

**ELECTRON TRANSPORT PROPERTIES OF
COPPER AND DILUTE Cu - ALLOY FILMS**

by

RITU SURI

*Thesis Submitted to the
Indian Institute of Technology, Delhi
for the Award of the Degree of
DOCTOR OF PHILOSOPHY*

**DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
APRIL, 1976.**

ACKNOWLEDGMENTS

It has been a privilege to be associated with Professor K.L. Chopra in this scientific endeavour. I am indebted to him for his valuable guidance at all stages of the work. In his inimitable way, he has inculcated in me a sense of devotion and discipline.

It has been of immense benefit to me to have had the close cooperation of all my colleagues in the Thin Film Group who generously lent their time and labour.

Thanks are due to V.N. Sharma who took great pains for the typing of the manuscript.

April, 1976

Ritu Suri

(RITU SURI)

Indian Institute of Technology, Delhi
New Delhi, India

ABSTRACT

The thickness dependence at 300 and 80 K of the electrical resistivity (ρ) and its temperature coefficient (α), Hall coefficient (R_H), mobility (μ) and thermoelectric power (TEP) of as-deposited and annealed 100-3000 Å thick evaporated polycrystalline copper films and films deposited at elevated temperatures have been studied. All transport properties, with the notable exception of TEP, in carefully prepared and well-characterised films exhibit monotonically increasing size effects with decreasing film thickness. Both annealing and deposition at elevated temperatures cause considerable reduction of the "apparent" size effects in all the transport properties of the room-temperature deposited films. A critical analysis of the observed size effects shows that the data in all cases depart markedly from the predictions of the Fuchs-Sondheimer theory (and also that of the Mayadas-Shatzkes theory which takes into account the grain boundary surface scattering). The departure from theory is different for each transport property. The annealing studies show that the enhanced size effects are due to the presence of a large concentration of structural defects in the films. The thermopower data suggest that the large concentration of defects causes distortion of the Fermi surface and thereby a strong energy dependence of the mfp or relaxation time at the Fermi surface.

Kinetics of annealing of the transport properties ρ , R_H , μ and TEP of thin (160-3000 Å) copper films deposited at temperatures ranging from 80 to 600 K have been studied. The activation energy for the associated recovery process has been obtained from the observed isothermal and isochronal changes in the resistance of the films. This energy increases from a value of 0.7 eV at 2000 Å to 1.4 eV at 180 Å for Cu films deposited at 300 K. Changes in ρ , R_H and μ on annealing are found to decrease with film thickness and deposition

and annealing temperatures. On the other hand, changes in TEP due to annealing increase with film thickness up to 3000 Å; the rate of change depends sensitively on deposition temperature. Annealing does not affect the temperature dependence of R_H and TEP. These results together with the information on the microstructure (particularly the grain size) of films and the known scattering behaviour of various types of structural defects in bulk Cu lead us to conclude that the reduction in ρ , R_H and μ on annealing is due to annihilation of point defects, primarily vacancies. The dislocations do not affect these properties significantly. However, the corresponding changes in TEP are due to the decrease in the concentration of vacancies as well as the density of dislocations. Quantitative effects of vacancies and dislocations on R_H and TEP have been deduced from the observed data. The enormously large contributions of these defects may be understood qualitatively in terms of the variations in the density of hole-like states and/or the energy dependence of conductivity at the Fermi surface, caused by changes in the extent and/or degree of curvature of the necks at the Fermi surface.

In order to understand the role of impurities in Cu films, the resistivity, R_H , α , μ and TEP of Cu-based alloy films containing 1, 2 and 5 at.% of Al, Ge and Sn, in the temperature range 80 to 600 K, have been investigated. Electronmicroscopy and electron diffraction studies have been carried out to study the structural details of the films. The composition of the alloy films has been ascertained by mass-spectrometer analysis. The resistivity increases linearly (and the TCR decreases correspondingly) with concentration of the impurities in accordance with Matthiessen's rule. The magnitude as well as the temperature of R_H and μ decrease on addition of impurities. Typically, the magnitude of R_H reduces from 5.5 (in units of $10^5 \text{ cm}^3 \text{ Coul}^{-1}$) to approximately 4.7 by 5 at.% Al, to 2.7 by 5% Ge and to 3.1 by 5% Sn for annealed films. At

a concentration of 5 at.% Ge and Sn, the temperature dependence of R_H of Cu is reversed. The addition of 5 at.% Al makes R_H independent of temperature. The TEP of Cu is reduced by the addition of all these impurities. The observed electron transport properties have been explained in terms of scattering behaviour of electrons and hole states in a mixed conduction mechanism (hence anisotropy of relaxation time) and distortions of the Fermi surface of Cu.

The investigations reported in this thesis are of direct interest in understanding the thermal and ageing stability of thin film resistors of high precision.

CONTENTS

| | Page |
|---|----------|
| ACKNOWLEDGMENTS | ... (iv) |
| ABSTRACT | ... (v) |
| | |
| CHAPTER I ELECTRON TRANSPORT PROPERTIES IN METAL FILMS | |
| 1.1 Introduction | ... 1 |
| 1.2 Geometrical Size Effects | ... 1 |
| 1.3 Role of Structural Defects | ... 9 |
| 1.4 Role of Impurities | ... 12 |
| 1.5 Objective of the Thesis | ... 16 |
| | |
| CHAPTER II EXPERIMENTAL TECHNIQUES | |
| 2.1 Vacuum Evaporation System | ... 20 |
| 2.2 Method of Deposition | ... 20 |
| 2.3 Electronmicroscopy Studies | ... 23 |
| 2.4 Measurements of Electron Transport Properties | ... 23 |
| | |
| CHAPTER III GEOMETRICAL SIZE EFFECTS IN COPPER FILMS | |
| 3.1 Introduction | ... 27 |
| 3.2 Experimental Details | ... 27 |
| 3.3 Results | ... 28 |
| 3.4 Discussion | ... 32 |
| 3.5 Conclusions | ... 38 |

| | Page |
|----------------------|--|
| CHAPTER IV | ROLE OF STRUCTURAL DEFECTS IN COPPER FILMS |
| 4.1 | Introduction ... 40 |
| 4.2 | Experimental Details ... 40 |
| 4.3 | Results ... 41 |
| 4.4 | Discussion ... 44 |
| 4.5 | Conclusions ... 51 |
| CHAPTER V | ROLE OF IMPURITIES IN COPPER FILMS |
| 5.1 | Introduction ... 53 |
| 5.2 | Experimental Details ... 53 |
| 5.3 | Results ... 54 |
| 5.4 | Discussion ... 56 |
| 5.5 | Conclusions ... 65 |
| REFERENCES | ... 67 |
| APPENDICES | ... 73 |
| LIST OF PUBLICATIONS | ... 76 |