

Rare-earth Information Center

Insight

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Interfacial Reactions between Thin RE_2O_3 Films and Si

The fabrication of sub- $0.1\mu\text{m}$ complementary metal-oxide-semiconductor devices requires that the gate dielectric layer be less than 1 nm thick. This requires that the traditional SiO_2 oxide layer be replaced by a material with a higher dielectric constant. This layer must be deposited on Si without significant oxidation of the Si. Thus, there is considerable interest in oxides that are thermodynamically more stable than SiO_2 . La_2O_3 and Gd_2O_3 have been reported to be suitable dielectrics. As a result, H. Ono et al. {*Appl. Phys. Lett.*, **78**, [13], 1832-34 (2001)} have performed a detailed investigation of the interfacial reactions between thin RE_2O_3 films and Si substrates. The films were prepared by depositing a thin film of a RE containing organic compound, $[\text{Ln}(\text{CH}_3\text{COCHCOCH}_3)_3\text{H}_2\text{O}]$, by thermal evaporation in vacuum. The organic films were then pyrolyzed at 400°C for 1 hr in air or Ar. The films were subsequently annealed at 600 and 800°C for 30 min in N_2 . After the 400°C treatment, FTIR measurements showed that there were significant levels of organic impurities remaining in the films. While the 600°C anneal significantly reduced this level, only the 800°C annealed samples had concentrations below the detection limit of FTIR. FTIR was also used to measure the number of Si-O-RE and Si-O-Si bonds in the sample. In the pyrolyzed samples, there were no detectable Si-O-RE bonds. The concentration of these bonds increased with annealing temperature, and for a given temperature decreased with RE radius approaching the detectability level for the heavy rare earths. The number of Si-O-Si bonds corresponded to a 1 nm thick SiO_2 layer for all samples.

Catalysts for Syngas Production

Synthesis gas (syngas) is a mixture of carbon monoxide and hydrogen produced on an enormous scale

for the manufacture of ammonia, hydrogen, methanol, and other chemicals. Less traditional uses of syngases continue to be developed and have increased in importance in recent years: viz., acetic acid and acetic anhydride. Syngas is produced from a wide variety of hydrocarbons ranging from methane to coal. A major strength of syngas appears to be that it provides a uniform feedstock from a diverse set of starting materials, including biogas. Ideally, one would like to have a syngas converter where a mixture of feedstocks could be simultaneously converted to syngas. Fluidized catalytic cracking or petroleum produces "tail gas" and refinery gas mixtures of CH_4 (methane), C_2H_6 (ethane), C_3H_8 (propane), and C_4H_{10} (butane). The complete separation of these gases is not economical, however, efforts are being made to develop catalysts that can simultaneously convert all these gases to syngas. Recently, S. Liu et al. {*Appl. Catalysis A: General*, **211**, 145-52 (2001)} have reported work on the partial oxidation of propane to syngas using Ni supported catalysts that have been modified by various RE-oxides and alkali metal oxides. The major concerns appear to be high conversion efficiency, selectivity (which I assume means producing the desired end product), and the absence of carbon deposition on the catalyst. The latter occurs when ethane or propane is thermally split at high temperature. This limits the temperature of operation for the reactor. The catalysts compared in this study were $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ and $\text{LiLaNiO}/\gamma\text{-Al}_2\text{O}_3$. The major effects of the RE additions appear to be related to enhancing the thermal stability of the $\gamma\text{-Al}_2\text{O}_3$ and also a substantial decrease in carbon deposition during the reduction of propane.

Amorphous Phase Formation by Hydrogen Absorption

Normally, amorphous metallic alloys are prepared by rapid quenching of molten alloys or deposition of metallic vapors. However, amorphous alloys

have been prepared by hydrogen absorption of intermetallic compounds. Recently, it has been demonstrated that the C15 Laves phases, REFe_2 , can be made amorphous by hydrogen absorption (*Mater. Sci. Eng. A*, **304-306**, 45-53 (2001)). In order to obtain the amorphous material, the hydrogenation must be performed at low temperature, below 100°C . The process also requires fairly high pressures, 5 MPa or roughly 50 atm. The hydrogenation times are given as 173 ks that translates to 48 hrs. Differential thermal analysis performed under 1 MPa H_2 suggests that the time and pressure are probably somewhat excessive. The curves exhibit clear exotherms associated with H_2 absorption into the crystalline material, followed by a second exotherm associated with the formation of the amorphous phase. As the temperature is raised, the precipitation of REH_2 results in a third exotherm. At high temperature, the REFe_2 is completely decomposed into $\text{REH}_2 + \text{Fe}$. This last reaction corresponds to the hydrogen decomposition used in the HDDR process for $\text{Nd}_2\text{Fe}_{14}\text{B}$. As all of these reactions are exothermic, the $\text{REH}_2 + \text{Fe}$ is clearly the ground state under this H_2 pressure. The paper contains a rather complete analysis of a large number of C15 phases, using not only Fe but also Co, Ni, Al, and Pt. They find that when the ratio of the RE atomic size to the other element exceeds 1.35, the amorphous structure is formed.

RE Additions to AB_2 -types Laves-phase Hydrogen Storage Alloys

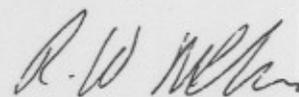
In Ni/MH batteries, the negative electrode is either a RE based AB_5 -type alloy (LaNi_5) or a non-rare earth containing AB_2 Laves-phase. The AB_2 based batteries are claimed to have higher discharge capacities and better cycle life. Zr-based Laves phase batteries however have a slow activation behavior, poor-high rate discharge and low electrocatalytic activity. The activation behavior refers to the fact that the battery must be cycled a number of times before the maximum capacity of the battery is reached. This behavior is attributed to the formation of a dense oxide layer on the surface of the alloy. Small amounts of RE to the Zr-based Laves alloys have been shown to greatly improve the ac-

tivation behavior, and W-X Chen (*J. Alloys Compds.*, **319**, 119-23 (2001)) has recently performed an extensive study of these materials. It should be noted that while AB_2 sounds like a simple system, in practice the alloy investigated is $\text{ZrNi}_{1.1}\text{Mn}_{0.5}\text{V}_{0.3}\text{Cr}_{0.1}$. The mixture of transition elements results from the optimization of a series of competing requirements, including the H potential. In the current study, Ce or mischmetal was nominally substituted for 10% of the Zr. I should note that no determination of the actual phases formed was made in this paper, but it is highly probable that the RE did not substitute in the AB_2 compound. The RE substitution did result in significant improvement in the activation properties, reducing from 27 to 4 the number of cycles required to reach maximum capacity. The electrocatalytic activity of the electrode was also significantly improved. Unfortunately, cycle life was degraded.

High Coercivity CoO YIG Bilayers

For high density magneto-optical recording, a large component of the magnetic field perpendicular to the film is required along with significant coercivities. Yttrium iron garnet (YIG) films, which have low coercivities and their easy axis of magnetization in the plane of the film, would therefore appear to be poor candidates for such applications. However, A. C. Rastogi et al. (*Appl. Phys. Lett.*, **78**, [12], 1709-11, (2001)) have produced high values of the out-of-plane coercivity and saturation magnetization by the simple process of depositing a CoO on top of the YIG film. YIG films of $\sim 5000\text{\AA}$ were covered with 200-4600 \AA layers of CoO. The magnetic properties of the films, which were grown on a hot substrate, showed a significant dependence on the growth rate of the CoO film with the properties of films grown at high rates being significantly poorer than those where the CoO film was grown at low rates. If the films were annealed at the growth temperature after deposition, this difference was largely eliminated. As a result, the authors conclude that the time the CoO interacts with the YIG film is crucial. They attribute the enhanced properties to a Co-Rich YIG interface layer, which results in strong uniaxial anisotropy due to the interface and stress.

Sincerely,



R. W. McCallum
Director of RIC