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Final Technical Report

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HIGH FIELD CONDUCTION AND SWITCHING PHENOMENA AND MAGNETIC SPIN RESONANCE IN METAL OXIDE THIN FILMS AND SURFACES

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number):

Investigation was performed on transport, dielectric, switching and optical properties of thin amorphous and polycrystalline films of a series of transition metal and other oxides films. The conduction and dielectric dispersion mechanisms were unambigously identified for each oxide studied in the parent metal-oxide-parent metal configuration. The switching phenomena and the observed RF oscillations in the negative resistance region were fully explained by the double injection model. Stable and

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) reproducible switching devices were fabricated and the properties of important switching parameters studied as a function of composition temperature and applied voltage.

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I PREFACE

This final report briefly reviews the results covering a three year period ending Oct. 31, 1976. The principal objectives of the research program were to study high field conduction properties, dielectric dispersion and switching pheonomena in amorphous and polycrystalline metal oxide thin films and their surfaces. Another objective was to improve the switching performance of thin film transition metal oxide devices.

The detailed results of this research program were presented in journal articles, national and international meetings, Ph.D. dissertations and patent applications. As a result of this program 18 papers were published and 4 papers are under preparation or in the submission stage, 8 presentations were made at different meetings, 4 Ph.D theses completed and 2 applications for patentable inventions were made. The list of published papers and other publications is presented in this report.

II SUMMARY OF RESULTS

II-1 General Review

An investigation was performed of transport, dielectric and switching properties of amorphous and polycrystalline thin films of NiO, NiO(Li), CoO, CoO(Li), Nb_2O_5, TiO_2 and of the optical and electrical properties of SiO_2, $A\ell_2O_3$, WC_4 and their layered structures with different noble and transition metals.

Experimental results on transport properties of CoO, CoO(Li), Nb_2O_5 and TiO_2 are found to be in excellent agreement with the generalized theory of the Poole-Frenkel field-assisted emission mechanism. The theory of small polaron hopping mechanism rendered the best agreement with the results of measurements on transport properties of NiO and NiO(Li) polycrystalline films.

Dielectric dispersion was found to be either due to the Debye type of thermally activated hopping mechanism, or to adiabatic hopping from the uncorrelated sites. Relaxation times of different dispersion mechanisms were determined by the use of Cole-Cole or Scaiffe plots. The dielectric breakdown process is fully explained in terms of a formation of four sequential conduction states.

The mechanism of switching from high to low resistance states and of the current controlled negative resistance region was explained on the basis of I-V characteristics, Balberg's double pulse test and the observed R-f relaxation oscillation in the negative resistance region. The analysis of the above experiments was found to be in excellent agreement with Lampert's double injection theory of switching mechanism. The work on surface switching has shown that devices with a surface electrode configuration resulted in better switching devices. A model and preliminary calculations were made for this type of a device.

Results on the optical, electric and mechanical properties of thin films of SiO_2, $A\ell_2O_3$ and WC_4 and their layered structures with noble and transition metals, have shown considerable improvement in mechanical properties and drastic changes in the optical properties of cosputtered metal-oxide films.

II-2 Transport Mechanism

The I-V-T relationship for a semicrystalline material is given in the generalized Poole-Frenkel field-assisted conduction mechanism by the following expression:

$$I = I_o(kT)^4 \, (\beta_{PF})^{-2} \exp(-E_i/kT) \quad \alpha^2 \sinh \alpha$$

where $\beta = \frac{e^{3/2}}{(\pi\varepsilon d)^{1/2}} \frac{1}{kT}$, E_i is the ionization energy and

$$\alpha = \left(\frac{\beta_{PF}}{kT}\right)\left(\frac{V}{d}\right)^{1/2}$$

A plot of $IT^{-4}\exp(E_i/kT)$ vs $V^{1/2}/T$ should produce an $\alpha^2 \sinh \alpha$ curve. This type of a plot was found to be in excellent agreement with the measurements on amorphous and polycrystalline films of Nb_2O_5 [1,5,11] CoO and CoO(Li)[2] and TiO_2[10]. The ionization energy E_i is found to vary between 0.145 eV for TiO_2 to 0.27 eV for Nb_2O_5.

The I-V and G-V measurements on thin NiO and NiO(Li) films are found to be in agreement with the following expression for a polaronic hopping conduction mechanism [3,4]:

$$G = \frac{ne^2a^2\varepsilon'}{kT} \nu_o \left[1 + \frac{E^2}{2} \left(\frac{ea\varepsilon'}{2kT}\right)^2 + \ldots\right] \exp\left(-\frac{W_H}{kT}\right)$$

where n is the free carrier concentration, a(4.1Å) is the lattice constant, $\varepsilon' = \frac{E_{local}}{E} = \frac{\varepsilon + 2}{3}$, $\nu \approx 10^{-12}$ sec is the hopping frequency, $W_H = 0.3$ eV is the activation energy for polaron hopping and E is the applied field. The experimental plots of G vs V^2 are found to be in agreement with the above relation.

II-3 Dielectric Dispersion

Dielectric dispersion and polarization are found to be due to hopping of charge carriers at higher frequencies and to interfacial polarization and blocking electrode effects at low frequencies. The observed frequency dependence of ac conductivity ($\sigma(\omega)$) $\sigma(\omega) \approx \omega$ at higher frequencies [8,10] is in agreement with the theory of non-correlated hopping of charge carriers where:

$$\sigma(\omega) = (\frac{\pi^3}{96}) N^2(E_F) kT\, a\, r_\omega^4\, e^2 \omega$$

Here $N(E_F)$ is the probability density of localized states at the Fermi level ($cm^{-3}\, eV^{-1}$), r_ω is the separation between a pair of localized states ($r_\omega = a\, \ell n\, (\nu_o/\omega)$ where $\nu_o \approx 10^{12} sec^{-1}$) and a is the lattice constant. The values of $N(E_F)$ ranged from $1.5 \times 10^{19} cm^{-3}\, eV^{-1}$ for Nb_2O_5 [8] to $7 \times 10^{19} cm^{-3}\, eV^{-1}$ for TiO_2 [10] and r_ω from 49Å to 65Å, respectively.

In the intermediate frequency range, the ac conductivity varies with frequency as $\sigma(\omega) \propto \omega^n$ where $0.75<n<0.8$ [2,8,16]. This corresponds to the theoretically predicted relationship for non-adiabatic hopping as given by:

$$R_e\, \sigma(\omega) \propto (14.8 - \frac{1}{2}\, \ell n\, \omega)^4$$

A plot of the right-hand side of the above relation shows that $\sigma(\omega) \propto \omega^{0.8}$ which is in close agreement with experimental results.

Relaxation times at low frequencies were obtained from the Cole-Cole plots when modified Debye relations were used in the form [2.8]:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{(1+j\omega\tau)^\beta}$$

with $\varepsilon_1 - \varepsilon_\infty = (\varepsilon_o - \varepsilon_\infty)(\cos\phi)^\beta \cos\beta\phi$

$$\varepsilon_2 = (\varepsilon_o - \varepsilon_\infty)(\cos\phi)^\beta \sin\beta\phi$$

Here $\tan\phi = \omega\tau$ and $\omega\tau_o = \tan\theta/\beta$, where $\theta = \tan^{-1}(\frac{\varepsilon_2}{\varepsilon_1 - \varepsilon_\infty})$; τ_o is is the relaxation time and $0<\beta<1$. The values for relaxation times ranged from $2x10^{-2}$sec [8] to 1.6×10^{-4}sec [2].

II-4 Switching Mechanism

Experimental results on switching mechanisms are found to be in excellent agreement with Lampert's theory of double injection mechanism (17). The I-V characteristics show an initial linear increase of I with increasing V followed by an $I \propto V^2$ relation on increasing the applied voltage. Following the negative resistance region I again becomes proportional to V^2, which is in complete agreement with Lampert's model.

Experiments on Balberg's double pulse method for testing the switching mechanism rules out the thermal runaway model and was in complete agreement with Lampert's model. The analysis of the observed RF oscillations in the negative resistance region (12) was found to be in agreement with the above model.

II-5 Switching Devices

Stable and reproducible switching devices were made of thin transition metal oxide films that could support an input power greater than 2 watts with a device lifetime greater than 10^8 switching cycles. The significant and novel features observed in the switching process are the following [7,8,9,11]: a) Switching occurs within <2.5 mV for triggering pulses in the range 2-4V; b) the delay time τ_d decreases exponentially with increasing applied voltage; c) recovery time τ_r is 20 n sec and d) the proper switching time τ_s is less than 3 n sec.

Switching devices with the surface electrode configuration were studied using NiO and NiO(Li) polycrystalline thin film devices. These devices have shown an increased lifetime by a factor of 10^3 switching cycles due to the improved heat exchange with the substrate.

A surface switching electrode configuration, similar to that of a unijunction transistor was studied and it was calculated that the delay time can be reduced below 10^{-9}sec. The experiments, however, were not carried out due to the cessation of the program and the lack of IC facilities.

II-6 Optical and Electrical Properties of Other Oxides

These studies were performed on thin films of SiO_2, $A\ell_2O_3$ and

WC_4, on the metal-dilectric thin film configuration and on the thin dielectric films codeposited with metals. Noble and transition metals were used in layered structures and codeposition studies. Vastly improved optical and electrical properties were observed in the layered and codeposited films. Since numerous compositions were studied it would be difficult to enumerate them in a report and the details can be found in the references 13, 14 and 15.

III PERSONNEL

Following is a list of professional personnel who participated in the investigations.

Investigators:

N. Fuschillo, died on Oct. 15, 1974, Professor of Electrical Engineering.

B. Lalevic, Associate Research Professor of Electrical Engineering.

Guest Scientist:

Dr. Bekir Kuliyev, Azerbaijan Academi of Science.

Graduate Students:

N.K. Annamalai, Ph.D.; B. Leung, Ph.D.; W. Slusark, Ph.D.; G. Taylor Ph.D.; W. Wang, M.S.

IV - Ph.D. DISSERTATIONS

1. N. K. Annamalai, "Transport, Dielectric and Switching Properties of Nb_2O_5 Thin Films in the Device Configuration of Nb - Nb_2O_5- Nb" Ph.D. Thesis, Rutgers University, March, 1974.

2. B. Leung, "Transport, Dielectric and Switching Properties of NiO and NiO(Li) Thin Films in the Device Configuration Ni - NiO - Ni", Ph.D. Thesis, Rutgers University, January, 1976.

3. G. Taylor, "Switching and Conduction Mechanisms, Dielectric Dispersion, and RF Oscillations in Polycrystalline Thin Films of TiO_2", Ph.D. Thesis, Rutgers University, June, 1976.

4. W. Slusark, "Dielectric Dispersion, Transport and Switching Properties of Thin Polycrystalline Films of Nb_2O_5", Ph.D. Thesis, Rutgers University, May, 1976.

V - PUBLICATIONS

The following papers were published as a result of research on the ONR contract:

1. "Non-linear Transport and Switching Properties of Transition Metal Oxides," N. Fuschillo and B. Lalevic, Jap.J. Appl. Phys. 13-Suppl. 2, part 1, 817 (1974).
2. "Transport and Dielectric Properties of Thin Polycrystalline Films of CoO," B. Lalevic, N. Fuschillo, B. Kuliyev and W. Wang, Appl. Phys. 5, 127 (1974).

3. "High Field Transport in NiO and $Ni_{1-x}Li_xO$ Thin Films," B. Lalevic, N. Fuschillo and B. Leung, Solid State Electronics 19, 394 (1976).

4. "Electrical Conduction and Dielectric Breakdown in Crystalline NiO and NiO(Li) Films," with N. Fuschillo, B. Lalevic and B. Leung, J. Appl. Phys. 46, 310 (1975).

5. "Atomic Implantation of Nb in Amorphous Nb_2O_5 Films by RF Sputtering," B. Lalevic, N. Annamalai and N. Fuschillo, J. Vac. Sci. Technol. 12, 52 (1975).

6. "Hopping Conduction in Amorphous Nb_2O_5 Films," N. Annamalai and B. Lalevic, J. Non-Cryst. Solids, 20, 651 (1976).

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8. "Dielectric Properties of Nb_2O_5 Films," with N. Annamalai, B. Lalevic and N. Fuschillo, Thin Solids Films, 30, 141 (1975).

9. "Switching in Nb-Nb_2O_5-Nb Devices with Doped Nb_2O_5 Amorphous Films, B. Lalevic, W. Slusark and N. Fuschillo, IEEE Trans. Electron Devices ED-22, 965 (1975).

10. "Electrical Conduction in Thin Polycrystalline TiO_2 Films," B. Lalevic and G. Taylor, J. A-pl. Phys. 46, 3208 (1975).

11. "Switching Processes and Dielectric Breakdown in Polycrystalline Nb_2O_5 Films," B. Lalevic and W. Slusark, J. of Elec. Materials, 5, 531 (1976).

12. "RF Relaxation Oscillations in Polycrystalline TiO_2 Films," G. Taylor and B. Lalevic, Solid State Electronics, 19, 669 (1976).

13. "Properties of Metal-Dielectric Co-Deposited Films," G. Taylor and W. Slusark, Thin Solid Films, accepted to be published in Sept.-Oct. 1976 Volume.

14. "Optical Mechanical and Corrosion Properties of Metal-Metal and Metal-Dielectric Thin Layered Films," W. Slusard, B. Lalevic and G. Taylor, Thin Solid Films, accepted to be published in Sept.-Oct. 1976 volume.

15. "Hard Transparent Dielectric Coatings," G. Taylor, B. Lalevic and W. Slusark, Thin Solid Films, accepted to be published in Sept.-Oct. 1976 volume.

16. "Schottky-Barriers Effects on the Dielectric Behavior of the Nb-Nb_2O_5-Nb System," B. Lalevic and N. Annamalai, Physica Status Solidi, 37, K 177 (1976).

17. "Dielectric Dispersion and Polarization Effects in Thin Transition Metal Oxide Films," B. Lalevic, N. Annamalai, B. Leung, G. Taylor and W. Slusark, Vacuum, accepted.

18. "Mechanism of Threshold Switching in TiO_2 Films," G. Taylor and B. Lalevic, J. Appl. Phys., April (1977).

VI TECHNICAL PRESENTATIONS:

N. Fuschillo and B. Lalevic, 6th Inter. Vacuum Congress, Kyoto, Japan, April 1974.

N. Fuschillo, B. Lalevic and N. Annamalai, Proc. 21st Nat. Symp. Am. Vacuum Soc., Annaheim, Calif., Oct. 8, 1974.

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B. Lalevic, G. Taylor and W. Slusark, 14th Inter. Conf. on Mettalurgical Coatings, San Francisco, Calif., April 5-7, 1976.

G. Taylor, B. Lalevic and W. Slusark, 14th Inter. Conf. on Metallurgical Coatings, San Francisco, Calif., April 5-7, 1976.

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B. Lalevic, N. Annamalai, B. Leung, G. Taylor and W. Slusark, Inter. Symposium on Thin Films, Uppsala, Sweden, Aug. 31-Sept. 3, 1976.

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