

# Rare-earth Information Center

# Insight

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Vol. 15

RIC Insight

February 2002

## RE Hydride Optical Switches

Since May of 1996, *Insight* has followed the development of switchable optical mirrors based on the metal insulator transition that occurs when  $REH_2$  is converted to  $REH_3$ . Huiberts et al. [*Nature*, **380**, 231-234 (1996)] produced thin films of La and Y, which were overlaid with a thin (5-20 nm) Pd film. This layer protects the RE hydride from oxidation but allows H to diffuse readily. Subsequent work demonstrated that the Pd layer is also required to catalyze the  $H_2$  disassociation. An undesirable property of the pure REH films is that while they are transparent, they are also colored. This problem was addressed by P. van der Sluis et al. [*Appl. Phys. Lett.*, **70**, 3356-8 (1997)] by adding Mg to the films. Alloys of Gd, Sm, Lu, and Y were found to reversibly absorb and desorb H with achieved transmission ratios of more than 1000. These early experiments controlled the H content of the films by varying the atmosphere around the film. Clearly, this is not suitable for a device. In 1999, R. Armitage et al. [*Appl. Phys. Lett.*, **75**, [13], 1863-5 (1999)] reported on a completely solid state device. The concept is fairly simple; a multilayer structure is created in which H may be moved from one layer to another by the application of a voltage across the layers. Starting with a glass substrate, an indium-tin-oxide (ITO) electrode film is deposited. The Gd-Mg film is deposited on top of that and is as before capped with Pd. A hydrated Zr-O solid electrolyte layer is then added. The hydrogen storage layer is  $WO_3$  that is then capped by another ITO electrode. When the base electrode is at -3.0 V relative to the  $WO_3$ , all layers except the Pd are fully transparent while at +3.0 V the device view through the glass substrate is reflecting. In this device, the switching of the prototype took 16 h. and required a current in excess of 40 mA. In 2000, R. Armitage et al.

[*Appl. Phys. A*, **71**, 615-8 (2000)] have investigated using a Pd grid rather than a continuous film in order to increase the transparency and reduce switching times. Recently, V. M. M. Mercier and P. van der Sluis [*Solid State Ionics*, **145**, 17-24 (2002)] have investigated the use of zirconium oxide as a proton conductor. The electrolyte must fulfil a number of conditions. It must be a good insulator with respect to electrons while providing high conductivity for the positive ions. It must be transparent and color neutral. Finally, it must not react with the insertion electrodes either during processing or operation. Pure  $ZrO_2$  is monoclinic and insulating at room temperature. YSZ, yttria stabilized zirconia is cubic and used as an ion conductor in a number of high temperature applications. Mercier et al. have hydrated  $ZrO_2$  ( $ZrO_2 \cdot 1.75H_2O$ ) produced by thin film reactive sputtering in and  $O_2$  and  $H_2$  as the electrolyte. They have produced a symmetric-GdMg stack device that contains two GdMg layers. One of these layers is hydrided by exposure to  $H_2$  gas and the H is then moved between layers by applying the voltage across the device. The switching was reversible. Due to multiple Pd layers in the device, the overall transmission was fairly low, however, switching time of about 200 seconds were achieved with average current values of about  $0.3mA/cm^2$ .

## Rare Earth Reinforcement of $MoSi_2$

The intermetallic molybdenum disilicide ( $MoSi_2$ ) is a leading candidate for high temperature structural applications. It has an extremely high melting temperature for an intermetallic due to the fact that it exhibits both metallic and covalent bonding. It has good high temperature corrosion and oxidation resistance. Unfortunately, it is brittle at room temperature, which limits its practical applications.

Numerous approaches have been taken to improve the room temperature fracture toughness of  $\text{MoSi}_2$  including additions of TiC, SiC,  $\text{Al}_2\text{O}_3$  and more. H. Zhang and X. Liu, {*J. Rare Earths*, 19, [14], 271-4 (2001)} have recently tried mechanically alloying with unspecified rare earths. A significant increase in fracture toughness is reported, which is claimed to exceed that obtained by SiC additions. The experimental process used is not entirely clear, as the alloying conditions are not given. A "0.9% RE/ $\text{MoSi}_2$ " mixture was prepared by mechanically alloyed and consolidated by isostatic pressing at 100 MPa for 3 min. The samples were sintered under hydrogen at 1400°C. Microstructural analysis showed the RE to be present as  $\text{RE}_2\text{O}_3$ . There was a significant reduction in grain size with the RE additions compared to the single-phase material. This reduced grain size is credited with causing the increased toughness.

### Ce<sub>2</sub>O<sub>3</sub> Nanoparticles

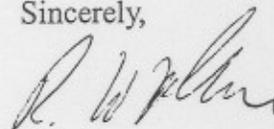
Ceria,  $\text{Ce}_2\text{O}_3$ , is widely used as a catalyst, as an ion conductor and as an insulator. For some of these applications, it is desirable to have nanoparticles, which have high surface areas for catalytic activity or rapid sintering at lower temperatures. Of course, for an ultrafine catalyst, sintering at low temperature reduces the surface area so that property is not necessarily desirable. F. Zhang et al. {*Appl. Phys. Lett.*, 80, [1], 127-9 (2002)} have concentrated not on the application of such particles but rather on producing nanometer sized particles with a narrow size distribution. Many processes produce fine particles with a wide distribution, but the authors point out that the yield of particles below 10 nm is typically very low. Using a room temperature reaction of equal volumes of 0.0375 M  $\text{Ce}(\text{NO}_3)_3$  and 0.5 M hexamethylenetetramine particle with a mean size of 3-12 nm may be

obtained by varying the reaction time. The particle size distribution is  $\pm 15\%$ , and the particles are found to be single crystals by TEM examination. It appears that patience is required when producing the particle as the reaction time for 8 nm particles is 10 h. The particle size is a linear function of reaction time. As the particle size decreases, there is an increase in the ceria lattice parameter that is attributed to an increasing concentration of point defects. For particles of 6 nm, the lattice parameter is 0.45% larger than the bulk value.

### YSZ – Gold Nanocomposite Films

YSZ, yttria stabilized zirconia, has been the subject of over 300 papers in the last year because of its wide variety of current and potential applications. The thermal expansion coefficient of YSZ matches that of metal alloys, and its elastic modulus is close to that of steels. This makes it attractive as a surface coating to protect against wear, oxidation and corrosion. The fracture toughness of YSZ is one of the highest for ceramic materials. Unfortunately, that value is not high enough to prevent cracking under surface-wear conditions where substrate deformation can take place. For these conditions, it is desirable to have 1  $\mu\text{m}$  thick films on steel substrates with even higher fracture toughness. This limits deposition temperatures, which in many processes effects the crystallinity of the material. A. A. Voevodin et al. have investigated the possibility of using pulsed laser deposition (PLD) of YSZ coupled with the simultaneous magnetron sputtering of Au to produce thin films containing crystalline YSZ nanoparticles in an amorphous YSZ/Au matrix. The Au concentration to obtain this structure was 10-15 at% Au, and the nanoparticles were 5-10 nm. This combination maintained a relatively high hardness and elastic modulus while improving the film toughness.

Sincerely,



R. W. McCallum  
Director of RIC