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The defect structure of epitaxial oxide thin films was investigated. Both binary and complex oxides were studied. Epitaxial oxides were synthesized by organometallic chemical vapor deposition (OMCVD). This technique has been found to be highly versatile for the the synthesis of a wide range of epitaxial oxide including dielectrics, ferroelectrics and high T_c superconductors. Systems investigated include the binary oxides ZnO and TiO_2 and ferroelectric oxides $BaTiO_3$, $BaSrTiO_3$ and $KNbO_3$. Techniques used to evaluate the defect structure included deep level transient spectroscopy (DLTS), photocapacitance spectroscopy, and photoluminescence (PL) spectroscopy. High purity, stoichiometric oxide films were deposited and their defect structure evaluated. Epitaxial ZnO was deposited at temperatures as low as 250° C. PL indicated only near band edge ultraviolet emission showing that both extrinsic and intrinsic point defects could be significantly lowered in OMCVD derived thin films compared to that of the bulk.This presumably was a result of low deposition temperatures and high purity starting materials.

Ferroelectric oxides epitaxial thin films of $BaTiO_3$ and the solid solution $BaSrTiO_3$ were synthesized and the defect structure determined. Photocapacitance spectroscopy was developed to quantify electrically active defects in the oxides. Defects with concentrations as low as 10^{14} cm^{-3} were observed and their properties determined. A new model was developed for the electronic transport properties of intrinsic and extrinsic $BaTiO_3$. A transport model was proposed whereby conduction in La doped films occurs via hopping in localized states within a pseudogap formed between a lower Hubbard band and the conduction band edge. The influence of the *size effect* on the ferroelectric phase transition in the thin films was investigated. The Curie temperature shifted more than 100° C as a result of strain stabilization of the low symmetry phase. The dielectric properties of $BaTiO_3$ showed a strong thickness dependence for films ranging from 15 to 320 nm. The dynamic dielectric and non-linear optical relaxation response of the ferroelectric thin films was studied over nine orders of magnitude in time from 1 nsec to 1 sec. A power law dependence of the relaxation response on time was observed and a model developed. The dynamic response was analyzed in terms of relaxation of ferroelectric domains with a continuous size distribution. Domain size ranged from nanometers to microns. This continuous size distribution also leads to a diffuse phase transition as observed for the thin films.

Future Work

This program has shown that highly perfect films of complex oxides can be synthesized by OMCVD at low temperature. Furthermore it was shown that spectroscopic techniques used for high purity semiconductors for electronic defect studies can be used for these oxides. We are now in a position to understand the electronic and optical properties of a wide range of nearly intrinsic complex oxides. Future work should be directed toward applying these techniques and developing models that explain the defect structure of these oxides.

DOE Patent Clearance Granted

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DOE Chicago Operations Office

DISCLAIMER

As a result of the transient electro-optic and dielectric response measurement techniques that were developed we can now explore the kinetics of phase transformations from picoseconds to hours on a single material system. We are now in a position to measure and model the dynamics of first order and second order phase transitions with unprecedented accuracy. This development should have wide applicability to a large class of complex oxides.

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