

Rare-earth Information Center

Insight

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Combinatorial Chemistry

In the late 1960's and early 1970's, researchers at the RCA Laboratories set up a deposition system to codeposit two or three elements. The geometry of the system was such that films of differing compositions could be simultaneously deposited. The system was used to study A15 superconductors that with transition temperatures in the >20 K region were the high temperature superconductors of the time. While the system produced arrays of samples, they still had to be individually analyzed. Recently, this idea has been revisited. Now, computer controlled deposition systems, which have the ability to change masks between sequentially deposited layers, allow control of composition and small individual sample size. Libraries, with thousands of samples, can be prepared on a single 3-inch diameter substrate. An article by R. Dagani {*C&EN*, 77, [10] 51-60 (1999)} reviews the progress in this area since 1995. Areas of interest to the rare earth community, where this approach has been applied, include high temperature superconductors, magnetoresistive materials, phosphors, ferroelectric and dielectric materials. Phosphors are relatively easy to evaluate as the color and intensity of light can be measured using instruments that are available or at least can be assembled from commercial modules. For large libraries, measurements that require contact with the sample are difficult. Electrical properties are now being measured at microwave frequencies using a tool dubbed "a scanning evanescent microwave microscope". X-ray microbeams available at synchrotron radiation facilities serve as x-ray microprobes to characterize 2 mm^2 samples. IR thermography is used to detect the exothermic reactions on active catalysts. Materials synthesis is no longer a limiting factor in these studies, but rather the problem of how you characterize thousands of tiny samples in a rapid automated fashion.

Automotive Catalysts

A major market for rare earth materials is the automotive catalyst. Driven by increasingly stringent emissions requirements, the catalytic converters on cars and trucks have become increasingly complex. An article by M. Jacoby {*C&EN*, 77, [4] 36-44 (1999)} discusses the major factors for automotive applications. Unlike catalysts in industrial chemical processes, automotive catalytic converters do not operate in a steady state environment. In fact, the major problem facing manufacturers is the emission during cold starts. Current converters do not become effective until their temperature reaches 300°C . Exhaust emissions are measured in a cycle that includes cold starts, and it is during these starts that the majority of emissions occur. Designs that place the converter close to the exhaust manifold, rather than under the passenger compartment, reach temperature faster, but must operate at higher temperatures. At these temperatures, which may exceed 1000°C , ceria in the catalyst sinters reduces its surface area and, hence, effectiveness. Ceria (cerium oxide) serves an

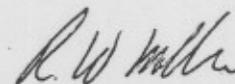
interesting function in the converter. For the converter to work efficiently, the oxygen level must be closely controlled. While modern engine control systems do a relatively good job of maintaining a constant level, short term fluctuations between oxygen rich and oxygen deficient conditions occur in the converter. Under oxidizing conditions, the ceria oxidizes as the Ce becomes tetravalent. Under reducing conditions, the Ce reverts to trivalent releasing oxygen. Thus, the ceria serves as a ballast, which controls fluctuations in the oxygen partial pressure. Unfortunately, high surface area materials are unstable against sintering at elevated temperatures. Pure ceria sinters above 850°C. Zirconia is used to stabilize the ceria, which raises its operating temperature, but higher temperatures are still desirable.

90° Magneto-optical Polar Kerr Effect.

When light reflects from a ferromagnetic material, the polarization of the light is rotated by a small amount. Magneto-optical recording uses this rotation to detect the direction of magnetization of domains in the recording media. Clearly, the larger the rotation, the higher the signal to noise ratio in the recording. CeSb has been shown to exhibit a polar Kerr rotation of 90°; but, unfortunately, this requires the material be at ~1.5K and a magnetic field of 5T. This makes the storage drive a bit bulky for your average laptop computer. Y. A. Uspenskii et al. {*Appl. Phys. Lett.*, 74, [11] 1618-20 (1999)} have examined the fundamental limitations of Kerr rotation. As is common in nature, there are two conflicting requirements in this case on the dielectric tensor. Uspenskii et al. have considered the properties of a theoretical layered material made up of magnetic semiconductor/metal bilayers. For these multilayers, if the periodicity of the multilayer is much less than the wavelength of light, the effective dielectric tensor can be tailored in such away as to satisfy the requirements for 90° Kerr rotation. The number of combinations on magnetic semiconductor/metal structures available greatly increases the chances of finding a useful material, and the authors make several suggestions.

Photoluminescence Superlattices

The Er³⁺ ion has an optical transition that emits at a wavelength of 1.54 μm that is highly desirable for fiber optic applications. Since Si processing is the basis for the vast majority of our microelectronics, a Si:Er light emitting diode would be highly desirable. While such a diode has been demonstrated at room temperature, the efficiency of these diodes is very low because of nonradiative decay of the excited state. The problem is that in a narrow band gap material, energy may be transferred to the electrons by phonons. The band gap of Si can be engineered by reducing the dimensions, and efficient Er³⁺ luminescence has been demonstrated in Er-doped silicon rich silicon oxide that consists of Si nanocrystals in a SiO₂ matrix. In this situation the Er may be either in the Si or the SiO₂. J. H. Shin et al. {*Appl. Phys. Lett.*, 74, [11], 1573-5 (1999)} have prepared Er-doped Si/SiO₂ superlattices. It was found that doping either layer with Er resulted in a substantial decrease in the nonradiative decay compared to pure Si. Doping the SiO₂ layer resulted in much more intense luminescence than doping the Si.



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