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On the optical properties of gadolinium hydride systems

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Abstract

Thin Pd-capped rare-earth metallic films switch reversibly from their initial reflecting state (metal phase) to visually transparent state (insulator or semiconductor phase) when exposed to gaseous hydrogen. Palladium-capped Gadolinium films were prepared by rf-sputtering technique to produce very homogeneous and high-quality metal films as indicated by X-ray and scanning electron microscope analysis. After preparation, a separate cell and experimental setup are used that allow both optical and electrical measurements of the films during hydrogen loading simultaneously. The thickness dependence of the switching properties of Gadolinium hydride system is presented. The complex refractive index, the thickness, as well as the energy gap, of GdH_3 films (transparent phase) were calculated from transmission data by use of a new technique based on "Forouhi–Bloomer" model, and by a recent "pointwise unconstrained minimization approach" method.
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1. Introduction

Static state-of-the-art glazings for architectural window applications are reaching their physical limits when it comes to the improvement of the energy efficiency of the building. A subsequent possible step towards improved glazing energy efficiency may be the use of switchable or smart windows.

A remarkable discovery by Huilberts et al. [1] initiated interest in metal hydride optical switching smart windows. When the hydrogen content in palladium-capped (5–20 nm) yttrium and lanthanum films (200–500 nm) was varied with H_2 pressure, they switched reversibly from opaque metal at lower hydrogen content to transparent semiconductor at high hydrogen content. The Pd cap prevents oxidation and catalyzes hydrogen absorption at room temperature. Recently, much progress has been made in the development of practical optical devices by the incorporation of metal hydrides [2].

In this paper, we study the switching properties of the gadolinium hydride system in the wavelength range from 300 nm to 2500 nm at room temperature and determine the optical constants and the optical energy gap. The optical properties of relatively thick films can be obtained from transmission spectra quite accurately with the so-called envelope method [3,4]. However, the main shortcoming of such method is that it cannot be used in the case of transmittance that does not display interference fringes. In the present study, the fringes are not satisfactory (they show only two broad maxima). So we report here two approaches—a pointwise unconstrained minimization approach, PUMA [5–8], that proved to be very useful to circumvent the difficulty of a lacking fringe pattern, and we suggest a simple adapted technique to calculate the spectral optical constants of GdH_3 films in the fundamental absorption band gap by using Forouhi–Bloomer formalism (FB) [9,10].

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2. Experimental details

2.1. Film production and characterization

The Gd films of various thickness (d=100–500 nm) are deposited onto glass and silicon substrates by rf-sputtering in Ar (2×10^{-5} Pa base pressure, and 4.5 Pa process pressure) at room temperature. The layer thickness is determined by an oscillating quartz microbalance. Before exposing the films to the ambient, they are covered with a thin palladium cap layer with a thickness of about 10–15 nm. The Pd films were grown at room temperature to prevent the alloy formation with the gadolinium. To avoid the plastic deformation of the Gd films by the loading with hydrogen, the preparation conditions were optimized. As demonstrated in Fig. 1, the produced Gd films show a strong preferential orientation.

Room-temperature X-ray diffraction measurements (XRD) were performed by the use of the symmetric geometry ($\theta-2\theta$) over a range of 10–120°, with a step of 0.02° for (2θ) and a fixed count time of 10 s for each step. Scanning electron microscope (SEM) pictures were received by use of a field emission microscope. The accelerating voltage was 10 kV.

2.2. Measurements of optical properties

In order to measure the optical properties of GdH_3 in equilibrium with hydrogen at various pressures, we develop an experimental setup consisting of two parts: (i) an optical gas-loading cell, and (ii) a gas-loading chamber (for higher pressure). The sample can be exposed to controlled hydrogen gas atmosphere during the measurements via two tubes connected to a vacuum pump and a hydrogen gas cylinder. The gas-loading cell is designed for vacuum but works also reliably up to a few bars of hydrogen pressure. The cell is also equipped with an electrical feed-through with several pins to permit measurements of the resistivity of a sample during hydrogenation. Since Gd is a metal and GdH_3 is a semiconductor, the time evolution of hydrogenation can be pursued in real time by monitoring the change of the resistivity. This allows us to optimize the hydrogen pressure (starting at low pressures and increasing it stepwise to a few bar).

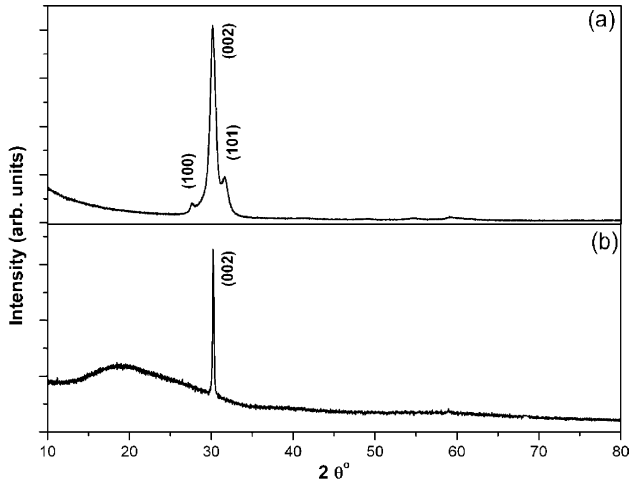

Fig. 1. XRD patterns of Gd (500 nm) films on (a) Si (111) and (b) glass, showing a strong preferential orientation.

3. Results and discussion

3.1. XRD and SEM patterns of Gd films

Fig. 1 shows X-ray diffraction patterns (XRD) of Gd films on Si (111) and on glass. In Fig. 1a, the intensity of the middle peak (2θ=30.135°) is considerably larger than the other two small peaks. The peak corresponds to the hexagonal Gd (002) plane. The peaks near the 002 are the 100 (2θ=27.77°) and 101 (2θ=31.41°), respectively. The other reflections, e.g., at 2θ=49.39°, and 59.27° are very small.

In Fig. 1b, only the (002) peak at 2θ=30.135° can be observed. One can say that, the intensity of (002) reflection is much higher than all other reflections in comparison with the results for isotropical distributed powder. These results illustrate that there are good crystalline structures and a strong preferential orientation along the (002) axis in the Gd films on both substrates.

Figs. 2 and 3 show the surface morphology of Gd films on glass covered with a thin Pd layer before and after hydrogenation, respectively. The scanning electron microscope (SEM) picture (Fig. 2) shows that the sample exhibits a smooth surface. There are grain-like structures in the films. Most of them have the same size with an average diameter of d=30 nm and a typical hexagonal shape. Fig. 3 shows nearly no difference in comparison with Fig. 2, which indicates that there is no evidence of any plastic deformation, if the sample is loaded with hydrogen [11]. As shown by Pedersen et al. [12] Gd can be switched reversibly between well-defined stress states of the dihydride and trihydride phases even though the stress involved is of the order of several gigapascals. Dornheim et al. [13] explained the relatively low net stress as the result of the fact that textured polycrystalline thin films benefit from a small in-plane tensile stress component. During the transformation from the dihydride to the trihydride phase, mostly the distance between the closed-packed planes increases. Since the films have a texture such that these planes are parallel to the substrate, most stress is relieved by an expansion of the film thickness.

3.2. Optical switching

Typical switching curves for Gd (200 nm and 400 nm thickness) films are shown in Fig. 4, the transmission at fixed wavelength (λ=500 nm) was measured as a function of time, i.e., the hydrogen concentration. At low hydrogen concentration, the transmission was nearly zero, ~1%, and

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