ELECTROMIGRATION IN THIN FILMS

By

Hans M. Breitling

A Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

University of Florida
1971
ACKNOWLEDGMENTS

The author would like to thank his advisor, Dr. R. E. Hummel, for the constant encouragement and support during the course of this research. Gratitude is extended to Dr. D. B. Dove, Dr. A. G. Guy and Dr. J. Kronsbein, the other members of the advisory committee. The author also would like to thank Dr. D. Hagmann of the IBM Germany Research Laboratory for suggesting the topic of this dissertation and for giving valuable help in the initial stages of the research project. Thanks go to Dr. G. L. Hofman for many fruitful and stimulating discussions.

The National Aeronautics and Space Administration provided the funding for this research under contract No. NGR 10-005-080, for which the author is very grateful.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>ii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>v</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>x</td>
</tr>
<tr>
<td>Chapter</td>
<td></td>
</tr>
<tr>
<td>I  INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II ELECTROMIGRATION IN METALS</td>
<td>5</td>
</tr>
<tr>
<td>III REVIEW OF PREVIOUS RESULTS ON ELECTROMIGRATION IN THIN FILMS</td>
<td>13</td>
</tr>
<tr>
<td>IV EXPERIMENTAL PROCEDURE</td>
<td>20</td>
</tr>
<tr>
<td>V  RESULTS</td>
<td>36</td>
</tr>
<tr>
<td>VI DISCUSSION</td>
<td>83</td>
</tr>
<tr>
<td>VII CONCLUSIONS</td>
<td>96</td>
</tr>
<tr>
<td>Appendices</td>
<td></td>
</tr>
<tr>
<td>I  DEVELOPMENT OF NUCLEAR EMULSION PLATES</td>
<td>98</td>
</tr>
<tr>
<td>II PREFERRED ORIENTATION OF SILVER FILMS</td>
<td>99</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>101</td>
</tr>
<tr>
<td>BIOGRAPHICAL SKETCH</td>
<td>105</td>
</tr>
</tbody>
</table>
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Comparison of Direction of Electrotransport and Sign of Hall Coefficient in Different Metals</td>
<td>9</td>
</tr>
<tr>
<td>6.1</td>
<td>Direction of Electrotransport in Thin Films and Bulk Specimens</td>
<td>85</td>
</tr>
<tr>
<td>A2.1</td>
<td>Relative Line Areas in Percent of the 111 Line for Silver Films Deposited on Glass at Ambient Temperature and at 300°C</td>
<td>100</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Specimen shape A</td>
<td>23</td>
</tr>
<tr>
<td>4.2</td>
<td>Specimen shape B</td>
<td>23</td>
</tr>
<tr>
<td>4.3</td>
<td>Sample holder used for resistance measurements</td>
<td>25</td>
</tr>
<tr>
<td>4.4</td>
<td>Schematic drawing of x-ray pinhole camera used for stress measurements</td>
<td>26</td>
</tr>
<tr>
<td>4.5</td>
<td>X-ray diffraction pattern on photographic plate for stress measurement</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>(schematic)</td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>Shielding of gold film with cadmium sheet during irradiation in the nuclear</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>reactor (schematic)</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>Activation of a small area in the middle of gold film by vapor depositing in</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>two steps. a) Film after first evaporation during irradiation in the reactor;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>b) after second evaporation</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>Arrangement used for electroplating of radioactive silver (schematic)</td>
<td>33</td>
</tr>
<tr>
<td>4.9</td>
<td>Equipment used for counting activity in scanning method</td>
<td>34</td>
</tr>
<tr>
<td>5.1</td>
<td>Temperature distribution in silver film</td>
<td>37</td>
</tr>
<tr>
<td>5.2</td>
<td>Resistance change and temperature versus time in silver film. Current</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>density ( j = 7 \times 10^5 \text{ A/cm}^2 ), film thickness 1,500 ( \text{Å} ),</td>
<td></td>
</tr>
<tr>
<td></td>
<td>thickness of electrodes 3,000 ( \text{Å} )</td>
<td></td>
</tr>
<tr>
<td>5.3</td>
<td>Hillock formation on cathode side of silver film (SEM micrograph, 10,000X,</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>( j = 7.2 \times 10^5 \text{ A/cm}^2 ), after 15 hours)</td>
<td></td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>5.4</td>
<td>Holes on anode side of silver film (SEM micrograph, 10,000X, ( j = 7.2 \times 10^5 \text{ A/cm}^2 ), after 15 hours)</td>
<td>40</td>
</tr>
<tr>
<td>5.5</td>
<td>Formation of holes and hillocks in the same area in silver film (SEM micrograph, 2,000X, ( j = 7 \times 10^5 \text{ A/cm}^2 ), after 50 hours)</td>
<td>41</td>
</tr>
<tr>
<td>5.6</td>
<td>Typical failure in silver film</td>
<td>42</td>
</tr>
<tr>
<td>5.7</td>
<td>Resistance change and temperature versus time in silver film coated with SiO. Current density ( j = 8 \times 10^5 \text{ A/cm}^2 ), film thickness 1,500 Å, thickness of electrodes 3,000 Å</td>
<td>45</td>
</tr>
<tr>
<td>5.8</td>
<td>Surface of silver film after deposition on glass substrate (SEM micrograph, 10,000X)</td>
<td>47</td>
</tr>
<tr>
<td>5.9</td>
<td>Grain boundary grooving in silver film after passing of current (SEM micrograph, 20,000X, ( j = 4.1 \times 10^5 \text{ A/cm}^2 ), 57 hours)</td>
<td>47</td>
</tr>
<tr>
<td>5.10</td>
<td>Silver film with grain size gradient; small grain size in central portion. Arrow marks location of failure site</td>
<td>48</td>
</tr>
<tr>
<td>5.11</td>
<td>Silver film with grain size gradient; large grain size in central portion. Arrow marks position of failure site</td>
<td>48</td>
</tr>
<tr>
<td>5.12</td>
<td>Silver film deposited on glass at room temperature (transmission electron micrograph)</td>
<td>49</td>
</tr>
<tr>
<td>5.13</td>
<td>Silver film deposited on glass at 300°C (transmission electron micrograph)</td>
<td>50</td>
</tr>
<tr>
<td>5.14</td>
<td>Resistance change versus time in silver film deposited at 300°C on glass. Current density ( j = 6.3 \times 10^5 \text{ A/cm}^2 ), film thickness 1,400 Å, thickness of electrodes 6,000 Å</td>
<td>53</td>
</tr>
</tbody>
</table>
Silver film deposited on air-cleaved rocksalt at room temperature (transmission electron micrograph) . . . . . . . . 55

Resistance change and temperature versus time in silver film deposited at ambient temperature on air-cleaved rocksalt crystal. Current density $j = 7 \times 10^5 \text{ A/cm}^2$, film thickness 1,350 Å, thickness of electrodes 6,000 Å . . . . . . . . 56

Electron diffraction pattern of single-crystal silver film deposited on air-cleaved rocksalt at 200°C . . . . . . . . 58

Resistance change and temperature versus time in single-crystal silver film deposited on air-cleaved rocksalt at 200°C. Current density $j = 8 \times 10^5 \text{ A/cm}^2$, film thickness 1,350 Å, thickness of electrodes 6,000 Å . . . . . . . . 59

X-ray diffraction pattern from anode side of silver film ($j = 3.3 \times 10^5 \text{ A/cm}^2$, after 100 hours) . . . . . . . . 61

X-ray diffraction pattern from cathode side of silver film ($j = 3.3 \times 10^5 \text{ A/cm}^2$, after 100 hours) . . . . . . . . 61

Resistance change and temperature versus time in gold film. Current density $j = 7 \times 10^5 \text{ A/cm}^2$, film thickness 1,300 Å, thickness of electrodes 5,000 Å . . . . . . . . 63

Resistance change and temperature versus time in copper film coated with SiO. Current density $j = 5.1 \times 10^5 \text{ A/cm}^2$, film thickness 2,450 Å, thickness of electrodes 5,500 Å . . . . . . . . 64

Resistance change and temperature versus time in magnesium film. Current density $j = 4.2 \times 10^5 \text{ A/cm}^2$, film thickness 1,300 Å, thickness of electrodes 8,000 Å . . . . . . . . 65
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.24</td>
<td>Resistance change and temperature versus time in indium film. Current density $j = 1 \times 10^5$ A/cm$^2$; film thickness 6,000 Å, thickness of electrodes 10,000 Å</td>
<td>66</td>
</tr>
<tr>
<td>5.25</td>
<td>Resistance change and temperature versus time in tin film. Current density $j = 1.2 \times 10^5$ A/cm$^2$. Film thickness 4,200 Å, thickness of electrodes 9,000 Å</td>
<td>67</td>
</tr>
<tr>
<td>5.26</td>
<td>Resistance change and temperature versus time in lead film. Current density $j = 1.4 \times 10^5$ A/cm$^2$, film thickness 1,700 Å, thickness of electrodes 13,200 Å</td>
<td>68</td>
</tr>
<tr>
<td>5.27</td>
<td>Whisker type growths on cathode side of gold film (SEM micrograph, 5,000X, $j = 5 \times 10^5$ A/cm$^2$, after 115 hours)</td>
<td>70</td>
</tr>
<tr>
<td>5.28</td>
<td>Holes and hillocks on anode side of gold film (SEM micrograph, 5,000X, $j = 5 \times 10^5$ A/cm$^2$, after 115 hours)</td>
<td>70</td>
</tr>
<tr>
<td>5.29</td>
<td>Whisker type growths on cathode side of gold film (SEM micrograph, 5,000X, $j = 5 \times 10^5$ A/cm$^2$, after 115 hours)</td>
<td>71</td>
</tr>
<tr>
<td>5.30</td>
<td>Cathode side of SiO coated copper film; no hillocks are formed because of coating (SEM micrograph, 1,000X, $j = 5.1 \times 10^5$ A/cm$^2$, after 150 hours)</td>
<td>72</td>
</tr>
<tr>
<td>5.31</td>
<td>Elongated holes on anode side of SiO coated copper film (SEM micrograph, 1,000X, $j = 5.1 \times 10^5$ A/cm$^2$, after 150 hours)</td>
<td>72</td>
</tr>
<tr>
<td>5.32</td>
<td>Holes on cathode side of tin film (SEM micrograph, 2,000X, $j = 1.2 \times 10^5$ A/cm$^2$, after 36 hours)</td>
<td>73</td>
</tr>
<tr>
<td>5.33</td>
<td>Growth on anode side of tin film (SEM micrograph, 1,000X, $j = 1.2 \times 10^5$ A/cm$^2$, after 36 hours)</td>
<td>73</td>
</tr>
<tr>
<td>5.34</td>
<td>Growth on anode side of tin film (SEM micrograph, 5,000X, $j = 1.2 \times 10^5$ A/cm$^2$, after 36 hours)</td>
<td>74</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES (cont.)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.35</td>
<td>Growth in indium film after passing of current (SEM micrograph, 1,000X)</td>
<td>75</td>
</tr>
<tr>
<td>5.36</td>
<td>Growth in indium film (SEM micrograph, 10,000X)</td>
<td>75</td>
</tr>
<tr>
<td>5.37</td>
<td>Location of radioactive zone in a gold film before (A) and after (B) the strip was subjected for 20 hours to a direct current of $7 \times 10^5$ A/cm$^2$. The probability that the actual value falls within the statistical &quot;standard error&quot; limit is 68 percent. Curve B is lower due to radioactive decay.</td>
<td>79</td>
</tr>
<tr>
<td>5.38</td>
<td>Location of radioactive zone in silver film before passing of direct current</td>
<td>81</td>
</tr>
<tr>
<td>5.39</td>
<td>Location of radioactive zone in silver film after passing of direct current for 72 hours ($j = 8 \times 10^5$ A/cm$^2$). Radioactive zone in left part of photograph serves as reference. Electric field is directed from top to bottom.</td>
<td>81</td>
</tr>
</tbody>
</table>
Abstract of Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

ELECTROMIGRATION IN THIN FILMS

By

Hans M. Breitling

June, 1971

Chairman: Dr. R. E. Hummel
Major Department: Metallurgical and Materials Engineering

An experimental study of electromigration in thin films of silver, copper, gold, magnesium, indium, tin and lead was carried out. Various experimental methods have been employed, including resistance measurements, observations with the scanning electron microscope, determination of stress with x-rays and the measurement of the displacement of radioactive tracers and inert markers under the influence of the electric field. The primary objective of the investigations was the determination of the direction of electrotransport in the different metallic films. The migration of ions is directed towards the cathode in films of silver, copper and gold, and towards the anode in magnesium, indium, tin and lead films. The results can be explained by using the concept that electromigration in thin films is
confined to grain boundaries, and that the electron concentration in a grain boundary is different from that in the regular lattice.
CHAPTER I

INTRODUCTION

Electromigration is a term used to describe the transport of mass in metallic conductors under the influence of an applied electric field. The effect is quite small and in bulk samples is observed only under conditions of high current densities and high temperatures. The first observation of electrotransport was made by Gerardin [1] in 1861, who noticed that after electrolysis in the molten state a lead-tin alloy became soft at one end and brittle at the other.

Electrotransport in solids occurs at a much slower rate, and it was not before the early 1930's that electromigration in solid metals was experimentally demonstrated. Since then, numerous investigations on electromigration have been published (for a review see Verhoeven [2]).

In the past few years electromigration has been identified as a cause of failure in thin aluminum conductors used for interconnection purposes in integrated circuits. The failures were at first attributed to gradual evaporation of the material. Soon it became evident, however, that this could not satisfactorily explain the observations. Detailed studies revealed that the interconnections failed
predominantly near the cathode [3] and that no failures occurred under alternating current. From this it was concluded that the breakdown occurred as a result of mass transport which took place under the influence of the applied direct current. Due to the small geometrical dimensions of microelectronic devices, very high current densities (of the order of $10^5 \text{A/cm}^2$) can be sustained with comparatively little joule heating. These high current densities and the unique structural properties of thin films lead to an appreciable amount of electrotransport at ambient temperatures.

Failure in the metallic interconnections of semiconductor devices is due to hole formation produced by local divergencies in mass transport, i.e., local changes in the electromigration rate [4]. These changes result from temperature gradients or structural and chemical inhomogeneities. In the absence of such gradients and inhomogeneities, the rate of mass transport is uniform along the strip, and no hole formation and failure are expected.

In aluminum films grain boundaries provide preferred diffusion paths for the migration of ions [5]. They also represent preferential sites for the heterogeneous precipitation of vacancies and the nucleation of voids [6]. It is therefore evident that the electromigration behavior is very sensitive to the structure and properties of grain boundaries.
Several methods have been suggested for preventing void formation in thin film conductors and thus improve the reliability of semiconductor devices. In these methods attempts are made to reduce the various gradients or to reduce the rate of mass transport. Temperature gradients can be reduced by proper design of the circuits. Structural and chemical inhomogeneities can be minimized by using films with uniform grain size and of high purity. It should be noted, however, that the improvements obtained by these measures are limited.

The rate of mass transport can be reduced in several ways. One method consists of restricting the number of paths available for the migrating atoms. This is done by increasing the grain size and thus decreasing the number of grain boundaries. A more promising method is to replace aluminum (the metal mostly used in the interconnections) by other metals or alloys with lower electromigration rates.

The research reported in this dissertation was prompted by the lack of experimental results for electromigration in thin films of metals other than aluminum. More information about electrotransport in different metal films is needed in order to assess the usefulness of various metals and alloys for forming the interconnections in semiconductor devices. The investigation of electromigration in thin films has significance, however, beyond the immediate practical applications in that it might lead to a better understanding
of the phenomenon of electrotransport in metals. The measurement of mass transport is complicated by the very small thickness of thin films, and various measuring techniques have been employed in this research. Their applicability to study electromigration in thin films has been evaluated. It is hoped that the information obtained in the course of this investigation can serve as a basis for further studies of electrotransport in thin films.
CHAPTER II

ELECTROMIGRATION IN METALS

2.1. Atomistic Description of Electrotransport

It is generally assumed that the force exerted by an electric field on a metal ion consists of two parts:
1) the Coulomb force $F_c$ on the positively charged ion, and
2) a force $F_{int}$ resulting from the transfer of momentum from the charge carriers to the migrating ion. This force is commonly called the electron drag force and is usually larger than $F_c$. Although the force from the electric field is acting on all atoms, only a limited number will be able to migrate under the influence of this force. An ion must be next to a lattice defect, i.e., next to a vacancy if mass transport occurs by a vacancy mechanism, to be able to change its position.

The force $F_c$ arises from the direct interaction of the charged ion with the electrostatic field. The charge of the ion is taken simply as the product of its nominal valence $Z$ and the unit charge $e$:

$$F_c = E_e Z \quad (1)$$
Possible screening effects by the surrounding electrons are neglected.

The force $F_{\text{int}}$ is due to the momentum transfer between the ion and the colliding electrons. According to Fiks [7], the momentum transfer can be calculated from the number of collisions per second and the extra momentum which the electrons acquire in the electric field between two collisions. The extra momentum per electron is given by

$$\Delta p = \frac{eE\xi}{v_e} \quad (2)$$

where $\xi$ is the mean free path of the electrons and $v_e$ the average velocity of the electrons. Using the atomic scattering cross section $\sigma$, the number $C$ of collisions per second can be expressed as follows

$$C = n_e v_e \sigma \quad (3)$$

where $n_e$ is the number of free electrons per cm$^3$. The total momentum transfer per second, which is equal to the interaction force $F_{\text{int}}$, is then given by

$$F_{\text{int}} = \Delta p C = eE\xi n_e \sigma \quad (4)$$

Equation (4) can be written in terms of resistivities if one uses the relations between scattering cross section and resistivity derived by Mott and Jones [8]. These relations are

$$\rho_o = \frac{m^* v_e}{n_e e^2 \xi} \quad (5)$$
\[ \rho_d = \frac{m^* v_e}{n_e e^2 N_d \sigma} \]  

(6)

where \(\rho_o\) and \(\rho_d\) are the resistivities due to the perfect lattice and to defects, respectively; \(N_d\) is the number of defects per \(\text{cm}^3\) and \(m^*\) is the effective mass of the electrons.

With \(n_e = Z N_o\), where \(N_o\) is the number of ions per \(\text{cm}^3\), equation (4) becomes

\[ F_{\text{int}} = eE Z \frac{N_o \rho_d}{\rho_o N_d} \]  

(7)

This derivation shows that the interaction force is proportional to the specific resistivity \((\rho_d/N_d)\) of the point defects responsible for the transport of the atoms.

The exact expression derived by Huntington and Grone [9] for the total force exerted by the electric field on the migrating ion is

\[ F = eE Z [1 - \frac{1}{2} \frac{\rho_d N_o}{\rho_o N_d} \frac{m^*}{|m^*|}] \]  

(8)

The factor \(\frac{m^*}{|m^*|}\) takes account of the fact that the sign of the electron drag force depends on the sign of the effective mass of the charge carriers. Similar expressions for the force were derived by other authors [7, 10].

The relationship between the atom drift velocity \(v_A\) and the driving force \(F\) is given by the Nernst-Einstein equation

\[ v_A = \frac{D^* F}{f k T} \]  

(9)

where \(D^*\) is the self-diffusion coefficient as measured by
tracers, \( f \) is a correlation factor, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature.

Using the relation \( E = j \rho \) (where \( j \) is the current density and \( \rho \) is the specific resistivity of the metal), equation (9) can be written

\[
\frac{v_A}{j} = \frac{D^*}{f k T} e \rho Z \left[ 1 - \frac{1}{2} \frac{\rho}{\rho^*} \frac{N_o}{N_d} \frac{m^*}{m^*} \right]
\] (10)

The atomic drift velocity is thus proportional to the current density and the diffusion coefficient.

2.2. The Direction of Electrotransport and the Sign of the Hall Coefficient

The direction of electrotransport and the sign of the force \( F \) is not the same in all metals. This is illustrated by the experimental data in Table 2.1, which were compiled by Hofman [11]. It should be noted that there is a correlation between the direction of electrotransport and the sign of the predominant charge carriers as measured by the Hall coefficient. Although investigations by Brown and Barnett [12] showed that the momentum of the electric current in hole and electron conductors has the same direction, the experimental data in Table 2.1 indicate that the sign of momentum transfer is different in hole and electron conductors. The force \( F_{\text{int}} \) seems to be directed towards the anode if electrons predominate in the current transport.
Table 2.1
Comparison of Direction of Electrotransport and Sign of Hall Coefficient in Different Metals [11]

<table>
<thead>
<tr>
<th>Metal</th>
<th>Electrode towards which electrotransport occurs</th>
<th>$R_{H}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>anode</td>
<td>-0.4**</td>
</tr>
<tr>
<td>Ag</td>
<td>anode</td>
<td>-0.8</td>
</tr>
<tr>
<td>Au</td>
<td>anode</td>
<td>-0.7</td>
</tr>
<tr>
<td>Cu</td>
<td>anode</td>
<td>-0.8</td>
</tr>
<tr>
<td>Ni</td>
<td>anode</td>
<td>-4</td>
</tr>
<tr>
<td>Li</td>
<td>anode</td>
<td>-1.3</td>
</tr>
<tr>
<td>In</td>
<td>anode</td>
<td>-0.04</td>
</tr>
<tr>
<td>Sn</td>
<td>anode</td>
<td>-0.025</td>
</tr>
<tr>
<td>Zn</td>
<td>anode</td>
<td>+0.4***</td>
</tr>
<tr>
<td>Cd</td>
<td>anode</td>
<td>+0.5</td>
</tr>
<tr>
<td>Pb</td>
<td>anode</td>
<td>+0.05</td>
</tr>
<tr>
<td>Fe</td>
<td>cathode</td>
<td>+14</td>
</tr>
<tr>
<td>Co</td>
<td>cathode</td>
<td>+4</td>
</tr>
<tr>
<td>Mo</td>
<td>cathode</td>
<td>+1.3</td>
</tr>
<tr>
<td>W</td>
<td>cathode</td>
<td>+1.2</td>
</tr>
</tbody>
</table>

*The values for the Hall coefficient are per unit atomic volume and are measured in units of 1/ec.

**- indicates predominant electron conduction.

***+ indicates predominant hole conduction.
and towards the cathode if holes predominate. The above considerations can be expressed in the following expression for \( F \) \[ N_{13} \]

\[
F = e E Z [1 - e \frac{N^0}{N_d} (n_e e \sigma_d - n_h \mu_h \sigma_d)]
\]

(11)

where the subscripts \( e \) and \( h \) refer to electrons and holes, respectively; \( n, \sigma_d \) and \( \mu \) are the number of charge carriers, the scattering cross sections of the ions for those charge carriers and the mobilities of the charge carriers, respectively.

In the case of cadmium, zinc and lead the sign of the Hall coefficient and the direction of electrotransport do not agree. It should be noted, however, that the Hall coefficients given in Table 2.1 were measured at room temperature, whereas the direction of electrotransport was determined at temperatures near the melting point of the metals.

Although the Hall coefficient in most metals does not change significantly with temperature, hexagonal metals are an exception. Measurements by Frey [14] in zinc and by Frank [15] in cadmium show that the value of \( R_H \) decreases sharply with increasing temperature. Although no actual reversal in the sign of \( R_H \) was found in the temperature interval examined, there are indications that the sign of \( R_H \) might change at high temperatures and become positive. No similar explanation is available for lead.
Experimental data on alloys also reveal anomalies in the migration directions, compared to those predicted from the sign of the charge carriers in these alloys. One would expect dilute solutes to migrate towards the anode in an electron conductor regardless of whether these solutes are electron or hole conductors. This relation holds for impurities in copper [16] and silver [17]; however, not for impurities in nickel [18].

The predominant conduction mechanism in alloys may change as a function of concentration. It is then expected that the migration direction of all the components should change accordingly. This was indeed observed in Ag-Zn alloys [19], where both components migrate towards the anode in the α, β and ε phases (predominant electron conduction), while in the γ phase (predominant hole conduction) the components migrate towards the cathode. Similar results were reported for Cu-Al and Cu-Sn alloys [20]. Different migration directions for the components of a single alloy were, however, found for transition metal alloys [21].

It should be noted that the Hall coefficient is given by the following equation [22]

\[ R_H = -\frac{1}{e} \frac{n_e \mu_e^2 - n_h \mu_h^2}{(n_e \mu_e + n_h \mu_h)^2} \]  \hspace{1cm} (12)

where the symbols have the same meaning as in equation (11). The sign of the Hall coefficient depends therefore on the
value of $n_e \mu_e - n_h \mu_h$, whereas the sign of the atomic
drift velocity $v_A$ in equation (11) depends mainly on the
value of $n_e \mu_e \sigma_{de} n_h \mu_h \sigma_{dh}$. A different direction of
electrotransport than that expected from the sign of $R_H$ is
thus also possible if the mobilities or the scattering
cross sections for holes and electrons are appreciably dif-
f erent. In addition, in the case of almost equal hole and
electron conduction (as indicated, for example, by the very
small value of $R_H$ in lead), the electrostatic force can no
longer be neglected.

To summarize, most experimental results support the
assumption that the direction of electrotransport and the
sign of the Hall coefficient are interrelated. The few
exceptions that exist are probably due to a strong tempera-
ture dependence of $R_H$ or to different mobilities or scattering
cross sections for electrons and holes. In general,
electrotransport is directed towards the anode in metals
with a negative Hall coefficient (electron conductors) and
towards the cathode in metals with a positive Hall coeffi-
cient (hole conductors).
CHAPTER III

REVIEW OF PREVIOUS RESULTS ON ELECTROMIGRATION IN THIN FILMS

The primary objective in studying electromigration in thin films in recent years has been to understand the mechanism that leads to failure of these films when subjected to high current densities. It has become evident that the failure process is decisively influenced by any gradients which cause divergencies in the atomic flux. Two major types of gradients may be distinguished: local gradients resulting from structural and chemical inhomogeneities and long-range temperature gradients resulting from joule heating during the passage of current. Most investigations have attempted to establish the relative importance of these effects and to relate them to structural parameters of the films.

Due to its low electrical resistivity, good adherence to the substrate and the formation of ohmic contacts with silicon, aluminum is used almost exclusively for metallizations in integrated circuits. For this reason, most of the previous electromigration studies have been done in aluminum films and only a few investigations have been carried out in other metal films [23-27].
One of the first investigations of electrotransport in thin films was carried out by Kleinn [23], dating back to 1958. He studied the formation and the growth of holes in very thin single-crystal silver films under the influence of a direct current. The in situ observations in the electron microscope showed that the holes which formed were rectangular in shape with edges parallel to certain crystallographic directions. The density of holes was highest on the cathode side of the strip, and it was concluded that the electrotransport was directed towards the anode. However, the direction of electrotransport was reversed in films which had been exposed to chlorine and also in films which were subjected to a direct current in air instead of in vacuum. The mass transport towards the cathode in the latter films was attributed to enhanced surface migration.

It was not until around 1965 that the subject of electromigration in thin films became again of interest. In a paper published in 1967, Ghate [3] reported that aluminum strips failed predominantly on the cathode side. This was interpreted as a migration of aluminum atoms in the same direction as in the bulk [28,29], namely from the cathode to the anode. Howard and Ross [30] detected holes near the cathode and material build-up in the form of hillocks in the vicinity of the anode. They concluded from their experiments that voids in aluminum films are formed whenever the temperature is increasing in the direction of
electron flow and hillocks in the regions where the temperature is decreasing. Blech and Meieran [6] made in situ observations of aluminum strips in the electron microscope. With a cine-film technique they could show that the holes on the cathode side grew predominantly along grain boundaries and that a change in the polarity of the electric field leads to a shrinkage of the holes which continued until some holes had completely disappeared. The rate of hole formation was used by these authors to estimate a characteristic activation energy for electromigration in thin aluminum films. The activation energy of 0.7 eV compared favorably with grain boundary diffusion data in bulk aluminum [31]. Occasional division and drifting of holes indicated that surface tension effects were involved in the formation and growth of voids.

Rosenberg and Berenbaum [5] measured the change in resistance of thin aluminum films as a function of time. The resistance versus time curves displayed two distinct stages which were interpreted as gross mass transport and void growth. An activation energy of 0.5-0.6 eV was attributed to the first stage. The resistance method was refined by Hummel and Slippy [32], who measured the resistance change as a function of time in five separate segments of an aluminum strip. Only the segment close to the cathode showed an appreciable increase in resistance. No resistance decrease in the segment near the anode, where mass accumulation is expected, was observed.
In lifetime tests conducted by Black [33] and Blair et al. [34] with aluminum films of different grain sizes, the mean time to failure increased with increasing grain size. This trend was confirmed by d'Heurle and Ames [35], who were able to prolong the lifetime by a factor of $10^4$ when using single-crystal aluminum films instead of polycrystalline films.

The results reported on the effect of a dielectric overcoating on the lifetime of aluminum films are contradictory. Black [33], as well as Spitzer and Schwartz [36], found a prolonged lifetime for overcoated films, whereas Attardo and Rosenberg [37] observed no difference in lifetime between coated and uncoated films. Blair et al. [34] attributed a lifetime increase in coated films to grain growth occurring during the glass overcoating process.

Partial overcoating of aluminum films by Hummel and Breitling [38] showed that the lifetime of the strips can be prolonged by this method. Most probably this results from a diminution of the existing temperature gradient by the SiO$_2$ overlayer.

The changes that occur on the surface of a film during electromigration were observed in situ by Berenbaum and Rosenberg [25] with the scanning electron microscope. Holes which seemed to be caused by grain boundary grooving were initially formed uniformly over the whole length of the specimen. Their growth rate later was drastically reduced.
No apparent connection seemed to exist between the initial hole distribution and the location of the final failure. Hillocks and holes were often found in the same area. It was proposed that the distribution of holes and hillocks in the initial stages is determined by local gradients rather than by the macroscopic temperature gradient. Once some holes and hillocks have formed, the microscopic gradients that produce the required driving forces disappear, and the location of the failure site is then determined by macroscopic gradients.

Formation of holes and hillocks across the whole length of the test strip was also reported by Hummel and Slippy [32]. The highest density of holes, however, occurred on the cathode side of the aluminum film. In contrast to this, Rosenberg and Berenbaum [5] found the largest density of holes in the middle of the aluminum strip where the temperature was highest. They attributed the formation of holes to partial nonadhesion of the film to the substrate with following development of hot spots in these regions.

Attardo and Rosenberg [37] determined activation energies for electromigration in fine-grained (2μ) and coarse-grained (8μ) aluminum films from lifetime tests. The activation energies found were 0.51 and 0.73 eV, respectively. The difference in activation energy was attributed to different types of grain boundaries in fine- and coarse-grained films. The coarse-grained samples showed a highly
preferred <111> orientation with small angle tilt boundaries, whereas the fine-grained films were more randomly oriented and therefore possessed boundaries with greater structural disorder. It is known from grain boundary diffusion measurements [39] that the diffusivity in grain boundaries is strongly anisotropic. For a tilt boundary diffusion in a direction parallel to the tilt axis proceeds at a rate several orders of magnitude higher than in a direction perpendicular to the tilt axis. Since in the coarse-grained films with strong <111> orientation electromigration occurred mostly perpendicular to the tilt axis, the lower activation energy in coarse-grained films seemed consistent with the results of grain boundary diffusion measurements. Calculations showed that a difference of 0.1-0.2 eV in the activation energy for diffusion in adjacent grain boundaries leads to a vacancy supersaturation of greater than 0.1 (sufficient for heterogeneous nucleation of voids). The same supersaturation is achieved if the grain size changes by a factor of 5.

A reduction of electromigration rate in aluminum films by copper doping was reported by Ames et al. [40]. Alloying with approximately 4 percent copper increased the lifetime by a factor of about 70. Agarwala et al. [41] developed a statistical model to explain the observed dependency of failure time on length and width of aluminum strips. The results could be interpreted in terms of randomly distributed defects with a few microns in diameter.
Recent thin film electromigration studies in metals other than aluminum were carried out by Berenbaum and Rosenberg [25] in silver, by Hartman and Blair [26] in gold, and by Kennedy [27] in indium. In all three cases, the mass transport was observed to be, as in aluminum films, directed towards the anode. It was concluded from observations in the scanning electron microscope that electromigration in silver films [25] is, in contrast to aluminum films, governed by surface diffusion. The measurements with the electron microprobe in gold films [26] indicated that material accumulation and depletion in these films is determined by temperature gradients to a much greater extent than in aluminum films. Electrotransport in indium films [27] was measured with a radioactive tracer method. The results obtained for the transport velocity were in agreement with previous measurements in bulk samples of indium.
CHAPTER IV

EXPERIMENTAL PROCEDURE

In this chapter the procedures used in depositing the thin films and the various methods employed to study electromigration will be described. In the simplest electrotransport experiment, a film was subjected to a direct current until failure, and the location and the appearance of the failure region was examined with a light microscope. This method, however, is not suited for the detection of any changes in film structure which might have occurred prior to the breakdown. In order to detect such changes, resistance measurements in five different segments of the strip were carried out as a function of time. For most films supplementary observations in the scanning electron microscope were made. To investigate the possibility that differences in stress might exist on the cathode and anode side, stress measurements with a special x-ray pinhole camera were conducted. Finally, radioactive tracer and marker methods were used in an attempt to obtain quantitative data for the rate of electromigration.
4.1. Preparation of Thin Films

The thin films were prepared by evaporation of high purity metals from resistance heated molybdenum or tungsten boats. The ambient pressure during deposition in the ion getter pump system (Ultek Model TNB) was lower than $10^{-6}$ Torr. Deposition rates were in the neighborhood of 100 Å/sec at a distance of about 15 cm between evaporation source and substrate. In most cases glass microscope slides (1 x 25 x 32 mm) were used as substrates. The slides were cleaned by scrubbing the surface with cotton swabs in a hot solution of water and detergent. They were thoroughly rinsed in acetone, alcohol and distilled water, then dried with oil-free compressed air. A small number of films was deposited on air-cleaved rocksalt crystals or on oxidized silicon wafers. In general, the substrate was held at ambient temperature during deposition. If a larger grain size was desired, the substrate temperature could be raised with a small heater made of tungsten wire enclosed between two copper sheets. Temperatures up to 400°C could be reached in this way. The various shapes of the thin film specimens were obtained by covering the substrate with molybdenum masks, which left only those areas open where the film was to be deposited. The thickness of the films was determined after each deposition with an interferometer to an accuracy of ±100 Å. A few films were overcoated with silicon monoxide, which was evaporated from a baffled chimney tantalum source.
4.2. **Shape of Thin Film Specimens**

Two parts can be distinguished in the specimens which were used in these investigations, namely the contact areas and the actual test strip (Fig. 4.1 and Fig. 4.2). The wider areas on each end were used to provide electrical contact to the film. They had a larger cross sectional area to minimize disturbing effects of the electrical contacts on the test strip.

Specimen shape A, shown in Fig. 4.1, was employed in most experiments other than resistance measurements. The film thickness in the contact areas was the same as that in the test strip. For resistance measurements, specimens of type B (Fig. 4.2) were used. It had been found previously [42], in experiments with aluminum films, that this specimen shape was best suited to monitor the resistance changes during electromigration. As can be seen from Fig. 4.2, the electrode areas extend into the narrow portion of the specimen and the resistance can be measured in five separate segments along the length of the film. This type of sample was obtained by successive depositions of the electrode areas and the test strip. In general, the same metal, but different thicknesses, were employed for the two parts. Typical thickness values were 6,000 Å for the electrode areas and 1,500 Å for the test strip.
Fig. 4.1. Specimen shape A.

Fig. 4.2. Specimen shape B.

first evaporation
second evaporation
4.3. Resistance Measurements

The sample holder which was used for resistance measurements is shown in Fig. 4.3. The pressure contacts were independently spring-loaded and provided contact to the two electrodes and the six potential leads. To minimize temperature fluctuations the holder, together with the sample, was placed in a styrofoam box during the experiment. The direct current was supplied by a constant current power supply and was typically between 1 and 2 A. The voltage drop in the different segments of the film was measured with a potentiometer (Leeds and Northrup Model K3). During the test a temperature reading was taken with a small thermometer positioned in the middle of the glass substrate about 1 mm to one side of the strip.

4.4. Stress Measurements with X-ray Pinhole Camera

The essential parts of the pinhole camera, which was used for stress measurements, are shown in Fig. 4.4. The monochromatic x-ray beam (Cu-Kα) is diffracted by the specimen and the reflected beam is recorded on a photographic plate. Knowing the indices of the reflection planes and the camera dimensions, the lattice parameter can be determined. For a stress measurement one compares the lattice spacing in different orientations in the film. From this,
Fig. 4.3. Sample holder used for resistance measurements.
Fig. 4.4. Schematic drawing of x-ray pinhole camera used for stress measurements.
the sign and the magnitude of the stress can be calculated. Two successive exposures are therefore needed for a stress measurement. During the first exposure the incident beam strikes the specimen surface under an angle of 90° (Fig. 4.4). The diffracted beam is recorded in the first and third quarters of the photographic plate (Fig. 4.5; the second and fourth quarters are covered with a shielding plate). During the second exposure, the incident beam strikes the specimen surface under an angle of 45°. This time the diffracted beam is recorded in the second and fourth quarters. A difference in diffraction ring diameter in the two exposures indicates a different lattice spacing in the two directions and therefore the presence of stress. The magnitude of the stress is obtained by using the following equation [43]:

$$\tau = K_1 \Delta S$$

(13)

where $K_1$ is the so-called stress factor and $\Delta S$ the difference in ring radius (Fig. 4.5).

4.5. Markers

The markers used in some experiments were small graphite and chromium particles, as well as slight scratches on the film surface and small holes ($\phi \approx 100\mu$). These types were chosen because of their ease of application and
Fig. 4.5. X-ray diffraction pattern on photographic plate for stress measurement (schematic).
availability. The following techniques were employed for applying the markers to the film surface:

Graphite markers: sprinkling of fine graphite powder (\(\phi \approx 50\mu\)) on the film surface, followed by overcoating with another layer of metal film.

Chromium markers: vapor deposition of chromium through a mask with small holes onto the film surface (\(\phi \approx 300\mu\)), again followed by overcoating with another layer of metal film.

Surface scratches: moving a fine brush over the film surface.

Small holes: use of standard photoresist procedures, followed by chemical etching.

During the experiment the positions of the markers were measured periodically with a precision travelling stage attached to a light microscope. An optical mark on the substrate served as reference point. The precision of this method was estimated to be \(\pm 10\mu\).

4.6. Radioactive Tracers

Radioactive tracer experiments were carried out in gold and silver films. The tracers used were Au\(^{198}\) and Ag\(^{110m}\), respectively. Because of widely different half-lives of the two isotopes (2.7 and 270 days, respectively), different procedures were employed for introducing radioactive atoms in gold and silver films.
Gold tracer atoms were introduced by exposing a part of a thin gold film to thermal neutrons (University of Florida training reactor). To keep the radiation from the substrate at a low level, the films were deposited onto oxidized silicon wafers. For irradiation, the sample was completely embedded in cadmium sheet-metal (0.8 mm thick) which had a small opening on one side (1 x 2 mm), opposite to the central portion of the strip (Fig. 4.6). When activating the sample in the thermal column of the nuclear reactor (in general between 6 to 8 hours), the cadmium sheet-metal acted as a shield for thermal neutrons. The flux of thermal neutrons at the particular site where the sample was placed was approximately $6 \times 10^{10}$ neutrons per cm$^2$ sec. To minimize the number of fast neutrons penetrating through the cadmium shield, the whole assembly was placed in a paraffin block which served as a moderator.

For a few experiments, a modified activation procedure was employed in which the film was vapor deposited in two steps (Fig. 4.7a and b). A small segment of the strip (2 x 2 mm) was first deposited and irradiated (Fig. 4.7a). When the activity of the silicon wafer had sufficiently decayed, the remaining parts of the film were deposited in a second evaporation (Fig. 4.7b).

For tracer experiments in silver films, a thin layer of radioactive silver was electrodeposited onto a small portion of the strip. The film was masked with lacquer.
Fig. 4.6. Shielding of gold film with cadmium sheet during irradiation in the nuclear reactor (schematic).

Fig. 4.7. Activation of a small area in the middle of gold film by vapor depositing in two steps. a) Film after first evaporation during irradiation in the reactor; b) after second evaporation.
(Microstop), leaving only the small area (2 x 2 mm) in the middle of the film open, where the radioactive silver was to be deposited (Fig. 4.8). Deposition was made from a solution of HNO$_3$, AgNO$_3$ and NaCN containing radioactive silver (AgNO$_3$ in HNO$_3$ solution purchased from the Union Carbide Corporation). Typical values were 10$\mu$A for the current and 5 minutes for the deposition time. Under these conditions, the thickness of the radioactive layer was approximately 200 Å. The films were subsequently annealed at about 200°C to diffuse the radioactive material into the film.

The position of the radioactive atoms was monitored either with a scanning method (gold) or by autoradiography (silver). The equipment used in the scanning method is shown in Fig. 4.9. The essential parts are a precision mechanical travelling stage, the photomultiplier tube with the scintillation crystal, a high-voltage power supply and a counting rate meter. A stainless steel shielding plate with a small slit (0.2 mm) was placed between specimen and scintillation crystal. In this way only $\beta$-radiation from a small area of the film (approximately the size of the slit) could reach the crystal. The dimensions of the scintillation crystal were kept very small (5 x 3 x 2 mm), thus minimizing contributions from $\gamma$-radiation. Fixed optical markers on the silicon wafer served as reference points. The micrometer readings were reproducible within $\pm20\mu$. 
Fig. 4.8. Arrangement used for electroplating of radioactive silver (schematic).
Fig. 4.9. Equipment used for counting activity in scanning method.
Autoradiography uses the radiation emitted from activated atoms to obtain an image on a photographic plate. For determining the shift caused by electromigration, exposures were taken before and after current was passed through the strip. Typically, the nuclear emulsion plates (Ilford L4) were kept in contact with the thin film for about 8 hours each time.* A radioactive spot outside the strip served as a reference point. For higher precision, the blackening of the plates was measured with a microdensitometer. The accuracy of this method is limited by γ-radiation from the activated area and was estimated to be ±10μ.

*For procedures used in developing the nuclear emulsion plates, see Appendix I.
CHAPTER V

RESULTS

In the first part of this chapter the experimental results in silver films will be described. Experiments in various other films were carried out when electrotransport in silver films was found to be in the opposite direction to that previously measured in bulk specimens of the same metal. These results are described in the second part. Results of experiments with markers and radioactive tracers are described in the final sections.

5.1. Results in Silver Films

5.1.1. Direction of Electromigration in Silver Films

As mentioned in Chapter III, electromigration in thin films results in preferred hole formation in areas where the ions migrate in the direction of a positive temperature gradient. Joule heating in the film and heat conduction through the electrical contacts of the specimen holder make the temperature highest in the middle of the strip. This can be seen from the experimentally determined temperature profile shown in Fig. 5.1. Ion migration in the
Fig. 5.1. Temperature distribution in silver film.
direction of a positive temperature gradient occurs therefore in the anode half of the specimen if the electrotransport is directed towards the cathode and in the cathode half if it is directed towards the anode.

Typical resistance curves obtained for silver films are shown in Fig. 5.2. Unlike in aluminum films, where the resistance increase was greatest in segment II, i.e., on the cathode side [42], the largest increase in resistance for silver films occurred in segment IV, i.e., near the anode. Examination of the silver films in the scanning electron microscope revealed that the density of holes in the anode half of the film was larger than that in the cathode half (Figs. 5.3 and 5.4). It should be noted, however, that holes were not confined to the anode side, but could be found over the whole length of the strip, and often holes and hillocks were located side by side (Fig. 5.5). A uniform distribution of holes and hillocks across the strip indicates that their formation is caused by local gradients, whereas limitation of holes to one half and hillocks to the other half indicates that the gross temperature gradient is responsible for their growth. A distribution of holes and hillocks as observed in our specimens results if both effects are superposed.

All the silver films failed in the anode half of the strip. A typical sample with an opening near the anode is shown in Fig. 5.6. It should be mentioned here that
Fig. 5.2. Resistance change and temperature versus time in silver film. Current density \( j = 7 \times 10^5 \text{ A/cm}^2 \), film thickness 1,500 Å, thickness of electrodes 3,000 Å.
Fig. 5.3. Hillock formation on cathode side of silver film (SEM micrograph, 10,000X, \( j = 7.2 \times 10^3 \) A/cm\(^2\), after 15 hours).

Fig. 5.4. Holes on anode side of silver film (SEM micrograph, 10,000X, \( j = 7.2 \times 10^3 \) A/cm\(^2\), after 15 hours).
Fig. 5.5. Formation of holes and hillocks in the same area in silver film (SEM micrograph, 2,000X, $j = 7 \times 10^5$ A/cm$^2$, after 50 hours).
Fig. 5.6. Typical failure in silver film.
Berenbaum and Rosenberg [25] reported failure on the cathode side for silver films, although holes formed initially near the anode.

It was concluded from the observations described above that the electrotransport in silver films is directed towards the cathode. This is opposite to the direction obtained in bulk samples of silver at temperatures near the melting point [44-46]. Electrotransport towards the cathode in silver was, however, observed also by other authors under special conditions. Klotsman et al. [47] measured the electrotransport in grain boundaries of bulk silver samples and found it directed towards the cathode. Kleinn [23] noticed that in thin single-crystalline and polycrystalline silver films, failure occurred on the anode side if the films were subjected to high current densities in air or under chlorine atmosphere, whereas they failed near the cathode when the experiments were carried out in vacuum.

5.1.2. Migration of Ions on the Surface and Along Grain Boundaries

Due to the small thickness of thin films, the ratio of surface area to volume is large. In addition, because of the small grain sizes usually involved (if the substrate is held near room temperature during film deposition), the grain boundary area per unit volume is also large. Therefore, it can be expected that electromigration on the surface or in the vicinity of grain boundaries will predominate
in thin films. This is especially true when the temperatures at which the experiments are conducted are relatively low, i.e., typically about 100°C, where the low activation energies for surface and grain boundary diffusion favor migration in grain boundaries and on the surface.

It has been found experimentally that electromigration in thin aluminum films is mainly confined to grain boundaries (see Chapter III). On the other hand, Berenbaum and Rosenberg [25] inferred from their experiments that electromigration in silver films is governed by surface diffusion. This was attributed to the low activation energy for surface diffusion (about half that for grain boundary diffusion) in silver [48]. To verify the observations of Berenbaum and Rosenberg [25] the experiments described below were carried out.

**Effect of dielectric overcoating.** The importance of surface electromigration can be examined by applying a dielectric overcoating, which greatly reduces the mobility of the ions on the surface. Some of the silver films were therefore coated with a thin layer of SiO. Typical resistance curves obtained for such films are shown in Fig. 5.7. By comparing Fig. 5.7 and Fig. 5.2, it can be seen that the overcoating has only a small effect on the resistance behavior. The resistance increase in segment IV (expressed in percent of the initial resistance) in a given time is of the same magnitude in both figures. Overcoating of silver
Fig. 5.7. Resistance change and temperature versus time in silver film coated with SiO. Current density $j = 8 \times 10^5 \ A/cm^2$, film thickness 1,500 Å, thickness of electrodes 3,000 Å.
films with SiO seems to prolong the lifetime only slightly (about 30 percent).

In contrast to this, a pronounced difference in the amount of resistance increase in segments II and III for the two types of films was observed. In uncoated films, segments II and III show an increase in resistance of about 15 to 20 percent which cannot be attributed solely to the temperature rise. Examination in the scanning electron microscope revealed that in uncoated specimens considerable grain boundary grooving occurred during the experiment. This can be seen from Figs. 5.8 and 5.9, which show the surface of a film before and after current was passed through the film. The relatively large resistance increase in segments II and III in uncoated films is therefore attributed to grain boundary grooving. It follows that the effect of grain boundary grooving in coated films is greatly reduced, which was indeed observed.

**Grain size gradient.** The effect of a grain size gradient on electromigration was studied in a film where the average grain size in the central portion was different from that in the electrode areas (Figs. 5.10 and 5.11). The two parts were prepared in subsequent vapor depositions and had approximately the same thickness. The large grain size was obtained by heating the substrate to about 300°C during film deposition, whereas the small grain size was obtained by deposition at ambient temperature. It can be seen from Figs. 5.12 and 5.13 that the average grain size
Fig. 5.8. Surface of silver film after deposition on glass substrate (SEM micrograph, 10,000X).

Fig. 5.9. Grain boundary grooving in silver film after passing of current (SEM micrograph, 20,000X, $j = 4.1 \times 10^5$ A/cm$^2$, 57 hours).
Fig. 5.10. Silver film with grain size gradient; small grain size in central portion. Arrow marks location of failure site.

Fig. 5.11. Silver film with grain size gradient; large grain size in central portion. Arrow marks position of failure site.
Fig. 5.12. Silver film deposited on glass at room temperature (transmission electron micrograph).
Fig. 5.13. Silver film deposited on glass at 300°C (transmission electron micrograph).
of the film deposited on the heated substrate is appreciably larger than that of the film deposited at ambient temperature.

The site where an opening developed in the two cases is marked by arrows (Figs. 5.10 and 5.11). It can be seen from the position of the arrows that the films failed on opposite sides, depending on whether the grain size was larger in the central portion or in the electrode areas. This indicates that the breakdown of the film was indeed caused by the grain size gradient and not by the gross temperature gradient. Since the number of grain boundaries differs in regions of different grain size, a divergence will occur at the interface. More material is transported per unit time in the region with the small grain size than in the region with the large grain size. Failure will occur at that interface where the ions migrate from an area with large grains into an area with small grains. Based on these arguments, the location of the failure site in Figs. 5.10 and 5.11 is consistent with the earlier finding that electrotransport in silver films is directed towards the cathode.

Electromigration in silver films with large grain size.

It had been found previously [37] that the activation energy for electromigration in aluminum films is a function of grain size. The increase in activation energy with increasing grain size was considered to be due to a difference in grain boundary structure in films of different grain size.
Grain boundaries in large-grained films were less disordered because of a higher degree of preferred orientation in these films. In order to examine the influence of grain size on electromigration in silver films, the resistance behavior of films with large grain size was studied and compared with that measured in films with smaller grain size.

Large-grained films were obtained as described earlier in this chapter by depositing films on a heated glass substrate. A typical example for the resistance increase obtained in these films is shown in Fig. 5.14. A comparison with the resistance curves measured in a fine-grained film (Fig. 5.2) reveals that in both types of films the largest resistance increase occurs in segment IV, i.e., near the anode. In both cases the opening which led to the breakdown of the film developed in this segment. This means that the direction of electromigration is the same in small- and large-grained silver films.* The kinetics of resistance change are, however, slightly different in the two films. It can be seen from Fig. 5.2 that in small-grained films during the whole experiment the resistance increase in segment IV is larger than that in segment III. In contrast, in large-grained films segment III shows initially the largest resistance change and only in the final

*The degree of preferred orientation was different in large- and small-grained films. For details see Appendix II.
Fig. 5.14. Resistance change versus time in silver film deposited at 300°C on glass. Current density $j = 6.3 \times 10^5$ A/cm$^2$, film thickness 1,400 Å, thickness of electrodes 6,000 Å.
stages of the experiment is surpassed by the resistance change in segment IV (Fig. 5.14).

The different resistance behavior in small- and large-grained films can be qualitatively explained by taking into account the smaller electromigration rate in large-grained films. It is assumed that the resistance increase in segment III is mainly due to grain boundary grooving. Two effects can therefore cause a resistance increase: grain boundary grooving and hole formation. It will depend on their relative rate which process predominates. The resistance curves indicate that in small-grained films the resistance increase due to hole formation (segment IV) dominates over the resistance increase due to grain boundary grooving (segment III), while in large-grained films it is just opposite.

When silver was deposited on air-cleaved rocksalt crystals at ambient temperature, the average grain size was of the same magnitude as in films deposited on glass at 300°C (see Fig. 5.15). Resistance measurements gave similar results as obtained in large-grained films deposited on glass at 300°C (see Fig. 5.16).

The results reported in this section show that electromigration in silver films is mainly—as in aluminum films—a grain boundary diffusion process. Although extensive grain boundary grooving occurs, ion migration on the surface does not seem to be of importance for the rate of electrotransport and hole formation.
Fig. 5.15. Silver film deposited on air-cleaved rocksalt at room temperature (transmission electron micrograph).
Fig. 5.16. Resistance change and temperature versus time in silver film deposited at ambient temperature on air-cleaved rocksalt crystal. Current density $j = 7 \times 10^5$ A/cm$^2$, film thickness 1,350 Å, thickness of electrodes 6,000 Å.
5.1.3. **Single-crystal Silver Films**

If electrotransport in silver films is mainly confined to the grain boundaries, as the results reported in the foregoing sections suggest, then the amount of electrotransport in single-crystal films should be negligibly small. Some resistance measurements were therefore carried out in silver films which had been deposited on air-cleaved rocksalt crystals at 200°C. Examination in the electron microscope showed that under these conditions the films were single-crystalline with the \{111\} plane parallel to the surface of the substrate (Fig. 5.17). Typical resistance curves obtained for such films are plotted in Fig. 5.18. The largest resistance increase and failure occurred in segment III, i.e., in the middle of the strip, where the temperature was highest. Failure in this segment indicates that the amount of electrotransport is indeed small and that processes other than electromigration lead to an opening in the film. The breaking of the film in the middle is most probably the result of nonadhesion due to the high temperature, as reported in [5].

This type of failure makes a determination of the direction of electrotransport from resistance measurements very difficult. The resistance increase in segment II, i.e., near the cathode, is slightly larger than that in segment IV, i.e., near the anode, which suggests that the direction of electrotransport in single-crystal silver films
Fig. 5.17. Electron diffraction pattern of single-crystal silver film deposited on air-cleaved rocksalt at 200°C.
Fig. 5.18. Resistance change and temperature versus time in single-crystal silver film deposited on air-cleaved rocksalt at 200°C. Current density $j = 8 \times 10^5$ A/cm$^2$, film thickness 1,350 Å, thickness of electrodes 6,000 Å.
is towards the anode. However, the difference is too small to be considered as conclusive.

5.1.4. Stresses on Cathode and Anode Sides of Silver Film

Several authors have reported the appearance of hillocks when thin films are heated on substrates of lower thermal expansion coefficient [49-52]. It was assumed that this phenomenon is caused by compressive stress in the films and is associated with a stress-relief process. These observations suggest that the growth of hillocks during electromigration in thin films will be accompanied by compressive stress, while the formation of holes will occur under tensile stress.

To test this hypothesis for silver films, the stress on the cathode and anode side of a strip was measured with a special x-ray camera (see Fig. 4.4). Although the measurements revealed the presence of considerable stress in the film, no difference in the amount of stress between cathode and anode side could be detected. On both sides the stress was compressive and of the order of $1 \times 10^3$ psi (see Figs. 5.19 and 5.20). For some films, stress measurements were taken in situ while a direct current was passed through the specimen. Here, too, the two halves showed the same amount of compressive stress.

These results cannot exclude the possibility that hole and hillock formation are associated with stress differences.
Fig. 5.19. X-ray diffraction pattern from anode side of silver film ($j = 3.3 \times 10^5 \text{ A/cm}^2$, after 100 hours).

Fig. 5.20. X-ray diffraction pattern from cathode side of silver film ($j = 3.3 \times 10^5 \text{ A/cm}^2$, after 100 hours).
The uncertainty stems from the fact that the x-ray beam covered about one-third of the strip length, and local stress gradients could have been averaged out. The measurements show, however, that the difference in average stress between the anode and cathode half of the strip is very small and cannot be detected with the applied method. This finding seems consistent with the observation that holes and hillocks often form in the same area.

5.2. Resistance Measurements and Observations with the Scanning Electron Microscope in Films of Gold, Copper, Magnesium, Indium, Tin and Lead

In the experiments with gold, copper, magnesium, indium, tin and lead films, the main objective was to determine the direction of electrotransport. As in the investigations on silver films, resistance measurements supplemented by observations in the scanning electron microscope were used for this purpose. It was concluded that the electrotransport was directed towards the cathode if the resistance increased most on the anode side of the strip (segment IV), and towards the anode if the largest increase in resistance was measured near the cathode (segment II).

Typical resistance curves for films of the above-mentioned metals are shown in Figs. 5.21 through 5.26. As can be seen from the figures, there are two distinct types of resistance behavior. In gold, copper (and silver) films,
Fig. 5.21. Resistance change and temperature versus time in gold film. Current density $j = 7 \times 10^5$ A/cm$^2$, film thickness 1,300 Å, thickness of electrodes 5,000 Å.
Fig. 5.22. Resistance change and temperature versus time in copper film coated with SiO. Current density \( j = 5.1\times 10^5 \text{ A/cm}^2 \), film thickness 2,450 Å, thickness of electrodes 5,500 Å.
Fig. 5.23. Resistance change and temperature versus time in magnesium film. Current density $j = 4.2 \times 10^5$ A/cm$^2$, film thickness 1,300 Å, thickness of electrodes 8,000 Å.
Fig. 5.24. Resistance change and temperature versus time in indium film. Current density $j = 1 \times 10^5 \text{ A/cm}^2$; film thickness 6,000 Å, thickness of electrodes 10,000 Å.
Fig. 5.25. Resistance change and temperature versus time in tin film. Current density $j = 1.2 \times 10^5$ $\text{A/cm}^2$. Film thickness 4,200 Å, thickness of electrodes 9,000 Å.
Fig. 5.25. Resistance change and temperature versus time in lead film. Current density $j = 1.4 \times 10^5$ A/cm$^2$, film thickness 1,700 Å, thickness of electrodes 13,200 Å.
the resistance increases most in segment IV, i.e., in the anode half of the strip. This means, as already pointed out, that the electrotransport in these films is directed towards the cathode. On the other hand, in magnesium, indium, tin and lead films, the increase in resistance is largest in segment II, i.e., in the cathode half of the strip. Electromigration in these films is therefore directed towards the anode.

Figures 5.27 through 5.36 show typical SEM micrographs of hillocks and holes in various films. It should be noted that the shape as well as the distribution of holes and hillocks varies for different films. In the gold and copper films, the areas of hole and hillock formation are rather extended, whereas in the tin films, the holes, i.e., growths, are largely restricted to the immediate neighborhood of the interface between test strip and electrode areas. The elongated shape of the holes on the anode side of the copper film seems to be produced by the SiO overcoating, which was applied to all copper films in order to prevent oxidation. A similar hole shape was observed in silver films when coated with SiO. An interesting feature of the holes in the copper film is the obvious asymmetry in hole shape with the thicker portion always located on the positive side.

In all films, the segment in which the resistance increase was largest also had the highest density of holes, whereas hillocks were concentrated on the opposite side.
Fig. 5.27. Whisker type growths on cathode side of gold film (SEM micrograph, 5,000X, $j = 5 \times 10^5$ A/cm$^2$, after 115 hours).

Fig. 5.28. Holes and hillocks on anode side of gold film (SEM micrograph, 5,000X, $j = 5 \times 10^5$ A/cm$^2$, after 115 hours).
Fig. 5.29. Whisker type growths on cathode side of gold film (SEM micrograph, 5,000X, \( j = 5 \times 10^5 \text{ A/cm}^2 \), after 115 hours).
Fig. 5.30. Cathode side of SiO coated copper film; no hillocks are formed because of coating (SEM micrograph, 1,000X, $j = 5.1 \times 10^5$ A/cm$^2$, after 150 hours).

Fig. 5.31. Elongated holes on anode side of SiO coated copper film (SEM micrograph, 1,000X, $j = 5.1 \times 10^5$ A/cm$^2$, after 150 hours). Direction of electric field from left to right.
Fig. 5.32. Holes on cathode side of tin film (SEM micrograph, 2,000X, \( j = 1.2 \times 10^5 \, \text{A/cm}^2 \), after 36 hours).

Fig. 5.33. Growths on anode side of tin film (SEM micrograph, 1,000X, \( j = 1.2 \times 10^5 \, \text{A/cm}^2 \), after 36 hours).
Fig. 5.34. Growth on anode side of tin film (SEM micrograph, 5,000X, \( j = 1.2 \times 10^5 \) A/cm\(^2\), after 36 hours).
Fig. 5.35. Growth in indium film after passing of current (SEM micrograph, 1,000X).

Fig. 5.36. Growth in indium film (SEM micrograph, 10,000X).
This indicates that void formation is indeed the process mainly responsible for the observed resistance increase.

5.3. Marker Experiments

The study of marker motion in thin films is of interest for two reasons. First, it allows one to determine quantitatively the rate of mass transport caused by the applied direct current. Second, it leads to a better understanding of the process of hole migration, which plays an important role in the electromigration-induced failure of thin films. Marker experiments were carried out in aluminum, indium and silver films. The types of markers used and the procedures employed for introducing the markers into the films are described in section 4.5:

No conclusive results about direction and magnitude of marker motion in thin films could be obtained from the measurements. The displacement of the markers measured with respect to a reference point on the substrate was always less than the estimated error of measurement (±10μ). In addition, no size or shape changes of the chemically etched holes were seen to occur when the films were subjected to a direct current over an extended period of time.

The expected marker shift was estimated by using an equation derived by Ho [53] for the migration of an inert marker in an electrical gradient. He obtained for this
special case

\[ V_M = - \frac{3D_S v \dot{\Omega}}{kT a} e^E Z_{S^*} \]  

where \( V_M \) = velocity of marker motion
\( D_S \) = diffusion coefficient for surface diffusion
\( v \) = effective number of atoms per unit surface area participating in diffusion
\( \dot{\Omega} \) = atom volume
\( a \) = radius of marker
\( Z_{S^*} \) = effective charge number for surface electromigration.

The other symbols have their usual meanings.

The following values were used for estimating the marker velocity in silver:
\( D_S = 10^7 \) cm\(^2\)/sec
\( \dot{\Omega} = 1.3 \times 10^{-23} \) cm\(^3\)/atom
\( v = \frac{\dot{\Omega}}{2/3} = 2 \times 10^{15} \) atoms/cm\(^2\)
\( T = 400^\circ \)K
\( a = 50\mu \)
\( E = 2V/cm \)
\( Z_{S^*} = 10 \)

The value for \( V_M \) obtained with these data was \( 10^9 \) cm/sec, which leads to a marker shift of about 0.3\( \mu \) in 100 hours.

Considering the fact that \( Z_{S^*} \) is not known and that the values for the surface diffusion coefficient measured by different authors differ by several orders of magnitude [48], this calculation represents only a very rough
estimate. It shows, however, that the magnitude of the expected marker shift is very small, which would explain why no marker shift could be detected in the experiments.

5.4. Radioactive Tracer Experiments

Radioactive tracers can be used to determine the direction and the rate of mass transport under the influence of a direct current. Due to the rather small thickness of thin films, not all the experimental methods usually applied in bulk samples can be employed in thin films. In particular, the sectioning method, which is widely used for diffusion and electrotransport measurements in bulk samples, is not applicable in the case of thin films. The small amount of radioactive material in thin films also reduces the accuracy obtained in tracer experiments and makes it difficult to find detection methods which are sufficiently sensitive.

As described in section 4.6, radioactive gold tracers were introduced by activating a small portion of a gold strip in a nuclear reactor. Figure 5.37 shows the radioactive profile, measured with the scanning method before and after a direct current (current density \( j = 5 \times 10^5 \) A/cm\(^2\)) was passed for 20 hours through the film. The counting time was 20 minutes for each point, and the counts were later corrected for radioactive decay. The standard
Fig. 5.37. Location of radioactive zone in a gold film before (A) and after (B) the strip was subjected for 20 hours to a direct current of $7 \times 10^5$ A/cm$^2$. The probability that the actual value falls within the statistical "standard error" limit is 68 percent. Curve B is lower due to radioactive decay.
deviation ($\pm \sqrt{n}$, where $n$ is total number of counts) is indicated for each point. A comparison of the two curves suggests that curve B is shifted slightly to the left with respect to curve A, which would mean that the radioactive gold atoms have migrated towards the cathode under the influence of the direct current. This is in agreement with conclusions reached from resistance measurements and observations with the scanning electron microscope in gold films. Because of the relatively large errors involved in these measurements and because of lack of more experimental data, the curves were, however, not used to determine any quantitative values.

Due to the relatively long half-life of silver, activation of this metal in the nuclear reactor would require too much time. A radioactive area in silver films was therefore obtained by electroplating on a small portion of a silver strip as described in section 4.6. The shape and the location of the active zone was determined by autoradiography (Figs. 5.38 and 5.39). The two exposures were taken before and after passing direct current for three days (current density $j = 8 \times 10^5$ A/cm$^2$). A radioactive zone, which was not connected with the strip (left part of the photographs), served as reference when measuring the shift. An evaluation of the autoradiography was carried out with a microdensitometer and revealed that the shift of the active zone was less than the experimental error limit of $\pm 10\mu$. 
Fig. 5.38. Location of radioactive zone in silver film before passing of direct current.

Fig. 5.39. Location of radioactive zone in silver film after passing of direct current for 72 hours ($j = 8 \times 10^5 \text{ A/cm}^2$). Radioactive zone in left part of photograph serves as reference. Electric field is directed from top to bottom.
An estimation for the migration rate was made by using the following values:

\[
D_b = 2.5 \times 10^{-13} \text{ cm}^2/\text{sec} \\
T = 400^\circ \text{K} \\
E = 2 \text{ V/cm} \\
|Z^*| = 10
\]

From this, the drift velocity \( v_A \) was estimated to be \( \pm 0.2 \mu/\text{day} \). Unless important improvements in the accuracy of the applied method can be made, it is not possible to monitor such a small shift.
CHAPTER VI

DISCUSSION

The following discussion is based predominantly on the results of resistance measurements and observations with the scanning electron microscope. The results are primarily of qualitative nature.

The most important information which can be obtained from resistance measurements of the type used here is the direction of electrotransport. For the interpretation of the resistance measurements, however, it has to be assumed that

1) an increase in resistance is largely due to a reduction of the cross sectional area by the formation of holes, and that

2) the majority of the holes always form in that portion of the strip where the ions migrate in the direction of a positive temperature gradient.

The validity of these assumptions was established by comparing resistance data with scanning electron micrographs. The largest density of holes was always observed in that segment of the strip in which the resistance increased most. In different films of the same metal the majority of the holes always formed in the same region, indicating that
in this area the ions were migrating in the direction of a positive temperature gradient.

The direction of electromigration in various thin films and bulk metals is given in Table 6.1. The data for the latter are taken from the literature [2], and were obtained in measurements at temperatures near the melting point. It can be seen from the table that silver, gold and copper have different directions of electrotransport in thin films and in the bulk.

Electromigration studies on various metallic films have been carried out before [24-26]. A difference in direction of electrotransport between thin films and bulk has not been observed, however, in those studies. No satisfactory explanation for this can be given at the moment. It seems, however, that the narrow strips, used by other investigators, are not too well suited to determine the direction of electrotransport. Samples with very small dimensions were used by these investigators to match as closely as possible the actual conditions under which failure occurs in integrated circuits. Failures in such strips are very likely the result of structural inhomogeneities, in which case the failure sites are randomly distributed over the length of the strip. This is confirmed by a comparison of previous results in narrow and wide aluminum strips. In narrow strips, failures occur on the cathode as well as on the anode side [37], whereas in wider strips, failures occur exclusively on the cathode side [32]. It should also be
Table 6.1

Direction of Electrotransport in Thin Films and Bulk Specimens

<table>
<thead>
<tr>
<th>Metal</th>
<th>Electrode towards which electrotransport is directed in thin films</th>
<th>Electrode towards which electrotransport is directed in bulk specimens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>cathode</td>
<td>anode</td>
</tr>
<tr>
<td>Gold</td>
<td>cathode</td>
<td>anode</td>
</tr>
<tr>
<td>Copper</td>
<td>cathode</td>
<td>anode</td>
</tr>
<tr>
<td>Aluminum</td>
<td>anode</td>
<td>anode</td>
</tr>
<tr>
<td>Magnesium</td>
<td>anode</td>
<td>anode</td>
</tr>
<tr>
<td>Tin</td>
<td>anode</td>
<td>anode</td>
</tr>
<tr>
<td>Lead</td>
<td>anode</td>
<td>anode</td>
</tr>
<tr>
<td>Indium</td>
<td>anode</td>
<td>anode</td>
</tr>
</tbody>
</table>
noted that the current densities used by other investigators [24-26] were in most cases about ten times larger than those usually employed in our experiments and that instead of glass, silicon wafers were used as substrate.

As mentioned already in Chapter III, Kleinn [23] assumed that the electromigration towards the cathode, which was observed in some silver films, was due to enhanced surface migration of silver ions under the influence of oxygen. The importance of surface diffusion for electrotransport in silver films was also emphasized by Berenbaum and Rosenberg [25]. The experimental results obtained in this research indicate, however, that ion migration on the surface plays only a minor role. If in our experiments mass transport to a large extent had occurred on the surface, overcoating should have prolonged the lifetime of silver films substantially. This has not been observed. Additional evidence that electromigration in grain boundaries predominates was obtained from experiments involving large-grained and single-crystalline films. The results of these measurements clearly indicate that the electrotransport in silver films is reduced by an increase in grain size. Mass transport in silver films under the influence of an electric field is therefore under the conditions used here, like in aluminum films, mainly confined to grain boundaries.

Since the activation energy for surface self-diffusion in silver is about half that for grain boundary self-diffusion [48], one would expect that surface diffusion predomi-
nates over grain boundary diffusion. An estimation shows also that in thin films the number of atoms on the surface is of the same order of magnitude as the number of atoms in grain boundaries (assuming that grain size and film thickness are equal). The predominance of grain boundary diffusion found in the present measurements is presumably due to a thin sulfide layer on the film surface [54]. It would be of interest to carry out similar experiments in high vacuum to prevent formation of the sulfide layer and compare the results with those obtained in experiments conducted in air.

The different direction of electrotransport in thin film and bulk specimens of silver, gold and copper is most likely caused by the fact that in bulk samples mass transport takes place predominantly in the regular lattice, whereas in thin films it occurs mainly in the grain boundaries. Measurements of electrotransport in grain boundaries of bulk samples were made by Klotsman et al. [47]. In their experiments, radioactive silver was plated on the end faces of two polycrystalline specimens having a grain size of 0.1 to 1 mm. The specimens were then put together with the active faces towards each other and subjected to a current density of about $10^4$ A/cm$^2$ at temperatures between 400 and 550°C. After the experiment the specimens were separated and layerwise analyzed by determining the activity as a function of the distance from the interface on anode and cathode sides. The effective valence $Z^*$ was
calculated from the difference in the slope of concentration versus distance curve in the two halves [55]. Under these conditions, electrotransport of silver in silver, copper and gold was found to be directed towards the cathode. The value for the effective valence $Z^*$ was about ten times larger than that measured in volume electromigration.

It was concluded by these authors that electromigration towards the cathode in grain boundaries is due to a different electron spectrum in the boundaries as compared to that in the regular lattice. The ion transport towards the cathode was attributed to the drag force exerted by the electronic holes, which predominate in the boundaries. The large value for the effective valence $Z^*$ was attributed to the energetically favored "correlated" migration of ions in grain boundaries of materials with low stacking fault energies [56].

The different surrounding of an ion in the grain boundary as compared to that in the regular lattice (number of neighbors and symmetry) is expected to have an effect on the Fermi surface. This has been experimentally demonstrated by measurements of the Hall coefficient in grain boundaries of semiconductors [57-59], where the type of conductivity in the boundaries can be opposite to that in the bulk. In metals, the Hall coefficient of grain boundaries cannot be determined directly and one has to rely on indirect evidence and theoretical calculations.
In the free electron approximation, a metal consists of positive ions, which are embedded in a uniform distribution of quasifree electrons. Grain boundaries can be represented as regions with an ion density low compared to that of the regular lattice. This fact leads to a surplus of negative charge in the grain boundary, which is screened by a rearrangement of the electrons, similar to the screening of an impurity in a metal [60]. The rearrangement of the electrons causes an increase in the electron gas energy and is the main contribution to the energy of a grain boundary [61]. The values for the grain boundary energy calculated on the basis of this model give good agreement with experimental measurements if the surplus negative charge of the boundary is assumed to be 0.6-0.7 electrons per unit cell of grain boundary [61]. Since in f.c.c. metals the unit cell has four atoms, the electron concentration in grain boundaries is, according to these calculations, increased by about 0.15 electrons per atom.

The s-valence bands in silver, gold and copper are approximately half filled. With the electron concentration increased in the grain boundaries, it is likely that the bands become further filled. Because the electrons in the upper part of an energy band behave like electron holes, this could cause a change in the type of conductivity. This trend is exemplified by cadmium and zinc, which have one valence electron more than silver and copper, respectively, and both of which are hole conductors.
It was mentioned in Chapter II that, as a rule, electrotransport has a different sign depending on the sign of the predominant charge carriers. When electron conduction predominates, the ion migration is directed towards the anode, whereas it is directed towards the cathode in hole conduction. This suggests that, because the electrotransport in thin films of silver, gold and copper is directed towards the cathode, hole conduction predominates in the grain boundaries of these metals.

To examine quantitatively the effect of additional electrons on the Hall coefficient in noble metals, one has, in principle, to study the change in shape of the Fermi surface caused by a raise in Fermi energy level. Some parts of the Fermi surface correspond to hole orbits, whereas other parts represent electron orbits [62]. The relative area of both depends on the position of the Fermi level and determines the sign of the Hall coefficient. Since one has to average over orbits in different directions in the reciprocal space, this method is, however, too complicated to be useful for any quantitative calculations.

In a more simple way, the influence of an increase in electron concentration on the Hall coefficient can be seen from Hall coefficient measurements in dilute copper and silver-based alloys, where the electron concentration per atom changes as a function of composition. Such measurements were made by Köster and Rave [63] and show that the Hall coefficient becomes less negative with increasing
electron concentration. However, when adding 0.15 electrons per atom, the Hall coefficient is still negative and extrapolation of the data suggests that more than 0.5 electrons have to be added before the sign of the Hall coefficient might change. This seems to indicate that the electron concentration in the grain boundaries might not be high enough to cause a change in the type of conduction.

It should be remembered, however, that the values for the electron concentration in the grain boundaries used above represent only estimations. It was also tacitly assumed that the electron theory of metals can be extended to the disordered and nonperiodic structure of grain boundaries and that the band structure in grain boundaries is similar to that of the regular lattice. The error introduced by this assumption could be considerable. In addition, the Hall coefficient in alloys is not only a function of the average electron/atom ratio, but is also influenced by the change in lattice spacing and the disturbance of the periodicity of the lattice.

The migration of solute atoms in alloys is treated in the theory of electrotransport by Bosvieux and Friedel [10]. It is shown that the force on a solute atom depends on the difference in valence between solute and solvent. This theory can be used to estimate independently the effect of the surplus negative charge in the grain boundary on the electromigration behavior of ions in the grain boundary.
In such an approach, ions in the regular lattice represent solvent atoms and ions in the grain boundary take the role of solute atoms. Due to the surplus negative charge in the grain boundary area, ions in grain boundaries correspond to solute atoms with a valence slightly less than that of ions in the regular lattice. It can be expected that the forces on ions in the grain boundary and on ions in the regular lattice differ by a certain amount $\Delta F$. Bosvieux and Friedel [10] give the following expression for $\Delta F$:

$$\Delta F = F' - F = -ZEe \frac{\lambda}{\rho_o} (Z' - Z)$$

(15)

where $F'$ is the force on a solute atom (atom in the grain boundary)

$F$ is the force on a solvent atom (atom in the regular lattice)

$Z'$ is the valence of the solute

$Z$ is the valence of the solvent

$\lambda$ is a constant

and the other symbols have their usual meanings.

In the case of ions in grain boundaries, $Z' < Z$ and $\Delta F$ is positive, i.e., parallel to the electrical field $E$. Since the electrical field is directed towards the cathode, $\Delta F$ is therefore opposite to $F$ (directed towards the anode in noble metals) and leads to a smaller force $F'$ for ions in grain boundaries. There is a possibility that $\Delta F$ might become larger than $F$, in case of which the mass transport reverses its direction. This approach leads thus to the
same qualitative result as the concept of a change in the type of conductivity by Klotsman et al. [55].

The question whether in a certain metal the direction of electrotransport in grain boundaries is different from that in the regular lattice (Table 6.1) will depend on the value of the effective charge $Z^*$ in the bulk. If $Z^*$ is large, it is unlikely that the increase in electron concentration in the boundaries will change the direction of electrotransport. Although values for $Z^*$ have been determined for all the metals listed in Table 6.1, these values are not valid for low temperatures, at which the thin film experiments are conducted. In general, $Z^*$ shows a strong temperature dependence (see [11]) and increases with decreasing temperature. Measurements show, however, that in Cu [64], Ag and Au [11], $Z^*$ is almost temperature independent, whereas for example in Al [28], Pb [65] and Sn [66], the effective valence increases strongly with decreasing temperature, suggesting very high values for $Z^*$ at lower temperatures. This is in agreement with the observation in Table 6.1 that a reversal in the direction of electromigration occurs only for silver, gold and copper films.

The concept of an increased electron concentration in grain boundaries can be used to examine the conditions under which the electrotransport rate might eventually become zero. Let us take the example of silver. Electrotransport towards the cathode in silver films seems to be
due to the predominance of hole conduction in grain boundaries. Alloying with an element of lower electron concentration (palladium) should increase the part of electron conduction and change the type of conductivity. At a certain composition, the drag force of the electron holes should be just equal to the drag force of the electrons and the rate of electrotransport should become zero.

The problem of understanding the exact nature of electromigration-induced void formation and failure in thin films remains mainly unresolved. It appears that the processes in question are more complicated than previously anticipated. The location of hillocks and holes in the same area indicates that their formation is caused by local gradients. The above reported stress measurements, which showed that no stress difference exists between anode and cathode side of the strip, support this concept. On the other hand, the fact that openings in films of a certain metal always occurred in the same half of the strip, shows that the gross temperature gradient determines the location of the failure site. It is not clear in exactly which way local and temperature gradients interact in the formation of holes and hillocks. Examining the shape of holes and hillocks, it appears that stresses and probably plastic deformation are involved in their formation. A good example is the hillocks at the interface on the anode side in tin films (see Figs. 5.33 and 5.34). The form of hillocks varies from metal to metal and makes it questionable whether
their growth in different metals is caused by the same mechanism.

Finally, the experiments with markers and radioactive tracers have shown the difficulties encountered in quantitative measurements of electromigration in thin films. It appears that, unless important improvements in the measuring accuracy can be made, the drift velocity is too small to be determined by the methods applied. Increasing the drift velocity by using higher temperatures and current densities will not help too much, since the films will fail earlier in this case. The ionic shift attainable in thin films is limited by failure of the films, which occurs sooner or later.
CHAPTER VII

CONCLUSIONS

The results presented in the preceding chapters lead to the following conclusions:

1. The types of resistance measurements used in this research, when supplemented by other methods, are suitable to study electromigration in thin films.

2. The transport of ions under the influence of an electric field is directed towards the cathode in films of silver, copper and gold, and towards the anode in magnesium, indium, tin and lead films.

3. The electrotransport in silver, copper and gold films is opposite to the direction of mass transport usually found in bulk samples of these metals. This is attributed to the fact that in thin films mass transport occurs predominantly in grain boundaries.

4. The interaction between electrons and ions in grain boundaries is not the same as in the regular lattice and is explained with a different electron concentration in grain boundaries. An increase in electron concentration can lead to a force, which is directed towards the cathode. This is especially true in the case of silver, copper and gold.
5. The displacement of radioactive tracers and inert markers under the influence of a direct current is very small and therefore difficult to measure quantitatively with the methods employed.

6. The results obtained here can be used to examine the conditions under which the rate of electromigration should become zero.
APPENDIX I

DEVELOPMENT OF NUCLEAR EMULSION PLATES

The following procedure was used for developing the nuclear emulsion plates:

1) Soak in water for 10 minutes.
2) Develop in 1:3 D-19 for 30 minutes at 0°C.
3) Stop for 10 minutes in 3 percent acetic acid solution.
4) Fix for 1.5 hours in standard x-ray fixing solution.
5) Wash 90 minutes in flowing water.
6) Rinse with methyl alcohol.
7) Dry in desiccator.
APPENDIX II

PREFERRED ORIENTATION OF SILVER FILMS

The preferred orientation of silver films deposited on glass at ambient temperature and at 300°C was determined by using an x-ray diffractometer. The area of a hkl diffraction line is an approximate measure of the volume of material in the \{hkl\} orientation. Table A2.1 below gives the relative line areas for the two types of silver films and lists also for comparison the relative intensities for a powder specimen (random orientation).
Table A2.1

Relative Line Areas in Percent of the 111 Line for Silver Films Deposited on Glass at Ambient Temperature and at 300°C-

<table>
<thead>
<tr>
<th>Line (hkl)</th>
<th>Silver film deposited at ambient temperature</th>
<th>Silver film deposited at 300°C</th>
<th>Powder specimen (random orientation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>200</td>
<td>6</td>
<td>1.5</td>
<td>40</td>
</tr>
<tr>
<td>220</td>
<td>0.2</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>311</td>
<td>0.8</td>
<td>0.2</td>
<td>26</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY


60. J. Friedel, Phil. Mag., 43, 153 (1952).
BIOGRAPHICAL SKETCH

Hans Martin Breitling was born March 13, 1941, in Rotfelden, West Germany. He attended public High School in Nagold, West Germany, where he was graduated in 1960. From 1960 to 1967, the author studied at the University of Stuttgart, majoring in physics. He was graduated with the degree of Diplomphysiker in May, 1967. Mr. Breitling entered Graduate School at the University of Florida in September, 1967, and has pursued the degree of Doctor of Philosophy in Metallurgical and Materials Engineering since that date.

The author is a member of the Society of Irreproducible Results.
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Rolf E. Hummel, Chairman
Associate Professor of Metallurgical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Derek B. Dove, Associate Professor of Metallurgical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Albert C. Guy, Professor of Metallurgical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

John Kronsbein, Professor of Physics
This dissertation was submitted to the Dean of the College of Engineering and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June, 1971

[Signature]
Dean, College of Engineering

[Signature]
Dean, Graduate School