MASTER

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PROTECTIVE OXIDE FILMS

Progress Report

August 1979 to February 1980

R. K. MacCrone and S. R. Shatynski
Materials Engineering Department
Rensselaer Polytechnic Institute
Troy, New York 12181

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Abstract

The progress made during the period from initiation of the grant August 1979 to the present time February 1980 is described.

This includes a description of

- (i) the construction of a thermogravimetric facility,
- (ii) the growth and characterization of CVD single crystal NiO films,
- (iii) I versus V measurements at different temperatures,
- (iv) I versus t curves at different voltages.

The progress made since the grant was initiated to the present time is described below.

Thermogravimetric Facility

The high temperature portion of this program is close to fully operational. During the initial year of this program great emphasis was placed on building and calibrating the thermogravimetric rig. Shortly after the award was made, a new graduate student, Bruce Quimby, was assigned to the program. During the summer of 1979 work proceeded on the building of the rig which is capable of monitoring the weight change as oxidation occurs as a function of both oxygen partial pressure and temperature. Gas impedance capillary manometers were built to accurately determine and control the gas flow rates and subsequently the partial pressure of the gases entering the reaction chamber. The rig was tested by monitoring the oxidation of pure nickel in 1 atmosphere oxygen at 900°C and comparing the resultant parabolic rate constant with the literature. Reasonable agreement was obtained. It was found that vibrations severely limited the sensitivity. To eliminate many of the vibrations we are currently building an isolated stand. By limiting the vibrations greater sensitivity needed for the interrupted thermogravimetric technique can be obtained.

Work has begun on determining the mechanism of oxidation initiation. The technique which is used is resistance relaxation. Using this technique, which monitors the electrical resistance of a thin foil relative to some standard, accurate determination of the rate determining step of the chemical reaction between the metal and oxygen on the metallic surface can be obtained. At present work is nearly complete on determining the mechanism at 900°C in a variety of oxygen partial pressures varying from 1 atmosphere to .001 atmosphere. Completed results are expected in late Spring 1980.

Electrical Measurements

While the furnaces and gas flow systems for the thermogravimetric measurements were being set up, we have continued with our measurements of NiO single

crystal films. This is an important aspect of the research, in that these films will provide a set of control specimens with which those grown under different oxidizing conditions will be compared. The work was carried out by a senior graduate student, M. G. Brown, and a new student, John Savi, who joined the project in August 1979.

During the time since the initiation of the grant, we have

- (i) grown several sets of specimens,
- (ii) characterized the films by x-ray diffraction, SCEM, and optical microscopy,
- (iii) measured the I versus V curves using gold and aluminum electrodes,
- (iv) determined the time dependent current curves at different voltages and temperatures.

Film Growth

The films of NiO were grown by a chemical vapor technique:

The films are deposited on MgO substrates, and electrodes of gold, silver or aluminum are deposited using standard lithographic methods. The electrodes consist of a set of interdigitated fingers.

Film Characterization

X-ray Laue photographs were taken of selected films, to investigate the structural perfection of the films.

A typical back reflection photograph is shown in Figure 1. As can be seen, the sharp spots are characteristic of a single crystal, with little strain. (Absorption calculations showed that the diffraction pattern shown is due to NiO, and not that from the MgO substrate.)

A typical optical photomicrograph is shown in Figure 2, taken under Nomarski conditions.

The cross hatched pattern results from the anti-ferromagnetic boundaries. The well developed pattern and the spatial extent can be taken as evidence that the crystals are of good quality. There is no evidence of sub-boundaries or other large scale imperfections.

The original micrographs show a structure resembling mountain peaks (or rivers in valleys). These we believe are ridges due to back etching. This process causes large scale undulations in the film surface and are of no consequence in the electrical measurements.

The SCEM micrographs were featureless. This we take again as evidence for the high quality of our films.

The I versus V Curves

Current-voltage curves have long been used by the thin film device workers to characterize electrical traps in insulators. Electrical traps and their identification are important in this work as they are associated with lattice defects, the defects associated with the film growth, the film adherence and the film degradation.

A typical set of I versus V curves are shown in Figure 3 at different temperatures. The amount of work in producing this curve can be estimated by noting that each point takes at least 15 minutes to obtain.

The important features of this curve are

- (a) that deep level trapping (or some forming process) occurs during the first I versus V measurement,
- (b) that there are three regions, labelled (a), (b) and (c),
- (c) that the activation energies in
 - region (a) is $.6 \pm .1$ eV,
 - region (b) is $.6 \pm .1$ eV,
 - region (c) is $.6 \pm .1$ eV.

Finally, we note that this is a very anomalous I versus V curve.

The Current Transients

Current transients are also dependent on the number and type of electrical trap in insulators, and therefore are of considerable interest in this work.

A schematic representation of the current transients at different voltages is shown in Figure 4. As can be seen there is clear shift in the time dependence of the current as the voltage ranges through the regions (a), (b) and (c).

Analysis

We are presently heavily involved in the analysis of our electrical measurements. It is too premature to present our conclusions here.

Summary

Construction of our thermogravimetric facility is now complete. We anticipate a productive summer using this facility to study the growth of films and to produce well characterized films for electrical measurements.

We have also constructed a high temperature device for electrical measurements. In addition, a power supply for our Xenon light source has been designed and constructed.

We have grown a series of NiO single crystal films by CVD, and characterized them by x-ray diffraction, optical microscopy (Nomarski) and SCFM.

We have obtained a set of I versus V curves at a series of different temperatures, using both gold and aluminum electrodes.

We have obtained a series of I versus t curves at different voltages and temperatures.

Figure 1

Figure 2

CURRENT, I (AMPS)

Figure 3

Figure 4