Rare-earth Information Center

Insight

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Oxygen Diffusion from Internal Friction

We are all familiar with the process of shaking a package to try and guess what is inside. If we are being sophisticated about the process, we may attempt to determine the resonant modes of the package, and if we are really sophisticated, we might observe the damping of those modes. If the package is a single crystal of yttria stabilized zirconia (YSZ), the process is referred to as measuring the internal friction of the material. Instead of shaking the crystal, the crystal is used as a vibrating reed. One end of the reed is fixed, and the other has a gold film deposited on one side. The film can then be used as one side of a capacitor, and an AC voltage across the capacitor causes a force that drives flexural vibrations in the reed. If the displacement of the end of the reed is measured, which can be done with a laser displacement meter, the resonance curve can be measured. The damping can be determined from the width of the resonance curve in frequency space and also by the decay time of the resonant mode if the driving field is shut off. The damping or internal friction results from energy transfer from the macroscopic flexing of the crystal to microscopic mechanisms, such as the jumping of an ion to an adjacent vacancy. If the temperature dependence of the internal friction is measured, the damping peaks at a temperature that is characteristic of the energy associated with the jump. M. Ohta et al. {*Jpn. J. Appl. Phys.*, **40**, 5377-81 (2001)} have used internal friction measurements to study oxygen diffusion in YSZ. As has been discussed frequently, YSZ is an oxygen ion conductor and is used in a variety of applications from oxygen sensors to fuel cell membranes. From a simplistic standpoint, the ion conductivity of YSZ should scale as the number of dopant ions, i.e. the yttria concentration. However, the ion conductivity peaks at about 8 mol% Y_2O_3. It has been suggested that bound oxygen vacancies are formed around the Y-ion due to symmetry breaking. Such vacancies would allow an oxygen ion to hop back and forth near the y-ion but not to contribute to the conductivity. The measurements of Ohta et al. support this hypothesis in that they see two closely overlapping absorption peaks in the internal friction spectrum confirming the existence of two relaxation modes. One of these, the associate with diffusion relaxation is what we would consider the useful process, and the other is a localized relaxation.

Rare Earth Oxide Gate Dielectric

Tunneling leakage currents and a low dielectric constant make it very difficult to form a MOSFET, metal oxide semiconductor field effect transistor, with a SiO_2 oxide layer of less than 20 Å. Designs for the next generation MOSFET call for an equivalent oxide thickness of 15 Å, so the search is on for a better dielectric material that is compatible with conventional semiconductor processing. As has been previously reported, there is considerable interest in using RE_2O_3 layers and an increasing number of reports of success in forming suitable layers. A. Dimoulas et al. {*J. Appl. Phys.*, **90**, [8], 4224-30 (2001)} have reported on direct heteroepitaxy of Y_2O_3 on Si (001). Heteroepitaxy unfortunately results in a complex microstructure since there are two orientations of the Y_2O_3 with respect to the Si substrate. This may cause problems in device applications. Highly crystalline films were grown at ~450°C. Unfortunately, at this temperature a nonuniform amorphous reaction layer formed with the Si substrate, this layer was 5 to 15 Å thick. The layer crystallized at reaction temperatures of 600°C. S. Pal et al. {*J. Appl. Phys.*, **90**, [8], 4103-7 (2001) have reported a comparative study of Gd_2O_3,

$Ga_2O_3(Gd_2O_3)$, Y_2O_3, and Ga_2O_3 for use as gate dielectrics on SiGe. The strained $Si_{0.74}Ge_{0.26}$ metal-oxide semiconductor devices are a promising means of extending the useful life of the current transistor design. Gd_2O_3 and Y_2O_3 provided the highest resistivity and breakdown strength, but $Ga_2O_3(Gd_2O_3)$ gave the lowest interface state density.

An alternative approach was taken by D. Landheer et al. {*Appl. Phys. Lett.*, 79, [16], 2618-20 (2001)}, who intentionally formed a $Gd_{0.23}Si_{0.14}O_{0.63}$ layer. Since this layer was formed at 1000°C, the diffusion of constituents beyond the layer thickness is a concern. While oxygen diffused into the films eliminating oxygen vacancies, there was no Si diffusion, and the electrical properties were promising.

A third approach was to try to improve on HfO_2 gate dielectrics by Dy doping. (I probably would have been unable to resist trying Ho doping as a hafnium – holmium compound has a certain appeal.) The Dy doping resulted in lower leakage currents and a smaller effective oxide thickness compared to the undoped material. This was attributed to the lower electronegativity and larger atomic radii of the Dy compared to Hf.

I should note that IBM has just announced a two gate transistor design that circumvents the entire problem by allowing one to live with a certain amount of leakage through each individual gate. They have stated that strained Si designs will probably be sufficient until 2007, after which the two gate design may be implemented.

Reactive Recording

There are two common methods of optical data recording. In magneto-optical recording, the direction of magnetization of the recorded bit is determined using the Kerr effect that rotates the polarization of light reflected from the structure. Writing of bits is accomplished by the simultaneous application of a laser pulse for local heating and a magnetic field. In phase change recording, amorphous film is locally crystallized by the application of a laser pulse. The difference in optical properties of the amorphous and crystalline material provides a read out of the data. In the design of recording media for these processes, care has been taken to avoid reactions with the layers in the media surrounding the storage layer. (Optical recording media is usually designed so that the light used to read the media is reflected back and forth through the recording layer several times, which greatly improves the signal to noise ratio.) In a recent paper by J. Kim et al. {*Appl. Phys. Lett.*, **79**, [16], 2600-2 (2001)}, a presumably write once architecture was created where an amorphous RE-TM (transition metal) film was placed between dielectric layers that were intentionally chosen to react with the recording layer during writing. Significant improvements in carrier to noise ratio and a much higher modulation were obtained than is achieved for conventional phase change recording.

CO_2 Sensor

As stated in the first review, yttria-stabilized zirconia (YSZ) is used as an oxygen ion conductor in a number of applications, including sensors. One such sensor is for CO_2. Building a solid state sensor that will detect CO_2 does not appear to be much of a problem; however, a carbonate auxiliary electrode is required, and many of the compounds that have been investigated for this application have been water soluble. This becomes a major problem in a combustion system that is cycled on and off since the water that is a by-product of combustion, can condense on the electrode during cool down when the system is shut off. Needless to say, this does not do a water soluble electrode much good. N. Imanaka et al. {*Chemistry Lett.*, 718-9 (2001)} have recently developed a sensor that uses a Sc^{3+} ion conductor $Sc_{1/3}Zr_2(PO_4)_3$ prepared by sol gel processing with a YSZ O- conductor and a Li and Ba codoped neodymium oxycarbonate solid solution as the auxiliary electrode. The result is a highly stable sensor with rapid reproducible response.

Sincerely,

R. W. McCallum
Director of RIC