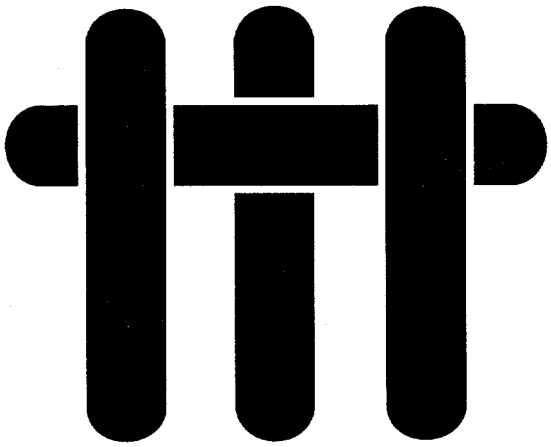
MATERIALS



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FINAL REPORT
to
U. S. DEPARTMENT OF ENERGY
OFFICE OF BASIC ENERGY SCIENCES

FUNDAMENTAL STUDIES OF THE INTER-RELATIONSHIP BETWEEN GRAIN BOUNDARY PROPERTIES AND THE MACROSCOPIC PROPERTIES OF POLYCRYSTALLINE MATERIALS

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DISCLAIMER

EXECUTIVE SUMMARY

The research performed under this grant has been principally devoted to understanding and quantifying the relationship between the macroscopic electrical transport properties of ZnO based materials and the properties of their grain boundaries. Two forms of polycrystaline ZnO have been extensively investigated, polycrystalline thin films, such as are used as optically transmitting, conducting electrodes and as piezoelectric films, and polycrystalline bulk forms, such as are widely used as surge arrestors. The former are essentially two-dimensional and the latter three-dimensional.

The research has included both simulation and experimental studies. The simulation studies have been primarily addressing how the macroscopic properties of bulk ZnO ceramics are determined by the electrical and crystallographic properties of their grain boundaries. (Reports #1,5,7,9). The behavior of varistors has been the focus since the highly nonlinear electrical characteristics provide an opportunity to test the models in much greater detail than is possible if the characteristics were simply ohmic. Furthermore, there is a continuing desire to improve varistor characteristics, such as the sharpness of the switching voltage and the degree of nonlinearity, so the effect of grain boundary variations on these parameters have been specifically addressed and found to quantitatively depend on the variation in both grain size and grian boundary barrier height. New methods of quantifying the effect of microstructural variations on the *I-V* characteristics have been introduced. The simulations have included both electrical network methods (reports#1,5,9) and effective medium methods (reports#7). During the course of the research, the studies were extended to describe electrical breakdown, specifically on how microstructural variations lead to current localization which in turn leads to a form of electrical discharge failure, a common form of failure of varistors under electrical loading (Report#9).

The question of the relationship between the *I-V* characteristics of a grain boundary, its crystallography and the charge distribution at the grain boundary is of profound importance in understanding the electrical properties of polycrystalline materials yet has not been systematically addressed. In report#10 we introduced a novel simulation approach for determining these relationships and developed quantitative relationships between the *I-V* characteristics and the charge and misorientation of tilt grain boundaries.

On the experimental side, we constructed a laser ablation system for the deposition of ZnO films and with this we have been able to fabricate all the films used in this work. Detailed studies of the crystallographic orientation of epitaxial growth on different substrate and substrate orientations were undertaken as well as the effect on the electrical transport properties. (Reports #3 and 4). The epitaxial films grown all have a mosiac structure as a result of the rather large lattice mismatch with most substrates. The crystallographic

studies led to a realization that the mosaic structure is a general feature of heterophase epitaxy. In report #15, a method for determining the in-plane crystallographic misorientation distribution of a mosaic structure from a series of out-of-plane X-ray rocking curves was described together with the concept of geometrically necessary dislocations to describe the mosiac structure. This has application to all heterophase epitaxially systems including such diverse systems as GaN on sapphire and GaAs on MgO.

One of the unusual features of polycrystalline ZnO is that the electrical properties can be altered by both doping the grain boundaries and the grains themselves. This has profound consequences on the electrical transport properties, the optical properties and the piezoelectric properties. The way in which they can be manipulated is described by the work in report # 6 and #8, so as to form thin-film varistors and nonlinear conductors. The properties are found to be sensitive to microstructural parameters, such as strain and grain size, as described in reports #11 and #12 in which the optical absorption properties of ZnO films are described. Our work on the effect of strain with the substrate (report#12) clarifies several long-standing discrepancies in the literature concerning questions such as the actual band-gap of ZnO itself and particle size effects. Another unexpected result of our research has been the demonstration of acousto-electric current saturation in polycrystalline films (report#13). The acousto-electric effect, a field induced piezoelectric coupling with the conduction electrons that limits the maximum current density, had previously only been reported in single crystals. Our work has shown that polycrystalline films can also exhibit this highly unusual phenomenon provided that the nature of the grain boundaries and their electrical properties are controlled during growth.

Finally, a physical model for the electrical impluse induced fracture of varistors was introduced (report#14). At very fast electrical loadings, for instance associated with arresting a surge produced by lightening, varistors can fail by what appears to be a mechanical failure and microstructural examination oftens reveals the existence of multiple failure origins on the fracture surface. An analysis based on the rapid resistive heating causing mechanical shock was developed that combines electrical and mechanical properties and successfully describes the failure modes observed.

√ = Pulled for Separate processing

REPORTS OF WORK SUPPORTED BY CONTRACT DE-FG03-91ER45447

Reprints

Report 1. Q. Wen and D. R. Clarke, **Modelling the Electrical Characteristics of Polycrystalline Varistors Using Individual Grain Boundary Properties**, Ceramics Transactions, **41** 217-230 (1994).

Report 2. V. Srikant, E. Tarsa, D. R. Clarke and J. S. Speck, **Crystallographic Orientation of Epitaxial $BaTiO_3$ Films: The Role of Thermal Expansion Mismatch with the Substrate**, Jouranl of Applied Physics, **77** [4] 1517-1522 (1995).

Report 3. V. Srikant, V. Sergo and D. R. Clarke, **Epitaxial Al-Doped Zinc Oxide Thin Films on Sapphire: I. Effect of Substrate Orientation**, Journal of the American Ceramic Society, **78** [7] 1931-1934 (1995).

Report 4. V. Srikant, V. Sergo and D. R. Clarke, **Epitaxial Al-Doped Zinc Oxide Thin Films on Sapphire: II. Electrical Properties**, Journal of the American Ceramic Society, **78** [7] 1935-1939 (1995).

Report 5. A. Vojta, Q. Wen and D. R. Clarke, **Influence of Microstructural Disorder On The Current Transport Behavior of Varistor Ceramics**, Computational Materials Science, **6** [1] 51-62 (1996) .

Report 6. V. Srikant and D. R. Clarke, **Manipulating The Electrical and Optical Properties of ZnO Based Films**, in *Polycrystalline Semiconductors IV. Physics, Chemistry and Technology*, edited S. Pizzini, H. P. Strunk and J. H. Werner, Trans. Tech. Publ., Zug, Switzerland 1996. pp 579-584.

Report 7. C.-W. Nan and D. R. Clarke, **The Effect of Variations in Grain Size and Grain Boundary Barrier Heights on the Current-Voltage Characteristics of ZnO Varistors**, Journal of the American Ceramic Society, **79** [12] 3185-3192 (1996).

Preprint

Report 8. V. Srikant and D. R. Clarke, **A Thin-Film Varistor Formed By Interdiffusion In A ZnO/Bi_2O_3/ZnO Heterostructure**, Applied Physics Letters, submitted.

Not Received with this submission

Report 9. A. Vojta and D. R. Clarke, **Microstructural Origin of Current Localization and "Puncture" Failures In Varistor Ceramics**, Journal of Applied Physics, **81** [2] 985-993 (1997).

Report 10. V. Srikant, D. R. Clarke and P. V. Evans, **Simulation of Electron Transport Across Charged Grain Boundaries**, Applied Physics Letters, **69** [12] 1755-1757 (1996).

Report 11. V. Srikant and D. R. Clarke, **Anomalous Behavior of the Optical Band Gap of Nanocrystalline ZnO Thin Films**, Journal of Materials Research, In Press.

Report 12. V. Srikant and D. R. Clarke, **The Optical Absorption Edge of ZnO Thin Films: The Effect of Substrate,** Journal of Applied Physics, In Press.

Report 13. T. Pompe, V. Srikant and D. R. Clarke, **Acousto-Electric Current Saturation In c-Axis Fiber-Textured ZnO Thin Films**, Applied Physics Letters, **69** [26] 4065-4067 (1996).

Report 14. A. Vojta and D. R. Clarke, **Electrical Impulse Induced Fracture of ZnO Varistor Ceramics**, Journal of the American Ceramic Society, In Press.

Report 15. V. Srikant, J. S. Speck and D. R. Clarke, **Mosaic Structure in Epitaxial Thin Films Having A Large Lattice Mismatch**, Journal of Applied Physics, submitted.

In Preparation:

Report 16. P. Verghese and D. R. Clarke, **Effect of Internal Residual Stress on the I-V Characteristics of Varistors.**