MECHANISMS OF VOLTAGE CONTROLLED REACTIVE SPATTERING AND PHYSICAL PROPERTIES OF REACTIVELY SPATTERED CERMET FILMS

By

JOHN DAVID AFFINITO

B.Sc., Lawrence Institute of Technology, 1975
B.Sc., Lawrence Institute of Technology, 1975
M.Sc., Wayne State University, 1978

THIS THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

in
THE FACULTY OF GRADUATE STUDIES
Department of Physics

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
January, 1984
© John David Affinito, 1984
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Physics

The University of British Columbia
1956 Main Mall
Vancouver, Canada
V6T 1Y3

Date April 6, 1984
This thesis deals with the mechanisms involved in reactively sputtering a metal target in an inert/reactive gas glow discharge and with the electrical transport and optical properties of Al/AlN granular metal (or cermet) films produced by this technique. Experiments are described in which an Al target is sputtered in Ar/N₂ and Ar/O₂ atmospheres. The relationships between chemical processes occurring on the target surface, substrate surface, and in the glow discharge of a dc planar magnetron sputtering system are studied for the purpose of controlling film composition. The positive feedback mechanisms which lead to the well known transitions between bare and covered target surfaces are correlated with glow discharge characteristics. These data are shown to be in agreement with a model which assumes two distinct mechanisms for target coverage: (1) chemisorption of neutral reactive gas species from the sputtering gas; and (2) ion plating of reactive gas species from the sputtering current. This model allows estimation of the stability of the glow discharge against the positive feedback mechanisms and indicates under what circumstances voltage control of the glow discharge will permit sustained operation at all degrees of target surface coverage. With the voltage control method, a one to one correspondence between target voltage and film composition is established. In addition, a method is presented for calculating the film composition from only the glow discharge characteristics.
My experiments show that voltage controlled, reactive dc, planar magnetron sputtering is ideally suited to the deposition of Al/AlN cermets of controlled composition. X-ray diffraction, transmission electron microscope (TEM), Hall, and resistivity vs. temperature data for these Al/AlN cermets are presented as a function of metal volume fraction (Xv) and correlated with the glow discharge characteristics of the deposition process. Metal precipitates are seen to form and, thereby, the film properties are interpreted in terms of granular composites of Al and AlN crystallites when the Al/N ratio becomes greater than one. A percolation threshold is observed in the conductivity at a critical volume fraction (Xvc) of 0.72 ± 0.02. The conductivity, σ, exhibits power law behavior both above and below Xvc. Above Xvc, σ ~ (Xv - Xvc)^t, with t = 1.75 ± 0.1, in excellent agreement with the theoretical prediction of 1.7 for a mixture of two "normal" conductors (i.e. metallic or semiconductor conduction, but not hopping or tunneling). Below Xvc, conduction is via hopping and σ ~ (Xvc - Xv)^-s, with s = 4.3 ± 0.1. For a mixture of normal conductors below Xvc, s is predicted to be 0.7, while there is no theoretical prediction for s when conduction is via hopping. This power law behavior of hopping conductivity warrants further theoretical, as well as experimental, investigation. Further, the temperature behavior of the conductivity is consistent with the view that hopping is from defect to defect within the AlN grains as opposed to direct metal grain to metal grain hopping. The temperature behavior of the conductivity also indicates that electron localization effects become important for Xvc < Xv < 0.8.
In spite of the obvious granular nature of these films, neither the effective medium or Maxwell-Garnett theories for granular materials appears adequate in describing their optical properties. Observable structure in the UV optical absorption and IR reflectivity seem to be properties of AlN and not due to the microgranular structure of the Al/AlN composite. That optical properties predicted in the granular theories are not observed, even though the films are granular, is attributed to the effect of a large number of single and multiple atom Al inclusions, with other than bulk optical properties, that are not taken into account in these theories.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>ix</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>xiii</td>
</tr>
<tr>
<td><strong>CHAPTER I - INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td>1.1 Sputtering</td>
<td>2</td>
</tr>
<tr>
<td>1.2 Electrical Transport and Optical Properties of Cermets</td>
<td>9</td>
</tr>
<tr>
<td>1.2-a Electrical Transport Properties of Cermets</td>
<td>10</td>
</tr>
<tr>
<td>1.2-b Optical Properties of Heterogeneous Mixtures</td>
<td>17</td>
</tr>
<tr>
<td>1.3 Physical Properties of AlN and Al</td>
<td>26</td>
</tr>
<tr>
<td>1.3-a AlN</td>
<td>27</td>
</tr>
<tr>
<td>1.3-b Al</td>
<td>28</td>
</tr>
<tr>
<td><strong>CHAPTER II - MECHANISMS AND CONTROL OF THE REACTIVE SPUTTERING PROCESS</strong></td>
<td>30</td>
</tr>
<tr>
<td>II.1 Apparatus and Experimental Method</td>
<td>34</td>
</tr>
<tr>
<td>II.2 Experimental Results and Discussion</td>
<td>39</td>
</tr>
<tr>
<td>II.2-a The Target Reaction</td>
<td>45</td>
</tr>
<tr>
<td>II.2-b Prediction of Film Composition from Plasma Characteristics</td>
<td>57</td>
</tr>
<tr>
<td>II.2-c Calculation of the Sputtering Yield</td>
<td>66</td>
</tr>
</tbody>
</table>
# CHAPTER III - FILM PROPERTIES - EXPERIMENTAL RESULTS AND DISCUSSION

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>III.1 Electrical Transport Properties of Al/AlN Cermetx</td>
<td>69</td>
</tr>
<tr>
<td>III.2 Optical Properties of Al/AlN Cermetx</td>
<td>79</td>
</tr>
</tbody>
</table>

# CHAPTER IV - CONCLUSION

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV.1 Reactive Sputtering Mechanisms</td>
<td>96</td>
</tr>
<tr>
<td>IV.2 Al/AlN Cermetx Deposited by Voltage Controlled Reactive Sputtering</td>
<td>97</td>
</tr>
<tr>
<td>IV.2-a Electrical Transport Properties</td>
<td>97</td>
</tr>
<tr>
<td>IV.2-b Optical Properties</td>
<td>98</td>
</tr>
</tbody>
</table>

**BIBLIOGRAPHY**

**APPENDIX ON OPTICAL CALCULATIONS**
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Schematic of sputtering process</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Schematic of sputtering chamber</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>Al-Ar/N₂ glow discharge characteristics</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>Comparison of voltage controlled and power controlled reactive sputtering discharge characteristics</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>Variations in Al-Ar/N₂ discharge characteristics with F₁Ar, F₁N₂, and S</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>Variations in Al-Ar/O₂ discharge characteristics with F₁Ar, F₁O₂, and S</td>
<td>51</td>
</tr>
<tr>
<td>7</td>
<td>Variation of P₁r/P₁t with P₁r/I at θ = 1</td>
<td>52</td>
</tr>
<tr>
<td>8</td>
<td>Deposition rate vs Al*</td>
<td>60</td>
</tr>
<tr>
<td>9</td>
<td>Variations of P₁N₂ and 1/P₁N₂ with Al*</td>
<td>62</td>
</tr>
<tr>
<td>10</td>
<td>ρ and TCR vs x (in AlNx)</td>
<td>64</td>
</tr>
<tr>
<td>11</td>
<td>Voltage dependence of the effective metal sputtering yield</td>
<td>68</td>
</tr>
<tr>
<td>12</td>
<td>X-ray diffraction data for Al/AlN cermet films correlated with deposition discharge characteristics</td>
<td>70</td>
</tr>
<tr>
<td>13</td>
<td>TEM data for Al/AlN cermet films correlated with deposition discharge characteristics</td>
<td>71</td>
</tr>
<tr>
<td>14</td>
<td>Resistivity vs T and lnT for Al/AlN cermet films of various metal volume fractions</td>
<td>73</td>
</tr>
<tr>
<td>15</td>
<td>Conduction activation energies for Al/AlN cermet films</td>
<td>75</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>16</td>
<td>Inverse Hall coefficient for Al/AlN cermet films with metal volume fractions near the percolation threshold</td>
<td>77</td>
</tr>
<tr>
<td>17</td>
<td>Critical exponents for conduction in Al/AlN cermets</td>
<td>78</td>
</tr>
<tr>
<td>18</td>
<td>Optical absorption data for Al/AlN cermet films correlated with deposition discharge characteristics</td>
<td>80</td>
</tr>
<tr>
<td>19</td>
<td>Optical absorption data for Al/AlN cermet films correlated with deposition discharge characteristics</td>
<td>81</td>
</tr>
<tr>
<td>20</td>
<td>MGT calculation of optical absorption for Al/AlN cermets as a function of Al volume fraction</td>
<td>83</td>
</tr>
<tr>
<td>21</td>
<td>MGT calculation of optical absorption in Al/AlN cermets as a function of AlN refractive index</td>
<td>84</td>
</tr>
<tr>
<td>22</td>
<td>EMT calculation of optical absorption in Al/AlN cermets as a function of Al volume fraction</td>
<td>85</td>
</tr>
<tr>
<td>23</td>
<td>Coated sphere-EMT calculation of optical absorption in Al/AlN cermets as a function of Al volume fraction</td>
<td>86</td>
</tr>
<tr>
<td>24</td>
<td>Comparison of optical absorption data for actual Al/AlN cermet films with coated sphere-EMT calculations</td>
<td>87</td>
</tr>
<tr>
<td>25</td>
<td>EMT calculation of reflectance of Al/AlN cermets as a function of Al volume fraction</td>
<td>88</td>
</tr>
<tr>
<td>26</td>
<td>Coated sphere-EMT calculation of reflectance of Al/AlN cermets as a function of Al volume fraction</td>
<td>89</td>
</tr>
<tr>
<td>27</td>
<td>IR reflectance data for Al/AlN cermet films correlated with deposition discharge characteristics</td>
<td>90</td>
</tr>
<tr>
<td>28</td>
<td>Optical constants of AlN</td>
<td>108</td>
</tr>
<tr>
<td>29</td>
<td>Optical constants of Al</td>
<td>109</td>
</tr>
</tbody>
</table>
## LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-D</td>
<td>Used as arbitrary constants.</td>
</tr>
<tr>
<td>A'-D'</td>
<td>Optical emission intensity of 3961.5 Å line of neutral Al atoms.</td>
</tr>
<tr>
<td>a-d, p</td>
<td>Radius of a particle in a cermet material.</td>
</tr>
<tr>
<td>a*</td>
<td>Radius of a spherical volume of cermet material.</td>
</tr>
<tr>
<td>E</td>
<td>Energy of a defect state.</td>
</tr>
<tr>
<td>E</td>
<td>Photon energy.</td>
</tr>
<tr>
<td>E_f</td>
<td>Fermi Energy.</td>
</tr>
<tr>
<td>E_0</td>
<td>Average electric field inside a cermet.</td>
</tr>
<tr>
<td>e</td>
<td>Electronic charge.</td>
</tr>
<tr>
<td>F</td>
<td>Electric field in hopping conduction.</td>
</tr>
<tr>
<td>F_{Ar}</td>
<td>Ar flow rate.</td>
</tr>
<tr>
<td>F_{N_2}</td>
<td>N_2 flow rate.</td>
</tr>
<tr>
<td>F_{O_2}</td>
<td>O_2 flow rate.</td>
</tr>
<tr>
<td>f</td>
<td>Fermi-Dirac distribution function.</td>
</tr>
<tr>
<td>f</td>
<td>Fraction of positive ions in sputtering ion current that are reactive gas species.</td>
</tr>
<tr>
<td>I</td>
<td>Total sputtering current (electronic + ionic).</td>
</tr>
<tr>
<td>k</td>
<td>Optical extinction coefficient.</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann's constant.</td>
</tr>
<tr>
<td>M</td>
<td>Generic chemical symbol for sputtered metal atom.</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>N</td>
<td>Density of states function for defects.</td>
</tr>
<tr>
<td>N</td>
<td>Total number of inclusions with dipole moment p.</td>
</tr>
<tr>
<td>n</td>
<td>Optical refractive index.</td>
</tr>
<tr>
<td>n_s</td>
<td>Total number of reactive gas molecules adsorbed on the surface of the sputtering target.</td>
</tr>
<tr>
<td>P_Ar</td>
<td>Ar partial pressure.</td>
</tr>
<tr>
<td>P_N2</td>
<td>N₂ partial pressure.</td>
</tr>
<tr>
<td>P_O2</td>
<td>O₂ partial pressure.</td>
</tr>
<tr>
<td>P_r</td>
<td>Reactive gas partial pressure.</td>
</tr>
<tr>
<td>P_t</td>
<td>Total pressure.</td>
</tr>
<tr>
<td>p</td>
<td>Dipole moment of an inclusion in a cermet material.</td>
</tr>
<tr>
<td>Q</td>
<td>For a coated sphere, ( Q = 1 - \frac{\text{coating thickness}}{\text{total radius}} ). The total radius includes the coating.</td>
</tr>
<tr>
<td>Q_i</td>
<td>Q for a coated dielectric (insulating) sphere.</td>
</tr>
<tr>
<td>Q_m</td>
<td>Q for a coated metal sphere.</td>
</tr>
<tr>
<td>R</td>
<td>Generic chemical symbol for a reactive gas molecule.</td>
</tr>
<tr>
<td>R</td>
<td>Optical reflectance.</td>
</tr>
<tr>
<td>R_H</td>
<td>Hall constant.</td>
</tr>
<tr>
<td>S</td>
<td>Pumping speed.</td>
</tr>
<tr>
<td>S(Ar)</td>
<td>Pumping speed for Ar gas.</td>
</tr>
<tr>
<td>S(N₂)</td>
<td>Pumping speed for N₂ gas.</td>
</tr>
<tr>
<td>S(O₂)</td>
<td>Pumping speed for O₂ gas.</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$s$</td>
<td>Critical exponent for conduction below $X_{vc}$.</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature.</td>
</tr>
<tr>
<td>$t$</td>
<td>Time.</td>
</tr>
<tr>
<td>$t_c$</td>
<td>Critical exponent for conduction above $X_{vc}$.</td>
</tr>
<tr>
<td>$t_{mc}$</td>
<td>Coating thickness on coated metal sphere.</td>
</tr>
<tr>
<td>$u$</td>
<td>Critical exponent for interparticle spacing.</td>
</tr>
<tr>
<td>$V$</td>
<td>Cathode voltage in sputtering.</td>
</tr>
<tr>
<td>$W$</td>
<td>Cathode power in sputtering</td>
</tr>
<tr>
<td>$X_v$</td>
<td>Volume fraction of metal in a cermet.</td>
</tr>
<tr>
<td>$X_{vc}$</td>
<td>Critical value of $X_v$ at the percolation threshold.</td>
</tr>
<tr>
<td>$x$</td>
<td>$x$ in AlN$_x$.</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Product of reactive gas impingement rate per unit $P_T$ and the coefficient for neutral reactive gas chemisorption on a sputtering target.</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Number of N$_2$ molecules gettered per Al atom sputtered.</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Secondary electron emission coefficient.</td>
</tr>
<tr>
<td>$\delta$</td>
<td>$\delta$Al$^*$ = the number of Al atoms sputtered per second.</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Ion plating sticking coefficient for positive reactive gas species impinging on a sputtering target.</td>
</tr>
<tr>
<td>$\epsilon_i$</td>
<td>Average dielectric constant of a cermet material.</td>
</tr>
<tr>
<td>$\epsilon_m$</td>
<td>Dielectric constant of metallic material in a cermet.</td>
</tr>
<tr>
<td>$\epsilon_{ic}$</td>
<td>Dielectric constant of material that is coating an insulating sphere in a cermet.</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>(\varepsilon_{mc})</td>
<td>Dielectric constant of material that is coating a metallic sphere in a cermet.</td>
</tr>
<tr>
<td>(\varepsilon_{ics})</td>
<td>Average dielectric constant of a coated insulating sphere in a cermet.</td>
</tr>
<tr>
<td>(\varepsilon_{mcs})</td>
<td>Average dielectric constant of a coated metallic sphere in a cermet.</td>
</tr>
<tr>
<td>(\eta_{\text{eff}})</td>
<td>Effective sputtering yield for metal atoms. (\eta_{\text{eff}} = \eta_m/(1 + \gamma)).</td>
</tr>
<tr>
<td>(\eta_m)</td>
<td>Sputtering yield for metal atoms.</td>
</tr>
<tr>
<td>(\eta_r)</td>
<td>Sputtering yield for reactive gas molecules.</td>
</tr>
<tr>
<td>(\theta)</td>
<td>Polar angle in a spherical coordinate system.</td>
</tr>
<tr>
<td>(\theta)</td>
<td>Fraction of the surface of a sputtering target that is covered with a target material-reactive gas compound layer.</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>Photon wavelength.</td>
</tr>
<tr>
<td>(\mu)</td>
<td>Mobility.</td>
</tr>
<tr>
<td>(\rho)</td>
<td>Resistivity.</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Conductivity.</td>
</tr>
<tr>
<td>(\tau)</td>
<td>Time duration of a sputtering current transient.</td>
</tr>
<tr>
<td>(\tau_r)</td>
<td>Time required for a pressure transient in the sputtering chamber to be damped out.</td>
</tr>
<tr>
<td>(\phi)</td>
<td>Electric potential.</td>
</tr>
<tr>
<td>(\Delta E)</td>
<td>(\Delta E = E - E_f) = the conduction activation energy.</td>
</tr>
<tr>
<td>(\Delta I)</td>
<td>Magnitude of sputtering current transient.</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

I am pleased to thank Dr. R.R. Parsons for the great amounts of time and effort he has invested in this project as my supervisor. His guidance was invaluable.

I also wish to thank Dr. R. Barrie, N. Fortier, M. Brett, and Dr. J.A. Rostworowski for the many illuminating discussions we have had. N. Fortier provided valuable assistance with the transport measurements, Mary Major assisted with the TEM work, and, using Dr. R.R. Haering's profilometer, M. Brett performed many of the film thickness measurements.

For financial support, I wish to thank the Natural Sciences and Engineering Research Council of Canada and the University of British Columbia.

To all my friends and relatives who encouraged and supported me throughout my studies I give my heartfelt thanks. To my father's repeated question, I would like to answer "Yes, I am finally through".

Thank you.
CHAPTER 1

INTRODUCTION

Microgranular mixtures of metallic and insulating materials (cermets or granular metals) are currently of great interest, both practically and theoretically. They are of practical interest as selective solar absorbers [1] and temperature stabilized, thin film resistors [2]. Theoretically, they represent real, macroscopic systems that may be used to study the critical phenomena associated with a percolation system near the percolation threshold [2-6]. As will be discussed shortly, these properties of interest, both practically and theoretically, depend crucially upon the microgeometrical configuration of the film, and not just upon the overall, bulk chemical composition.

This thesis focuses, in part, on some of the physical properties of Al/AlN cermets reactively sputtered from an Al sputtering target in an Ar/N₂ atmosphere. However, in developing the fabrication technique some very interesting results concerning the mechanisms involved in reactive sputtering were uncovered, and these results seem to be at least as important as the physical properties of the films produced. Therefore, in view of the ever increasing role of reactive sputtering in thin film deposition during the last twenty years [7-9], fully half of this treatise will concern experiments performed to determine and to model the mechanisms involved in the reactive sputtering process. Due to the large number of interrelated parameters involved in the reactive sputtering process, little in the way of general, systematic studies
relating film properties or process control to deposition parameters has been published [7]. Therefore, a study of the mechanisms involved in reactive sputtering, with the goal of determining some fairly universal guidelines for control of the deposition process, is of considerable importance.

This thesis is organized as follows. The remainder of this introductory chapter will be a review of: (1) the principles of the sputtering process; (2) the electrical transport and optical properties of cermets; and (3) the electrical and optical properties of AlN and Al. In chapter two, I present my experimental and theoretical results concerning the mechanisms of reactive sputtering. In chapter three, I give experimental data concerning the electrical transport and optical properties of reactively sputtered Al/AlN cermet films, and an analysis of these data.

I.1 Sputtering

"Sputtering" is associated with the impingement of a particle (ion, atom, cosmic ray, etc.) on a material body with the result that, through momentum transfer, some particles of the material body are ejected ("sputtered") [7-14]. The word "sputtering" is used in conjunction with a large number of modifiers to describe an equally large number of related processes. The modifiers are generally employed to indicate what type of particles are causing the sputtering, what technique is used to generate these particles, and, in the case of controlled deposition of thin films, what conditions exist on the substrate upon which the sputtered flux lands [7-14].
Ions are generally used to cause sputtering for the controlled deposition of thin films [13,14]. The two broad classes of ion sputtering are called "ion beam" sputtering and "glow discharge" sputtering. In either of these cases the material to be sputtered (or the target) is thick enough that the sputtered particles are ejected only from the surface that is under ion bombardment. The particles that are ejected are generally atoms or small molecules of the target material and "secondary" electrons. In the case of ion beam sputtering, a collimated beam of ions of rather well defined kinetic energy causes the sputtering, and the technique is further categorized by the method of producing the beam [13]. In glow discharge sputtering, the material to be sputtered forms the cathode in a glow discharge and is bombarded primarily by positive ions from the glow [7]. In this latter process, the incident ions are not collimated and their kinetic energies are distributed (in some cases rather widely) due to collisions in transit from the glow to the target. This distribution in incident ion energies is related to: the potential difference between the cathode (target) and the glow; the temperature; the total and partial pressures of the gases in the glow discharge environment; and the cross section for charge transfer between the various atoms, molecules, and ions present [7,15]. These glow discharge sputter techniques are further described by modifiers indicating: the target shape (planar, cylindrical, belt...); the frequency of the electrical discharge (dc, ac, or rf); any external agent used to support the glow discharge (magnetic fields, thermionic emitters, tesla coils...); the reactivity of the discharge
gases with respect to the target material (inert or reactive); the conditions existing at the substrate (temperature, state of motion with respect to the target, substrate bias, is there a glow discharge at the substrate, and if so, at what frequency) [8,10-12]. This seemingly endless addition of modifying words can lead to some fairly long names. For instance, the experimental work to be discussed in this thesis is concerned with "voltage controlled, dc, reactive, planar magnetron sputtering". This name indicates that: the target is flat (planar); a magnetic field is used to help confine the glow to a region very near the target, to make better use of the ionizing abilities of the secondary electrons and to create the ions close to the target where they are needed (magnetron); at least some component in the gas mixture will chemically combine with the target material (reactive); the discharge is dc (dc); the electrical characteristics of the glow discharge are altered or maintained by monitoring and controlling the cathode voltage (voltage controlled).

Fig. 1 schematically depicts the various processes which occur simultaneously inside a sputtering chamber while sputtering a metal target (M) in the presence of an Ar/reactive gas (R) mixture. These processes may be broadly divided into three categories according to the physical location at which the process takes place. They are target reactions, wall (or substrate) reactions, and gas reactions.

The target surface is continuously bombarded by energetic ions and thermal neutrals of the gases present in the discharge. The ion
Schematic depiction of processes occurring during reactive sputtering of a metal target (M) in an Ar/Reactive gas (R) atmosphere.
bombardment can cause sputtering of the target surface material and the emission of secondary electrons. Further, the bombarding ions of the reactive gas may chemically bond with the target material and produce a target material-reactive gas compound layer on parts of the target surface. If neutral R molecules chemisorb on the bulk target material, then the flux of thermal neutrals of R will also contribute to the formation of the compound layer. Since the yield of sputtered target atoms and secondary electrons is different for bare metal and compounded targets [8], these yields will be highly dependent on the degree of target coverage. Also, the presence of a compound layer on the target surface means that the constituents of R will also be sputtered from the target surface.

Sputtered flux will condense and react with the thermal flux of R neutrals on the walls and substrates [16-21]. Note that even if R molecules do not chemisorb on the bulk target material, the condensing flux is largely atomic in nature [7-8] and is expected to be much more reactive than the bulk material. This compound formation on the walls (sometimes called gettering) also serves to lower the partial pressure of the reactive gas in the chamber. The speed of this getter pumping is controlled by the sputtered flux, which, in turn, is controlled by the number and energy of ions incident on the target surface as well as the degree to which the target surface is covered by a reactive gas-target material compound layer.

Ar and R are allowed to flow into the vacuum chamber through a controlled leak while they are simultaneously pumped out by mechanical
means (such as a partially throttled diffusion pump). In steady state, this produces partial pressures of the two gases that are determined by their individual leak rates and pumping speeds, provided that there is no glow discharge. In the presence of the glow discharge, the gettering action of the sputtered flux on the reactive gas acts as another pumping port in parallel with the diffusion pump. In the glow region, secondary electrons emitted from the target help to sustain the discharge through electron impact ionization of the gaseous species present. Therefore, the glow may act as a source of positive and negative ions of Ar and R which serve to drive a variable speed reactive gas getter pump. The potential drop between the target and the glow region that is needed to maintain the discharge will depend on the yield of secondary electrons from the target surface (more electrons mean a lower voltage). This implies that this potential difference will depend strongly on the yield of secondary electrons, which, in turn, is largely controlled by the degree of target coverage. In addition, R molecules may dissociate into ions and neutrals of their various constituents. The positive ions in the glow will be accelerated towards the target, however, due to collisions (mostly symmetric charge transfer reactions [15]) many of the ions that reach the cathode have considerably less kinetic energy than expected by merely considering the potential difference between the cathode and the glow discharge (cathode fall) [7,15].

The previous discussions show that the gaseous ambient is coupled to the target, wall, and glow discharge regions. Therefore, these three regions are all coupled to each other through the sputtering gas. A longstanding problem in controlling reactively sputtered film
compositions is that positive feedback between the gettering rate at the wall and the metal sputtering rate conspire to force the target surface to either remain bare metal or become completely covered with a compound layer [16-21]. If the sputtering rate is becoming great enough to uncover some portions of the target surface then the sputtering yield increases from these bare regions. This causes an increase in the gettering rate which reduces the number of reactive gas species available to cover the target. This, in turn, allows the bare spots to grow larger and further increases the sputtering yield. This positive feedback cycle quickly leads to a completely bare target surface. This abrupt change in the degree of surface coverage also causes an abrupt change in the secondary electron emission yield, which results in an abrupt change in the cathode fall. Also, with the abrupt increase in sputtering yield, an abrupt increase in sputtered flux occurs that is accompanied by an abrupt decrease in reactive gas partial pressure due to increased gettering. If one starts from a bare target, the opposite reaction, which leads to a covered target, occurs if the sputtering rate becomes too low to keep the entire surface cleared of the compound layer. There is considerable hysteresis observed in the discharge characteristics between these two directions [16-21], with the result that a gap exists in the I-V-$P_R$ characteristics under which stable operation of the discharge is possible. Since it has been found that films sputtered from a bare target are nearly pure metal, while films sputtered from a completely covered target are stoichiometric metal-reactive gas compound [16,20,21], this positive feedback cycle is
seen to severely restrict the attainable film compositions. Since the composition of sputtered films will depend on the relative arrival rates of sputtered atoms and reactive gas molecules at the substrate, knowledge of the nature and strength of the coupling between the target, gas, and substrate would be very important in any attempt at controlled deposition of thin films. The nature of this coupling will be explored in this thesis through a detailed balance analysis of the movements of sputtered flux and reactive gas molecules in the sputtering chamber. This study will show why it is possible to maintain stable operating conditions at all degrees of target coverage for an Al target in an Ar/N₂ atmosphere (and other metal-reactive gas combinations in which rapid chemisorption of the neutral reactive gas on the bulk metal does not occur), provided that cathode voltage is controlled. This stability at all degrees of target coverage gives access to AlNₓ films for all x between zero and one. In addition, this analysis yields a technique by which x may be calculated from knowledge of the glow discharge characteristics alone.

1.2 Electrical Transport and Optical Properties of Cermets

Cermets (or granular metals) are microgranular mixtures of insulating and metallic particles. This term is sometimes applied to similar mixtures of insulator-semiconductor or semiconductor-metal particles. When the volume fraction of the metallic constituent (Xᵥ) is near zero or one the properties of the cermet are close to those of a pure phase. However, at intermediate values of Xᵥ some properties
(resistivity, average temperature coefficient of resistance (TCR), and density) [2,22] appear to be intermediate to those of the pure phases, while other properties (optical absorption and details of the temperature dependence of resistivity) [4-6] exhibit behaviour that is fundamentally different from either pure phase and arises primarily from the geometric properties of the mixture. A brief discussion of some of these geometry dependent properties will now be given.

**I.2-a Electrical Transport Properties of Cermets**

Previous experimental studies [23] of W/Al₂O₃ cermets have shown power law behaviour of conductivity (σ) for Xᵥ higher than the percolation threshold (Xᵥc). Theoretical studies [24] for mixtures of two "normal" conductors (not hopping or tunneling conduction) predict power law behaviour both above and below Xᵥc. By power law behaviour it is meant that the property under study, in this case the electrical conductivity, is seen to vary as some power of |Xᵥ - Xᵥc| for values of Xᵥ in the neighborhood of Xᵥc [3,24]. The particular power is expected to be different on either side of Xᵥc. The expression that relates the exponent on one side of Xᵥc to the exponent on the other side is called the scaling relation. The scaling relation and these exponents are expected to depend only on the spatial dimensionality of the sample [3,24]. For more detailed discussions on this power law behaviour and scaling, the reader is referred to the literature on percolation theory [3] and the theory of critical phenomena and phase transitions [25,26].
When the conductivities of the two phases differ by as much as in Al/AlN or W/Al₂O₃ cermets normal conduction does not occur below Xvc, instead conduction proceeds via tunneling between isolated metal particles and through the intervening insulator particles [2,5,23,27]. The resistivities of Al and AlN are \(3 \times 10^{-6} \ \Omega\cdot\text{cm} [28]\) and greater than \(10^{15} \ \Omega\cdot\text{cm} [29]\), respectively. This added complication of tunneling conduction below Xvc has not yet been treated in the context of a critical theory of phase transitions, nor has any experimental evidence for critical behaviour of tunneling in this regime been presented. The method of theoretical treatment seems straightforward enough. One should express \(\sigma\), for tunneling between isolated metal islands [30,31], in terms of the island size and interisland separation, then substitute the power law relations for these two distances into the expression for \(\sigma\). Unfortunately, while the power law relation for the metal cluster size is well known [3] the relation for the intercluster spacing is not. A measurement of the power law behaviour of tunneling for \(X_v \lesssim X_{vc}\) should, however, allow this relation to be determined by inverting the expression for the tunneling conductivity.

Previous treatments of tunneling far below Xvc, which were not meant to deal with critical phenomena, in cermets have predicted [2] and observed [2,32] \(\ln \rho \sim \frac{1}{\sqrt{T}}\) temperature behaviour for the resistivity in cermet films with average metal grain sizes less than \(\sim 40 \ \AA\). The explanation, however, involved assumptions for the relation between the distribution of grain sizes and intergrain spacings that did not reflect the true structure of these granular materials [6,33]. In particular,
Abeles et al. [2] derived an expression for hopping conduction in granular metals by considering the charging energy involved when an electron is removed from one isolated metallic grain and placed on a neighboring grain. This charging energy was found to be a function of both the intergrain spacing and the grain size. The two controversial assumptions [6,33] that they made were; that the intergrain spacing was proportional to the grain size, both microscopically and macroscopically; and that there was a very broad distribution of grain sizes. With these two assumptions, conduction was taken to be dominated by paths of an "optimal" grain size and intergrain spacing which resulted in the highest hopping probability. For low field conduction, as the temperature changed the energy available to the tunneling electrons changed which caused the optimal grain size to change also. Therefore, as the temperature changed the conduction path changed in order to always make use of a path with optimal grain sizes. As long as there was a sufficiently large distribution of grain sizes to accomodate this process, the temperature behaviour of \( \rho \) was predicted to be \( \ln \rho \sim 1 / \sqrt{T} \).

More recently, detailed studies of the grain size and intergrain spacing distributions in granular metals, that are found to follow the \( \ln \rho \sim 1 / \sqrt{T} \) law, have been done [6,33]. These studies showed that, given the hopping theory just described, the distribution in grain sizes was far too narrow to account for the range of temperature over which the \( \ln \rho \sim 1 / \sqrt{T} \) behaviour was observed.

The classic treatment of variable range hopping given by Mott [34] contained this same idea of an optimal hopping path. However, in
Mott's treatment the trade off was between the exponential dependences of the hopping frequency on distance between localized states and the difference in energy of these states (where it is assumed that hopping between states of equal energy is favored). Mott took the density of states to be a constant and found $\ln \rho \sim 1 / T^{1/4}$.

More recent theoretical studies [35,36] have indicated that the Coulomb interaction between localized electrons gives rise to a "Coulomb gap" in the density of states near the Fermi level and results in a parabolic density of states near the Fermi level. If this parabolic density is incorporated in the Mott theory for variable range hopping, $\ln \rho \sim 1 / \sqrt{T}$ behaviour is obtained, provided that the localization length is small compared to the hopping length [36]. This last restriction is not satisfied very near to $X_{vc}$, or when the ratio of metal island size to interisland separation is large, but will be expected to hold for values of $X_v$ well below $X_{vc}$.

All of these variable range hopping theories predict an apparent temperature dependent "activation" energy (i.e. Arrhenius plots of resistivity do not yield straight lines). This is because of the nature of the competition between available conduction pathways. Paths of a given particle size or separation will have conduction activation energies that differ from paths with different particle sizes or separations. The paths of least resistance (or optimal paths) will be the ones that carry the most current. Since the competition between the various pathways is affected by the temperature, as the temperature changes the optimal paths will also change. Since each class of
pathways has an activation energy that differs from the other classes of pathways, the apparent activation energy for the sample as a whole will vary with temperature as the optimal paths switch with changing temperature.

One other treatment of hopping conduction in cermets below $X_{vc}$ has been presented by Devenyi et al. [37] regarding conductivity data for Nb/Al₂O₃ composites. In these composites, Devenyi found the conduction activation energy to vary as a power of the temperature. His approach assumed that the insulating material contained such a large number of defect states due to excess Nb that a continuous, nonuniform distribution of defect states existed in the forbidden gap. Conduction was taken to be via hopping from defect to defect in the insulator as opposed to hopping directly across the insulator. To model this problem, Devenyi followed an approach presented by Croitoru et al. [38]. Using a relaxation time approximation to the Boltzmann transport equation, Croitoru showed that the hopping conductivity could be written as

$$\sigma \sim \int \mu(E,T,F) f(E,T,F) N(E,T,F) \, dE$$

where $e$ is the electronic charge, $\mu$ is the carrier mobility, $f$ is the statistical occupation function, $N$ is the density of defect states, $E$ is the defect state energy, $T$ is the temperature, and $F$ is the electric field. At this point Croitoru makes an assumption that is equivalent to a generalization of the optimal path method used by Mott [34], Abeles
The assumption is that the integrand of Eqn. 1-1 is sharply peaked at a particular energy so that conduction can be assumed to be only via states of this (optimal) energy. Various functional forms may then be used for N, \( \mu \), and \( f \) to calculate the conductivity due to the optimal path.

Devenyi et al. pointed out that if \( f \) is a Maxwell-Boltzmann distribution then the maximum of the integrand of Eqn. 1-1 occurs at an energy \( E \) given by the solution of the following equation:

\[
\frac{\partial (\ln(N\mu))}{\partial (E-E_f)} = \frac{1}{kT}.
\]  

To explain their data, which showed the conduction activation energy to vary as \( T \) to some power, Devenyi et al. took the density of states–mobility product to be

\[
N\mu \sim N_f\mu_f \exp(A[E-E_f]^p)
\]

where \( E \) and \( E_f \) are the state and Fermi energies respectively, \( N \) and \( N_f \) are the density of states in general and at the Fermi level respectively, \( \mu \) and \( \mu_f \) are the mobilities in general and at the Fermi level respectively, \( A \) and \( p \) are constants that are determined experimentally. No physical reason was given for choosing this functional form other than it gave the correct temperature behaviour for the conduction activation energy. Making use of Eqn. I-3 in Eqn. I-2 yields
\[ E - E_f = \frac{1}{(Ak_T p)^{1-p}} = \Delta E \]  \hspace{1cm} (I-4)

and

\[ \ln \Delta E = \ln ([A_p k]^{1-p}) + \frac{1}{1-p} \ln (T), \]  \hspace{1cm} (I-5)

where \( \hat{E} \) is the optimal energy which maximizes the integrand of Eqn. I-1. The result of this analysis, as shown in Eqn. I-5, was that, given Eqn. I-3, the conduction activation energy should vary as some power (related to \( p \)) of \( T \). Since the defect density will depend strongly on the sample composition, this power of \( T \) should be different for each value of \( x_v \) and, therefore, no characteristic temperature behaviour should exist from sample to sample.

Even though, in the Nb/Al\(_2\)O\(_3\) samples studied by Devenyi, this type of behaviour was observed, a physical model for the functional form of the \( Nu \) product, shown in Eqn. I-3, would be very desirable. Nevertheless, the idea of a large number of continuously distributed defect states within the forbidden gap leading to a continuously changing activation energy is certainly valid. Indeed, it is implicit in all of the previously mentioned optimal path approaches to hopping conduction [2,34-36]. Also, optical transitions between band tails have shown the density of states in the conduction band tails to exhibit an exponential dependence on \( E - E_b \), where \( E_b \) is the energy of the band edge under consideration [39]. The more heavily doped the sample the more...
prominent the presence of these exponential tails become. It is certainly possible that the metallic impurities within the insulating grains of a cermet could exhibit a similar exponential density of states with respect to their distribution near the Fermi level. If one has only resistance data it is not possible, however, to separate the density of states and mobility contributions in Eqn. 1-3. Devenyi suggests that nonlinear effects at high fields may allow for such a separation.

For $X_v$ just above $X_{vc}$ other investigators [5,40,41] have observed a metal to insulator transition as a function of $T$. On the low $T$ side of this transition, electron localization effects were observed as $\rho \sim \ln T$ behaviour, a negative magnetoresistance, and a relatively temperature-independent Hall coefficient. Either of these last two measurements served to determine that the $\rho \sim \ln T$ behaviour was due to electron localization and not electron-electron interaction.

I.2-b Optical Properties of Heterogeneous Mixtures

There are a great many mean field type approaches that have been used to predict the optical properties of heterogeneous mixtures of materials of differing dielectric properties. In fact, one review article by Van Beek [42] summarizes 29 different methods. While the details of these many approaches may differ considerably, in essence each is based on one of only two different fundamental assumptions: that particles of one material are randomly embedded in an amorphous matrix of another material; or, a random mixture of two different types
of particles is assumed. In either case, after making one of these two basic assumptions, along with other less important assumptions, an effective dielectric constant for the composite is derived in terms of the dielectric constants and volume fractions of the component materials [42,43]. These calculations are done by averaging over volumes that are large compared with the inhomogenities and small compared with the wavelength of light involved [42,43]. In the first case, the dielectric constants of the matrix and embedded materials appear in an asymmetric manner in the derived effective dielectric constant of the composite, while optical properties of both particles enter symmetrically in the second case. This is to be expected from the symmetries (or asymetries) inherent in the basic assumptions. While secondary assumptions (such as the distribution of particle shapes and sizes) lead to quantitative differences in the results, major, and fundamental, qualitative differences follow from choosing one or the other of the two basic assumptions mentioned earlier [42]. In addition, each of these approaches has been generalized to allow for mixtures of more than two materials [42,43].

At this point I briefly present the basics of these two fundamental approaches, as well as one generalization to more than two materials. This presentation is meant to be useful in the analysis of the optical properties of reactively sputtered thin film cermets, and does not even approach a comprehensive exposition on all of the various subtleties that have been introduced in the literature to date on the general topic of heterogeneous mixtures.
Perhaps the simplest approach to an asymmetric theory is a generalization of a calculation of Rayleigh's for a cubic array of spheres, of radius \(a\) and dielectric constant \(\varepsilon_m\), in an external electric field, \(E_0\). In such an array, the field seen by any sphere is, to a first approximation, just \(E_0\) because the fields due to dipoles induced in other spheres cancel due to the cubic symmetry and higher order multipoles are neglected. These higher order terms become more important as the spheres packing density (volume fraction, \(X_v\)) increases. A spherical portion of this array, of radius \(a^*\), is then centered on the origin of a spherical coordinate system embedded in a material of dielectric constant \(\varepsilon_1\). Then, by making use of the Clausius-Mossotti relation for polarizable spheres immersed in a dielectric medium, far away from the array, at a position \((r, \theta)\), one may calculate the potential as [44].

\[
\phi = \left[ N \frac{\varepsilon_m - \varepsilon_1}{\varepsilon_m + 2\varepsilon_1} \frac{a^3}{r^3} - 1 \right] E_0 \cos \theta 
\]  

where \(r\) and \(\theta\) have the usual meaning in reference to a spherical coordinate system, and \(N\) is the total number of spheres. Similarly, if the spherical section of the cubic array of spheres embedded in the dielectric medium is assumed to have an effective dielectric constant, \(\varepsilon\), one may also write this potential as...
\[ \phi = \frac{N}{\varepsilon + 2\varepsilon_1} \frac{a^3}{r^3} \cos \theta \]  

(I-7)

Upon equating Eqns. 1-6 and 1-7 one obtains

\[ \frac{\varepsilon - \varepsilon_1}{\varepsilon + 2\varepsilon_1} = X_v \frac{\varepsilon_m - \varepsilon_1}{\varepsilon_m + 2\varepsilon_1} \]  

(I-8)

or

\[ \varepsilon = \varepsilon_1 \left[ 1 + \frac{3X_v (\varepsilon_m - \varepsilon_1)}{\varepsilon_m + 2\varepsilon_1 - X_v (\varepsilon_m - \varepsilon_1)} \right] \]  

(I-9)

One should note the asymmetric appearance of \( \varepsilon_m \) and \( \varepsilon_1 \) in Eqns. 1-8 and 1-9, as well as the fact that \( \varepsilon \) diverges when \( \varepsilon_m + 2\varepsilon_1 = X_v (\varepsilon_m - \varepsilon_1) \). This divergence has been labeled "the dielectric anomaly" [4], and this type of feature is common to all asymmetric theories. Expressions similar to Eqn. 1-9 have been arrived at by many other authors [42, 43] with less restrictive assumptions (such as not requiring cubic symmetry or spherical particles) and more involved mathematics. In keeping with the literature, I will refer to asymmetric theories of optical properties as Maxwell-Garnett Theories (MGT). This nomenclature arises because James Clerk Maxwell Garnett was the first to arrive at Eqn. 1-9 based on an analysis of Maxwell's equations for propagating electromagnetic waves [45], whereas others, as
I have just outlined, had previously arrived at Eqn. I-9 from static considerations.

Symmetric theories are generally referred to as "Effective Medium Theories" (EMT), the first example of which seems to have been put forward by D.A.C. Bruggeman in 1935 [46]. Bruggeman sought the effective dielectric constant, $\varepsilon$, of a randomly dispersed mixture of two types of particles, with dielectric constants $\varepsilon_m$ and $\varepsilon_1$ and with respective volume fractions $X_v$ and $(1-X_v)$. If the average electric field within the composite is $E_0$, and if any particular particle is assumed to be immersed in a medium of effective dielectric constant $\varepsilon$, then the induced dipole moment of that particle, say one with dielectric constant $\varepsilon_m$, may be written as [4]

$$p = \frac{3}{4\pi} v \frac{\varepsilon_m - \varepsilon}{\varepsilon_m + 2\varepsilon} E_0$$  \hspace{1cm} (I-10)

where $v$ is the volume of the particular particle under scrutiny. Since these induced dipoles produce deviations from $E_0$ in proportion to $p$, the sum, over all particles, of these deviations (or dipole moments) must equal zero, by definition of $E_0$. Therefore, summation of equations like I-10 for each type of particle leads to

$$X_v \frac{\varepsilon_m - \varepsilon}{\varepsilon_m + 2\varepsilon} + (1-X_v) \frac{\varepsilon_1 - \varepsilon}{\varepsilon_1 + 2\varepsilon} = 0$$  \hspace{1cm} (I-11)
or

\[ \varepsilon = \frac{1}{4} (\Delta + \sqrt{\Delta^2 + 8 \varepsilon_m \varepsilon_1}) \]  \hspace{1cm} (I-12)

where

\[ \Delta = \left[ 3X_v - 1 \right] \varepsilon_m + \left[ 3(1-X_v) - 1 \right] \varepsilon_1 \]  \hspace{1cm} (I-13)

Note the symmetric roles of \( \varepsilon_m \) and \( \varepsilon_1 \) in Eqns. I-11 through I-13, as well as the lack of any dielectric anomaly. This lack of a dielectric anomaly is common to all symmetric theories. An EMT formulation that has been seen to agree more closely than others tested, when well defined mixtures of known \( \varepsilon \), \( \varepsilon_m \), and \( \varepsilon_1 \) were measured [43] was

\[ \varepsilon = \left[ X_v \varepsilon_m^{1/3} + (1 - X_v) \varepsilon_1^{1/3} \right]^3 \]  \hspace{1cm} (I-14)

Eqn. I-14 has been arrived at by at least two fairly different approaches. Landau and Lifshitz [48] obtained it by; expanding, to second order, the local dielectric constant, electric field, and electric displacement fields about their average values; making substitutions based upon the fact that the divergence of the unaveraged displacement field should vanish; then, with the help of several vector
identities, calculated the average electric displacement in the composite. Looyenga's [49] approach to Eqn. I-14 was very different. Looyenga assumed that the effective dielectric constant for the mixture was the same as for another mixture of the same overall composition but in which the different types of particles themselves had different volume fractions of the two materials. Then, to second order, the dielectric constants for each type of particle were expanded in powers of the volume fractions of the particles about the overall composition of the mixture. In the limit of going to particles composed of only one material, a second order differential equation for the effective dielectric constant as a function of $X_v$ was developed and solved, subject to the boundary conditions $\varepsilon(0) = \varepsilon_1$ and $\varepsilon(1) = \varepsilon_m$. The symmetry between $\varepsilon_m$ and $\varepsilon_1$, as well as the lack of any dielectric anomaly is even more apparent in Eqn. I-14 than in Eqn. I-12. Further, the more compact formulation and transparent symmetry of Eqn. I-14 make it easier to apply in actual calculations, particularly when all of the dielectric constants are complex numbers.

MGT has been found to describe, quite satisfactorily, the optical properties of mixtures that were quite obviously particles of one material embedded in a matrix of another material [4,50-54]. Of particular importance to this work, it was found adequate in describing the optical properties of cosputtered cermets. These are cermets that were prepared by sputtering, simultaneously, from two targets (a metal and an insulator) onto a single substrate. The dielectric anomaly manifests itself as a peak in the optical absorption spectrum of the
composite. The position of this peak is predicted, and observed, to move towards longer wavelengths as Xv is increased. While the peak positions are fairly well described by MGT, the peak heights and widths are generally different from the predicted values. A number of authors [54-57] have investigated the effects of distributions in particle sizes and shapes in an effort to explain these discrepancies. The results of these investigations were that peak widths should broaden as the particle size becomes less than the electron mean free path causing the conductivity to lower, and that peak positions and heights varied with particle shape. Inclusion of size and shape effects is found to still leave some discrepancy between the predicted and observed magnitude of optical absorption. In particular, the peak height of the dielectric anomaly is found to vanish with Xv much more rapidly than predicted, and the general background absorption is higher than predicted, especially at longer wavelengths [8,50-53].

EMT has been found to describe the optical properties of composites that were obviously a randomly dispersed mixture of two types of particles [43]. However, there are no reported cases of sputtered (or cosputtered) films displaying EMT behaviour, rather, these composites were mechanically mixed.

One method of extending either EMT or MGT to more than two materials may be particularly well suited to treating the optical properties of cermets that have been reactively sputtered from a single metal target. The method, introduced by H.C. van de Hulst [58], assumes that a particle in either EMT or MGT consists of a particle of radius a
and dielectric constant $\varepsilon_m$ (or $\varepsilon_i$) coated with another material of thickness $t_{mc}$ (or $t_{ic}$) and dielectric constant $\varepsilon_{mc}$ (or $\varepsilon_{ic}$).

Since one of these composite particles is just a particle of one material embedded in a matrix of another material, the effective dielectric constant of a coated sphere, $\varepsilon_{mcs}$ (or $\varepsilon_{ics}$), may be obtained from Eqn. I-9, with the following substitutions

$$
\varepsilon \Rightarrow \varepsilon_{mcs} \text{ (or } \varepsilon_{ics})
$$

$$
\varepsilon_m \Rightarrow \varepsilon_m \text{ (or } \varepsilon_i)
$$

$$
\varepsilon_i \Rightarrow \varepsilon_{mc} \text{ (or } \varepsilon_{ic})
$$

$$
X_v \Rightarrow Q_m^3 = \left[1 - \frac{t_{mc}}{a}\right]^3 \text{ (or } Q_i^3 = \left[1 - \frac{t_{ic}}{a}\right]^3\right)
$$

If, for instance, one has a mixture of coated metal particles and uncoated insulating particles, then $\varepsilon_{mcs}$ is calculated from Eqn. I-9, with the appropriate substitutions from Eqns. I-15. $\varepsilon$ is then calculated from either Eqn. I-12 or Eqn. I-14, where $\varepsilon_m$ is replaced by $\varepsilon_{mcs}$. In this way, a randomly dispersed mixture of two types of particles may exhibit a dielectric anomaly, due to a dielectric anomaly in $\varepsilon_{mcs}$. Observations of this type of behaviour have not yet been reported.
It should be remembered that these theories are based upon averaging over volumes that are large compared with particle size and small compared to the wavelength of light. Also, if the particle size is so small that bulk optical properties no longer apply to it then allowance for this effect must be made. This latter correction may be very difficult if particle sizes are distributed from isolated atoms on up to crystallites with bulk optical properties.

1.3 Physical Properties of AlN and Al

The previous section was concerned with physical properties of granular metals. The discussion focused primarily upon those properties that resulted from the geometry of the mixture, with the physical properties of the mixture's materials being of secondary importance. Of course, for at least two reasons, one must know the properties of the mixture's materials when modelling the physical properties of a cermet. The first reason is so that one can indeed know that observed behaviour is not just the behaviour of one of the materials present in the mixture. The second reason is that most of the quantitative aspects of the various mixture theories depend on the physical properties of the materials in the mixture (with the critical exponents in percolation theory being the exception). Therefore, at this time a brief review of the physical properties of AlN and Al, that are relevant to the experimental work discussed in this thesis, will be presented.
I.3-a AIN

While the literature on AlN is less extensive than for many other semiconductors (Si, Ge, GaAs, ZnO, etc.), a reasonable body of knowledge has been built up over about the last 20 years [22,29,59-78]. Pure AlN is a colorless solid that crystalizes in the hexagonal wurtzite structure [66]. At atmospheric pressure, it sublimes at about 2400°C [66]. At room temperatures and pressures, it readily oxidizes to form a surface layer of ~100 Å of amorphous Al₂O₃ within 24 h. This oxide layer then serves as a protective barrier against further oxidation. This rapid oxidation (roughly three times the rate of Al metal) leads to oxygen being the main unintentional impurity found in AlN, regardless of the method of preparation [66]. The tendency towards forming nitrogen deficient AlN is also a common problem [66]. AlN produced by reactive sputtering, under most conditions, crystalizes with the c-axis perpendicular to the substrate [70,71]. This results in the (002) peak being the dominant feature in x-ray diffraction patterns.

Pure AlN has a resistivity in excess of 10¹⁵ Ω-cm [29]. It has been doped n-type with Si, while C, S, and Mg doping produces p-type conduction [66]. N-vacancies or Al interstitials in nitrogen deficient AlN are expected to produce n-type behaviour, as should O substituting for N [65-73]. The reported defect conduction activation energies for AlN lie between 0.5 and 5 eV, depending on which impurities are present, while the band gap is 6.2 eV [60-66].

Optically, pure AlN exhibits a direct band gap of 6.2 eV. In cathode luminescence measurements [62], peaks at 3.33 and 3.55 eV were
correlated with nitrogen deficiency, while peaks at 2.71 and 2.78 eV were correlated with oxygen contamination. Pastrnak et al. observed a broad optical absorption band in AlN centered at 4.8 eV [60]. They attributed this broad band to oxygen contamination, however, their method of producing AlN (high voltage arcing of Al electrodes in an N\textsubscript{2} atmosphere) is known to also produce AlN that is quite deficient in nitrogen [66]. This technique of arcing Al electrodes in N\textsubscript{2} also seems likely to yield Al inclusions. Others [63,65] have claimed that their optical absorption measurements on nitrogen deficient AlN show the band edge shifting to about 4 eV. In hindsight, it appears that the dynamic range of their equipment was not sufficient to measure large enough absorptions (they appeared limited to transmittances > 1%). From data of Pastrnak, as well as the present work to be shown later, this limited dynamic range was not enough to observe the top of the peak at 4.8 eV, which is on the rapidly rising tail of the direct gap absorption.

Pastrnak also measured the dispersion of the AlN refractive index (n) [59], with wavelength, as the band edge was approached. These measurements are given in Fig. 28 in the appendix on optical calculations. In the infrared, AlN exhibits a reststrahlen band in the wavelength region between 11 μm and 15 μm [68,69].

I.3-b Al

Al is a metal that melts at 659°C and crystalizes in an fcc lattice. Exposed to air it will form ∼30 Å of amorphous Al\textsubscript{2}O\textsubscript{3} on it's
surface in 24 h [66], which serves as a protective barrier against further oxidation. The resistivity of pure Al is $3.6 \times 10^{-6} \Omega \cdot \text{cm}$ [28] at room temperature, and it exhibits p-type behaviour in Hall measurements [79]. Optically, it behaves qualitatively like most metals. A detailed tabulation of $n$ and $k$ (the real and imaginary parts of the refractive index, respectively) for Al from the far infrared to the far ultraviolet is presented by Powell [80]. Over the photon energy range of interest in this work, Powell's data shows the optical properties of Al to be smoothly, and slowly, varying with photon energy, with the exception of a peaked structure in both $n$ and $k$ near 1.5 eV. Figure 29, in the appendix on optical calculations, shows Powell's data.
CHAPTER II

MECHANISMS AND CONTROL OF THE REACTIVE SPUTTERING PROCESS

Planar magnetron sputtering of a metal target in a reactive gas atmosphere is a well known and useful technique for high rate deposition of either insulating or conducting films. For most applications it is desirable to maximize both the rate of deposition and the control over film stoichiometry. A technique to achieve these goals has been developed for the case of a dc planar magnetron with an Al target and an Ar/N$_2$ sputtering gas mixture. The method is described in this thesis and is expected to be applicable to other systems in which the reactive gas does not undergo rapid chemisorption on the target surface.

To control film stoichiometry it is necessary to regulate the relative rates of arrival of metal atoms and reactive gas species at the substrate [22,67]. The former is determined by the sputtering rate; the latter by the reactive gas partial pressure and sticking coefficient. Since sputtered metal deposits getter (combine chemically with) reactive gas species on the substrate and on inner surfaces of the vacuum chamber, these two rates are not independent of each other. As a result, one observes a decrease in the reactive gas partial pressure as the sputtering rate increases. The method, described here, for the control of these two quantities in order to produce a film of the desired composition has been to use the cathode voltage to monitor the degree to which the target surface becomes covered with an insulating compound of metal atoms and reactive gas species. A similar technique
for reactive sputtering (at constant pressure) employed by Schiller et al. has used the target voltage to determine one particular state of target coverage [81]. I have developed a model which allows for two distinct mechanisms by which this insulating layer may form on the target surface. One mechanisms is chemisorption of the neutral reactive gas species on the target surface (which can occur without a glow discharge); the other, target coverage by ions and atomic species of the reactive gas which is activated by the glow discharge. I call this latter process "ion plating". This differs from the generally accepted definition of ion plating only in that I am considering the target, rather than the substrate, in the plating process [8]. Sputtering of Al in the presence of O$_2$ is an example of the former mechanism while sputtering of Al in the presence of N$_2$ represents the latter. The model predicts differences between the glow discharge characteristics for the two mechanisms, which are in agreement with experiment.

If one could smoothly and monotonically increase the sputtering current (I) or power (W), thus increasing the sputtering rate, to produce a correspondingly smooth and monotonic decrease in reactive gas partial pressure (P$_r$), the control of film composition would be easily achieved [22,67]. At sufficiently low values of W and high values of P$_r$ the films would be expected to be nearly stoichiometric. With increasing W, as the sputtering rate increased and P$_r$ decreased due to getter pumping by the sputtered metal, the film composition would vary continuously until it was nearly a pure metal at some higher value of W. Such a smooth variation of P$_r$ with I or W does not occur for many
metal-reactive gas combinations of interest. In fact, it is well known that an abrupt change is observed in the value of \( P_r \) if \( W \) or \( I \) is varied while the rate of flow of reactive gas \( (F_r) \) into the chamber is held constant [16-21]. A similar transition is observed if \( F_r \) is varied and \( I \) or \( W \) is fixed.

The explanation of this transition is as follows. At low \( F_r \), the gettering rate is sufficient to keep \( P_r \) low enough to prevent formation of an insulating layer on the target surface so that sputtering is from a metal target. When the gettering rate can no longer match \( F_r \) an insulting layer begins to form on parts of the target surface. The reduced sputtering rate from the partially covered target lowers the gettering rate and permits further target coverage to occur. This positive feedback cycle repeats itself until the target is completely covered. With the gettering rate now much reduced, \( P_r \) rapidly increases. Since the secondary electron emission coefficients for the compound layers are generally different than for the pure metals [16,19,20], an abrupt change in the value of cathode voltage \( (V) \) is also observed as the target becomes covered. The opposite transition of going from a covered to a bare surface also occurs, with considerable hysteresis between the two directions. This hysteresis results in a gap in the operating ranges of both \( V \) and \( P_r \). For the Al-Ar/N\(_2\) system, it is found that films deposited on the low \( V \) and high \( P_r \) side of this gap are stoichiometric AlN, while films produced on the other side of the gap are deficient in nitrogen and contain Al precipitates (as seen by x-ray diffraction and TEM). Films deposited at \( V-P_r \) points within the gap are expected to have intermediate compositions.
I have found previously [21] that a single valued, monotonic functional relationship exists between $V$ and $P_r$ for the Al-Ar/N$_2$ system, while a range exists where each value of $I$ corresponds to three values of $V$ or $P_r$. When the discharge was operated by controlling $V$, I was able to operate over the full range of $I$-$V$-$P_r$ combinations. Thus, I could operate at any degree of target coverage (or film composition) of interest. Subsequent experiments with Al, Zn, In, and Mo in Ar/O$_2$ atmospheres revealed that voltage control was not possible across the transition between bare and completely covered target states. Also, in Ar/N$_2$ atmospheres control was not possible with Mo but was possible with Zn. The systems that were not controllable were the ones in which rapid chemisorption of the neutral diatomic gaseous species occurs, while this type of chemisorption does not occur in the others [82]. This implies that the presence of the glow discharge is totally responsible for activating the coverage process in the latter case, while it may be only partly responsible in the former.

Earlier models by Heller [17] or Shinoki [19] have treated the transition as described above with the only target coverage mechanism being chemisorption of reactive gas species from the sputtering gas. In this work I have included the ionic bombardment mechanism also. Further, for the Al-Ar/N$_2$ system, with the equations for conservation of flux of N$_2$ gas flowing into the chamber, flowing out through the pumping port, and flowing into sputter deposits it becomes possible to calculate the average film composition. In this procedure it is not necessary to know the system volume if one knows the actual gettering rate for some
specific range of values of sputter rate and \( N_2 \) partial pressure.

Fortunately, the sputter rate-\( N_2 \) partial pressure characteristics show a change of slope when the films pass from the stoichiometric region to the non-stoichiometric region. This procedure is facilitated by counting (via optical emission measurements) the number of Al atoms sputtered and counting the number of \( N_2 \) molecules gettered by monitoring \( P_r \). One may then obtain the average ratio of Al/N atoms in the film.

It should be noted that knowledge of the ratio of Al/N in the film gives no information about the chemical bonding between these species. Therefore, whether the film consists merely of AlN\( x \) or a mixture of AlN\( x \) and Al must be determined by other means.

II.1 **Apparatus and Experimental Method**

A schematic cross section of the planar magnetron sputtering chamber is shown in Fig. 2. The chamber is pumped by an oil diffusion pump with a freon cold trap. For operation while sputtering, the pumping speed is regulated by a throttling valve located between the cold trap and the diffusion pump. The 15 cm diameter target of 99.999\% Al is firmly clamped by a metal ring to a water cooled backing plate. A ground shield and water cooled anode are placed in front of and concentric to the target. The discharge is powered by a 5 kW, unfiltered, full wave rectified, constant current, dc power supply (Plasma Therm MDS-5000D, 0-10 A, 0-1000 V). Operation is possible with the anode either floating or grounded to the metal chamber. Pressure is measured with a capacitance manometer (MKS Baratron). An electromagnet
Schematic cross section of sputtering chamber.
is used to confine the plasma in the shape of a torus directly in front of the target, and thereby causes the sputtering erosion of the target to be a ring with outer diameter of about 7.5 cm and inner diameter of about 2.5 cm. A differentially pumped quadrupole mass spectrometer (UTI 100C) is mounted in a side arm and maintained at $10^{-3}$ Pa. It is used for leak detection, residual gas analysis, and in conjunction with the capacitance manometer for partial pressure measurements. Ar, N$_2$, and O$_2$ gas flows are controlled through independent leak valves (Granville Phillips model 203) and measured by independent mass flow meters (Hastings H-5 model All-5). Light from the plasma, seen perpendicular to the target surface, is focused through a quartz window onto the entrance slits of a 3/4 m Spex optical spectrometer (model 1702) to allow monitoring of the plasma emission lines.

A microprocessor system is used to monitor, record, and/or control all aspects of the experiment; e.g. gas flow rates, gas pressure, mass and optical spectra, substrate bias and temperature, cathode current, power and voltage.

The substrate holder-shutter arrangement accommodates a 5 cm x 5 cm substrate area. This area can be a single substrate or 6 rectangles of equal size (1.67 cm x 2.5 cm). The rotating shutter allows for exposure of the entire substrate area, none of the substrate area, or any one of the small rectangular areas to the sputtered flux.

Prior to any sputtering experiment the chamber was baked at about 75°C for at least 12 hours followed by 2 to 4 hours of sputter cleaning of the target and chamber in an Ar atmosphere ($\sim 0.25$ Pa) with a cathode
power of about 250 watts. This starting procedure was used to minimize contamination through extensive outgassing, followed by encapsulation of the inner surfaces of the chamber with an Al layer. Further precautions against contamination were exercised at the end of each experiment in preparation for the next one. These were to sputter for about 10 minutes in an N\textsubscript{2} atmosphere (P_{N_2} > 1 Pa) at low power (\approx 100 watts) to encapsulate the target with a nitride layer and then to bake the system for several hours in an N\textsubscript{2} atmosphere before briefly opening the chamber to exchange substrates. The reason for baking was to prevent condensation after the chamber was opened. The chamber was taken to atmospheric pressure with dry nitrogen gas as a further safeguard against condensation.

The experiments were of essentially two types. In one, the gas flows and pumping speeds were fixed while the cathode voltage was incremented through the range from about 200 to 500 volts. In the second type, the pump speed and Ar flow were fixed, as was either cathode power or current, and the reactive gas flow rate was scanned upwards from zero and then back again.

In the experiments where voltage was controlled, the first step was adjustment of the pumping speed. This was done by admitting the desired flow of Ar and then adjusting the diffusion pump throttle valve to obtain the desired pressure. The reactive gas flow rate was then set and the further increase in pressure recorded. Next, the discharge was started and allowed to equilibrate (\approx 200 V, \approx 0.1 A). A mapping of the I-V characteristics of the discharge was then performed by incrementing
the cathode voltage up to the desired value in step sizes ranging from 0.1 to 5 volts. Along with each I-V point, all other experimental parameters were recorded (i.e. pressure, mass and optical spectra, elapsed time, substrate bias and temperature, etc.). After obtaining the I-V characteristic, the curve was retraced to points of interest and films deposited. During the deposition, all parameters were again monitored for drift and, if need be, corrected by the computer so that fluctuations were held to within a few tenths of a percent.

In the experiments where cathode current or power was held constant along with Ar flow and pumping speed, while the reactive gas flow rate was scanned, the first step was again to adjust the pumping speed to a given Ar flow rate. The discharge was then ignited and set to the desired current or power. Then the reactive gas flow rate was scanned up at a rate between 1 and 4 SCCM/hour (1 SCCM = 1 standard cubic centimeter per minute) and then down again. During the scan, all parameters were recorded at intervals of from 30 seconds to several minutes.

Film thicknesses were measured both optically (by comparing interference maxima at two different angles of incidence), and with a profilometer. The two methods agreed to within about 10%. Investigations of other physical properties of the films were conducted by a variety of techniques, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction, IR reflectivity, UV-visible-near IR absorption, and conductivity measurements.
II.2 Experimental Results and Discussion

Using the methods discussed in the previous section, I monitored the following sputtering parameters: the total and partial pressures of the sputtering gases, up to three different gas flows into the chamber, the optical emissions of the species in the plasma, and the electrical characteristics of the discharge. The pump speed was set at the beginning of each experiment. Gas flows and one of either cathode current, power, or voltage are maintained at the desired setpoints. Typical sputtering parameters (or discharge characteristics) measured when Al is sputtered in an Ar/N₂ gas mixture are shown in Fig. 3 for the case when the glow discharge is maintained by controlling the cathode voltage. Here P_{N₂} is the N₂ partial pressure, Al* is the intensity of the 3961.52 Å optical emission line of neutral Al, and I and V refer to the cathode current and voltage respectively. The pumping speed for these data was such that, when no discharge was present, a flow into the chamber of 1.00 SCCM of Ar resulted in a chamber pressure of 0.93 Pa and the further addition of 1.50 SCCM of N₂ raised the pressure to 2.01 Pa.

It should be noted that the I-V curve of Fig. 3 is not a dynamic characteristic but rather the loci of stable operating points for the system. All points along the apparently negative resistance region are reached through positive resistance steps away from the equilibrium curve and back again. These steps must be much smaller than the width or height of the negative resistance region or oscillations will develop with the likelihood of the target surface ending in one of the extreme states of surface coverage. If I, rather than V, is the controlled parameter in the experiment then, for increasing I, upon reaching point
Typical glow discharge characteristics for the Al-Ar/N\textsubscript{2} system. I and V are the cathode current and voltage, respectively, P\textsubscript{N\textsubscript{2}} is the N\textsubscript{2} partial pressure, and Al\textsuperscript{*} is the optical emission intensity of the 3961.5 Å line of neutral Al atoms in the discharge. The Ar partial pressure is 0.93 Pa.
C in Fig. 3 the discharge characteristics would shift abruptly to those at point E. Similarly, for decreasing I, a shift would occur from point D to point B. The sets of points (C,E) and (D,B) will be shown to be related to the transitions from covered to bare and bare to covered target surfaces, respectively. Point A represents the discharge characteristics immediately after the glow is ignited.

In Fig. 3, no abrupt changes in the discharge characteristics, which are normally associated with the transitions between bare and covered target surfaces, are observed. Therefore, one does not know whether a smooth and continuous traversal through all degrees of target coverage has occurred in Fig. 3. To know this one must be able to relate the discharge characteristics in the experiments where the abrupt changes occur to the same parameters in the experiments where smooth control is achieved. All of the discharge characteristics at one operating point in one of the experiments must be identical to those at an operating point in the other experiment if the state of the target is to be assumed identical at these two operating points in the two different experiments.

Using Fig. 4, I now demonstrate that the points C and D of Fig. 3 are the points where the target surface is just beginning to uncover or has just become completely bare, respectively. Fig. 4-c shows the nitrogen partial pressure \((P_{N_2})\) versus the nitrogen flow rate \((F_{N_2})\) with the discharge power, \(W\), held at 295 watts with 1.00 SCCM of Ar producing a chamber pressure of 1.00 Pa. The transition from C' to E' and from D' to B' in Fig. 4-c are well known as transitions from covered
Comparison of discharge characteristics for the Al-Ar/N\textsubscript{2} system when voltage control is employed (a and b), or at constant \( W \) with variable \( F_{N_2} \) (c). The peaks in the curves (a) are identified as points where the target is just beginning to uncover (i.e. \( \theta=1 \)) and the minima are points where the target is just becoming bare (i.e. \( \theta=0 \)).
to bare and bare to covered target surfaces, respectively [16-21].

Fig. 4-a shows two W versus cathode voltage, V, curves from experiments with identical pumping speeds and Ar flows as the run of Fig. 4-c. Note that $F_{N_2}$ for the lower power W-V curve is the same as $F_{N_2}$ at the C' to E' transition of Fig. 4-c while $F_{N_2}$ for the higher power W-V curve is the same as $F_{N_2}$ at the D' to B' transition. Note also that W is 295 watts at points B, C, D, and E; the same power as at all points of Fig. 4-c. Figs. 4-b and 4-c show that the values of $P_{N_2}$ are equal for points B and B', C and C', D and D', and E and E'. Likewise, other plots demonstrate the equality of I, V, A etc. for the prime-unprimed pairs of operating points in the two experiments. This indicates that point C is the point at which the target begins to uncover and that point D is the point at which the target becomes bare.

The hysteresis in the experiment of Fig. 4-c is readily understood in terms of the discharge characteristics of Fig. 3 (or Figs. 4-a and 4-b). As the target starts to uncover at point C the secondary electron emission coefficient ($\gamma$) starts to decrease resulting in a lower total current, for the same voltage, than it would have with the higher $\gamma$. As $\gamma$ continues to decrease so does I until the target is bare at point D and $\gamma$ is once again essentially constant. With $\gamma$ constant at point D, I begins to increase with V again. As well, $P_{N_2}$ continuously decreases with increasing V for all values of V. In experiments similar to that of Fig. 4-c, where in one case, I or W is constant and $F_{N_2}$ varied and in the other case $F_{N_2}$ is fixed while I or W is varied, a problem arises. This problem is that a point is
reached (either of points C' or D' of Fig. 4-c) when the power supply is trying to maintain a given value of I or W but the combination of values [V, P_{N_2}, I] does not belong to the loci of stable operating points of the system shown in Fig. 3. The system is then forced to shift to an operating point that is consistent with the given I or W. Mathematically stated, V and P_{N_2} are not single valued functions of I; whereas, I and P_{N_2} are single valued functions of V as seen in Fig. 3. Therefore, if one does not alter the pumping speed or gas flow rates, operation between the points C and D requires control over target voltage. I will now demonstrate that the ability to control the voltage through the transition region is crucially dependent upon the dominant mechanism of target coverage being ion plating from the discharge current instead of chemisorption of the neutral reactive gas species.

In the absence of a discharge, it is known that O_2 chemisorbs on Al metal while N_2 does not [82,83]. Since both gases cover Al sputtering targets in the presence of a glow discharge, it is apparent that the discharge is totally responsible for the N_2 coverage, while it may be only partly responsible for the O_2 coverage. Thus, I now analyze and compare the discharge characteristics for the reactive sputtering of Al in an Ar/N_2 gas mixture to those for Al in an Ar/O_2 atmosphere in order to see the effect of the different mechanisms for target coverage. The changes in the discharge characteristics of the two systems caused by variations in the gas flow rates (F_{N_2} and F_{Ar}) and pumping speed (S) are examined, and the results analyzed in terms of a model for the sputtering process which allows for the two previously mentioned mechanisms for target coverage.
II.2-a The Target Reaction

The rate equation for absorption and emission of reactive gas molecules from the target surface may be written as follows [17-19]:

\[
\frac{dn_s}{dt} = \alpha(\theta) \frac{P_r}{P_t} + f(\frac{P_r}{P_t}) \varepsilon(\theta) \frac{I}{[1+\gamma(\theta)]e} - \frac{\eta_r(\theta) I}{[1+\gamma(\theta)]e} \tag{II-1}
\]

where, \( n_s \) is the total number of reactive gas molecules adsorbed on the target surface, \( P_t \) and \( P_r \) are, respectively, the total pressure and reactive gas partial pressure, \( I \) is the total discharge current, \( e \) is the electronic charge, \( f(\frac{P_r}{P_t}) \) is the fraction of positive ions in the discharge current that are reactive gas species, and \( \theta \) is the fraction of the target surface that is covered with a metal-reactive gas compound layer. The remaining parameters have different values on bare or covered portions of the target and, therefore, their values, when averaged over the entire target surface, will depend on \( \theta \). These average values are used in Eqn. II-1. The parameter \( \alpha(\theta) \) represents the product of impingement rate per unit \( P_r \) and the sticking coefficient for neutral reactive gas molecules on the target surface, \( \varepsilon(\theta) \) is the sticking coefficient for reactive gas ionic species impinging on the target surface, \( \eta_r(\theta) \) is the average sputtering yield of reactive gas molecules from the target, and \( \gamma(\theta) \) is the average secondary electron emission coefficient for the entire target surface. Target coverage by atomic neutrals has not actually been neglected in Eqn. II-1. Since, to first order, their contribution to target coverage will also be
proportional to the ion current [8], their effect is already accounted for in the current dependent ion plating term of Eqn. II-1.

The first term on the right hand side of Eqn. II-1 accounts for chemisorption of neutral reactive gas molecules on the target surface; the second term, for ion plating associated with the discharge current; the third term, sputtering of reactive gas molecules from the target. In steady state, Eqn. II-1 reduces to

$$f(P_r/P_t) = \frac{\eta_r(\theta)}{\epsilon(\theta)} - \frac{\alpha(\theta)}{\epsilon(\theta)} [1 + \gamma(\theta)] e \frac{P_r}{I} \quad (II-2)$$

To continue the analysis a particular functional form for $f(P_r/P_t)$ is required. One expects $f(P_r/P_t) = BP_r/P_t$, where $B$ is a positive constant, if the different gas species present in the plasma do not affect each other's ionization mechanisms. However, work by Lounsbury [84], Aita [85], and Karulkar and Nordman [86] on Ar–O\textsubscript{2} plasmas has indicated that the concentration of Ar\textsuperscript{+} ions in the plasma actually increases when small partial pressures of O\textsubscript{2} ($P_{O_2}/P_t < 0.15$) are present. When $P_{O_2}/P_t$ exceeds 0.15, the Ar\textsuperscript{+} ion concentration begins to decrease in the manner expected for a mixture of independent gases. The mechanisms involved in the plasma which leads to this behavior is related to the high electron affinities of both O\textsubscript{2} and O. Either will readily form negative ions through combination with the electrons present in the plasma. This negative ion formation reduces the number of electrons available to neutralize positive Ar ions which,
therefore, leads to an increase in the concentration of positive Ar ions. If enough reactive gas is added, a point is eventually reached when the decreasing Ar atom concentration offsets this effect and the Ar\(^+\) ion concentration begins to decrease. Regarding the positive oxygen species, work of Aita et al. [87] has shown that, for oxide targets, the number of positive oxygen species has the form \(a + bP_{O_2}/P_t\). The constant term \(a\) arises because, even with no \(O_2\) added to the gas, some oxygen species appear in the gas after being sputtered from the oxide target. Therefore, if the number of Ar\(^+\) ions is increasing like \(c + dP_{O_2}/P_t\), then the fraction of the positive ions in the discharge current that are oxygen species has the form \((a + bP_{O_2}/P_t)/(a + c + (b+d)P_{O_2}/P_t)\). This function is found always to decrease with increasing \(P_{O_2}/P_t\) provided that the fractional increase in Ar\(^+\) ions is greater than the fractional increase in positive oxygen species. For \(0 < P_{O_2}/P_t < 0.15\) this ratio is found to be about 2 from mass spectrometric and optical data of Aita [87] and Lounsbury [84]. In this work I have a metal target that is oxidized. As long as I operate the discharge in the oxidized regime the above expression for the concentration of positive oxygen species should be valid. Further, since my data extends over such a small range of values for \(P_{O_2}/P_t\), I will approximate the concentration of positive oxygen species as a linearly decreasing function of \(P_{O_2}/P_t\) for \(0 < P_{O_2}/P_t < 0.15\). Therefore, this propensity for negative ion formation decreases the concentration of positive oxygen species as well as increases the Ar\(^+\) ion concentration for low values of \(P_{O_2}/P_t\). This mechanism leads to
$f(P_{O_2}/P_t)$ being given as $(A' - B' P_{O_2}/P_t)$ when $P_{O_2}/P_t$ is less than 0.15, and $f(P_{O_2}/P_t)$ behaving as $(A'' + B'' P_{O_2}/P_t)$ when $P_{O_2}/P_t$ exceeds 0.15, where $A'$, $B'$, $A''$ and $B''$ are positive constants. My data involving Ar-O$_2$ plasmas in the range of partial target coverage shows $P_{O_2}/P_t$ to be always less than 0.10, therefore I take $f(P_{O_2}/P_t) = (A' - B' P_{O_2}/P_t)$.

In the case of Ar-N$_2$ plasmas, neither N$_2$ nor N is able to form negative ions; therefore the gases are expected to act independently of each other with $f(P_{N_2}/P_t) = B P_{N_2}/P_t$.

The above-mentioned forms for $f(P_r/P_t)$ lead to the following predictions for the steady state pressure quotient $P_r/P_t$.

$$\frac{P_{O_2}}{P_t} = \frac{1}{B'} [A' - \frac{\eta_r(\theta)}{\epsilon(\theta)}] + \frac{1}{B'} [1 + \gamma(\theta)] e^{\frac{\alpha(\theta)}{\epsilon(\theta)} \frac{P_{O_2}}{I}} \quad (II-3-a)$$

for the Ar-O$_2$ plasma when $P_{O_2}/P_t$ is less than 0.15; and

$$\frac{P_{N_2}}{P_t} = \frac{1}{B} \frac{\eta_r(\theta)}{\epsilon(\theta)} - \frac{1}{B} \frac{\alpha(\theta)}{\epsilon(\theta)} [1 + \gamma(\theta)] e^{\frac{P_{N_2}}{I}} \quad (II-3-b)$$

for the Ar-N$_2$ plasma at all values of $P_{N_2}/P_t$. The parameters $\{\alpha, \epsilon, \gamma, \text{ and } \eta_r\}$ will depend on the reactive gas-target combination under study. This dependence was not explicitly shown in Eqns. II-3 in order to minimize the number of symbols. If the neutral reactive gas molecules do not chemisorb on the target material, $\alpha$ is equal to zero in either of Eqns. 3. I now present data to compare with these equations.
Figs. 5-a to 5-i show how independent variations of nitrogen flow
\((F_{N_2})\), argon flow \((F_{Ar})\), or pump speed \((S)\) affect the
current-voltage \((I-V)\), \(P_{N_2}-V\), and \(P_{N_2}/P_t-V\) characteristics when
Al is sputtered in an \(Ar/N_2\) gas mixture. Similar experiments for an Al
target and an \(Ar/O_2\) gas mixture are summarized in Figs. 6-a to 6-i. To
more clearly present the relevant data in Figs. 6 I have not shown the
transition to a bare target surface. Instead, the highest voltage data
point in each curve presented is the last one recorded before the abrupt
shift in the discharge characteristics. This data from the bare target
discharge would be at higher voltages than those shown in Figs. 6 and at
\(P_{O_2}\) values of \(\sim\) zero. Peaks in the \(I-V\) characteristics of the \(N_2\) data
and the points where the abrupt changes occur in the \(O_2\) data are
identified as the points where \(\theta = 1\), as explained in the previous
section and depicted in Fig. 4 for \(N_2\). Because \(P_r/P_t\), as given in
Eqns. II-3, is strongly dependent on \(\theta\) through the parameters \(\{\alpha, \epsilon, \gamma, \text{ and } \eta_r\}\), I will limit the analysis to the operating points
corresponding to \(\theta = 1\).

Fig. 7 shows the plots of \(P_r/P_t\) vs. \(P_r/I\), for \(\theta = 1\), taken
from the \(N_2\) and \(O_2\) data of Figs. 5 and 6. One sees immediately that
\(P_{N_2}/P_t\) is constant, within experimental error, as predicted by Eqn.
II-3-b with \(\alpha = 0\); i.e. no chemisorption of neutral reactive gas
molecules. Further, \(P_{O_2}/P_t\) can be better described by a linearly
increasing function of \(P_{O_2}/I\) as predicted by Eqn. II-3-a with a
non-zero \(\alpha\). The tendency of \(P_{O_2}/P_t\) vs. \(P_{O_2}/I\) to flatten out for
higher values of \(P_{O_2}/P_t\) is attributed to the breakdown of the linear
Variation of Al-Ar/N$_2$ discharge characteristics with F$_{Ar}$, F$_{N_2}$, and S. In (a)-(c), F$_{N_2}$ is varied with 1.00 SCCM(Ar) giving S(Ar) = 1.00 SCCM(Ar) per 0.76 Pa(Ar) and o-2.00 SCCM(N$_2$), x-1.50 SCCM(N$_2$), and e-1.00 SCCM(N$_2$). In (d)-(f), F$_{Ar}$ is varied with 1.50 SCCM(N$_2$) giving S(N$_2$) = 1.50 SCCM(N$_2$) per 0.84 Pa(N$_2$) and x-1.50 SCCM(Ar), e-1.00 SCCM(Ar), and + -0.50 SCCM(Ar). In (g)-(i), S is varied with 1.50 SCCM(Ar) and 1.50 SCCM(N$_2$) and o-S(Ar) = 1.50 SCCM(Ar) per 1.48 Pa(Ar), x-S(Ar) = 1.50 SCCM(Ar) per 1.07 Pa(Ar), e-S(Ar) = 1.50 SCCM(Ar) per 0.81 Pa(Ar), and + -S(Ar) = 1.50 SCCM(Ar) per 0.42 Pa(Ar).
Variation of Al-Ar/O\textsubscript{2} discharge characteristics with F\textsubscript{Ar}, F\textsubscript{O\textsubscript{2}}, and S. In (a)-(c), F\textsubscript{O\textsubscript{2}} is varied with 3.00 SCCM(Ar) giving S(Ar) = 3.00 SCCM(Ar) per 1.13 Pa(Ar) and o-0.90 SCCM(O\textsubscript{2}), + -0.60 SCCM(O\textsubscript{2}), and •-0.30 SCCM(O\textsubscript{2}). In (d)-(f), F\textsubscript{Ar} is varied with 0.60 SCCM(O\textsubscript{2}) giving S(O\textsubscript{2}) = 0.60 SCCM(O\textsubscript{2}) per 0.21 Pa(O\textsubscript{2}) and o-6.00 SCCM(Ar), +'-5.00 SCCM(Ar), •-4.00 SCCM(Ar), and x-3.00 SCCM(Ar). In (g)-(i), S is varied with 3.00 SCCM(Ar) and 0.60 SCCM(O\textsubscript{2}) and o-S(Ar) = 3.00 SCCM(Ar) per 2.84 Pa(Ar), + - S(Ar) = 3.00 SCCM(Ar) per 2.06 Pa(Ar), and •-S(Ar) = 3.00 SCCM(Ar) per 1.33 Pa(Ar).
Variation of \( \frac{P_r}{P_{r_1}} \) with \( \frac{P_r}{I} \) at the \( \theta = 1 \) points of the data of Figs. 5 and 6.
relationship for \( f(P_{O_2}/P_t) \) as \( P_{O_2}/P_t \) nears \( \approx 0.15 \). Despite the similarities in the transitions between bare and covered targets when sputtering at constant power or current, it is now evident that the mechanism leading to target coverage is fundamentally different when sputtering Al in the presence of \( N_2 \) from that involved with \( O_2 \) present. From the above analysis of the target processes I conclude that chemisorption of neutral reactive gas molecules is an important target coverage mechanism when the latter gas is present, but is unimportant when considering the former.

I now address the question of why operation at points between \( \theta = 1 \) and \( \theta = 0 \) is possible for the Al-Ar/\( N_2 \) system and not for the Al-Ar/\( O_2 \) system. The stability of \( dn_g/dt \), as given by Eqn. II-1, with respect to fluctuations in the discharge current is examined for the cases of no chemisorption (Ar-\( N_2 \) plasma) and chemisorption (Ar-\( O_2 \) plasma). The change in the rate of target coverage caused by a fluctuation in the current (\( \Delta I \)) is given by

\[
\Delta(\frac{dn_g}{dt}) = [\alpha_r \frac{\partial P_r}{\partial I} + \frac{fe}{(1+\gamma)e} + \frac{\epsilon I}{(1+\gamma)e} \delta f_r \frac{\partial P_r}{\partial I} + \frac{\eta_r}{(1+\gamma)e}] \Delta I, \quad (II-4)
\]

where, in the interest of clarity, I have discontinued writing the arguments associated with the various functions in Eqn. II-4.

If, prior to the fluctuation in discharge current, the system existed under steady state conditions, then since \( -\alpha_r \frac{P_r}{(1+\gamma)e} = \frac{f_r}{(1+\gamma)e} \) by virtue of Eqn. II-2, Eqn. II-4 may be rewritten as
Using Eqns. II-1, II-2 and II-3 together with the data contained in Figs. 5, 6, and 7, one finds that each term on the right hand side of Eqn. II-5 produced a fractional change in $\frac{dn_s}{dt}$ of the order of $(\Delta I)/I$. In my system, in steady state operating conditions, $(\Delta I)/I$ is roughly 10% at 360 Hz due to the nature of the dc current supply (i.e. unfiltered full wave rectified 3-phase). Note, however, that Eqn. II-5 portrays two fundamentally different mechanisms by which a fluctuation in the current can cause a change in the rate of target coverage. Firstly, the term $\alpha(P_r/I)(\Delta I)$ represents an immediate change in both the rate at which ions are brought to the target surface by the ion current and the rate at which reactive gas species are resputtered. This term is seen to vanish when $\alpha = 0$ (i.e. no chemisorption). Secondly, the other two terms involve slower changes in both the chemisorption and ion plating rates caused by the change in $P_r$, which results from the change in the gettering rate that accompanies a change in the current. One of these two terms also vanishes when $\alpha$ is zero. This second type of response is slower because of the processes involved: the movement of sputtered flux to the gettering surfaces; the actual gettering at the surface; and the diffusion of the pressure fluctuations from the gettering surfaces back to the target. As a result of the time required for these processes to occur, changes in

\[
\Delta \left( \frac{dn_s}{dt} \right) = \left[ - \frac{\alpha P_r}{I} + \left\{ \alpha + \frac{eI}{(1 + \gamma)e} \frac{\delta f}{\delta P_r} \right\} \frac{\delta P_r}{\delta I} \right] \Delta I
\]

(II-5)
pressure do not follow the current fluctuation. In the limit of the duration ($\tau$) of the current transient being much less than the time required for the pressure to equilibrate ($\tau_R$), continuity of flux requires that the magnitude of the pressure response terms of Eqn. II-5 be reduced, by a factor of order $\tau/\tau_R$, as the response is spread out in time. If this factor were small enough, the effects of current induced pressure transients in Eqn. II-5 would be negligible. For my system and operating pressures, a minimum estimate of this reduction is roughly 100 fold. For a minimum estimate of $\tau_R$, I consider only the process of the $N_2$ partial pressure transient diffusing from the wall back to the target. Taking the $N_2$ mean free path and thermal velocity as $\sim 0.5$ cm and $\sim 5 \times 10^4$ cm/s [88], respectively, yields a mean diffusion time of $\sim 0.06$ s for an $N_2$ molecule to traverse the 40 cm of the vacuum chamber. Assuming $\tau_R$ to be several of these diffusion times gives $\tau_R$ as about a quarter of a second. The time that passes between arrival of some sputtered atoms at a wall and their combination with a reactive gas molecule may be significant in the $N_2$ case. While $N_2$ will not chemisorb on the surface of bulk Al metal it will react with Al atoms (as in the condensing sputtered flux) [66], but the $N_2$ dissociation step is still expected to be much longer than that for $O_2$ dissociation. Therefore, one expects $\sim 0.25$ s to be a reasonable lower limit for $\tau_R$. With $\tau \sim 1/360$ one finds a 90 fold reduction. From this analysis I conclude that the stability of the discharge characteristics should be much better for systems where chemisorption of the sputtering gas does not occur than for systems where it contributes significantly to the target coverage mechanism. In the regime of partial target...
coverage, where small fluctuations result in positive feedback, this increased stability of non-chemisorbing systems should be most apparent.

In the case of the Al-Ar/N$_2$ system $\alpha = 0$ and, therefore, one expects only the slow response of the target coverage due to current induced fluctuations in $p$. I am able to control the discharge at all degrees of target coverage in this system. The method of control exploits the single valued relationship between $V$ and $\theta$ discussed in the previous section. I control target coverage by monitoring the target voltage for drift away from a setpoint on the loci of stable operating points for the discharge (as in Fig. 3) and, when drift is detected, small changes are made in the discharge current to bring the voltage back to the desired value. Since the fast first order changes in the rate of target coverage vanish, the positive feedback effect of these small current pulses is small and the runaway transition between covered and bare target states will take a "long" time to get out of control.

With the microcomputer control system, the voltage is read about every 0.1 s and, if drift of more than 0.5 volts is detected, the current is changed in order to drive the voltage back to the desired value. The time lag between detection of drift and the change in the current is less than 0.1 s. However, another change in current is not initiated until roughly 0.5 s has elapsed. This 0.5 s delay is necessary in order to allow the full effect of the previous change to be realized. If shorter delays are used oscillations develop and the positive feedback cycle runs out of control. The fact that the necessary delay time is about 0.5 s indicates that $\tau_r$ is about 0.5 s instead of the lower limit of about 0.25 s mentioned earlier.
When chemisorption occurs, as in the Al-Ar/O₂ system, α is not zero and the immediate response in the rate of target coverage is the major factor affecting control of the process. When drift is detected and a current change is initiated, as described above, a second change cannot be made in a rational way until another voltage measurement is made. This results in a minimum delay in initiating the second change of at least 0.1 s and, evidently, this delay is too long to prevent the positive feedback from running out of control. In fact, the literature indicates [83] that the monolayer formation time for chemisorbing O₂ on Al is on the order of 1/360 s for O₂ partial pressures in the range that I am working at. Therefore, a highly filtered dc power supply may be needed in order to control the Al-Ar/O₂ discharge in the region of partial target coverage, rather than a faster computer control algorithm. It is well known that O₂ chemisorbs on Si; however the monolayer formation time at P₀₂ ∼ .25 Pa (sputtering pressures) is on the order of an hour [89]. Therefore, voltage control of a Si target in an Ar/O₂ atmosphere should be possible. Recently, Steenbeck et al. [90] reported an "N-shaped" I-V characteristic for sputtering in the Si-Ar/O₂ system that is similar to that in the Al-Ar/N₂ system.

II.2-b Prediction of Film Composition from Plasma Characteristics

For most applications of thin film deposition an accurate knowledge of film composition during film growth is required. I present a method by which the film composition may be calculated from the sputtering discharge characteristics such as those given in Fig. 3. The
basis of the technique is to use the optical emission data to determine the flux of metal atoms sputtered, and to obtain the gettering rate by monitoring the reactive gas partial pressure. For purposes of demonstration I will use data for the Al-Ar/N\textsubscript{2} system.

I assume the rate of reaction of Al with N\textsubscript{2} on the substrate is proportional to only the Al concentration when N\textsubscript{2} is in extreme over-abundance, but that the rate is proportional to the product of both reactant concentrations when both N\textsubscript{2} and Al are in limited supply. The former condition means that in the low V and high P\textsubscript{N\textsubscript{2}} region of the discharge characteristics, where stoichiometric AlN is deposited, the gettering rate will be proportional to the sputtered Al flux only, while the latter condition says that the gettering rate will be proportional to the product of the sputtered Al flux and P\textsubscript{N\textsubscript{2}} in the region of the discharge characteristics where nitrogen deficient AlN is deposited. Based on these two different gettering regimes I now present a rate equation analysis of the flow of N\textsubscript{2} gas into and out of the vacuum chamber that will allow prediction of the Al/N ratio in the sputter deposits from data such as in Fig. 3. Under steady state conditions one may write

$$SP_{N_2} = F_{N_2} - \frac{1}{2} \text{(Al flux)}, \text{ for } P_{N_2} > P_{N_2}^* \quad (II-6-a)$$

when N\textsubscript{2} is in over-abundance, and
\[ \text{SP}_{N_2} = F_{N_2} - \beta P_{N_2} \text{ (Al flux)}, \] for \( P_{N_2} \leq P^*_{N_2} \) \hspace{1cm} \text{(II-6-b)}

when both reactants are in limited supply. In these equations all variables except \( P^*_{N_2} \) and \( \beta \) have been previously defined; \( P^*_{N_2} \) represents the \( N_2 \) partial pressure at which the gettering behavior changes from the regime of \( N_2 \) over-abundance to the case where both reactants are in limited supply; \( \beta \) is the constant of proportionality which relates the product \( P_{N_2} \) (Al flux) to the gettering rate. The factor of \( 1/2 \) in Eqn. II-6-a arises because two Al atoms are required to getter one \( N_2 \) molecule to form two AlN molecular units in the stoichiometric AlN region of the discharge characteristics. Physically, \( \text{SP}_{N_2} \) is the flow of \( N_2 \) out of the chamber through the pumping port; \( F_{N_2} \) is the \( N_2 \) flow deliberately let into the chamber through the leak valve; \( 1/2 \text{(Al flux)} \) in Eqn. II-6-a or \( \beta P_{N_2} \text{ (Al flux)} \) in Eqn. II-6-b) represent the flow of \( N_2 \) into sputtered deposits. Note that, in Eqn. II-6-b, \( \frac{1}{2} \frac{1}{\beta P_{N_2}} \) gives the average, over all gettering surfaces, of the ratio of Al/N atoms in the sputtered deposits when \( P_{N_2} < P^*_{N_2} \) (or \( 2\beta P_{N_2} = x \) in AlN\( x \)). Therefore, \( \beta \) is of central importance in the determination of film composition.

One now needs to determine the Al flux in terms of the discharge characteristics. I take the number of Al atoms sputtered per second to be directly proportional to the intensity of optical emission from neutral Al atoms in the glow discharge. This assumption is justified by Fig. 8, which is a plot of the deposition rate versus Al\( ^* \), where Al\( ^* \) is the intensity of the 3961.52A optical emission line of neutral Al.
Variation of film thickness deposition rate with $\text{Al}^*$ from data of Fig. 3. In reference to Fig. 3, $\times$-between points A and C, $\bullet$-between points C and D, $+$ - at point D, and $\circ$-between points D and E.
from the data of Fig. 3. The transition from one linear dependence to another in Fig. 8 is accounted for by the change in density as the composition changes from AlN to Al. I have assumed densities of 3.26 gm/cc and 2.7 gm/cc for AlN and Al, respectively [66]. I therefore write \( \text{(Al flux)} = \delta \text{Al}^* \) over the entire operating range, where \( \delta \) is a constant of proportionality which relates the intensity of the emission line to the sputtered flux from the target. This allows one to rewrite Eqn. II-6-a and Eqn. II-6-b as

\[
P_{N_2} = \frac{F_{N_2}}{S} - \frac{\delta}{2S} \text{Al}^*, \quad \text{for } P_{N_2} > P_{N_2}^* \tag{II-7-a}
\]

and

\[
\frac{1}{P_{N_2}} = \frac{S}{F_{N_2}} + \frac{\beta \delta}{F_{N_2}} \text{Al}^*, \quad \text{for } P_{N_2} < P_{N_2}^* \tag{II-7-b}
\]

Since \( S \) is known, \( \delta \) may be determined through Eqn. II-7-a from a plot of \( P_{N_2} \) vs. \( \text{Al}^* \) in the region between A and C of Fig. 3. Once \( \delta \) has been determined, \( \beta \) may be determined from the slope of a \( \frac{1}{P_{N_2}} \) vs. \( \text{Al}^* \) plot in the region after point D. For the data of Fig. 3 the plot associated with Eqn. II-7-a is given in Fig. 9-a while Fig. 9-b should be used in conjunction with Eqn. II-7-b.

The value of \( \frac{\beta P_{N_2}}{N_2} \) calculated at point D of Fig. 3 is about \( \frac{1}{4} \), indicating the ratio of Al/N in the film is about 2. Point D is also
Variations of $P_{N_2}$ (a) and $1/P_{N_2}$ (b) with Al$^*$ from the data of Fig. 3.
the point where film conductivity begins to rise quite rapidly in
concert with a rapid increase in the number of Al precipitates. Fig. 10
shows room temperature resistivity ($\rho$) and temperature coefficient of
resistance (TCR) as a function of $x$ in AlNx films deposited along the
I-V characteristic of Fig. 3, where $x$ is calculated by the method just
discussed. The volume fraction of Al in the samples ($X_v$) is also shown,
where $X_v$ was calculated by assuming that all Al in excess of what is
needed to form stoichiometric AlN from the incorporated $N_2$ is present as
Al precipitates. Since no attempt was made to account for cross doping
between Al and AlN phases, these values for $X_v$ are only upper limits.
Of course, the Al precipitates are expected to contain nitrogen
impurities, while the AlN crystals will contain excess Al. Also
included is similar data of Itoh and Misawa [22] for reactive, rf
sputtered AlNx films, where $x$ was obtained from electron microprobe
analysis. One sees that the agreement between the two sets of data is
excellent for the low resistivity films (more metallic), but that my
films show a percolation threshold at a much lower value of $x$ (higher
$X_v$) than Itoh's. I believe this difference arises, in part because
Itoh's deposition rate is much higher than mine ($\sim x 4$) and in part
because his films are much thicker than mine ($> 3500 \AA$ as compared with
$< 1400 \AA$ for my samples).

I explain this in terms of the Al-$N_2$ reaction mechanism which
takes place on the substrate (I observe no AlN emission lines in the
glow discharge [91]). The Al-Al reaction is expected to proceed more
quickly than the Al-$N_2$ reaction due to the $N_2$ dissociation step of the
Fig. 10

Variations of $\rho$ (a) and TCR (b) with $x$, $x$-my data where $x$ is calculated from the data of Fig. 9 and Eqns. II-7-a and II-7-b, the solid line is a fit to data of Itoh and Misawa where $x$ was measured by electron microprobe analysis.
latter. Therefore, high absolute Al sputter rates should result merely in nitrogen doped Al if there is not sufficient time for N\textsubscript{2} dissociation, reaction with Al, and formation of crystalline AlN. This implies that higher absolute Al sputter rates lead to more Al inclusions and smaller and less prevalent AlN crystals. Further, increasing the Al sputter rate may just lead to increasingly dirty (nitrogen doped) Al if enough time for the reaction is not allowed. From films deposited in the stoichiometric region of the I-V characteristics there is evidence for smaller AlN crystal size with increasing Al rate from x-ray diffraction studies. At constant Xv I have also observed, for films on the insulating side of Xvc, that $\rho$ is constant for thicknesses less than $\sim 2000$ Å, but decreases rapidly (by $\sim x$ 5) for thicknesses between $\sim 2000$ Å and 4000 Å, and becomes constant again for thicknesses over $\sim 4000$ Å. I believe this effect may be due to the sensitivity of the hopping mechanism to the dimensionality of the film. If the film thickness is not many metallic grain sizes thick the hopping may be 2-dimensional [92]. For the essentially metallic samples the sample is 3-dimensional for normal conduction processes and grain size should not be a major factor affecting $\rho$ in a metallic matrix, especially when the metal is very impure in each case. For these reasons I think it is reasonable to assume that my deduced compositions are correct even after the point where the $\rho$ vs. x plot departs from Itoh's data.

I am now in a position to discuss how one may obtain a given film composition and deposition rate. I have observed that films deposited on the low V side of the I-V maximum, as in Fig. 3, appear to be
stoichiometric AlN while x in AlNx steadily decreases with increasing V on the high V side of the peak. Further, if variations in pump speed or gas flow are introduced, as in Figs. 5, equivalent operating points along different characteristics (i.e. A, B, C etc. as in Fig. 3) appear to yield identical film compositions as well as calculated values of \( \beta \) \( P_{N_2} \) that agree to within 10%. Therefore, increasing the \( N_2 \) flow rate will increase the discharge power (and therefore sputtering rate) for equivalent points along the I-V curve, while the position along the characteristic may be used to predict the composition.

II.2-c Calculation of the Sputtering Yield

If one equates the standard expression for calculating the sputtered flux from the sputtering current [19] to \( \delta Al^* \) of Eqn. II-7, the resulting expression is

\[
\frac{\eta_m(\theta)I}{[I + \gamma(\theta)]e} = \delta Al^* 
\]  

(II-8)

where \( \eta_m \) is the sputtering yield in Al atoms per incident ion, \( \gamma \) is the effective secondary electron emission coefficient for the target, e is the electronic charge, and I is the discharge current. It follows from Eqn. II-8 that a plot of \( e\delta Al^*/I \) vs V will give the voltage dependence of \( \eta_{\text{eff}} \) for the particular target and gas composition used. Where the effective sputtering yield \( (\eta_m/(1 + \gamma)) \) has been
labeled $\eta_{\text{eff}}$. The data of Fig. 3 has been used to make such a plot which is presented as Fig. 11.

In the high $V$ and low $P_{N_2}$ region one might expect the effective sputtering yield to approach the values recorded in the literature for normal incidence sputtering yields of Al in an Ar atmosphere. These values in Fig. 11 are less than half the accepted values [93] (about 40%). In addition, the data of Fig. 11 was obtained from a new target and as the target is used more, causing the erosion channel to deepen, the effective sputtering yield can rise to about 60% of the accepted value for this geometry. The rise is attributed to increased sputtering at oblique incidence as the erosion channel deepens [94].

There are several mechanisms that could serve to lower $\eta_{\text{eff}}$ from the accepted values. The ion energies may be lower than those given by the cathode voltage drop because of collisions [15]. Some of the ion current is still $N_2$ species with a lower sputtering yield than Ar. Also, while the target appears bare and $P_{N_2}$ is very low, the $N_2$ that is present may still be keeping $\gamma$ high.

In any event, Eqn. II-8 and Fig. 11 should give a good indication of the relative magnitudes of the effective sputtering yields for various degrees of target coverage.
The voltage dependence of the effective sputtering yield. •-I from Fig. 3 and o-\( \eta_{\text{eff}} \) calculated from Eqn. II-8 and the data of Fig. 3.
CHAPTER III

FILM PROPERTIES - EXPERIMENTAL RESULTS AND DISCUSSION

At this point I will present electrical transport and optical data from measurements made on Al/AlN cermets produced by voltage controlled, reactive, dc, planar magnetron sputtering of an Al target in an Ar/N\textsubscript{2} atmosphere, as described in the previous section. Much of the data will be presented graphically along with an inset of the deposition glow discharge I-V characteristic (as in Fig. 3) in order that, in the end, an intuitive feeling may be developed for the relationship between film properties and deposition conditions.

III.1 Electrical Transport Properties of Al/AlN Cermets.

As discussed earlier, Fig. 10 and the text of pages 63 and 64 shows resistivity ($\rho$) and temperature coefficient of resistance (TCR) data that demonstrates that the method of calculating film compositions from the glow discharge characteristics does work. X-ray diffraction measurements of AlN\textsubscript{x} films are correlated with the deposition I-V characteristic in Fig. 12, while Fig. 13 shows transmission electron microscope (TEM) data correlated in like manner. One sees the AlN crystals becoming smaller and fewer for increasing $V$, while the Al crystals become larger and more prevalent. In particular, one sees; the AlN crystal size to be roughly 300 Å for films deposited on the low $V$ side of the I-V maximum (the stoichiometric region); between the I-V maximum and minimum the AlN crystal size decreases steadily to about 150 Å while more and more Al inclusions appear with diameters less than
X-ray diffraction data for films deposited at the positions indicated on the inset I-V curve.
TEM for films deposited at the positions indicated on the inset I-V curve. The films are about 1500 Å thick.
50 Å; just past the I-V minimum an abrupt decrease, to about 50 Å, occurs in the AlN crystal size; after the abrupt drop in AlN crystal size, with increasing V the Al crystal size grows steadily larger while the AlN size grows steadily smaller. Also, in this last region, one will notice the tendency of the Al inclusions to form large single particles instead of labyrinthian interconnections of smaller particles, and that, even at very high volume fractions of Al, the tendency is to form AlN barriers between the Al inclusions. To this tendency to form barriers has been attributed [2] the fact that cermet films invariably exhibit an $X_{vc}$ that is higher than theory predicts for a random percolation network ($X_{vc} = .33$ in theory for 3-dimensions [3]). This barrier formation is undoubtedly a thermodynamic effect related to the surface tension of the different inclusions, and serves to remove the randomness from the system. However, theoretical studies have shown [59,96] that a correlated percolation system like this may have a much higher value for $X_{vc}$, but the critical exponents should remain unchanged.

In Fig. 14 is shown normalized $\rho$ vs. $T$ data for four samples that are representative of the three types of behavior seen near $X_{vc}$. For $X_{v} > .8$ the behavior is typical of an impure metal with $\rho$ decreasing linearly with $T$ to some lower limit. For $.72 < X_{v} < .8$, $\rho$ decreases with $T$ at high $T$, reaches a minimum, and then increases with decreasing $T$ from the minimum. In this region where $\rho$ is increasing with decreasing $T$, $\rho \sim \ln T$ and the temperature at which the minimum occurs moves to higher $T$ as $X_{v}$ is reduced. This $\rho \sim \ln T$ behavior and the temperature behavior of $\rho_{\text{min}}$ is characteristic of electron
Normalized $\rho$ vs. $T$ (a) and vs. $\ln T$ (b) for samples near $X_{vc}$. ($X_v$, $\rho_{\text{min}}$, $\rho_{\text{max}}$), with resistivities in $\mu\Omega\cdot\text{cm}$, for each sample are: squares - (.66, 840, 984), solid circles - (.75, 299.0, 292.5), open circles - (.79, 128.3, 128.7), and triangles - (.84, 41.6, 52.8).
localization in a cermet just above $X_v c$ [5,40,41]. (Detailed magnetoresistance and Hall coefficient measurements (as a function of temperature) are presently being performed by Normand Fortier on the samples exhibiting $\rho \sim \ln T$ behavior in order to differentiate between electron localization or electron-electron interaction effects.) For $X_v \leq .72$, $\rho$ is increasing with decreasing $T$ with no well known temperature dependence, and definitely not as $\ln \rho \sim 1/\sqrt{T}$ as others have seen with smaller grain sizes and lower values for $X_v c$ [2,32].

Using the method of Denvenyi et al. [37], discussed earlier, I have made ln-ln plots of activation energy versus $T$ for samples just below $X_v \sim .72$ and found that, indeed, the activation energy varies as some power of $T$. The activation energies are found by taking the slope at many points along a $\ln \rho$ vs. $1/T$ plot. Fig. 15 is a typical example of this procedure, and the power of $T$ is seen to vary from sample to sample also, in accordance with Devenyi's model.

The view [37] that a very large number of defect states exists in the insulating grains, due to excess Al, seems extremely likely when one considers the way in which these films grow. In the composition range just below $X_v \sim .72$ the $N_2/Al$ arrival rate at the substrate is very low, the AlN crystal size is extremely small (less than $\sim 50 \, \AA$), the Al islands are becoming very large and prevalent, and there is not yet a continuous metallic pathway across the sample. One, therefore, expects a large amount of Al atoms dispersed in the AlN, and that conduction does not proceed via a continuous metallic channel. The island sizes
Fig. 15

In–ln plots of conduction activation energies vs. $T$ (a) and $\ln \rho$ vs. $1/T$ at $X_v = .66$ (b). The data (squares) in (b) was used to calculate the data (triangles) in (a), then the slope and intercept in (a) were used to find $A$ and $p$, as in Eqn. I–5. The solid line in (b) is calculated from Eqn. I–5, with the $A$ and $p$ values from (a).
(estimated from the x-ray and TEM data of Figs. 12 and 13) indicate the typical charging energies for the metal islands to be of the order of $0.1\text{eV}$ at $X_v = 0.65$. Therefore, it is unlikely that many of these islands are charged below 300 K. The conduction mechanism is then likely to be hopping between isolated defects. However, the physical nature of these filled and unfilled defect states is not immediately apparent.

As $X_v = 0.72$ is crossed from the insulating to the metallic side one observes (see Fig. 16) the carrier type in room temperature Hall measurements to change from $n$ to $p$. Hopping should yield $n$-type [97] while Al is $p$-type [79]. While either Al interstitials or N-vacancies are also expected to produce $n$-type conduction in AlN through doping, the data of Figs. 12 through 15 indicate that hopping conduction is the more likely mechanism in this case. The composition ranges for the $\rho - \ln T$ behavior and the changing Hall sign coupled with TCR, in Fig. 10, changing sign at $X_v = 0.72$ strongly indicates that $X_{vc} = 0.72$.

Using the conductivities extrapolated to $T = 0$ K to fit $\sigma$ to a power law form, both above and below $X_{vc}$, with $X_{vc}$ as a free parameter gave a best fit of $X_{vc} = 0.72 \pm 0.02$. This value is in good agreement with the value from the TCR, Hall, and $\rho - \ln T$ data discussed earlier. Fig. 17 shows $\log(\sigma)$ vs. $X_v$ and $\log(\sigma)$ vs. $\log|X_v - X_{vc}|$ with $X_{vc} = 0.72$. Above $X_{vc}$ one finds $\sigma \sim (X_v - X_{vc})^t$ with $t = 1.75 \pm 1.1$, in excellent agreement with the theoretical value [3] of 1.7. Below $X_{vc}$ one finds $\sigma \sim (X_v - X_{vc})^{-s}$ with $s = 4.3 \pm 1.1$. This last exponent does not agree with the theoretical value of 0.7 for a mixture of normal conductors and, of course, this is due to the conduction mechanism being tunneling.
Inverse Hall constant vs. $X_v$ for films deposited near $X_v = X_{vc} = 0.72$. 
(a) The theoretical form for $\ln(\sigma)$ vs. $X_v$, with the scaling relations shown for a 3-dimensional mixture of "normal" conductors. (b) $\ln(\sigma)$ vs. $X_v$ from data from films deposited near $X_v = X_{vc} = .72$. (c) $\ln(\sigma)$ vs. $\ln |X_{vc} - X_v|$ for data in (b). As depicted in (a), from (c) one obtains the critical exponents $t = 1.75 \pm .1$ and $s = 4.3 \pm .1$. The discrepancy between the observed and predicted values of $s$ arises because, for the data, conduction proceeds via hopping.
If one adopts Neugebauer's formula for tunneling [30]

\[
\sigma \sim \frac{R^2}{r} \exp(-\alpha R) \exp\left(-\frac{e^2}{kT}\right) \tag{III-1}
\]

where \( R \) is the particle separation and \( r \) is the particle size, then in the limit of both \((\alpha R)\) and \( (e^2/kTr) \) being small one finds that \( R \sim (X_{vc} - X_v)^u \) with \( u \sim 0.9 \). \( r \) has been taken to vary as \((X_{vc} - X_v)^{-1/\delta}\) with \( \delta = 0.4 \) [3]. Of course, in hopping from defect to defect the particle size may not be as big a factor in the tunneling process and the hopping conduction may only depend on the interdefect spacings.

III.2 Optical Properties of Al/AlN Cerments

The optical absorption of Al/AlN films, deposited at various positions along the I-V characteristic of Fig. 3, was measured. Fig. 18 shows the product of film thickness (d) and optical absorption coefficient (\( \alpha \)) vs. wavelength for films of thicknesses between 4000 Å and 7000 Å. Taking account of film thicknesses, Fig. 19 shows \( \sqrt{\alpha} \) vs. photon energy for the same films as in Fig. 18. On the high voltage side of the I-V minimum the films turn from clear, to yellow brown, to dark brown, to black, and finally silvery (like Al metal) by film #8 of Fig. 18. The absorption peak at 4.8 eV in Fig. 18 and 19 is identical in position and appearance to that observed by Pastrnak et al. [60], as described in the introduction. Pastrnak concluded that this absorption peak was due to oxygen impurities in the film. This conclusion was
Product of film thickness (d) and optical absorption coefficient (α) vs. wavelength for films deposited at the positions shown in the inset I-V curve.
$\sqrt{\alpha}$ vs. E for the films shown in Fig. 18.
based upon diffuse reflectance measurements on crushed AlN crystals prepared by high voltage arcing of Al electrodes in an N₂ atmosphere, where the general background reflectance (after crushing) and 4.8 eV absorption intensity (before crushing) seemed correlated with oxygen content in the powdered samples (after crushing). In view of the known granular nature of the films of Figs. 18 and 19, and the fact that the arc discharge method of making AlN is known to produce varying degrees of nitrogen deficiency [66] (and possibly Al inclusions), the question arises as to whether the absorption at 4.8 eV could be due to some form of the dielectric anomaly, associated with granular materials, as described in the introduction.

In order to determine whether or not the 4.8 eV absorption is due to the granular nature of the films, calculations, based upon the MGT, EMT, and coated sphere approximations presented earlier, for Al/AlN cermets were performed and the results are displayed in Figs. 20 through 27. For these calculations: the Al optical constants given by Powell were used [80]; the refractive index data of Pastrnak [59], including dispersion, was used; and the extinction coefficient for AlN was obtained from optical absorption measurements on AlN deposited in the stoichiometric portion of the I-V characteristics. Details of these calculations are given in the appendix on optical calculations.

Fig. 20 shows the result of the MGT calculation. The position of the dielectric anomaly is seen to shift appreciably with Xᵥ, whereas the data of Pastrnak and of Figs. 18 and 19 indicates a constant peak position. Since Irene and Zirinsky [65] reported a lowering of refractive index in AlN with Al enrichment (to ~ 1.7), Fig. 21 shows the
$\sqrt{\alpha}$ vs. $E$ calculated in the MGT approximation for Al/AlN composites at various values of $X_v$. See Eqn. I-9 and the appendix on optical calculations.
$\sqrt{\alpha}$ vs. $E$ calculated in the MGT approximation for Al/AlN composites at $X_v = 0.10$, but at various values of AlN refractive index. See Eqn. I-9 and the appendix on optical calculations.
$\sqrt{\alpha}$ vs. $E$ calculated in the EMT approximation for Al/AlN composites at various values of $X_v$. See Eqn. 1-14 and the appendix on optical calculations.
$\sqrt{\alpha}$ vs. E calculated in the coated sphere-EMT approximation for Al/AlN composites at various values of $X_v$. See Eqns. 1-14 and 1-15 and the appendix on optical calculations.
Comparison of $\sqrt{\alpha}$ vs. $E$ data of Fig. 19 (a) with calculations, from Fig. 23 (b) in the coated sphere-EMT approximation.
Reflectance vs. E calculated in the EMT approximation for Al/AlN composites at various values of Xv. See Eqn. I-14 and the appendix on optical calculations.
Reflectance vs. E calculated in the coated sphere-EMT approximation for Al/AlN composites at various values of Xv. The coating parameters are the same as those used in Fig. 23. See Eqns. 1-14 and 1-15 and the appendix on optical calculations.
Infrared reflectance data for: films deposited at the positions indicated in the inset I-V curve; bulk AlN; and the substrates used for the deposited films.
effect, in the MGT calculation, of changing \( n \). It does not seem reasonable to assume that the shift (to lower energies) in peak position with increasing \( X_v \) could be exactly cancelled out, for all \( X_v \), by the shift (to higher energies) in peak position as \( n \) decreases with increasing \( X_v \), especially since such a low index is required, even at \( X_v \sim 0 \), to shift the peak to 4.8 eV. Therefore, one must rule out the MGT dielectric anomaly as the source of the 4.8 eV absorption.

Fig. 22 reveals the results of the EMT calculation for Al/AlN cermets. No absorption peak is observed, and the general background level of absorption is seen to increase with \( X_v \). Therefore, one must also rule out the EMT model as an explanation of the 4.8 eV absorption.

Fig. 23 is based on coated Al spheres in an EMT approximation for Al/AlN cermets. The coating material was taken to have a refractive index of 1.6 and an extinction coefficient varying as that of AlN, but at five times the intensity. The value of \( Q \) (i.e. \( 1 - \text{coating thickness/inclusion radius} \)) was taken as 0.2. The results of Fig. 23 are seen to resemble the experimental results, aside from absolute absorption intensity, quite well. However, the assumption of constant \( Q = 0.2 \), regardless of \( X_v \), means that as \( X_v \) and inclusion size change the fraction of the inclusion radius that is the coating material remains constant at 0.8. This may or may not be a reasonable assumption. The coating of inclusions has, in the past, been attributed to thermodynamic effects, such as surface tension [2], and used to explain the raising of the percolation threshold in cosputtered granular metals. In these Al/AlN films, condensing Al atoms cease growing as crystalline Al at
some particular crystal size. According to the x-ray and TEM data of Figs. 12 and 13, this size is dependent on the relative arrival rates of Al and N₂ at the substrate. The absolute arrival rates are, most likely, important in this respect as well. A similar situation obtains for the growing AlN crystals. It is possible that the "bridge" between the two types of particles is an amorphous, metal enriched AlN coating, and that the thickness is related to the incident flux of condensing atoms and is in some way proportional to the particle sizes for some thermodynamic reason. The values of Q, n, and k for the coating material used in the calculation would then represent average values for this "bridge" of amorphous material. Fig. 24 compares the results of the coated sphere calculation of Fig. 23 with the data of Fig. 19, and one sees good qualitative agreement. However, without further evidence to support the assumption of constant Q, this coated sphere-EMT approximation can only be thought of as a possibility, perhaps only a remote possibility, for the description of the origin of the 4.8 eV absorption band. The remoteness of this possibility becomes even more apparent when one considers that Q is actually Xv₁/₃ in an MGT calculation for a single sphere and, therefore, small changes in Q will produce noticeable shifts in the peak position, as in Fig. 20. Since it seems reasonable that Q should be related to both the absolute and relative condensation rates for Al and N₂ at the substrate, it seems unlikely that Pastnak's arc discharge and the reactive sputtering technique of this work would produce the same Q and, therefore, the same peak position.
Oxygen impurities do not seem to be a likely origin for the 4.8 eV absorption either. In this work, the base pressures before throttling the diffusion pump were less than \(10^{-5}\) Pa, and less than \(10^{-4}\) Pa after throttling. These base pressures are independent of where on the I-V characteristic the film was deposited. Therefore, oxygen incorporation should manifest itself in all films in an absorption peak at 4.8 eV. Measurements on films deposited in the stoichiometric region of the I-V characteristics with thicknesses varying from 300 Å to 50,000 Å have shown no evidence of either browning or an absorption band at 4.8 eV.

The films of this work which display an optical absorption band at 4.8 eV are all Al/AlN cermets where the AlN is most likely doped with excess Al atoms and/or N-vacancies and the Al is most likely doped with nitrogen. It seems likely that Pastrnak's samples have, at least, excess Al and/or N-vacancies in an AlN matrix [66], while the possibility of Al inclusions can not be ruled out. Also, Noreika et al. performed absorption measurements on dark brown, rf, reactively sputtered AlN films [63] and obtained results similar to film #8 of Figs. 18 and 19, but observed no Al lines in electron diffraction patterns. Therefore, it seems possible that either N-vacancies or included Al atoms give rise to the optical absorption band at 4.8 eV in AlN.

If the absorption band at 4.8 eV is due to some defect state in AlN (such as N-vacancies or Al interstitials), the EMT theory should describe the optical properties of the granular films, and the 4.8 eV band should be superimposed upon it. Infrared reflectance measurements
on these Al/AlN cerments do not support this supposition very well. Figs. 25 and 26 are reflectance vs. E (photon energy) curves calculated in the EMT and coated sphere-EMT approximations, respectively, for Al/AlN cerments. The coated sphere-EMT calculations show the IR reflectivity of Al/AlN cerments to be identical to that of AlN, whereas the EMT calculation shows the reflectivity to increase fairly rapidly with Xv.

Actual IR reflectance data, as a function of deposition I-V characteristics, for Al/AlN cerment films, between 4000 Å and 7000 Å thick, are presented in Fig. 27. The various peaks present in these data can be attributed to the quartz substrate or the AlN reststrahlen bands. Assuming these peaks to be superimposed upon the reflectivities calculated for granular Al/AlN composites, one sees, in these data, the IR reflectivity of the cerments to be very close to that of the pure AlN, with much of the difference accounted for by differing interference maxima for films of differing thickness. The coated sphere-EMT approximation seems to fit these data much closer than the EMT approximation does. However, if the coated sphere-EMT approximation describes the optical behavior of these films, a dielectric anomaly would be expected in the optical absorption, and the previous discussions indicated that no dielectric anomaly is observed. Since it is common that absolute magnitudes of absorption are not well predicted by these granular theories [54,57], it may be that the films are EMT-like. However, the difference between the observed and predicted levels of absorption are much greater (by ~10) than the observed
differences reported to date [4,50-54]. The complexity of the microstructure of these films, however, may not be adequately accounted for in any of the relatively simple theories I have discussed in this work, since there are, undoubtedly, a great many single and multiple atom inclusions with optical properties far different than bulk Al. A model which, more realistically, incorporates the true microstructure of these films is, most likely, needed to accurately described the optical properties of these films.

While the absorption at 4.8 eV is most likely due to either excess Al atoms or N-vacancies in AlN, the coated sphere-EMT approximation for granular Al/AlN composites remains a remote possibility.
CHAPTEIV
CONCLUSION

IV.1 Reactive Sputtering Mechanisms

This work has shown that two separate mechanisms are at work in covering a sputtering target with a reactive gas compound layer: chemisorption of reactive gas neutrals from the sputtering gas and ion plating of reactive gas species from the sputtering ion current. The degree to which either mechanism contributes to target coverage will depend on the particular target-reactive gas combination under study. However, since the chemisorption rates of most common gasses on most metals are known [82], one should be able to predict, in advance, which mechanism will dominate.

When ion plating is the dominant target coverage mechanism, voltage control of the glow discharge will permit stable operation at all degrees of target coverage. Under these circumstances, the ratio of sputtered flux to reactive gas molecules impinging on the substrate will be a single valued function of the target voltage. Since this ratio determines the film composition [22,67], voltage control allows film composition control when ion plating is the dominant target coverage mechanism. Since thermodynamic considerations should dictate a solubility limit for any particular defect in a chemical system, when the sputtered film becomes too deficient in the reactive gas constituent precipitates of the sputtered material should appear in the film.

Therefore, voltage control in reactive sputtering is well suited to the
controlled composition deposition of thin film cermets from a single target when target coverage is dominated by the ion plating mechanism.

**IV.2 Al/A1N Cermets Deposited by Voltage Controlled Reactive Sputtering**

**IV.2-a Electrical Transport Properties**

The volume fraction (Xv) of Al inclusions in Al/A1N cermets was found to be readily controllable through regulation of the target voltage in the manner discussed in Chapter II. At the precolation threshold the temperature coefficient of resistance (TCR) was seen to be zero. Therefore, the techniques of Chapter II have a very practical application in the controlled composition deposition of temperature stabilized thin film resistors. The granular nature of these films, coupled with the highly controllable Xv, also makes these techniques well suited to the study of electron localization effects as well as the critical phenomena associated with percolation systems near the percolation threshold (Xvc). Above Xvc, it was found that $\sigma \sim (Xv - Xvc)^t$ with $t = 1.75 \pm 0.1$, in excellent agreement with the theoretical prediction (of 1.7) for a 3-dimensional mixture of normal conductors. Below Xvc, conduction appears to be via hopping from defect to defect within the AlN grains and $\sigma \sim (Xvc - Xv)^s$, with $s = 4.3 \pm 0.1$. For mixtures of normal conductors, $s$ is predicted to be 0.7. No theoretical predictions for $s$ exist, at present, when hopping is the conduction mechanism because the divergence of the interparticle (or interdefect)
spacing, as the percolation threshold is approached, is not known. Therefore, this method of cermet fabrication, which favors this defect hopping conduction mechanism below $X_{vc}$, may be very useful in verifying future predictions of the power law behaviour of the interparticle spacing in percolation systems. The rather tortuously interconnected labyrinthian conduction pathways in a system near the percolation threshold are predicted \[5,40,41\] to give rise to electron localization within the labyrinth. Again, the precise control over $X_v$ makes the fabrication methods of this thesis ideally suited to the study of these phenomena. Towards this end, Normand Fortier is presently undertaking an in depth study of percolation and electron localizatin effects in thin films sputtered by the techniques of this Ph.D. thesis study.

**IV.2-b Optical Properties**

It appears that the optical absorption band observed at 4.8 eV, for $0.5 < X_v < 0.7$ in my films, is more likely due to excess Al or N-vacancies in AlN than to the granular geometry or, as Pasttnak has suggested, oxygen contamination. The lack of any observed "dielectric anomaly" in the optical absorption seems to rule out the MGT or coated sphere-EMT approximations for describing the optical properties of the Al/AlN cermets of this work. However, the extremely large difference, in magnitude, between the observed and EMT-predicted optical absorption seems to also rule out the EMT approximation. This lack of agreement probably arises because neither of these three theories is equipped to deal with a distribution of inclusion sizes ranging continuously from
single atoms to crystallites with bulk optical properties. A distribution in Al inclusion sizes like this is almost certainly present in the films discussed in this work. Both the EMT and MGT theories have been generalized to any number of types of inclusions [43,55-57]. One of these generalizations may apply if the single, double, triple, etc. Al atom clusters are each thought of as "different types of inclusions" with different optical properties. Such an effort does not seem particularly worthwhile in this case.


34. N.F. Mott, Phil. Mag., 17, 1259 (1968).


APPENDIX ON OPTICAL CALCULATIONS

In this appendix, the steps involved in calculating optical absorption coefficients ($\alpha$) and reflectivities ($R$) from any of Eqns. I-9, I-14, or I-15 will be detailed. This procedure may be subdivided into the following four (4) steps:

1. Standard techniques are used to obtain the real and imaginary parts of the dielectric constants of the constituent materials of a granular composite from data on their refractive indices ($n$) and extinction coefficients ($k$).

2. The real and imaginary parts of the dielectric constants of the mixture components (calculated in step 1) are substituted into either Eqn. I-9 or Eqn. I-14 to obtain the effective values for the real and imaginary parts of the dielectric constant ($\varepsilon$) of the mixture of the two materials.

3. Using standard techniques, the mixture's effective $n$ and $k$ values are calculated from the real and imaginary parts of $\varepsilon$ (obtained in step 2).

4. $\alpha$ and $R$ are then calculated, by standard techniques, from the $n$ and $k$ values from step 3.

Mathematical details of this method, and the standard techniques, will now be presented.

The following expressions are some standard formulas [39] which interrelate many of the optical constants of a single material.
\[ \varepsilon = \varepsilon_1 + j\varepsilon_2 = |\varepsilon| \exp(j\theta) = |\varepsilon|(\cos\theta + j\sin\theta), \]

with

\[ |\varepsilon| = (\varepsilon_1^2 + \varepsilon_2^2)^{1/2}, \]

and

\[ \theta = \tan^{-1}(\varepsilon_2/\varepsilon_1). \]

\[ \varepsilon_1 = n^2 + k^2, \]

\[ \varepsilon_2 = 2nk \]

\[ n^2 = \frac{1}{2}[(\varepsilon_1^2 + \varepsilon_2^2)^{1/2} + \varepsilon_1] \]

\[ k^2 = \frac{1}{2}[(\varepsilon_1^2 + \varepsilon_2^2)^{1/2} - \varepsilon_1] \]

\[ R = [(n - 1)^2 + k^2]/[(n + 1)^2 + k^2] \]

\[ \alpha = 4\pi nk/\lambda \]

The symbols in Eqns. A-1 through A-5 are defined as follows:

\( \varepsilon \) = dielectric constant

\( \varepsilon_1 \) = the real part of \( \varepsilon \)
\[ \varepsilon_2 = \text{the imaginary part of } \varepsilon \]
\[ j = \sqrt{-1} \]
\[ n = \text{the refractive index} \]
\[ k = \text{the extinction coefficient} \]
\[ R = \text{the reflectivity} \]
\[ \alpha = \text{the absorption coefficient} \]
\[ \lambda = \text{the wavelength of light} \]

The dielectric constant of AlN is obtained from the \( n \) and \( k \) data of Fig. 28 and Eqns. A-2 and A-1. For use in Eqns. I-9, I-14, and I-15 the dielectric constant of AlN is written as

\[ \varepsilon_i = \varepsilon_{i1} + \varepsilon_{i2} = |\varepsilon_i| \exp(j\theta_i), \quad \text{A-6} \]

where the conventions of Eqns. A-1 are followed and the subscript \( i \) stands for insulator. Similarly, Fig. 29 and Eqns. A-2 and A-1 are used to write the dielectric constant of Al as

\[ \varepsilon_m = \varepsilon_{m1} + j\varepsilon_{m2} = |\varepsilon_m| \exp(j\theta_m), \quad \text{A-7} \]

where the subscript \( m \) stands for metal.

Eqns. A-6 and A-7 may now be used with either of Eqns. I-9 or I-14 to calculate \( \varepsilon \) for a granular mixture of Al and AlN. The details of this procedure for the MGT, EMT, and coated sphere approximations for granular materials will now be discussed.
Optical constants for AlN. The refractive indices \((n)\) are from data of Pasternak et al. [59], while the extinction coefficients \((k)\) were calculated from my optical absorption data for stoichiometric Aln films.
Fig. 29

The optical constants of Al from the data of Powell [80].
Substitution of Eqns. A-6 and A-7 into Eqn. I-9 permits, upon extensive rearrangement, $e$ to be written as

$$e = \frac{A + jB}{C + JD}, \quad \text{A-8-a}$$

where

$$A = 2X_v(R_1 - R_2) + R_1 + 2R_2, \quad \text{A-8-b}$$

$$B = 2X_v(I_1 - I_2) + I_1 + 2I_2, \quad \text{A-8-c}$$

$$C = X_v(\varepsilon_{11} - \varepsilon_{m1}) + \varepsilon_{ml} + 2\varepsilon_{i1}, \quad \text{A-8-d}$$

$$D = X_v(\varepsilon_{12} - \varepsilon_{m2}) + \varepsilon_{m2} + 2\varepsilon_{i2}, \quad \text{A-8-e}$$

and

$$R_1 = \varepsilon_{i1} \varepsilon_{ml} - \varepsilon_{i2} \varepsilon_{m2}, \quad \text{A-8-f}$$

$$R_2 = \varepsilon_{i1}^2 - \varepsilon_{i2}^2, \quad \text{A-8-g}$$
The results of Eqns. A-8 allow $\varepsilon_1$ and $\varepsilon_2$ to be written as

$$
\varepsilon_1 = (AC + BD)/(C^2 - D^2) \quad \text{A-9-a}
$$

and

$$
\varepsilon_2 = (BC - AD)/(C^2 - D^2) \quad \text{A-9-b}
$$

Equations A-9 may then be used in concert with Eqns. A-3, A-4, and A-5 to calculate the optical properties of an Al/AlN cermet in the MGT approximation.

**The EMT Approximation**

Substitution of Eqns. A-6 and A-7 into eqn. I-14 yields

$$
\varepsilon = |\varepsilon| \exp(j\theta)
$$

$$
= [(1 - Xv) \{|\varepsilon_1| \exp(j\theta_1)\}^{1/3} + Xv \{|\varepsilon_m| \exp(j\theta_m)\}^{1/3}]^3. \quad \text{A-10}
$$
Since \( \exp(j \theta) \)^{1/3} has three (3) solutions it is apparent that
Eqn. A-10 has more than one solution. However, only one of the
solutions to Eqn. A-10 satisfies the physical requirement of being
symmetric with respect to the roles of the two types of particles.
Therefore, the symmetric solution is used, and it is written as follows:

\[
\varepsilon = (1 - Xv)^3 |\varepsilon_i| \exp(j \theta_i) + Xv^3 |\varepsilon_m| \exp(j \theta_m) \\
+ 3Xv(1 - Xv)^2 |\varepsilon_i|^{2/3} |\varepsilon_m|^{1/3} \exp\{j(2 \theta_i + \theta_m)/3\} \\
+ 3Xv^2 (1 - Xv) |\varepsilon_i|^{1/3} |\varepsilon_m|^{2/3} \exp\{j(\theta_i + 2 \theta_m)/3\}. \tag{A-11}
\]

Using the identity \( \exp(j \theta) = \cos \theta + jsin \theta \) in Eqn. A-11 allows the
real and imaginary parts of \( \varepsilon \) to be written as

\[
\varepsilon = (1 - Xv)^3 |\varepsilon_i| \cos(j \theta_i) + Xv^3 |\varepsilon_m| \cos(j \theta_m) \\
+ 3Xv(1 - Xv)^2 |\varepsilon_i|^{2/3} |\varepsilon_m|^{1/3} \cos\{j(2 \theta_i + \theta_m)/3\} \\
+ 3Xv^2 (1 - Xv) |\varepsilon_i|^{1/3} |\varepsilon_m|^{2/3} \cos\{j(\theta_i + 2 \theta_m)/3\}. \tag{A-12-a}
\]

and

\[
\varepsilon = (1 - Xv)^3 |\varepsilon_i| \sin(j \theta_i) + Xv^3 |\varepsilon_m| \sin(j \theta_m) \\
+ 3Xv(1 - Xv)^2 |\varepsilon_i|^{2/3} |\varepsilon_m|^{1/3} \sin\{j(2 \theta_i + \theta_m)/3\} \\
+ 3Xv^2 (1 - Xv) |\varepsilon_i|^{1/3} |\varepsilon_m|^{2/3} \sin\{j(\theta_i + 2 \theta_m)/3\}. \tag{A-12-b}
\]
Eqns. A-12 may be used in concert with Eqns. A-3, A-4, and A-5 to calculate the optical properties of an Al/AlN cermet in the EMT approximation.

The Coated Sphere Approximation

The coated sphere approximation is used in conjunction with either the MGT or EMT approximations. The only modification being that, in Eqns. A-9 or A-12, either or both of $\varepsilon_i$ or $\varepsilon_m$ are replaced with the effective dielectric constant for a sphere of the original material ($i$ or $m$) that is coated with a layer of another material. The effective dielectric constant for such a sphere is calculated in the MGT approximation where the coating material is taken as the amorphous dielectric matrix that the original sphere is embedded in. With the effective dielectric constants for coated spheres in place of the uncoated sphere dielectric constants, a random distribution of two types of coated spheres is treated in the EMT approximation (Eqns. I-14 and A-12), while a random distribution of one type of coated sphere embedded in an amorphous matrix of another material is treated in the MGT approximation (Eqns. I-9 and A-9).