3.3 Surface Morphology Measurements

3.3.1 Atomic force microscopy

An atomic force microscope (Digital Instruments MMAFM-2) was used in tapping mode to obtain real space images of surfaces ex-situ after processing. The AFM gives a direct measure of the surface height $h$ on a grid of 512×512 points at maximum resolution. The size of a scan can be adjusted up to a maximum of 50 $\mu$m×50 $\mu$m. The lateral resolution of the AFM is limited by the size of the tip that is used to scan the surface. The geometry of an AFM tip is sketched in Fig. 3.9. Silicon tips (Mikromasch NSC15/100) with a radius $r$ of $\approx 10$ nm and a cone angle $\Phi$ of $\approx 10^\circ$, as specified by the manufacturer, are used. This means that the lateral resolution of the AFM images is of the order of 10 nm whereas atomic resolution is achieved for the surface height. The cone angle $\Phi$ limits the maximum slope that can be imaged to approximately $80^\circ$. All surfaces discussed in this work have maximum slopes that are much smaller than the limit set by the AFM tip geometry. This means that for these surfaces no tip effects are expected on length scales that are significantly larger than the tip radius.

The power spectral density of a surface can be calculated directly from the
AFM data for the surface height according to Eq. (2.1). This is done by using a Fast Fourier Transform algorithm. This results in a 512×512 points matrix representing the two-dimensional PSD of the surface at the discrete values of the wavevector \( \vec{q} \), with the smallest \( q \)-values in the center of the matrix. For one-dimensional plots of the PSDs as shown in Chapter 4, lines of data are extracted from this matrix which run through the center of the matrix and along the direction of interest. In the case of isotropic roughness, as it is found for chlorine etched surfaces, lines are extracted along all directions and then averaged. In the case of anisotropic PSDs, as in the case of MBE grown surfaces, lines are extracted and averaged in a fan of ±5° around the direction of interest. Because of the effects of the finite size of the tip on the images as described above, the PSDs are only deemed reliable for wavevectors \( q \leq 200 \mu m^{-1} \) corresponding to a length scale of 30 nm and the plotting range is restricted to these values of \( q \). On the other end of the scale, the accessible \( q \)-range is limited fundamentally by the maximum scan size. Practically, for large scale AFM scans, a long wavelength image distortion is caused by the way that the piezoelectric controllers move the sample during the scan. A flattening algorithm can be applied to correct for this distortion but nevertheless the lower cutoff for \( q \) to obtain reliable PSDs is \( \approx 1 \mu m^{-1} \) corresponding to a length scale of 6 \( \mu m \). To access the full range of length scales and to improve the statistics, PSDs are obtained by superimposing the PSDs obtained from a series of AFM scans of a sample with different scan sizes, typically consisting of a 2 \( \mu m \times 2 \mu m \), a 5 \( \mu m \times 5 \mu m \), a 10 \( \mu m \times 10 \mu m \) and a 20 \( \mu m \times 20 \mu m \) scan.

### 3.3.2 Light scattering and diffraction

Light scattering and diffraction experiments were carried out to monitor surface roughness in real time during etching and growth. For the surfaces used in this work the surface roughness is much smaller than the wavelength of the light used in the experiment, and in this case the differential intensity \( dI \) scattered into the solid angle element \( d\Omega \) is given by [15]:

\[
\frac{dI}{I_0 d\Omega} = 4 \left( \frac{\omega}{c} \right)^4 \cos \theta_i \cos^2 \theta_s Q_P(\theta_i, \theta_s, \phi_s) P(\vec{q})
\]  

(3.3)

where \( I_0 \) is the intensity of the incident light, \( \omega \) is the the angular frequency of the light, \( c \) is the speed of light and \( P \) is the power spectral density as before. The angles are defined in Fig. 3.10, and the subscripts \( i \) and \( s \) refer to incident
Figure 3.10: Definition of the scattering angles used in Eq. (3.3). This figure is taken from Ref. [64].

and scattered radiation respectively. The factor of $Q_p$ in (3.3) depends on the polarization of the incident and scattered light and explicit expressions are given in Appendix B of Ref. [15]. The argument of the power spectral density is the momentum transfer in the plane of the surface, $\bar{q} = \vec{k}_{s,||} - \vec{k}_{i,||}$ where $\vec{k}_{s,||}$ and $\vec{k}_{i,||}$ are the components of the wavevector of the incident and scattered light parallel to the surface. It is determined by the scattering geometry and the wavelength of the light. The most important consequence of Eq. (3.3) is that the scattered intensity is directly proportional to the value of the power spectral density at a wavevector equal to the lateral momentum transfer.

For light scattering measurements during etching, light from a He:Ne laser (Uniphase 1125P) which delivers 10 mW of power at a wavelength of $\lambda = 633$ nm was incident on the sample through one of ports A to C (see Fig. 3.4) and the scattered intensity was measured through another port with a photomultiplier tube (Hamamatsu R955). The different port configurations and the corresponding momentum transfers are listed in Table 3.2. The polarization of the incident beam is a superposition of s- and p-polarization. To improve the signal to noise ratio, the incident beam was chopped (typically
Table 3.2: Port configuration and corresponding momentum transfer for the light scattering experiments.

<table>
<thead>
<tr>
<th>Input Port</th>
<th>Detection Port</th>
<th>Momentum Transfer (μm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>A</td>
<td>16</td>
</tr>
<tr>
<td>C</td>
<td>A</td>
<td>9</td>
</tr>
<tr>
<td>C</td>
<td>B</td>
<td>6</td>
</tr>
</tbody>
</table>

with a frequency of ≈ 250 Hz) and the modulated signal was detected using a lock-in amplifier. An adjustable aperture was used in the path of the incident beam after the last mirror to minimize the amount of light scattered from optical elements. The diameter of the laser beam is ≈ 5 mm and since no focussing was used on the incident beam this was also the spot size on the sample. A 1 inch diameter lens with a focal length of 10 cm was used on the detection port to collect the scattered light and focus it on the detector aperture. The detector was fitted with a 10 nm wide line filter around 633 nm to protect it from the room light.

Just as for the specular reflection discussed in the previous section, interference fringes can be observed in the light scattering signal during the etching or growth of multilayer structures. These fringes are found to be out of phase with the fringes in the specular reflectivity. A simple theory for this phenomenon as well as a derivation of Eq. (3.3) for the case of scattering of s-polarized light using a Green’s function approach are presented in Appendix B.

During the etching of samples with microfabricated surface gratings, the intensity of the first-order diffraction was measured. The same He:Ne laser as for the scattering experiments was used on port B. Since the grating period was relatively large (3 μm pitch), the first-order diffraction was close to the specular reflection and it was possible to align the input beam so that the diffracted beam could be detected on the “specular port” D. As for the light scattering measurements, the beam was chopped and the diffraction was detected using a silicon photodiode and a lock-in amplifier. Care was taken to not saturate the photodiode and the linearity was checked by inserting neutral density filters into the path of the beam. Diffraction from a grating is just a special case of light scattering from a periodic surface. The PSD of the grating consists of a series of discrete peaks at multiples of the wavevector...
that corresponds to the grating period. Equation (3.3) then means that the measured diffracted intensity is proportional to the square of the first coefficient of the Fourier expansion of the grating height profile.

3.4 Sample Preparation

3.4.1 Smooth and randomly rough surfaces

The combination of the etch chamber with the MBE system allows one to prepare clean surfaces for etching and growth with the standard methods used for MBE crystal growth. The wafers used for the work presented in this thesis are either mechanical grade or epi-ready (001)-oriented, on-axis (± 0.5°) GaAs substrates. The only preparation necessary prior to growth on these samples is the removal of the native surface oxide; however, it is common to apply a UV-ozone treatment that improves the substrate/buffer layer interface quality by trapping contaminants in a thicker oxide layer that is subsequently removed. For this treatment the sample surface is exposed to UV radiation from a nearby Hg vapor bulb for approximately 10 minutes. The setup is described in [44].

Two common ways of removing the surface oxide in the MBE growth chamber prior to growth are atomic hydrogen etching and thermal desorption of the oxide. Hydrogen is supplied to the sample through a nitrogen plasma source installed on the chamber for the growth of dilute nitride films. For hydrogen etching the source is simply used as a convenient way to feed hydrogen gas into the growth chamber. By opening the leak valve for the hydrogen, the chamber is brought to a pressure of $1.5 \times 10^{-6}$ mbar as measured with the growth chamber ion gauge. A tungsten filament is brought into close proximity of the sample and resistively heated to $\approx 1800^\circ C$ to crack the hydrogen molecules. During the hydrogen etch the sample is heated to approximately $200^\circ C$. The oxide is typically removed from the surface within less than 10 min. This can be monitored by observing the appearance of a streaky reflection high energy electron diffraction (RHEED) pattern, corresponding to an oxide free, smooth surface. An AFM image of a H-etched substrate is shown in Fig. 3.11 on the left. The surface is very smooth and almost featureless with a RMS roughness of only 0.23 nm.

Alternatively, the oxide can be removed by thermal desorption, which is still the most common GaAs substrate preparation due to its simplicity. In
Chapter 3. Experimental Method

Figure 3.11: 5 μm×5 μm AFM images of GaAs surfaces after removal of the native oxide. The left image shows a H-etched substrate which has a RMS roughness of 0.23 nm and the right image shows a surface after thermal desorption of the oxide. Its RMS roughness is 5.2 nm. The gray scale is 2 nm for the left image and 20 nm for the right image (full scale from black to white).

In this case the substrate is heated to ≈620°C (measured by DRS as described in Section 3.2.2) for a period of 5-10 minutes with a flux of arsenic on the surface. The flux of arsenic (As₂ produced by a standard valved cracker source) is necessary to avoid the formation of gallium droplets on the surface due to the evaporative loss of arsenic. It is the same as is used under typical growth conditions, i.e. between 3-10 monolayers per second. A substrate after thermal oxide desorption is shown on the right side of Fig. 3.11. The desorption of the oxide causes significantly more roughness than the H-etch, in fact at 5.2 nm the RMS roughness is more than 20 times higher than that of the H-etched sample. The surface morphology exhibits characteristic pits with diameters of up to 500 nm and depths of up to 30 nm. The roughness that develops during thermal desorption depends on the amount of surface oxide. The sample in Fig. 3.11 was treated with UV-ozone as described above but untreated surfaces show significantly less roughness after desorption. From the point of view of surface morphology studies during growth or etching, the two methods for removing the oxide provide a simple means of creating distinctly different starting surfaces, the H-etched one being almost atomically...
Table 3.3: Recipe for contact photolithography.

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Spin on photoresist (type AZ 4110) at 9000 rpm for 60 seconds, let dry for 30 min</td>
</tr>
<tr>
<td>2</td>
<td>Cover center area of sample, where the pattern should be written, with a piece of silicon and expose in mask aligner for 60 s.</td>
</tr>
<tr>
<td>3</td>
<td>Develop the exposed edges in mixture of H₂O:AZ400K developer=3:1 ( \text{takes} \approx 15 \text{ sec} ), rinse with H₂O and blow dry with N₂</td>
</tr>
<tr>
<td>4</td>
<td>Softbake on hot plate at 100°C for 10 min</td>
</tr>
<tr>
<td>5</td>
<td>Expose photoresist for 30 sec in mask aligner with grating mask in contact</td>
</tr>
<tr>
<td>6</td>
<td>Develop the pattern in mixture of H₂O:AZ400K developer=3:1 ( \text{takes} \approx 2 \text{ min} ), rinse with water and blow dry with N₂</td>
</tr>
</tbody>
</table>

...and the thermally desorbed one randomly rough.

### 3.4.2 Grating fabrication

Surfaces patterned with microfabricated gratings are used to study the shape evolution during growth and etching discussed in Chapter 5. Gratings with a pitch of 3 μm and a peak to peak amplitude of 100 nm were fabricated by standard contact lithography and wet etching. The detailed fabrication steps for the lithography and the wet etching are given in Tables 3.3 and 3.4 respectively. Contact lithography is generally limited to feature sizes greater than \( \approx 1 \) μm, and the duty cycle of the gratings was found to vary between 30% and 50% from run to run. The wet etching solution (step 1 of Table 3.4) is a commonly used mixture for GaAs processing. Steps 4-6 of the wet etching recipe are surface cleaning steps: In step 4 a thin sacrificial surface layer is etched away, in step 5 the surface is oxidized and in step 6 this surface oxide is dissolved in H₂SO₄ which also removes organic residues left on the surface. The surface can be observed to change from hydrophobic to hydrophilic after the H₂SO₄ dip. This makes the blow drying with nitrogen much easier since there is no formation of water droplets which are hard to remove.

A 3D view of a 20μm×20μm AFM image of a grating fabricated according to this recipe is shown in Fig. 3.12. The shape of the ridges is trapezoidal and independent of the orientation of the grating with respect to the crystal axes. The sidewalls are at an angle of 25°±5° to the flat sections as measured by the...
Table 3.4: Recipe for wet etching and surface cleaning.

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mix wet etching solution: 75 ml H₂O, 2 ml concentrated H₂SO₄, 2 ml H₂O₂ (30%), use immediately</td>
</tr>
<tr>
<td>2</td>
<td>Dip sample into etching solution under slight agitation, etch depth ≈ 100 nm in 30 s, rinse with H₂O</td>
</tr>
<tr>
<td>3</td>
<td>Remove photoresist with acetone and methanol, rinse with H₂O</td>
</tr>
<tr>
<td>4</td>
<td>Dip sample into above etching solution for 1 s, rinse with H₂O</td>
</tr>
<tr>
<td>5</td>
<td>UV-ozone treatment for 10 min, as described in previous section.</td>
</tr>
<tr>
<td>6</td>
<td>Dip sample into conc. H₂SO₄ for 30 s, rinse with H₂O</td>
</tr>
</tbody>
</table>

Figure 3.12: AFM image of a microfabricated grating made by photolithography and wet etching as described in the text in a 3D view. The pitch of the grating is 3 μm and the peak to peak amplitude is 100 nm.

AFM. This does not correspond to a low index crystal plane that might be expected to become exposed in the wet etch. At such low angles, however, no artifacts are expected from the AFM other than a rounding off of the corners and the slopes are therefore believed to be measured correctly. It is well known that the etching reaction can become diffusion-controlled for high etch rates, causing a drastic change of the etch profiles [26]. A reason for the formation of these low angle sidewalls may therefore be that the wet etching occurs in an intermediate regime between kinetically and diffusion controlled etching.

Two-dimensional square gratings were fabricated in the same way as the one-dimensional ones by double exposure of the photoresist with a 5 μm pitch grating mask which was rotated by 90° for the second exposure. This way a two-dimensional array of 100 nm high, 2 μm×2 μm squares with slightly
rounded corners was produced. This was done for two orientations, with the sides of the squares along the [110] and [110] directions and along the [100] and [010] directions. An optical micrograph of a 2D grating is shown in Fig. 3.13.

In addition, a limited supply of gratings with a pitch of 300 nm fabricated by UV holography at McMaster University by Brad Robinson were available. These were shipped to UBC with a patterned photoresist mask and then wet etched by the author according to the recipe of Table 3.4; however, due to the small pitch, the achievable etch depth is only approximately 40 nm and the etch time was changed accordingly.

After the wet etching procedure the patterned samples are brought into the growth chamber and the surface oxide that may have formed after the processing is removed by an H-etch in the case of successive etching experiments and by thermal desorption for successive growth.
Chapter 4

Roughness Evolution

Results of AFM and light scattering studies of surface morphology evolution during MBE growth and thermal chlorine etching of GaAs are presented and compared to the theory of kinetic roughening described in Section 2.2. In both cases the theory is found to give an excellent quantitative description of the evolution of smooth and randomly rough surfaces. The first section is a brief discussion of the results on MBE grown surfaces which are very well described by the KPZ equation. This was first published by Anders Ballestad et al. [3] as an alternate explanation for mound formation during growth which had previously been attributed to unstable growth [32]. A more extensive study was carried out subsequently to which the author contributed experimental results and which confirmed that the KPZ equation is a better fit to the observed morphology than the so-called MBE equation [4].

The central part of the chapter is the application of kinetic roughening theory to thermal chlorine etched surfaces. For this the KPZ equation has to be extended to include the fourth order linear term. It is found that with this extension the equation gives an excellent fit to both the roughening of initially flat surfaces and the smoothing of randomly rough surfaces during etching. The main results presented in this section were originally published in Refs. [66, 67].

4.1 MBE Growth

4.1.1 KPZ equation for GaAs growth

The morphology of MBE grown films is strikingly different for growth on H-etched and thermally desorbed surfaces. This can be seen in Fig. 4.1 which shows two 10 µm×10 µm AFM images of a 500 nm thick film grown on a H-etched surface (left) and a 1.2 µm thick film grown on a thermally desorbed surface (right). Both films were grown at a substrate temperature of 550°C and with an As/Ga flux ratio of approximately 5. The corresponding
Figure 4.1: $10 \mu m \times 10 \mu m$ AFM images of MBE grown GaAs films. The left image shows a 500 nm thick film grown on a H-etched substrate with a RMS roughness of 0.19 nm and the right image is a 1.2 $\mu m$ thick film grown on a thermally desorbed surface with a RMS roughness of 1.0 nm. The gray scale is 2 nm for the left image and 5 nm for the right image.

Figure 4.2: Numerical simulations of the grown films in Fig 4.1. The images are obtained by a numerical solution of the KPZ equation using the surfaces shown in Fig. 3.11 as a starting condition. The parameters are given in the text and the gray scales are the same as for Fig. 4.1.
starting surfaces are shown in Fig. 3.11. In both cases the RMS roughness decreases during growth, but in the case of the thermally desorbed substrate, the formation of characteristic mounds is observed. These mounds have an amplitude of several nanometers and a typical spacing of several micrometers, comparable to the spacing of the largest pits on the thermally desorbed surfaces. This suggests that the mounds are remnants of the rough starting surface.

In fact, good reproductions of the surface morphology can be obtained by numerically solving the KPZ equation (2.33) using AFM images of the starting surfaces such as the ones shown in Fig. 3.11 as initial conditions. Two simulations corresponding to the experimental surfaces of Fig. 4.1 are shown in Fig. 4.2. The code used to generate these images uses a finite-difference algorithm to solve the KPZ equation and was written by Anders Ballestad and Ben Ruck. Details on the numerical implementation can be found in [4]. The code allows for an asymmetry of the coefficient $\nu$, i.e. the $\nu$-term (2.21) is written as $\nu_x \frac{\partial h}{\partial x^2} + \nu_y \frac{\partial h}{\partial y^2}$, where $x$ and $y$ correspond to the [110] and the [110] directions respectively, whereas the coefficient $\lambda$ has to be isotropic. To simulate the effect of the random fluctuations $\eta$ on the morphology, a matrix of random numbers from a uniform distribution is generated and added to the surface at each time step. Although the amplitude of the expected noise, i.e. the width of the distribution, is fixed by relation (2.27), a fitting parameter $\Gamma$ is used to multiply the expected amplitude. For noise according to (2.27), $\Gamma = 1$. The parameters used for the simulations in Fig. 4.2 are $\nu_x = 10 \text{ nm}^2/\text{s}$, $\nu_y = 1 \text{ nm}^2/\text{s}$, $\lambda = 12 \text{ nm/s}$ and $\Gamma = 10$.

The reason for the formation of mounds in the simulation on a thermally desorbed substrate is the outward growth of surface features as discussed in Section 2.2 and illustrated in Fig. 2.3. On the H-etched surfaces there are no surface features initially present that can develop into mounds by outward growth. It has also been shown in [4] that the time dependence of the power spectral density can be fitted well with the KPZ equation using the parameters given above. This is illustrated for the case of the thermally desorbed surfaces in Fig. 4.3 in which experimental PSDs obtained from AFM images are compared with PSDs obtained from simulated images such as the ones in Fig. 4.2 (solid lines). The PSD of the initial, thermally desorbed surface has a pronounced peak at a wavevector of $\approx 5 \mu\text{m}^{-1}$ corresponding to the average spacing between the pits. During growth the PSD decreases at all length scales and reaches an equilibrium value for large wavevectors corresponding
Figure 4.3: Power spectral density of GaAs films grown on thermally desorbed surfaces obtained from AFM images as a function of wavevector for three growth times and for two crystal directions. The numerically simulated PSDs (solid black lines) are obtained from surface images of simulations of the KPZ equation using AFM images as the initial condition. The dotted vertical lines indicate the wavevector corresponding to the correlation length. Originally published in [4].
to length scales shorter than the correlation length. The correlation length for the two growth times is indicated in Fig. 4.3 as dashed lines. As indicated in the figure, for long wavevectors the PSD decays as $q^{-2}$. According to Table 2.1 and Eq. (2.8) this is the behavior expected for the Edwards-Wilkinson equation whereas a decay $\propto q^{-2.8}$ would be expected for the KPZ equation. The reason for this is that at short length scales, where the surface roughness is small, the nonlinear term is unimportant. In fact, it can be shown that the nonlinearity only becomes dominant if the RMS roughness is larger than $2\nu/\lambda$ [54].

It is interesting to note that a pure scaling analysis as is very commonly done to analyze morphology evolution would therefore lead one to conclude that the KPZ equation is not the correct equation to describe MBE growth. This shows that the comparison of experimental and simulated surface images and PSDs as a function of growth time is a more reliable way to analyze morphology data than a scaling analysis.

Good fits of the simulations to the data can be obtained for a range of the parameters $\nu$, $\lambda$ and $\Gamma$; however, for any reasonable fit $\lambda > F$ (the experimental growth rate is $F = 0.2$ nm/s) and $\Gamma > 1$. This rules out the simple physical interpretation of the KPZ-term as growth along the local surface normal and of the noise term as shot noise from the flux.

### 4.1.2 Effect of surfactants on the growth of AlGaAs

In addition to the adjustment of growth conditions, surfactants can be used to alter the morphology of growing surfaces. For GaAs growth it was found by C. Lavoie et al. [45] that significantly smoother surfaces can be obtained at a growth temperature of 590°C when a flux of indium is incident on the surface. This substrate temperature is high enough that only a small amount of indium is incorporated into the films (InGaAs alloy films are typically grown at 500°C or less for this reason). Bismuth has been shown to have a surfactant effect on the growth of GaNAs and InGaNAs films at a much lower substrate temperature of 460°C [78]. In this section it is shown that both indium and bismuth also act as surfactants during the growth of AlGaAs.

In Fig. 4.4 three 5×5 μm AFM images of 780 nm thick Al$_{0.3}$Ga$_{0.7}$As layers grown on thermally desorbed substrates at a temperature of 600°C are shown. The left image shows a film grown with no surfactant. This film exhibits strongly anisotropic roughness with surface features elongated along the [110] crystal direction. At 4.3 nm, the RMS roughness is large compared to GaAs.
Figure 4.4: 5×5 μm AFM images of Al$_{0.3}$Ga$_{0.7}$As films grown with no surfactant (left), with indium as a surfactant (center) and with bismuth as a surfactant (right). The corresponding RMS roughness of these films is 4.3 nm (no surfactant), 0.18 nm (In surfactant) and 0.49 nm (Bi surfactant) and the gray scales of the images are 16 nm, 0.8 nm and 3 nm respectively.

Films grown under similar conditions. In the middle image a film grown under the same conditions but with a concurrent indium flux corresponding to a beam equivalent pressure (BEP) of 1.8×10$^{-7}$ mbar is shown. In this case the RMS roughness is 0.18 nm and atomic steps can be seen on the surface. The anisotropy of the morphology is also reduced significantly. Larger scale AFM images of the same sample show line defects on the surface which may originate from the formation of dislocations due to the strain of the AlGaAs film. High resolution X-ray diffraction measurements show that the difference between the lattice constants of the GaAs substrate and the film in the growth direction is approximately three times larger than when no indium surfactant is used. This difference corresponds to an incorporation of indium into the crystal at a level of 1% (approximately 10% of the indium that is incident on the surface). The additional strain caused by the indium incorporation may cause the film to strain relax. The image on the right shows an AlGaAs film grown with a concurrent flux of bismuth with a BEP of 1.7×10$^{-6}$ mbar. The RMS roughness of this film is 0.49 nm, larger than for the indium surfactant but still almost a factor of ten lower than without a surfactant. A similar anisotropy as in the case of no surfactant is observed.
X-ray measurements show no measureable incorporation of bismuth into the film.

The use of bismuth as a surfactant also leads to an improvement of the electronic quality of the grown material. This is demonstrated in Fig. 4.5 which shows room temperature photoluminescence (PL) from a 6.5 nm thick GaAs quantum well sandwiched between two 400 nm thick layers of Al$_{0.3}$Ga$_{0.7}$As. The experimental setup for the PL measurement has been described in [1]. For the structure grown with a bismuth flux of the same magnitude as above, the emitted intensity is larger by a factor of two, whereas the spectral width is unchanged. This is comparable to the improvement that is observed in the PL of InGaNAs quantum wells embedded in GaAs when grown with Bi as a surfactant [78].

There are various possible explanations for the observed effects of surfactants on the growth process. The presence of surfactant atoms on the surface changes the surface free energy and the diffusion constant of adatoms. This changes the smoothing coefficients of the growth equation (2.33). Furthermore, the incorporation of impurity atoms from the background gas in the growth chamber may be reduced due to a lowering of their sticking coefficients. This could be an especially large effect in the case of AlGaAs due to
the high reactivity of the Al atoms with oxygen which means that the sticking coefficient for impurities is intrinsically large and likewise for InGaNAs which is grown at a comparatively low substrate temperature. A lower number of impurities would explain the improvement of the PL. It is also possible that the incorporation of impurity atoms contributes to the noise term in the growth equation since the crystal structure is perturbed in the vicinity of an impurity atom which could lead to local surface roughening during successive growth. It is noteworthy that the observed effects of the surfactants such as reduced surface roughness, formation of larger atomic terraces and decreased sticking coefficients for impurities can also be expected at higher substrate temperatures. It could therefore be said that the use of a surfactant increases the effective substrate temperature during growth.

4.2 Thermal Chlorine Etching

4.2.1 Morphological phase transition

During thermal Cl$_2$ etching, GaAs surfaces can become visibly rough or remain smooth depending on the substrate temperature and the Cl$_2$ pressure. This was first observed by optical microscopy by Furuhata et al. [25]. In their work they found that, after etching at a pressure of $5 \times 10^{-4}$ mbar, a mirrorlike surface was obtained for a substrate temperature of 300°C but a rough morphology resulted from etching at 150°C and 500°C.

The transition from smooth to rough etching can be observed by in-situ light scattering measurements. Randomly rough samples were prepared by thermal oxide desorption in the growth chamber as described in Section 3.4.1 and then moved into the etch chamber. The substrate temperature was brought to 200°C and etching was initiated by opening the Cl$_2$ leak valve until the chamber pressure reached the desired value. During the etch the light scattering signal at 16 $\mu$m$^{-1}$ was recorded. The substrate temperature was then slowly ramped up to 500°C over a period of 40 minutes while keeping the Cl$_2$ pressure constant. The light scattering signal for an etch at a pressure of $6 \times 10^{-5}$ mbar is shown in Fig. 4.6. After the start of the etch, the scattered intensity decreases at first until it reaches a background level after $\approx 5$ min of etching. This decrease will be discussed in Section 4.2.3. The scattered intensity remains at the background level until the substrate temperature reaches 420°C (after 37 minutes of etching) where there is a
very sharp onset of surface roughening. The surface roughness continues to increase until it stabilizes at a high level at a substrate temperature of 500°C.

This measurement shows that, at the given pressure, a smooth surface after etching can only be obtained for substrate temperatures lower than 420°C. The same measurement was carried out at different pressures and in each case a similar sharp onset of surface roughening is observed at a substrate temperature that depends on the pressure. This way a phase diagram for rough and smooth etching can be obtained which is shown in Fig. 4.7. In general, the onset of surface roughening occurs at higher temperatures for lower pressures. Although no attempt was made to correlate the surface roughening with the etch rate in these measurements, the transition from smooth to rough etching occurs in the same temperature range as the transition from the temperature independent to the exponentially increasing etch rate (regions II and III in Fig. 3.1 respectively). Su et al. found that this transition also occurs at lower temperatures for higher pressures (see Fig. 22 in Ref. [76]). Similarly, the roughness of surfaces found after etching at 150°C may be related to the fact that the etch rate is also exponentially increasing with temperature in this range (region I in Fig. 3.1). The emerging picture is that smooth surfaces can only be obtained by etching in temperature region
Figure 4.7: Phase diagram for rough and smooth etching obtained from light scattering measurements such as the one shown in Fig. 4.6.

II where the etch rate is independent of temperature.

Fig. 4.8 shows a scanning electron microscope (SEM) image of a rough surface after etching. It appears that the surface is covered with a layer of porous material. A possible explanation is that there is an imbalance of the reaction or desorption rates between the Ga-containing and the As-containing species in the temperature regions where roughness is observed. This leads to the formation of a non-stoichiometric surface layer during the etch as described by Balooch et al. [6]. If this layer is porous, as the SEM image indicates, the etching can continue through this layer and the slowly reacting species can accumulate on the surface thus causing the surface roughening; however, x-ray photoelectron spectroscopy (XPS) measurements on a rough sample failed to provide clear evidence for a depletion of the surface of one of the constituents of the crystal.

4.2.2 Roughening of initially smooth surfaces

Surfaces etched under the “smooth conditions” as described in the preceding section look mirrorlike, i.e. no surface roughness is detectable by eye; however, AFM measurements reveal that the surface roughness does increase during etching. This surface roughness is intrinsic in the sense that it cannot
be reduced by changing the etch conditions. The surface height fluctuations associated with this roughness can therefore be considered a fundamental limitation to one's ability to control the etch depth. In this section the surface roughness is characterized quantitatively and compared to the predictions of kinetic roughening theory. To observe this roughening it is essential that the starting surface be as smooth and clean as possible. This was achieved by using MBE grown films that were transferred into the etch chamber directly after growth without intermediate exposure to air.

Fig. 4.9 shows the PSDs of surfaces etched at a substrate temperature of 200°C and a pressure of $1.3 \times 10^{-4}$ mbar for two etch times. The dashed-dotted line shows the starting condition which is a 500 nm thick film grown on an H-etched substrate (see Fig. 4.1 for an AFM image of this surface$^1$). There is a slight crystallographic anisotropy in the PSD of the grown starting condition.

$^1$In each case the etch depth is smaller than the thickness of the grown film to avoid artifacts that could result from etching through the interface between the substrate and the epi-layer. Therefore a thicker film (2 μm) was used as the starting condition for the longer etch and its simulation. Its PSD is very similar to the starting PSD of Fig. 4.9.
Figure 4.9: PSDs of surface after 1 min and after 30 min of etching compared to numerical simulations based on Eq. (2.33). The starting surface is a buffer layer grown on a H-etched substrate.
surface (see Fig. 11 in [4]). The PSD shown in Fig. 4.9 is averaged over the [110] and the [110] directions. After 1 minute of etching, the surface has become significantly rougher on short length scales but has hardly changed for spatial frequencies smaller than about 10 µm\(^{-1}\). After 30 minutes of etching, the sample is much rougher at large length scales whereas for spatial frequencies of more than 80 µm\(^{-1}\) the PSD has remained unchanged from the 1 minute long etch. This behavior is analogous to the theoretical PSDs shown in Fig. 2.2. The limiting slope at large spatial frequencies of the PSD on a log-log plot is close to -4, indicating that the fourth order linear term is the dominant term in an evolution equation describing the etch at these length scales. The simplest equation (i.e. the shortest truncation of the expansion (2.34)) that can describe the surface evolution is then Eq. (2.33). PSDs obtained from numerical simulations of this equation are plotted in Fig. 4.9 alongside the experimentally measured PSDs. The simulations are based on a finite-difference integration of Eq. (2.33) using AFM images of the starting surface as the initial condition. The code used for these simulations is a modified version of the KPZ-code discussed in Section 4.1. The match between the simulations and the experimental data is excellent for both etch times over the entire range of wavevectors probed by the AFM measurements. The parameters used for the simulations are \(\nu = 4\) nm\(^2\)/s, \(\lambda = -1\) nm/s, \(K = 600\) nm\(^4\)/s and \(\Gamma = 12\) where \(\Gamma\) is the multiplier to the noise amplitude as discussed in the previous section on MBE growth.

Experimental AFM images and surface images obtained from numerical simulations corresponding to the PSDs shown in Fig. 4.9 are compared in Figs. 4.10 and 4.11. No anisotropy is observed in the experimental data justifying the directional averaging of the PSDs in Fig. 4.9. After the 1 minute long etch the surface is dominated by short length scale roughness. The visibly dominant length scale of the image corresponds to the knee in the PSD which is given by the correlation length. After 30 minutes of etching the correlation length is larger and this leads to a longer length scale for the roughness in Fig. 4.11. The simulation of the 30 minute etch (Fig. 4.11, right) shows slightly more roughness at long length scales than the AFM image. This is also visible in the PSDs of Fig. 4.9.

The parameter \(\lambda\) used in the simulations is fixed to the etch rate of \(-1\) nm/s, as theoretically expected for etching that proceeds along the local surface normal; however, as mentioned in the previous section, the nonlinear term in Eq. (2.33) only plays a dominant role in the morphology evolution if the RMS roughness is larger than \(2\nu/\lambda = 8\) nm. For all the etched surfaces
Figure 4.10: Left: $5 \mu m \times 5 \mu m$ AFM image of a surface etched for 1 min (corresponding to the PSD shown in Fig 4.9). Right: Numerically simulated surface according to Eq. (2.33). The RMS roughness is 0.5 nm and the gray scale for both pictures is 1.4 nm.

Figure 4.11: Same as Fig. 4.10 for a 30 min long etch. The RMS roughness is 0.8 nm and the gray scale is 3 nm. The simulation has the same parameters as in Fig. 4.10 except for the etch time.
Figure 4.12: Comparison of the PSDs obtained from a numerical simulation of the nonlinear equation (2.33) for a 30 min long etch and the analytical solution (2.30) for the purely linear model Eq. (2.24) with the same noise amplitude $\Gamma$ and coefficients for the linear terms $\nu$ and $K$. 
discussed in this section the RMS roughness is smaller than 8 nm. This means that the effect of adding the nonlinear term to the equation is negligible. This is demonstrated in Fig. 4.12 which compares the simulated PSD of the 30 minute etch from Fig. 4.9 to the exact solution for the PSD for the linear equation according to Eq. (2.30). The nonlinear simulation and the linear theory match almost perfectly for all but the shortest wavevectors.

Etch experiments were also carried out using the mounded surfaces that result from growth on thermally cleaned substrates as a starting condition. An AFM image of a mounded surface after 10 minutes of etching is shown on the left side in Fig. 4.13. The remnants of the mounds are still clearly visible in the AFM image. It is remarkable that the mound pattern which has an amplitude of only ≈3 nm can be retained over an etch depth of ≈600 nm. On shorter length scales the AFM image shows the same increasing roughness that was found for the etches on flat substrates. A numerical simulation that was carried out in the same way and with the same parameters as described above, but with a mounded surface as the initial condition, is shown on the right side of Fig. 4.13. The resulting surface looks very similar to the AFM image, showing both the increased short length scale roughness and the mound structure on longer length scales. In fact, the AFM image shown on
Figure 4.14: Comparison of the PSDs from the experimental and simulated images shown in Fig. 4.13. The large broad peak at small wavevectors corresponds to the mounds on the surface.

The right side in Fig. 4.1 was used as the initial condition for this simulation and it can be seen that the original mound structure is still retained on the surface. The different direction of elongation of the mounds in Fig. 4.13 is due to the fact that the sample orientation was different for the two AFM scans whereas the mounds are always elongated along the [110] direction.

The PSDs of the mounded surfaces are shown in Fig. 4.14. As discussed in Section 4.1 the mounds cause a characteristic peak in the PSD at small wavevectors \((q \approx 20 \mu m^{-1})\) which is visible in all of the PSDs. After 10 minutes of etching the peak due to the mounds is unchanged whereas there is a significant increase in the PSD for large wavevectors. The shape of the PSD for large wavevectors is identical to the PSDs of the etched surfaces using a flat starting condition shown in Fig. 4.9. The match between experiment and simulation is excellent.
Figure 4.15: Bottom: AFM scan line of a rough surface obtained by the thermal oxide desorption process. Middle: Numerical simulation of a 20 min long etch according to Eq. (2.33) using the profile below as the initial condition. Top: AFM scan line of a thermally desorbed surface after a 20 min long etch. The scan lines are offset for clarity.

4.2.3 Smoothing of randomly rough surfaces

Kinetic roughening theory predicts that surfaces that are etched for a long time reach a steady state roughness or constant PSD independent of the initial condition. Therefore a surface that is initially rougher than this steady roughness should become smoother during etching. It is interesting to check this prediction and investigate the evolution of initially rough surfaces during etching. Rough starting surfaces can be prepared by thermal oxide desorption as described in Section 3.4.1. After the desorption process was carried out in the MBE growth chamber, the samples were transferred into the etch chamber.

Surface profiles that demonstrate the evolution of the rough surfaces are shown in Fig. 4.15. An AFM scan line of the thermally desorbed starting surface is plotted on the bottom. It shows the profiles of the desorption
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Figure 4.16: PSDs of the surfaces corresponding to the scan lines shown in Fig. 4.15. The three curves are for a thermally desorbed substrate, a surface after a 20 min long etch and a numerical simulation of the 20 min etch.

pits that are visible in Fig. 3.11 (right hand side image). This scan line was used as a starting condition to simulate the surface evolution according to Eq. (2.33) numerically, with the same parameters as for the kinetic roughening simulations. The result of the simulation of a 20 minute etch is plotted in Fig. 4.15 above the initial condition. Clearly, evolution according to Eq. (2.33) causes the randomly rough surface to become smoother. The amplitude of the deepest desorption pits has decreased to less than half of the initial value while their widths have increased significantly. The scanline shown at the top of Fig. 4.15 is experimental data taken from the AFM image of a rough surface after a 20 minute etch. The same smoothing effect as discussed for the simulated profile is visible in the data. In fact, the experimental and simulated profiles look strikingly similar by eye. The similarity of the experimental and simulated profiles shown in Fig. 4.15 translates into good agreement between their respective PSDs, as shown in Fig. 4.16.

The roughness of the thermally desorbed surfaces can be monitored as
Figure 4.17: Light scattering measurements of the surface smoothing during etching for three values of the wavevector $q$ compared to simulated signals using Eq. (2.33) (dashed lines).
a function of time during etching by elastic light scattering measurements. According to Eq. (3.3) light scattering measures the PSD at a wavevector $q$ given by the lateral momentum transfer. A purely exponential decay with a $q$-dependent rate constant is expected for a linear evolution equation. This is a consequence of Eq. (2.30). Deviations from an exponential decay are a signature of nonlinear terms in the evolution equation. The light scattering signals for the three accessible $q$-values (see Table 3.2) are plotted on a logarithmic scale in Fig. 4.17. As expected, the surface becomes smoother at all length scales but at different rates. This is the initial smoothing that can also be seen in Fig. 4.6. Since there is a small background from light scattered inside the etch chamber, a constant background was subtracted from the data, adjusted so as to produce an exponential decay at long times when the nonlinear contributions become negligible. The dashed lines are simulations of Eq. (2.33) with the same parameters as before. Both the time and the $q$-dependence of the surface smoothing is well described by the simulations. A small deviation from the exponential decay can be observed at early times and the inclusion of the nonlinear term in the simulations does improve the fit to the data; however, the effect is quite small. The RMS roughness of the thermally desorbed starting surface is 5 nm which is significantly larger than the grown surfaces discussed in the previous section but still smaller than $2\nu/\lambda = 8$ nm where the nonlinear term is expected to become dominant.

Finally, the dependence of the smoothing rate on the substrate temperature was measured. It is typically assumed to be Arrhenius-like [7]; however, Eqs. (A.5) and (A.11) predict a more complicated behavior since the density $n$ depends on the substrate temperature.

The decay of the light scattering signal at $16 \mu m^{-1}$ shown in Fig. 4.17 can be fitted by a single exponential with a rate constant of $\tau^{-1} = 0.2$ min$^{-1}$. The same measurement was then carried out for a range of substrate temperatures and for two different Cl$_2$ pressures. The results for the smoothing rates are shown in Fig. 4.18. The lines between the data points are guides to the eye. No smoothing, i.e., a smoothing rate of zero, was measured at $140^\circ$C for a pressure of $1.3 \times 10^{-4}$ mbar and at $350^\circ$C for a pressure of $1.3 \times 10^{-5}$ Torr. These data points are indicated by the two extrapolating lines in Fig. 4.18. At both pressures the smoothing rate has a maximum which seems to be shifted to a higher temperature at the lower pressure. This shift corresponds well to the temperature shift of the phase transition from smooth to rough etching in Fig. 4.7. Since, as mentioned in Section 4.2.1, another rough phase exists at low substrate temperature, the fact that the smoothing rate has a
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Figure 4.18: Smoothing rate of randomly rough surfaces as a function of substrate temperature for two Cl₂ pressures.

maximum in between these two transition temperatures is not surprising. It confirms that at $1.3 \times 10^{-4}$ mbar, etching at a substrate temperature of $\approx 200^\circ$C results in the smoothest surface morphology.

4.3 Summary and Discussion

The comparison of AFM and light scattering data with numerical simulations of the surface evolution is a powerful tool to determine the applicability of kinetic roughening theory to a particular system and to find out which terms of the evolution equations are the essential ones on the length and time scales probed by the experiment. In particular, in the case of MBE growth it was shown that a pure scaling analysis can be misleading while in the case of thermal Cl₂ etching, the scaling behavior of the evolution equation is too complex to be measured with confidence over the restricted time and length scales that are accessible to experiments.

MBE growth of GaAs is found to be well described by the KPZ equation. To simulate the evolution during thermal Cl₂ etching the KPZ equation has
to be extended to include the fourth order linear term, yielding Eq. (2.33). Thus, both MBE growth and thermal Cl₂ etching on flat and randomly rough substrates can be modelled with good success by two of the simplest possible evolution equations discussed in Section 2.2. Considering the complexity of the growth process of the two-component GaAs system and even more so the complexity of the etching process, this is a remarkable result.

The physical interpretation of the various terms in the evolution equations has been discussed at length in Section 2.2. The values of the coefficients obtained from the fitting of experimental data raise some interesting questions. For MBE growth the nonlinear coefficient \( \lambda \) is approximately fifty times larger than the growth rate, which rules out the simple explanation arising from growth along the local surface normal. The outward growth is rather a consequence of the underlying atomistic processes that occur at the surface during film growth, namely the incorporation and release of adatoms at step edges and surface diffusion. This can be concluded both from atomistic Monte-Carlo simulations and from the coupled equations continuum models discussed in Section 2.3 [5].

For both etching and MBE growth the amplitude of the noise that has to be added in the simulations is an order of magnitude larger than expected from the fluctuations in the arrival rate of atoms from the vapor which is assumed to be Poisson distributed. This means that the noise is associated with the entire growth dynamics including all atomistic surface processes, not just the flux noise. For example, thermal fluctuations associated with repetitive attachment and detachment from step edges may contribute to the observed roughness. Furthermore, as mentioned in Section 2.2, due to thermal fluctuations the equilibrium surface at typical growth temperatures is not atomically smooth whereas the smoothing terms in Eq. (2.33) are driving the system towards a perfectly flat surface. It is plausible that this discrepancy is solved by additional noise input. Another possibility is that a number of atoms is added or removed from the surface at a time rather than individual atoms. For growth, it may be energetically favorable for the atoms to incorporate as one unit cell of the reconstructed surface at a time. For etching it has been found in a scanning tunneling microscopy study [62] that the atoms are removed in patches. As noted in [4] this changes the noise coefficient from \( D = F a_0^3 \) to \( D = n F a_0^3 \) in Eq. (2.27) where \( n \) is the number of atoms which are removed at the same time. Finally, it is possible that the noise in the rate of arriving atoms is non-Poissonian.

If the differential desorption and the surface diffusion corresponding to
the two linear terms in Eq. (2.33), were due to the chlorine on the surface, the terms would have to be negative, leading to a surface instability. Looking back at the surface chemistry of the etching reaction Eq. (3.1) it then appears logical to associate these terms with desorption and diffusion of the chlorinated etch products. For example, if these products are desorbing faster from regions with negative curvature (a peak) than from a valley, this could lead to a lower coverage of the surface with these products on the peaks than in the valleys, giving the incoming chlorine more sites to attach to, and thus increasing the etch rate. Directional diffusion towards the valleys could have the same effect, thereby leading to the required smoothing terms. In this interpretation the desorbing and diffusing species on the surface are the same and Eq. (2.23) applies. From the values of the linear coefficients used to fit the data, \( \nu = 4 \text{ nm}^2/\text{s} \) and \( K = 600 \text{ nm}^4/\text{s} \), the difference of the activation energies for desorption and diffusion can be calculated to be \( \Delta E = E_{\text{des}} - E_{\text{diff}} = 0.27 \text{ eV} \).

In spite of the success in fitting data with the stochastic equation models, from the preceding discussion one may conclude that the main weakness of these models is that little can be learned conclusively about the microscopic physics underlying the surface evolution. Questions about the presence of an Ehrlich-Schwoebel barrier, the origin of the noise, and the reason for the KPZ nonlinearity are all left to speculation. In this sense, the coupled equations models discussed in Section 2.3 and applied to the shape evolution of gratings in the following chapter are a step forward, as their physical interpretation is much clearer.
Chapter 5

Pattern Evolution

In this chapter, experimental results of the evolution of microfabricated gratings during MBE growth and thermal Cl₂ etching are shown. The evolution of the grating shapes is found to be significantly more complex than predicted by the single evolution equations described in Section 2.2 that have been applied very successfully to the evolution of flat substrates during growth and etching in the previous chapter. Therefore, the coupled equations models discussed in Section 2.3 have to be used to model the pattern evolution. The fit of the experimental shapes with these models provides significant insights into the underlying atomistic surface dynamics during growth and etching. The results on MBE growth on patterned substrates have been partly published in [5] and those on pattern evolution during Cl₂ etching in [68, 69].

5.1 MBE Growth on Patterned Substrates

AFM data on grating shapes after regrowth is shown in Figs. 5.1-5.4 as heavy lines together with numerical solutions of the noise free KPZ equation (thin lines). For the KPZ simulations trapezoidal gratings with the same dimensions as the experimental ones are used as the initial condition. The values used for the parameters ν and λ in these simulations are summarized in Table 5.1. It is obvious that the KPZ equation fits some aspects of the experimentally observed shapes but not all. The key feature of the data that is reproduced is the outward growth that leads to the formation of mounds and cusps. The KPZ fits therefore allow one to quantify in a simple way how fast this outward growth occurs, or in other words, how nonlinear the shape evolution is, as a function of the growth parameters. This is useful for predicting how fast the surface gratings decay during growth.

The shape evolution as a function of growth time (or thickness) is shown in Fig. 5.1 for gratings aligned along the [110] crystal direction. The substrate temperature is 580°C for all growths. In the early phase of the growth a rapid filling in of the lower corners of the gratings takes place. This leads
Figure 5.1: AFM line scans (heavy lines) of 3 μm pitch gratings aligned along the [110] crystal direction for different thicknesses of the overgrown GaAs film as indicated on the right side of each scan line. The thin lines are simulations using the KPZ equation. The lines are arbitrarily offset for clarity.
to the formation of concave sidewalls at intermediate growth times. The upper plateau, on the other hand, evolves into a convex shape which has a slightly pointed peak (seen most clearly for the 2 μm thick film in Fig. 5.1). The crossover point between the convex and concave regions is a corner that moves outward during growth until it disappears as two neighboring sidewalls merge together (between 2 μm and 2.6 μm of growth in Fig. 5.1). As the sidewalls merge together a sharp cusp is formed in the valley between them. None of these details is reproduced by the KPZ equation. The only way to create a concave sidewall in a KPZ simulation is by choosing a large ratio of ν/λ; however, in this linear regime the formation of a sharp cusp is precluded and a sine wave pattern is obtained instead.

A series of growths at different substrate temperatures is shown in Fig. 5.2 for two orientations of the gratings. At low substrate temperature little or no outward growth of the grating ridges is observed and the original pattern is fairly well preserved during growth. For higher temperatures the growth becomes increasingly nonlinear. At 550°C the shapes develop a strong convex curvature and for gratings along [110] the formation of secondary mounds on the lower plateau is observed (these are also visible in Fig. 5.1 at 200 nm thickness but they are much less dominant there). At 610°C the concave sidewalls described above are formed. Again it can be seen that the KPZ equation cannot reproduce all of the features of the shape evolution. The thin lines next to the starting surface in Fig. 5.2 show the initial condition used for the KPZ simulation. It has a slightly smaller duty cycle than the particular AFM scan line shown. This duty cycle is believed to be more typical of the fabricated gratings. Changing the duty cycle of the initial condition within the limits of the experimental uncertainty does not affect the analysis significantly.

A comparison of the shape evolution during growth of GaAs and AlAs is shown in Fig. 5.3. The growth rate (13 nm/min) and the V:III flux ratio (≈3) are the same for AlAs and GaAs growth. The resulting shapes after regrowth are very different for GaAs and AlAs. No significant outward growth is observed in the case of AlAs. This means in terms of the KPZ description that λ = 0 for AlAs. In this respect the growth of AlAs resembles the growth of GaAs at low substrate temperatures as shown in Fig. 5.2. As a result of this lack of outward growth, the grating amplitude of ≈100 nm is retained even after the growth of a 3 μm thick film. The fact that grating shapes are conserved during AlAs growth but wiped out during GaAs growth is also observed in metal-organic chemical vapor deposition (MOCVD) and can
Figure 5.2: AFM line scans of overgrown 5 μm pitch gratings as a function growth temperature (indicated on the right side of each line) for two orientations (heavy lines). The thin lines are KPZ simulations with the parameters indicated on the left side of each line (see also Table 5.1). The lines are arbitrarily offset for clarity.
Figure 5.3: AFM scan lines of 5 μm pitch gratings overgrown with GaAs and AlAs (heavy lines) and simulations of the KPZ equation (thin lines) with the parameters indicated on the left side of each corresponding line. The lines are arbitrarily offset for clarity.
be an important issue in the design and fabrication of distributed feedback lasers [57]. In addition the shapes of the gratings overgrown with AlAs show interesting details such as a waviness of the upper grating plateau (grating along [110], 3 \( \mu \text{m} \) growth) and the formation of two distinct sidewall slopes, a feature that is also observed in the Cl\(_2\) etched gratings that will be discussed in the following section. The emergence of these features during growth is not understood.

The effect of shape conservation during AlAs growth can also be observed on a much shorter length scale as demonstrated in Fig. 5.4 which shows AFM data on the regrowth on 300 nm pitch gratings oriented along [110]. The growth conditions were the same as for the previous case of the 5 \( \mu \text{m} \) pitch gratings and the parameters of the KPZ simulations were also kept unchanged. The GaAs gratings flatten out significantly faster on this short length scale and the fits show that the KPZ equation gives a good description of this length scale dependence of the smoothing rate. On this length scale the shapes of the overgrown gratings look significantly less complex and the KPZ simulations give a very reasonable fit to the experimental data; however, the details of the shapes may not all be measured correctly by the AFM as the lateral resolution due to the finite tip size is only about one tenth of the grating period in this case.

As demonstrated in this section, the KPZ equation cannot explain some of the main features of the grating shape evolution during growth. A much better understanding of the shape evolution and of the growth process in general can be gained from simulations of the coupled equations (2.39). Fig. 5.5 shows a sample calculation using Eqs. (2.39), which was performed by Anders Ballestad, compared to the temperature dependent AFM data shown at the bottom of Fig. 5.2. Clearly, the simulations give a spectacular reproduction of the main features of the shape evolution, such as the formation of secondary mounds on the lower plateaus and the transition from convex to concave sidewalls at high substrate temperatures. This indicates that the shape evolution can indeed be understood in terms of the atomistic processes included in Eqs. (2.39) and explained in Chapter 2. An inverse Schwoebel barrier favoring downhill migration of adatoms is necessary to obtain good fits of the simulations to the experimental data. This is explained in more detail in Ref. [5] and the results of more simulations and discussion of the general properties of these equations will be given in the Ph.D. thesis of Anders Ballestad.

Since the evolution of surface roughness can be altered significantly by the
Figure 5.4: AFM scan lines (heavy lines) and KPZ simulations (thin lines, with parameters indicated on the top left) of short length scale gratings (300 nm pitch) oriented along [110], overgrown with GaAs and AlAs. The thickness of the regrown film is indicated on the right side of each scan line. The lines are arbitrarily offset for clarity.
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Figure 5.5: Comparison of the temperature dependent AFM data shown at the bottom of Fig. 5.2 (left) and simulations of grating shapes for different substrate temperatures obtained from a numerical solution of the coupled equations (2.39) (right). This figure is taken from Ref. [5].

Table 5.1: Parameters of the KPZ equation used for the simulations shown in Figs. 5.1-5.4. The subscripts $x$ and $y$ refer to the [110] and [110] crystal directions respectively.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\nu_x$(nm$^2$/s)</th>
<th>$\nu_y$(nm$^2$/s)</th>
<th>$\lambda_x$(nm/s)</th>
<th>$\lambda_y$(nm/s)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>420</td>
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<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>15</td>
<td>10</td>
<td>0.5</td>
<td>0</td>
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<td>610</td>
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<td>10</td>
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<td>2</td>
</tr>
<tr>
<td>AlAs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>620</td>
<td>2</td>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 5.6: AFM scan lines of gratings after regrowth of 600 nm of GaAs for three different fluxes of indium demonstrating the strong surfactant effect of In on the GaAs growth. The scan lines are arbitrarily offset for clarity and the upper line corresponding to the highest In flux is stretched vertically by a factor of 5 for clarity.
use of surfactants during growth as shown in Section 4.1.2, it is interesting to investigate the effect of surfactants on the shape evolution during regrowth. Indium is known to have a strong surfactant effect during the growth of GaAs at substrate temperatures that are high enough that indium does not incorporate into the crystal [45]. Fig. 5.6 shows AFM scan lines of gratings after regrowth of 600 nm of GaAs for three different fluxes of indium. The substrate temperature was 600°C for all growths and the As:Ga flux ratio was ≈3. The indium-induced smoothing of the grating structure is dramatic for the higher indium flux of 0.1 monolayers per second (approximately one tenth of the gallium flux), and the amplitude of the grating is reduced by a factor of 25 compared to the case of no indium flux. There appears to be a transition from outward to inward growth of the grating ridges as the indium flux is increased. In terms of the KPZ description this corresponds to a transition from positive to negative values for \( \lambda \) and in fact, for the high indium flux, the grating develops inverse mounds and cusps comparable to the KPZ simulation with negative \( \lambda \) shown in Fig. 2.3. Interestingly, the same transition is observed in kinetic Monte-Carlo simulations of growth for increasing temperatures\(^1\). This matches well with the simple picture given in Section 4.1.2 that the effects of surfactants can be understood as an increase of the effective substrate temperature. While this effect has so far not been modeled with the coupled equations (2.39) it seems likely that the reason for the inward growth is an increase in the release rate of atoms from step edges (which are concentrated on the slopes of the grating) in combination with the downward drift caused by the inverse Schwoebel barrier.

5.2 Evolution of Gratings during Chlorine Etching

The most striking feature of the shape evolution of gratings during thermal Cl\(_2\) etching is a widening or narrowing of the ridges depending on the orientation of the grating with respect to the crystal axes. The widening and narrowing of grating ridges is due to a crystal orientation dependent etch rate which causes the sidewalls of a trapezoidal grating to etch at a rate that is different from the flat sections. The effect is illustrated in Fig. 5.7 for the case of a sidewall etch rate \( R(\theta) \) which is higher than the etch rate of the

\(^1\)Anders Ballestad, private communication
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Figure 5.7: Narrowing of a trapezoidal grating due to a high sidewall etch rate \( R(\theta) \). The expansion velocity \( v \) can be calculated from Eq. (5.1).

flat surface \( R_{001} \). This leads to inward growth of the ridge with an expansion velocity \( v \) as defined in Fig. 5.7. From trigonometry this velocity can be expressed in terms of the etch rates \( R_{001} \) and \( R(\theta) \) as:

\[
v = \frac{R_{001}}{\tan \theta} - \frac{R(\theta)}{\sin \theta}
\]

(5.1)

As mentioned in Section 3.1, for thermal Cl\(_2\) etching the etch rate depends on the crystal orientation with the following etch rate sequence for different substrate orientations: \{111\}B > \{011\} = \{001\} > \{111\}A. The sidewalls of the wet etched gratings have angles of \( \theta \approx 25^\circ \) with respect to the \{001\} surface and thus do not correspond to low-index crystal facets. Nevertheless, the sidewalls of a grating oriented along the [110] direction will be between a \{001\} and a \{111\}A facet and can therefore be expected to etch slower than the \{001\} surface leading to a widening of the ridges. The sidewall orientation of a grating along [110] on the other hand is between that of a \{001\} and a \{111\}B facet which etches faster than a pure \{001\} facet and the sidewall of a grating along [100] is between a \{001\} and a \{011\} facet. This geometry is illustrated for the three cases in Fig. 5.8.

The orientation dependent widening or narrowing leads to a characteristic shape distortion of 2-dimensional gratings. Fig. 5.9 (left column) shows two

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\(^2\)By definition, a positive expansion velocity corresponds to outward growth and a negative velocity to inward growth.
Figure 5.8: Orientation of the gratings and their sidewalls with respect to the crystal axes for three cases. The plane of the substrate is the \{001\} plane.

10 μm×10 μm AFM images of square gratings, such as the one shown in Fig. 3.13, after a 1 μm deep etch. The etch, as all etches described in this section, was carried out at a substrate temperature of 200°C and a pressure of $1.3 \times 10^{-4}$ mbar. The sides of the initial squares are oriented along the [110] and the [110] crystal directions for the grating in the upper image and along the [100] and [010] directions for the grating in the lower image. In both cases the resulting shape after etching is characteristically elongated along the [110] direction and the width of the initial shape has decreased significantly along the [110] direction. The resulting shapes can be reproduced remarkably well by a simple numerical calculation shown in the right column of Fig. 5.9. The initial shape for the calculation is the square plotted as a dashed line. As explained above, the expansion velocity $v$ depends on the crystal orientation and therefore, an angle $\phi$ is defined as the angle between the local normal to the circumference of the shape and the [100] direction. In each time step $\Delta t$ of the simulation the angle $\phi$ is calculated for each point on the circumference and then the point is translated outward by a distance $v(\phi)\Delta t$. The functional form of $v(\phi)$ is not known a priori. The simplest function that gives a good fit to the experimentally observed shapes is

$$v(\phi) = 2 + 18 \cdot \sin(2\phi) - 2 \cdot \cos(4\phi), \quad [v] = \text{nm/min} \quad (5.2)$$

This function is plotted in Fig. 5.10. The shapes resulting from this angle dependent outward expansion are plotted in Fig. 5.9 as solid lines. It should be noted that the expansion velocity is only constant as long as
the sidewall slope remains constant, but in reality the sidewall slopes are slowly changing during the etch as will be shown below. The assumption of a constant expansion velocity can therefore only be an approximation. Nevertheless, the comparison of the simulated shapes with the corresponding AFM images to the left of them demonstrates the usefulness of this simple calculation in predicting the shape evolution of 2-dimensional patterns.

From the measured value for the expansion velocity \( v \), the etch rate of the sidewall can be calculated using Eq. (5.1) if the sidewall inclination \( \theta \) and the etch rate of the flat surface are known. In the present case, where \( \theta \approx 25^\circ \) for all sidewalls and \( R_{001} = 20 \text{ nm/min} \), the sidewall etch rates can be calculated to be 18 nm/min for inclination towards \{011\} (\( \phi = 0 \)), 10 nm/min for inclination towards \{111\}A (\( \phi = 45^\circ \)) and 24 nm/min for inclination towards \{111\}B (\( \phi = 90^\circ \)). The comparison of the shape evolution of the microfabricated grating with the simple numerical calculation thus constitutes a measurement of the etch rate for a crystal plane which is intermediate between two high symmetry planes. A different approach to measure these intermediate etch rates for many orientations simultaneously, which also uses microfabricated surface patterns, has been developed by Wind and Hines [82] for silicon; however, their measurements rely on the fact that the silicon crystal, unlike GaAs, is inversion symmetric.

There is no general theory that allows one to interpolate etch rates for surface orientations between high symmetry planes with known etch rates. Fig. 5.11 shows two possible ways of deriving such an etch rate interpolation for the present case, which are different yet lead to the same mathematical result. Fig. 5.11a) is a schematic of a surface with a macroscopic inclination \( \theta \) with respect to the (001) surface. This macroscopic slope is the one that is measured by the AFM. Microscopically the surface consists of flat terraces and atomic steps. For the purpose of deriving a mathematical expression for the etch rate of this surface, the atomic steps are thought to be spaced equidistantly across the surface so as to produce the macroscopic inclination \( \theta \) as shown in Fig. 5.11a). The slope of the atomic step \( \alpha \) is the angle of the next high symmetry plane and the (001) plane, e.g. for inclination towards a (111) surface \( \alpha = 54.7^\circ \), the angle between the (001) and the (111) planes. The reason for choosing this angle is that the surface atoms that comprise an atomic step on a (001) plane form a row of atoms with the bond configuration of the nearest high symmetry plane. The atomic step can therefore be looked at as a one unit cell high part of this neighboring high symmetry plane. This is shown in a projected sideview for the case
Figure 5.9: Shape evolution of two-dimensional square gratings with Cl₂ etching. The left side shows two 10 μm×10 μm AFM images of gratings after a 1 μm deep etch (gray scale is 160 nm). The sides of the squares before the etch were oriented along [110] and [110] (top), and along [100] and [010] (bottom). The right side shows numerical simulations of the evolution of an initially square shape (dashed lines) as described in the text. The final shapes (solid lines) are to be compared with the corresponding AFM image to the left.
Figure 5.10: Lateral expansion velocity $v$ of the circumference of a surface feature as a function of the circumference orientation $\phi$ as explained in the text. The arrows indicate the angles for which the normal to the circumference is along the [110] and the [110] directions.

of a (111)-step in Fig. 5.11b). Comparison with Fig. 3.2 shows that the atom that comprises the step (labelled “B” in the figure) has the same bond configuration as a (111) surface atom. The same is also valid for inclination towards (011) in which case the atoms comprising the step are part of a (011) surface and $\alpha = 45^\circ$. The terraces and slopes in Fig. 5.11a) are then assumed to etch along the local surface normal at the rates of the (001) surface $R_{001}$ and the next high symmetry plane $R_s$ respectively. Applying the same geometrical construction as in Fig. 5.7 to the steps and terraces, the following expression for the etch rate $R$ can be obtained:

$$R(\theta) = R_{001} \cos \theta + \left( \frac{R_s}{\sin \alpha} - \frac{R_{001}}{\tan \alpha} \right) \sin \theta$$

(5.3)

The same formula (5.3) can be derived by considering the total removal rate of atoms from the stepped surface of Fig. 5.11. With the same reasoning as above it is assumed that all atoms comprising the terraces, including atoms “A” and “C” in Fig. 5.11b), are removed at a rate corresponding to the etch rate of the (001) surface whereas the atoms comprising the step (atom “B”) are removed at the rate corresponding the etch rate of the (111) surface. The explicit derivation for the case of a (111) step is contained in the M.Sc. thesis of Richard Mar [50]. This model is similar to the one used in [82] to
Figure 5.11: a) Schematic representation of a surface consisting of terraces and atomic steps that result in a macroscopic inclination at an angle $\theta$ with respect to the (001) surface. The etch rate $R$ is determined by the etch rates of the terraces and the steps according to Eq. (5.3). b) Projected side view of an atomic step on a (001) surface off-cut towards (111). The step atom “B” has the same surface bond configuration as a (111) surface atom.
Figure 5.12: Interpolated etch rate as a function of surface inclination between {001} and {111} as well as {001} and {011} according to Eq. (5.3) (solid lines) and interpolations used for the simulations in Figs. 5.15-5.17 as explained in the text (dashed lines). The markers (x) indicate the etch rates obtained from the simulations of the outward expansion of 2-dimensional gratings shown in Fig. 5.9

describe step-flow etching. The etch rate interpolation Eq. (5.3) is plotted in Fig. 5.12 as solid lines for the three cases of inclination towards {111}A, {111}B and {011}. The model predicts, for the intermediate orientations, an etch rate that is higher than that obtained from a linear interpolation. The dashed lines in Fig. 5.12 are interpolations used to model the evolution of 1D gratings as explained below.

The markers in Fig. 5.12 indicate the values of the sidewall etch rate obtained from the fit to the outward expansion of the 2D gratings discussed above. They agree with the interpolations used for the 1D simulations (explained below) within error\(^3\). It is interesting to note that the fits to all experimental data require etch rates which are lower than predicted by the

\(^3\)The uncertainty in the sidewall angle is estimated to be \(\approx 5^\circ\). The starting surface used for simulations has a sidewall slope of 22.5°.
simple model that is the basis of Eq. (5.3).

The shape evolution of one-dimensional gratings during etching with a directional molecular beam and with non-directional Cl₂ exposure is shown for three crystal orientations in Figs. 5.13-5.15. In each case the heavy lines are AFM scan lines obtained from gratings after etching and the thin lines are numerical simulations using Eqs. (2.35).

Fig. 5.13 shows the evolution of gratings (3 μm pitch, 100 nm amplitude) oriented along the [110] direction. The wet etched starting surface is shown on top. For this orientation the sidewalls of the grating are intermediate between {001} and {111}A (see Fig. 5.8). As seen before for the 2D gratings, the etch rate of the sidewalls is significantly slower than that of the plateaus and this leads to a widening of the ridges. This is clearly visible in the AFM data both in the case of etching with a non-directional Cl₂ flux (left column) and with a directional molecular beam at approximately normal incidence (right column). The etch depths are indicated next to the corresponding scan lines in the figure. The anisotropic etch rates limit the achievable etch depth for pattern transfer without significant loss of fidelity to less than 1 μm. Interestingly, in the intermediate times (400 and 600 nm etch depth) the sidewalls develop two distinct slopes, a low slope of approximately 6° higher up on the sidewall and a steeper slope at the bottom which is the same as the initial slope of the wet etched sidewalls (≈ 25°). Eventually, as the ridges merge together the steep slope disappears, resulting in a V-shaped valley with the lower slope. Another noticeable feature of the shape evolution is the formation of two small bumps on the upper plateau next to the sidewalls. There appears to be only a small difference for non-directional versus directional Cl₂ exposure.

The simulations shown in Fig. 5.13 as thin lines are obtained from a numerical solution of Eqs. (2.35) with the following parameters: \( a^2_0 F_0 = 0.33 \) nm/s, \( D = 6000 \) nm²/s and \( \tau = 0.5 \) s. As explained in Section 2.3 the difference between non-directional and directional supply of Cl₂ is a cosine-facor multiplying the flux term \( F_0 \) in the case of the directional beam, see Eq. (2.36). Since the beam is incident approximately normal to the surface, \( \theta_0 = 0 \) in Eq. (2.36). As discussed in Section 2.3, the crystal anisotropy of the etch rate is simulated by using an inclination dependent sticking coefficient \( S(\theta) \). This sticking coefficient is related to the etch rate interpolation \( R(\theta) \) discussed above by the relation\(^4\) \( a^2_0 S(\theta) F_0 = R(\theta)/\cos \theta \). The interpo-
Figure 5.13: AFM scan lines (heavy lines) and simulations (thin lines) with Eqs. (2.35) of gratings oriented along [110]. The scan lines are offset for clarity and the etch depths are indicated on the right next to each line. The widening is due to the crystal anisotropy of the etch rate.
lations \( R(\theta) \) that are used in the simulations are shown as the dashed lines in Fig. 5.12. Since the initial sidewall slope is the largest slope that occurs in any of the simulations, the functional form of the interpolation \( R(\theta) \) for slopes larger than 25° has no effect on the results. For the simulations shown in Fig. 5.13, i.e. sidewall inclination towards \{111\}A, a good fit to the shape evolution requires an etch rate interpolation that is flat for small angles around (001) and then drops sharply to the lower value required for the sidewalls. This is accomplished by using the functional form of a Fermi-function for the etch rate \( R(\theta) = 20 \cdot (\exp(20 \cdot (\theta - 0.34)) + 1) \) nm/min where \( \theta \) is in radians. These simulations show not only the correct outward growth but also the development of two distinct sidewall slopes and little bumps on the upper flat sections next to the sidewalls during the etch. The bumps are caused by the combination of a low concentration of chlorine on the sidewalls (due to the lower sticking coefficient) and surface diffusion. The development of the two distinct sidewall slopes is an impressive success of the model, even though the lower sidewall slope in the simulations is only \( \approx 1.5° \) and therefore significantly lower than the one observed in the experiment. Presumably this shortcoming is due to the lack of a more detailed knowledge of the interpolation function \( R(\theta) \).

The evolution of gratings oriented along the [110] crystal direction is shown together with numerical simulations in Fig. 5.14. The sidewalls of the gratings are intermediate between {001} and {111}B and etch faster than the plateaus. Therefore the gratings decay due to a narrowing of the ridges, eventually forming triangularly shaped peaks, opposite to the behavior of gratings oriented along [110]. The narrowing can be slowed down significantly by the use of a directional molecular beam: The gratings etched with a Cl\(_2\) beam have not lost any amplitude after a 1.5 \( \mu \)m deep etch whereas gratings etched with a non-directional Cl\(_2\) exposure have already become triangular after a 1 \( \mu \)m deep etch.

The simulations use the same parameters but a different etch rate interpolation as for the gratings along [110]. A parabolic etch rate interpolation between {001} and {111}B is used. The functional form is \( R(\theta) = (20 - 0.37\theta + 11.2\theta^2) \) nm/min if \( \theta \) is in radians. This function is plotted as \( R(\theta)/\cos \theta \) which is simply the evolution equation resulting from etching at a rate \( R \) along the local surface normal. In fact, this simple equation gives a good description of the outward growth for any function \( R(\theta) \) which has the correct sidewall etch rate of \( \approx 8 \) nm/min at \( \theta \approx 25° \) as shown in [68]; however, it cannot explain the details of the shape evolution.
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Figure 5.14: AFM scan lines (heavy lines) and simulations (thin lines) with Eqs. (2.35) of gratings oriented along [110]. The scan lines are offset for clarity and the etch depths are indicated on the right next to each line.
a dashed line in Fig. 5.12. This gives a good fit to the inward growth in Fig. 5.14. The difference between non-directional and directional etching is reproduced very well by the simulations. The fact that there is a significant difference between directional and non-directional etching for [110]-oriented gratings but not for [110]-oriented gratings may seem surprising at first. It can be understood from Eq. (5.1) for the expansion velocity. The change from non-directional to directional exposure causes a change in the etch rate of the sidewall from \( R(\theta_S) \) to \( R(\theta_S) \cdot \cos \theta_S \) (\( \theta_S \) = sidewall angle). For the [110] oriented grating for which \( R(\theta_S) \) is smaller than \( R_{001} \) this leads to a much smaller change in the lateral velocity \( v \) of the grating than for the [110]-oriented gratings which have a large \( R(\theta_S) \). In addition to the lateral shrinking the model predicts the formation of small trenches at the foot of the sidewalls due to the diffusion of the higher sidewall chlorine concentration; however, these features are small and not observed in the experimental data.

The results for gratings oriented along the [100] direction, i.e. at 45° to the cleave planes, are shown in Fig. 5.15. In this case gratings can be transferred to much larger etch depths than for the other orientations. The AFM scan lines for non-directional etching show very little distortion and no significant outward or inward growth of the grating ridges after a 3 μm deep etch. This indicates that the etch rate of the sidewall is slightly lower than that of the plateaus. In fact, perfect pattern replication requires that \( R(\theta) = R_{001} \cos \theta \) which means that each point of the surface is transferred downward by the same amount in each time step. This cosine function is therefore used for \( R(\theta) \) in the simulations and is plotted in Fig. 5.12 as a dashed line. This is not a proper interpolation function since it does not reach the required value of 20 nm/min for the \{011\} surface; however, as mentioned above, the maximum surface inclination that occurs in the simulations is \( \approx 25^\circ \) and therefore the functional form of \( R(\theta) \) for angles larger than this is irrelevant. In combination with a uniform flux of Cl\(_2\) to the surface, which is assumed for the non-directional case, this etch rate interpolation leads to good pattern replication in the simulations in agreement with experiment. The rounding of the corners is caused by the addition of a small “Edwards-Wilkinson”-term as explained in Section 2.3.

\( ^5 \)Due to the fabrication tolerances in the duty cycle of the wet etched starting surfaces this conclusion may not seem entirely convincing on the basis of the data presented in Figs. 5.13 and 5.14 alone; however, the diffraction measurements discussed below and shown in Fig. 5.16 leave little doubt about its validity.
Figure 5.15: AFM scan lines (heavy lines) and simulations using Eqs. (2.35) (thin lines) of gratings oriented along [100]. The amplitude of the starting surface is \( \approx 100 \text{ nm} \), as indicated by the scale bar in the top right corner. The etch depths are marked on the right next to the corresponding scan lines and simulations. All lines are offset for clarity.
When a directional beam is used the gratings develop a strong asymmetric shape distortion during etching as shown in Fig. 5.15. The shape of this distortion is strongly reminiscent of the evolution discussed in Section 2.3 and shown in Fig. 2.5. These experiments were performed for two different angles of the gas injector with respect to the sample surface: normal to the surface or at an angle of 40° to the normal. The size of the patterned part on the samples is \( \approx 8 \times 8 \) mm. Due to the proximity of the gas injector to the sample, this means that the angle of incidence of the molecular beam varies across the pattern. In the case of the normally incident beam, the injector was situated such that the normally incident beam was at one edge of the pattern. According to the geometry described in Section 3.2.1, the angle of incidence at the opposite edge was \( \approx 20° \). This non-uniformity makes the exact angle of incidence (\( \theta_0 \) in Eq. 2.36) uncertain and it was therefore adjusted in the simulations to obtain a good fit to the experimental shapes. This was achieved for an angle of 12° which is a very reasonable value since the AFM scans were taken close to the center of the pattern.

The beam was also slightly off-normal for the other etches carried out with a directional beam described above; however, the anisotropic etch rates cause these gratings to decay much faster than the [100] oriented ones, and the effects of the off-normal beam are not clearly visible after these shorter etch times. The origin of the asymmetric shape distortion as a result of the off-normal incidence and surface diffusion was explained in Section 2.3. The formation of the bump on the lee side of the upper plateau causes a significant increase of the grating amplitude for the 3 \( \mu m \) deep etch at \( \theta_0 = 12° \). For the etches at \( \theta_0 = 40° \) the gratings evolve into a sawtooth shape with a superimposed waviness. The waviness originates from the formation of more pronounced bumps and trenches than observed for the lower angle of incidence. These features are reproduced very well by the numerical simulations with the same parameters as above.

The solid lines in Fig. 5.16 show the measurements of the first order diffracted light intensity from gratings during etching for the three orientations and for directional (thin lines) and non-directional \( \text{Cl}_2 \) flux (heavy lines). For gratings along the [110] and the [110] direction the diffracted light intensity decays rapidly. This is due to the smoothing of the grating caused by the lateral growth or shrinking as seen in the AFM scan lines. For the case of a square grating with a constant amplitude the first Fourier coefficient varies as a function of the duty cycle \( \xi \) (where \( \xi \) is a number between 0 and 1) as \( \sin(\pi \xi) \). At the early phase of the etch, when the amplitude
Figure 5.16: Measurements of the first order diffracted intensity of a He:Ne laser incident on the gratings during the etch. Heavy lines are for non-directional etches and thin lines are for etches with a directional molecular beam and in each case the solid line is experimental data and the dashed line is a simulation as explained in the text.
is still constant, the dominant part of the evolution of the grating is the change of the duty cycle. In a first approximation the diffracted intensity is therefore expected to follow a $\sin^2(d)$-dependence as a function of the etch depth $d$. Since the initial duty cycle of the gratings is smaller than 50%, this means that the diffracted intensity is expected to go through a maximum if the etch increases the duty cycle. This explains why there is an initial increase in diffracted intensity from the [110]-oriented gratings but not for the [110]-oriented gratings. The light scattering measurements confirm that the difference between etching with a non-directional and a directional flux is smaller for the [110]-oriented gratings. For [110]-oriented gratings, on the other hand, the diffracted intensity decays more slowly in the directional case, meaning that the pattern transfer can be improved significantly with the use of a directional beam. For the gratings oriented along [100] the diffracted intensity is almost constant for non-directional Cl$_2$ exposure, as expected from the good pattern replication observed in the AFM scans of Fig. 5.15. For directional etching there is a significant increase of the diffracted intensity due to the increase in amplitude of the gratings caused by the off-normal incidence as shown in Fig. 5.15.

The simulation results in Fig. 5.16 (dashed lines, thin for directional and heavy for non-directional Cl$_2$ flux) were obtained by doing a Fourier expansion of a time series of simulated gratings as shown in Figs. 5.13, 5.14 and 5.15 and plotting the square of the first coefficient. The agreement with the measured intensity is excellent in all cases. For the [110]-oriented gratings the simulations decay to a lower background level than the data. This can be understood from the scan lines in Fig. 5.13 that show that the amplitude of the simulated gratings for the deepest etches is smaller than the measured amplitude. This is due to the secondary sidewall slope which is too low in the simulations as pointed out above.

Finally, results of gratings with a smaller pitch of 300 nm, oriented along the [110] direction, are shown. AFM scan lines (heavy lines) and simulations with Eqs. (2.35) (thin lines) of these gratings are shown in Fig. 5.17. The amplitude of the initial wet etched grating is $\approx$40 nm in this case. The fabrication tolerances and the non-uniformity of the grating duty cycle are higher than for the larger gratings which makes it harder to draw definite conclusions about the pattern transfer. As in the case of the [110]-oriented 3 $\mu$m pitch gratings it can be seen that the gratings disappear due to the high sidewall etch rate which leads to a shrinking of the ridges. This limits the pattern transfer to an etch depth of less than 40 nm in the case of
Figure 5.17: AFM scan lines (heavy lines) and simulations (thin lines) with Eqs. (2.35) of 300 nm pitch gratings oriented along [110]. The scan lines are offset for clarity and the etch depths are indicated on the left next to each line.
Chapter 5. Pattern Evolution

non-directional exposure. As for the larger gratings this can be improved by using a directional beam, in which case the grating amplitude remains almost unchanged after a 55 nm deep etch. In any case the pattern transfer is limited to less than 100 nm etch depth. The important result is that the lessons learned from the 3 \( \mu \text{m} \) pitch gratings seem to be applicable to these smaller length scales which are important for the fabrication of optoelectronic devices. The simulations confirm that there should be a measurable effect of the directionality of the incident \( \text{Cl}_2 \) beam. In addition they predict an upward bowing of the lower plateau, which is larger for non-directional exposure, due to the increased chlorine concentration next to the sidewalls; however, this is not observed in the AFM data.

5.3 Summary and Discussion

Experimental results and simulations on surface grating evolution during MBE growth and thermal \( \text{Cl}_2 \) etching of GaAs were presented. In both cases a rich and complex shape evolution is observed that cannot be explained in terms of the single differential equation (2.33). The coupled equations (2.35) have to be used instead. In the case of MBE growth these equations are written in the form (2.39) which gives a description of the shape evolution in terms of the underlying microscopic processes which are incorporation and evaporation of adatoms at step edges, surface diffusion, the Schwoebel effect and island nucleation. Overgrown GaAs films exhibit good pattern replication at low growth temperatures whereas the growth becomes increasingly nonlinear for higher temperatures leading to a rapid decay of the pattern. The smoothing of the grating can be accelerated drastically by using indium as a surfactant during overgrowth. This also leads to a change from outward growth of the grating ridges to inward growth. The use of a surfactant therefore introduces an additional degree of freedom that allows for a certain degree of engineering of these self-organized surface patterns.

The dominant effect of the evolution of gratings during thermal \( \text{Cl}_2 \) etching is the crystal orientation dependent widening or narrowing of the gratings. Pattern transfer can be optimized by orienting the gratings along the [100] crystal direction. The coupled equations (2.35) can be applied with excellent results to all the data sets presented. This is even more impressive considering that the only true fitting parameters of the model are the diffusion length \( l = \sqrt{D \tau} \) and the etch rate interpolations \( R(\theta) \) for which very simple
functional forms are used. The success of this model means that the shape evolution of gratings during thermal Cl\textsubscript{2} etching is indeed dominated by the effects of the crystal anisotropy of the etch rate and spatial variation of the Cl\textsubscript{2} flux across the pattern in combination with surface diffusion of chlorine.

For the gratings with a 300 nm pitch the correspondence between the model and the observed shapes is not as good. Since the aspect ratio is very different for these smaller gratings, shadowing and reemission effects become more important. From the measured etch rate of 20 nm/min at 1.3×10\textsuperscript{-4} mbar one can calculate that only ≈5% of the Cl\textsubscript{2} flux to the surface contributes to the etching. This means that 95% of the Cl\textsubscript{2} is reemitted from the surface. In the case of the small pitch gratings the probability of these reemitted Cl\textsubscript{2} molecules hitting the surface at another point is much higher than for the larger gratings. The importance of shadowing also increases with the aspect ratio of the small pitch gratings. Shadowing leads to the formation of U-shaped valleys and therefore this effect could counteract the formation of the upward bowing, which is predicted by the model for the 300 nm pitch gratings which does not include shadowing.

Given the parameters used in the simulation a diffusion length of \( l = \sqrt{D\tau} \approx 55 \text{ nm} \) is obtained; however, the model does not specify which species is diffusing on the surface. According to the surface chemistry described in Section 3.1 both Cl\textsubscript{2} and chemisorbed Cl are present on the surface during etching. Diffusion of either of these species may therefore contribute to the observed effects. A recent scanning tunneling microscopy study [51] has shown that chemisorbed Cl can be surprisingly mobile on GaAs even at room temperature. The Cl hopping rate on the surface depends strongly on the surface structure [48]; however, using as a typical number from Ref. [48] for the activation energy for diffusion \( E_a=0.8 \text{ eV} \), a hopping distance of \( a = 4 \text{ Å} \) and an attempt frequency \( \nu_0 \) of \( 10^{12} \text{ Hz} \), the diffusion constant can be calculated to be \( D = a^2\nu_0 \exp(-E_a/kT) =1500 \text{ nm}^2/\text{s} \) at 200°C. Within a monolayer etch time \( \tau_{ML} \) of one second this leads to a diffusion length of \( l = \sqrt{D\tau_{ML}} =40 \text{ nm} \). The diffusion length of 55 nm used in the simulations therefore seems entirely reasonable and could be explained on the basis of the diffusion of atomic Cl alone. The diffusion length might also be direction dependent. To restrict the number of parameters in the model this dependence was not included but it should be noted that the fit to the gratings along [110] in Figs. 5.14 and 5.17 might be improved by using a shorter diffusion length which would lead to less prominent trenches in the simulated profiles.
Conclusions

The combination of in-situ thermal Cl₂ etching and MBE regrowth is a promising method for fabricating interesting novel semiconductor nanostructures with high quality. An experimental setup combining a standard MBE growth system and an etching chamber that enables one to carry out multiple etch and growth steps inside a common vacuum system has been described. Typical fabrication schemes involve the transfer of surface patterns by etching and regrowth and therefore a good understanding of surface pattern evolution is crucial in order to make use of these methods in a nanofabrication process. The surface roughness that develops during etching and growth processes sets a fundamental limit to one’s ability to control the etch depth and growth thickness. Roughness evolution is therefore an important consideration for a nanofabrication process. The work presented in this thesis contains the first comprehensive study of surface roughness and pattern evolution in thermal Cl₂ etching of GaAs as well as new experimental results on surface morphology evolution during MBE growth of GaAs.

This study shows that morphological evolution can be treated on the same mathematical footing for both etching and growth, at least for the length scales where continuum models are applicable. Nanometer scale surface roughness evolution can be described accurately by simple stochastic differential equations for the surface height whereas the evolution of larger amplitude patterns on the scale of hundreds of nanometers requires a different approach consisting of two coupled differential equations for the concentration of a mobile surface phase and the surface height. These two approaches and their physical interpretations for the cases of etching and growth have been discussed in detail. The models give significant insights into the physical issues that fundamentally limit the fabrication of nanoscale patterns, for example the combination of noise and smoothing terms in the case of roughness evolution and anisotropic etch rates and directionality of the etchants in the case of shape evolution during etching.

The general approach to identifying the appropriate equations has been
Conclusions

To compare experimentally obtained surface images and light scattering data with numerically generated surfaces and scattering data derived from these. This direct comparison has been shown to be a very powerful tool to determine the correct mathematical model to describe surface evolution and is more generally applicable and less ambiguous than a scaling analysis which is commonly done in the case of surface roughness.

The evolution of nearly flat GaAs surfaces during MBE growth is described by the KPZ equation. The value of the parameter $\lambda$ of the KPZ equation is found to be significantly larger than expected from the simple interpretation of the KPZ nonlinearity as originating from locally normal growth. Similarly, the noise that has to be used in the simulations to achieve a good fit with experiment is much larger than the shot noise in the arrival rate of atoms at the surface. The reason for these deviations has only been speculated upon so far and more detailed microscopic models are needed to really understand this problem in terms of the underlying surface processes. A step in this direction is the coupled equations model used to model shape evolution during growth. This model explains not only the rate of outward growth but the entire shape evolution of gratings during overgrowth in terms of atomistic processes. The success of this model warrants further investigations into its applicability for a wider range of parameters and different materials. It is also possible that this model can explain the excess noise used in the KPZ equation in terms of all the noisy processes that occur at the surface during growth, for example the noise in the rates of incorporation and release of adatoms from step edges. This has so far not been attempted. Finally, it has been shown that the morphology evolution can be altered drastically by the use of surfactants. The effect of a surfactant on the surface morphology is qualitatively similar to the effect of increasing the substrate temperature.

For thermal chlorine etching it was found that an accurate description of surface roughness evolution is obtained with the KPZ equation extended by a fourth order linear term that is normally associated with surface diffusion. This equation correctly predicts both the roughening of initially smooth surfaces and smoothing of randomly rough surfaces. As in the case of MBE growth the noise input needed to model the surface roughness is found to be significantly larger than the expected flux noise again indicating that other noisy surface processes are dominant. A non-trivial dependence of the smoothing parameter $\nu$ on the substrate temperature and Cl$_2$ pressure is found.
Pattern evolution during etching is dominated by anisotropic etch rates which cause gratings to decay due to the different etch rates of flat and inclined surface sections. The decay of the gratings can be used to measure etch rates of the inclined sidewalls which are intermediate between two low-index crystal planes with known etch rates. For one-dimensional gratings pattern transfer can be optimized by orienting them along the [100] crystal direction and the evolution of two-dimensional gratings can be understood with a simple model for the outward expansion velocity of the shapes. The shape evolution can be altered by using a directional molecular beam of Cl\(_2\) rather than a non-directional background gas phase. Most notably etching with a molecular beam improves the pattern transfer of gratings oriented along [110] and, at off-normal incidence, causes a large asymmetric shape distortion for gratings oriented along [100]. These phenomena are modelled successfully with the coupled equations model. From fits of the model to the surface shapes the diffusion length of chlorine on the surface can be determined to be approximately 55 nm at 200°C. More experiments on smaller structures are needed to determine conclusively if the same model can be applied at length scales relevant to the fabrication of nanostructures without modifications, or if additional physical effects have to be included. Finally, it would be interesting to explore different etching reactions with the methods and models developed for this study. In particular finding a UHV compatible etching reaction that produces atomically smooth GaAs surfaces would be of great interest. The different models and some of the main conclusions are summarized in Table 5.2.

In conclusion, this work demonstrates that surface morphology evolution of a prototype semiconductor material system can be understood with the same continuum models for both etching and growth. It thus contributes to finding a unified approach to the modeling and understanding of surface pattern evolution. This understanding is essential for making fabrication processes that rely on etching and regrowth meet the stringent requirements that are likely to be needed for the nanodevices of the future.
Table 5.2: Summary of models used to describe surface morphology evolution in this thesis.

<table>
<thead>
<tr>
<th>Small amplitude texture (max. surface slope $\lesssim 3^\circ$)</th>
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<tbody>
<tr>
<td>Single stochastic equation</td>
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<tr>
<td>Thermodynamic description</td>
</tr>
<tr>
<td>Mass transport driven by surface chemical potential</td>
</tr>
<tr>
<td>No distinction between adatoms and surface</td>
</tr>
<tr>
<td>Noise included</td>
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<tr>
<td><strong>MBE Growth</strong></td>
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<tr>
<td>Equation</td>
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<tr>
<td>Dominant Physics</td>
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<td>Comments</td>
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<tr>
<th>Grating Patterns (max. surface slope $\lesssim 30^\circ$)</th>
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</thead>
<tbody>
<tr>
<td>Coupled deterministic equations</td>
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<tr>
<td>Kinetic description</td>
</tr>
<tr>
<td>Adatom transport by diffusion</td>
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<tr>
<td>Separate equations for adatoms and surface height</td>
</tr>
<tr>
<td>Noise not included</td>
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<tr>
<td><strong>MBE Growth</strong></td>
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<tr>
<td>Equation</td>
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<td>Dominant Physics</td>
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Appendix A

Derivation of Expressions for the Coefficients \( \nu \) and \( K \)

First, an expression for the coefficient \( \nu \) in Eq. (2.24) can be derived by observing that the rate of desorption of atoms from the surface \( R_{\text{des}} \) is given by:

\[
R_{\text{des}} = \nu_0 \exp \left( -\frac{E_{\text{des}}}{kT} \right) \quad (A.1)
\]

where \( \nu_0 \) is an attempt frequency of the order of a typical phonon frequency and \( E_{\text{des}} \) is the activation energy for desorption. The activation energy is the sum of the activation energy for atoms on a flat surface \( E_{\text{des}}^0 \) and the change due to the curvature dependent chemical potential \( \mu \) (Eq. 2.20). The difference between the desorption rate on a flat surface \( R_{\text{des}}^0 \) and a curved surface is therefore:

\[
\Delta R_{\text{des}} = R_{\text{des}} - R_{\text{des}}^0 = R_{\text{des}}^0 \left( \exp \left( \frac{\mu}{kT} \right) - 1 \right) \approx R_{\text{des}}^0 \frac{\mu}{kT} \quad (A.2)
\]

The last step follows from an expansion of the exponential and is valid for \( \mu < kT \). By multiplying the differential rate with the surface concentration of the desorbing adatoms \( n \), the differential flux of adatoms away from the surface is obtained:

\[
\Delta j = n \Delta R_{\text{des}} \approx \frac{n R_{\text{des}}^0}{kT} \mu \quad (A.3)
\]

This flux translates into a rate of change for the surface height \( h \) according to:

\[
\frac{\partial h}{\partial t} = a_0^3 \Delta j = a_0^3 \frac{n R_{\text{des}}^0}{kT} \mu = v^2 n_0 \frac{R_{\text{des}}^0}{kT} \nabla^2 h \quad (A.4)
\]

where the last equality follows from Eq. (2.20) and \( a_0^3 = v \). The coefficient \( \nu \) can be identified as:

\[
\nu = v^2 n_0 \frac{R_{\text{des}}^0}{kT} = \frac{v^2 n_0}{kT} \nu_0 \exp \left( \frac{E_{\text{des}}^0}{kT} \right) \quad (A.5)
\]
Appendix A. Derivation of Expressions for the Coefficients \( \nu \) and \( K \)

To derive an analogous expression for \( K \), one can start with the equation of motion for the velocity \( v \) of a diffusing particle biased by a force \( f \):

\[
\frac{m}{\partial t} = f - \gamma v \tag{A.6}
\]

where \( \gamma \) is the friction constant. This leads to a drift velocity

\[
v_{\text{drift}} = \frac{f}{\gamma} = -\frac{\nabla \mu}{\gamma} \tag{A.7}
\]

since the driving force is the gradient of the chemical potential. The friction constant is related to the diffusion constant \( D \) by the Einstein relation:

\[
\gamma D = kT \tag{A.8}
\]

Combining (A.7) and (A.8), the surface current of atoms is given by:

\[
j = \frac{n}{a_0} v_{\text{drift}} = -\frac{n}{a_0} D \frac{\nabla \mu}{kT} \tag{A.9}
\]

By inserting (A.9) into the continuity equation \( \frac{dh}{dt} = -a_0^4 \nabla \cdot j \) and using (2.20) one obtains:

\[
\frac{\partial h}{\partial t} = a_0^3 n D \frac{kT}{kT} \nabla \cdot \nabla \mu = -v^2 \sigma n D \frac{kT}{kT} \nabla^4 h \tag{A.10}
\]

Therefore \( K \) is given by:

\[
K = v^2 \sigma n D \frac{kT}{kT} = \frac{\nu^2}{\sigma \nu \nu_0} a_0^2 \exp \left( -\frac{E_{\text{diff}}}{kT} \right) \tag{A.11}
\]

From (A.11) and (A.5) the ratio of \( K \) and \( \nu \) is given by:

\[
\frac{K}{\nu} = \frac{D}{\nu R_{\text{des}}} = \frac{D}{\nu_0 \exp \left( -\frac{E_{\text{diff}}}{kT} \right)} = \frac{a_0^2 \exp \left( -\frac{E_{\text{des}}}{kT} \right)}{\nu_0 \exp \left( -\frac{E_{\text{des}}^0}{kT} \right)} \tag{A.12}
\]

In this expression \( E_{\text{diff}} \) is the activation energy for surface diffusion. This is the same as Eq. (2.23) in which the superscript 0 has been omitted from the activation energy for desorption from a flat surface.
Appendix B

Green's Function Method for Elastic Light Scattering from Multilayer Structures

This appendix gives a derivation of Eq. (3.3) for the case of scattering of s-polarized light and shows how the expression has to be modified to calculate the scattering from multilayer structures. The derivation uses a Green’s function approach originally developed by J. E. Sipe [73] and recently employed by P. Paddon and Jeff Young to calculate photon dispersion in planar photonic crystals [59, 58]. The work on this derivation was in fact inspired by a lecture by Jeff Young on the topic. The more conventional theories for light scattering in general are reviewed for example in [74, 55] and a theory for scattering from multilayers is described in [10].

The wave equation for the time-Fourier transform of the electric field is:

$$\nabla^2 \tilde{E}(\vec{r}, \omega) + \left(\frac{\omega}{c}\right)^2 \epsilon(\vec{r}, \omega) \tilde{E}(\vec{r}, \omega) = 0 \quad (B.1)$$

The dielectric function is 1 above the sample surface and \(\epsilon\) below. Thus the susceptibility \(\chi\) can be expressed in terms of the height function \(h(\vec{x})\) of the interface as:

$$\chi(\vec{r}) = \frac{\epsilon(\vec{r}) - 1}{4\pi} = \frac{(\epsilon - 1)}{4\pi} \Theta(z - h(\vec{x})) \quad (B.2)$$

where \(\vec{x} = (x, y)\) is the coordinate in the plane of the surface, \(\vec{r} = (x, y, z)\) and \(\Theta\) is the Heaviside function.

The dielectric function of the system is now split into two parts: The first one is a step function as for an interface with no roughness and the second is the contribution that arises from the difference of this flat interface and the actual surface, i.e. from the roughness. Thus a solution is sought to the wave equation
\[ \nabla^2 \vec{E}(\vec{r}, \omega) + \vec{\omega}^2 \varepsilon(z) \vec{E}(\vec{r}, \omega) = -4\pi \vec{\omega}^2 \chi_s(\vec{r}) \vec{E}(\vec{r}, \omega) = -4\pi \vec{\omega}^2 \vec{P}_s(\vec{r}, \omega) \]  

where \( \vec{\omega} = \omega / c \), the dielectric function \( \varepsilon(z) \) is now simply a step function in \( z \) and \( \chi_s(\vec{r}) = \chi(\vec{r}) \Theta(-z) \). \( \vec{P}_s \) denotes the polarization of the surface layer which will now conceptually be considered a source term in the wave equation (B.3), see Fig. B.1. This is similar to the surface current density defined in [10]. The homogeneous solution to (B.3) for an incident plane wave is now simply given by a superposition of the incident field and the usual Fresnel expressions for the reflected and transmitted field at a planar interface. It can be written as:

\[ \vec{E}_{\text{hom}} = \left( e^{-i\omega(\vec{\beta})z} \vec{1} + e^{i\omega(\vec{\beta})z} \vec{r}(\vec{\beta}) \right) \cdot \vec{E}_{\text{inc}} e^{i\vec{\beta} \cdot \vec{z}} e^{-i\omega t} \Theta(z) \]  

where \( \vec{\beta} \) is the in-plane wavevector of the electric field, \( w = \sqrt{\omega^2 - \vec{\beta}^2} \) is its perpendicular component and \( \vec{r}(\vec{\beta}) = r_s(\vec{\beta}) \hat{s}(\vec{\beta}) + r_p(\vec{\beta}) \hat{p}_+(\vec{\beta}) \hat{p}_-(\vec{\beta}) \) is the Fresnel reflection tensor (in dyadic notation) where \( r_s \) and \( r_p \) are the Fresnel reflection coefficients of the interface for s and p polarizations and \( \hat{s} \) and \( \hat{p} \) are unit vectors in the direction of s- and p-polarization. The subscripts + and − refer to waves travelling in the positive and negative z-direction respectively.

The diffuse scattering from the surface is entirely contained in the particular solution to (B.3). A particular solution to (B.3) is given by:

\[ \vec{E}(\vec{r}) = \sum_{m} \vec{E}(\vec{\beta} + \vec{q}_m, z) e^{i(\vec{\beta} + \vec{q}_m) \cdot \vec{z}} \]  

with

\[ \vec{E}(\vec{\beta}, z) = \int \vec{\tilde{g}}(\vec{\beta}, z, z') \cdot \vec{P}_s(\vec{\beta}, z') \, dz' \]  

where \( \vec{\tilde{g}} \) is a generalized Green’s function tensor that above the surface \( (z > 0) \) is given by:

\[ \vec{\tilde{g}}(\vec{\beta}, z, z') = \vec{\tilde{g}}_+(\vec{\beta}) \Theta(z - z') e^{i\omega(\vec{\beta})(z-z')} + \vec{\tilde{g}}_-(-\vec{\beta}) \Theta(z' - z) e^{-i\omega(\vec{\beta})(z-z')} + \vec{\tilde{r}}(\vec{\beta}) \cdot \vec{\tilde{g}}_-(\vec{\beta}) e^{i\omega(\vec{\beta})(z+z')} - 4\pi \delta(z - z') \hat{\vec{z}} \hat{\vec{z}} \]  

The notation follows [58] and a proper definition of all the quantities can be found there. The first three terms correspond to waves that are radiated
Figure B.1: Theory of light scattering from a rough surface: The surface is decomposed into a smooth surface (at $z = 0$) and a 2-dimensional sheet of polarization $P_s$ just above the surface (at $z = z'$). The surface polarization is proportional to the unperturbed electric field at $z = z'$, i.e. the field in the absence of any roughness, and has the same relative Fourier components as the surface height function. This polarization sheet radiates and the light scattering is calculated as the radiated field in the presence of the smooth interface at $z = 0$.

from the surface into the free space above, towards the substrate below and to the substrate and reflected back into the free space. The last term is a depolarization term that is important for p-polarized waves. Next $\chi_s$ is expanded into a Fourier series according to:

$$\chi_s(\vec{x}, z) = \sum_m \chi_{q_m}(z) e^{i(\vec{q}_m \cdot \vec{x})}$$  \quad \text{(B.8)}$$

In a first order approximation the surface polarization $P_s$ which enters (B.3) as a source term is the product of the susceptibility and the homogeneous solution at the surface:

$$\bar{P}_s(\vec{x}, z) = \chi_s(\vec{x}, z) \bar{E}_{\text{hom}}(\vec{x}, z)$$  \quad \text{(B.9)}$$

Inserting (B.8) and (B.4) into (B.9) the surface polarization is:

$$\bar{P}_s(\vec{x}, z) = \left( \sum_m \chi_{q_m}(z)e^{-iw(\beta)z_1} + e^{i\omega(\beta)z_2} \bar{E}_{\text{inc}} e^{i(\vec{q}_m + \vec{q}_s) \cdot \vec{x}}} \right) e^{i\omega t}$$  \quad \text{(B.10)}$$
Comparing (B.10) with the general Fourier transformation $\tilde{P}_s(x, z) = \sum_m \tilde{P}_s(q_m, z)e^{iq_m x}$ it can be seen that:

$$\tilde{P}_s(\beta + \bar{q}_m, z) = \chi_{\bar{q}_m}(z)(e^{-iw(\beta)z} \bar{1} + e^{iw(\beta)z} \bar{\tau}(\beta)) \cdot \vec{E}_{inc}e^{i\omega t} \quad (B.11)$$

If the surface layer that contains the roughness is thin compared to the wavelength of the incident light, $h_{\text{max}} \ll 1/\omega$, the integrand in (B.6) is approximately constant as a function of $z$ and the equation can be transformed into an algebraic equation. An average susceptibility of the surface layer can be defined as:

$$\bar{X}_{\bar{q}_m} = \frac{1}{h_{\text{max}}} \int_0^{h_{\text{max}}} \chi_{\bar{q}_m}(z) dz = \frac{\varepsilon - 1}{4\pi h_{\text{max}}} h_{\bar{q}_m} \quad (B.12)$$

which is related to the power spectral density of the surface by:

$$h_{\text{max}}^2 |\bar{X}_{\bar{q}_m}|^2 = \frac{(\varepsilon - 1)^2}{4A} P(q_m) \quad (B.13)$$

Then (B.6) can be rewritten as:

$$\vec{E}(\beta + \bar{q}_m, z) = \sqrt{2\pi h_{\text{max}}} \bar{g}(\beta + \bar{q}_m, z, z' = 0) \cdot \tilde{P}_s(\beta + \bar{q}_m, z' = 0). \quad (B.14)$$

where $\bar{P}_s(\beta + \bar{q}_m, z' = 0)$ is given by (B.11) with $\chi_{\bar{q}_m}(z)$ replaced by $\bar{X}_{\bar{q}_m}$ from (B.12), explicitly:

$$\vec{E}(\beta + \bar{q}_m, z) = \sqrt{2\pi h_{\text{max}}} \bar{X}_{\bar{q}_m} \bar{g}(\beta + \bar{q}_m) \cdot \left(1 + \bar{r}(\beta)\right) \cdot \vec{E}_{inc} \quad (B.15)$$

The factor of $\sqrt{2\pi}$ in the last two equations is due to the fact that the time-Fourier transform of $\tilde{P}_s$ has to be used in these expressions.

In the following this formula is evaluated for the simplest case of $s$-polarization. Using the expressions for $\bar{g}_+$ and $\bar{g}_-$ given in [58] and keeping only the terms that are important for both $s$-polarized incident and scattered field, Eq. (B.15) becomes for $z > 0$:

$$\vec{E}(\beta + \bar{q}_m, z) = \frac{(2\pi)^{3/2} i\bar{\omega}^2}{\omega(\beta + \bar{q}_m)} h_{\text{max}} \bar{X}_{\bar{q}_m} e^{iw(\beta + \bar{q}_m)z} \hat{s}(\beta + \bar{q}_m) \hat{s}(\beta + \bar{q}_m) \left(1 + r_s(\beta)\hat{s}(\beta)\hat{s}(\beta)\right) \vec{E}_{inc} \hat{s}(\beta) \quad (B.16)$$
The dyadic products of the unit vectors can easily be evaluated in a basis of \( \hat{s}, \hat{\beta}, \) and \( \hat{z} \), where 
\[
\hat{s}(\hat{\beta} + \hat{q}_m) = \cos \phi \hat{s} + \sin \phi \hat{\beta} \quad \text{and} \quad w(\hat{\beta} + \hat{q}_m) = \tilde{\omega} \cos \theta_s
\]
in terms of the angles \( \phi \) and \( \theta_s \) defined in Fig. 3.10. The result of solving (B.16) for the ratio of scattered to incident field amplitude is:

\[
\frac{|E_s(\hat{\beta} + \hat{q}_m)|^2}{|E_{inc,s}|^2} = (2\pi)^3 \tilde{\omega}^2 \frac{\cos^2 \phi}{\cos^2 \theta_s} (h_{max} \chi q_m)^2 (1 + r_s(\theta_s)^2 (1 + r_s(\theta_i))^2 \quad (B.17)
\]

To compare this result with Eq. (3.3) it has to be converted to the power \( dP \) that is scattered into the solid angle \( d\Omega \) normalized to the incident power \( P_0 \). The incident power on the area \( A \) is given by the scalar product of the Poynting vector \( \vec{S} \) and the surface normal \( P_0 = A\vec{S} \cdot \vec{n} = A \frac{\tilde{\omega}}{2\pi} |\vec{E}_{inc}|^2 \cos \theta_i \).

Next, the power scattered into the solid angle element \( d\Omega \) has to be calculated. The width of a Fourier component is \( \Delta q_m = 2\pi/L \) leading to an angular spread \( \Delta \theta_s = \frac{2\pi}{\Delta \theta_s} \) and \( \Delta \phi = \frac{(2\pi)^3}{\Delta \phi} \). Thus one can write

\[
dS = \frac{\tilde{\omega}}{8\pi} |\vec{E}(\hat{\beta} + \hat{G}_m)|^2 \frac{(\Delta L)^2 \cos^2 \theta_s}{(2\pi)^3} d\Omega
\]

for the Poynting vector, which describes the power flux from a point source into the solid angle \( d\Omega \). To get the power incident onto a detector this needs to be multiplied by the illuminated area as seen from the detector, i.e. \( A \cos \theta_s \). Putting everything together, using

\[
(1 + r_s(\theta_s))(1 + r_s(\theta_i)) = \frac{2 \cos \theta_s}{\cos \theta_s + \sqrt{n^2 - \sin^2 \theta_s}} \frac{2 \cos \theta_i}{\cos \theta_i + \sqrt{n^2 - \sin^2 \theta_i}}
\]

and Eq. (B.13) one arrives at:

\[
\frac{dP}{P_0 d\Omega} = 4\tilde{\omega}^4 (\epsilon - 1)^2 \cos^2 \phi \cos^2 \theta_s \cos^2 \theta_i \frac{P(\tilde{q}_m)}{(\cos \theta_s + \sqrt{n^2 - \sin^2 \theta_s})(\cos \theta_i + \sqrt{n^2 - \sin^2 \theta_i})^2} \quad (B.18)
\]

This is exactly Eq. (3.3) with

\[
Q_P = \left| \frac{\epsilon - 1}{\cos \theta_s + \sqrt{n^2 - \sin^2 \theta_s}} \right|^2 \quad (B.19)
\]

in agreement with [15]. This coefficient is usually referred to as \( Q_{ss} \) since it is valid for both s-polarized incident and scattered light. The coefficients for p-polarization \( Q_{sp}, Q_{ps} \) and \( Q_{pp} \) are also given in [15].

Just as in the case of specular reflectivity, the diffuse reflection from multilayer structures exhibits interference effects that can be observed as fringes in the scattered signal as a function of time during etching or growth. The Green's function approach presented in this appendix can also be used to
Appendix B. Green's Function Method for Elastic Light Scattering

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 nm GaAs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 nm Al$<em>{0.98}$Ga$</em>{0.02}$As</td>
<td></td>
<td></td>
</tr>
<tr>
<td>185 nm GaAs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500 nm superlattice</td>
<td></td>
<td></td>
</tr>
<tr>
<td>95 nm Al$<em>{0.65}$Ga$</em>{0.35}$As</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 nm GaAs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaAs substrate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure B.2: Schematic of the GaAs/AlGaAs multilayer structure used for the light scattering measurement shown in Fig. B.3.

calculate the scattering from multilayer structures. Since the surface roughness of the samples of interest in this work is small, multiple scattering can be ignored. Furthermore since for semiconductor samples the index contrast between air and the semiconductor is much higher than the index contrast at any of the multilayer interfaces, only surface scattering needs to be taken into account. Under these conditions the only modification that has to be made to the theory above is the replacement of the Fresnel reflection coefficients $r_s(\theta_s)$ and $r_s(\theta_i)$ in Eq. (B.17) with their respective values for the multilayer structure $\tilde{r}(\theta)$. For reference, the Fresnel reflection coefficient of a two-layer structure (substrate and cap layer) can be calculated to be:

$$\tilde{r}(\theta) = r(\theta) + \frac{t(\theta)t^{-}(\theta')r_{\text{sub}}(\theta')e^{i\phi}}{1 - r_{\text{sub}}(\theta')r^{-}(\theta')e^{i\phi}}$$  \hspace{1cm} (B.20)

where $r$ and $r_{\text{sub}}$ are the reflection coefficients for the air-cap layer and the cap layer-substrate interfaces respectively and $t$ is the transmission coefficient for the air-cap layer interface (the superscript "-" marks the coefficients for light travelling towards the surface from inside the sample). The prime on the angle $\theta$ indicates that the coefficients have to be evaluated at a different angle for light travelling inside the cap layer because of refraction. The factor $e^{i\phi}$ is the phase shift of the wave due to the path associated with one round trip in the cap layer. Eq. (B.20) can easily be generalized for arbitrary multilayers by replacing $r_{\text{sub}}$ with the appropriate coefficient for this multilayer structure.
Figure B.2 shows a multilayer structure that was grown by Dr. Zbig Wasilewski of the National Research Council in Ottawa. This sample was used for light scattering measurements of a GaAs/AlGaAs structure since at the time of the measurements no aluminum source was available on the MBE system. To start with the cleanest possible surface, the sample was first oxidized in an ozone ambient for 10 minutes. The surface oxide was then removed with a standard thermal desorption procedure in the growth chamber. The procedure is described in detail in Section 3.4.1. It was then moved into the etch chamber where thermal Cl₂ etching was performed at a substrate temperature of 200°C. During the etch a light scattering measurement was performed with a lateral momentum transfer of 16 μm⁻¹ as described in Section 3.3.2. The scattered intensity measured with the photomultiplier tube as a function of etch time is shown in Fig. B.3 a). The interference fringes are clearly visible and superimposed is a decay of the signal. The decay is due to the smoothing of the surface during the etch as discussed in Section 4.2.3. In Fig. B.3 b) the diffuse reflectivity calculated using the experimental parameters for the film thicknesses and indices of refraction, incident and scattering angles and laser wavelength according to the theory presented in this section is shown. Since the decay due to decreasing roughness is not part of the light scattering theory, only the interference fringes should be compared to the data. The correspondence of data and theory is very good. For comparison, the specular reflectivity is also plotted and the fringes are found to be 180° out of phase with the diffuse reflectivity. This has been previously observed and described in the Ph.D. thesis of Christian Lavoie [44].
Figure B.3: a) Light scattering signal during etching of the multilayer structure shown in Fig B.2. The etch was stopped after 19 min. b) Calculated diffuse and specular reflectivity as a function of etch depth for the same multilayer structure.
Bibliography


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