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Steric effects on the metal–insulator (mirror–transparent) transition in YH_x

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Abstract

In order to further study the role of structure on the metal–insulator (mirror–transparent) transition in yttrium-hydride (YH_x) films [Nature 380 (1996) 231], we have substituted scandium (Sc) into the Y lattice. This substitution shows the effect of reduction of unit cell size on this transition. Electron-beam evaporation was used to deposit 100-nm-thick films of $Y_{1-z}Sc_z$ alloys for $0 \leq z \leq 1$. The films are capped with a 10 nm overlayer of palladium (Pd) to prevent oxidation and to catalyze hydrogen absorption. Fully hydrogenated alloys with $z \leq 0.10$ exhibit optical transmittance of up to 0.14 in agreement with the literature [J. Alloys. Comp. 253–254 (1997) 41]. This transmittance decreases by a factor of 3–12 for scandium concentrations of 20% and greater. The cell volume for $z \geq 0.20$ is consistent with rare-earth elements that do not form trihydrides. Details of sample synthesis, lattice structure, and optical transmission spectra are discussed.

Keywords: Metal hydrides; Switchable mirror; Yttrium scandium alloys; Metal–insulator transition; Optical properties

PACS: 61.66.Dk; 71.30.+h; 78.66.-w; 73.61.-r

1. Introduction

Thin films of yttrium (Y) and lanthanum (La) have been shown to undergo quick and reversible transitions from a metallic-mirror to a transparent-insulator upon absorption of hydrogen. The transition occurs between the dihydride and trihydride phases. Local density approximation (LDA) calculations fail to reproduce the optical bandgap observed experimentally [3]. Parameter-free GW calculations result in a fundamental gap of 1 eV; however, an optical gap of nearly 2.9 eV can be predicted when electric dipole interactions are considered [4,5]. Further photoemission spectroscopy experiments are required to verify the calculated fundamental gap. In addition, some structural studies on alloys of La–Y have been reported by van Gogh et al. [6] and continue to be pursued in both the LaH_x and YH_x systems [7–12]. Yttrium undergoes a structural phase transition from a hexagonal lattice in the pure metal phase to fcc in the dihydride phase and again to a hexagonal structure (larger than the pure metal lattice) in the trihydride phase. Lanthanum, on the other hand, remains cubic throughout the dihydride and trihydride phases where the optical transition occurs. The metal–insulator transition is, therefore, not mediated by evident structural phase transitions because such transitions do not occur in either of these systems. It has been observed that trihydride-forming alloys (e.g. $La_{1-z}Y_z$) undergo different switching mechanisms than combinations of trihydride- and dihydride-forming metals (e.g. $Mg_{0.50}Y_{0.50}$) that phase separate [13].

In order to further understand the mechanisms causing the metallic-mirror to transparent-insulator transition, we have substituted the smaller atom Sc for Y. Scandium is unable to form a trihydride due to its smaller unit cell that cannot incorporate octahedral hydrogen. For this reason, Sc does not undergo a phase transition from a metallic-mirror to a transparent-insulator. Here we report that optical transmission spectroscopy for this alloy series reveals that the optical gap seen in $YH_{3-\delta}$ is strongly suppressed for concentrations of 20% and greater scandium. For alloys with greater than twenty percent Sc, dihydride transmittance is observed as in the YH_x and $La_{1-z}Y_zH_x$ systems [1,13]. In addition, optical transmittance of these fully loaded films behaves more dihydride-like with increasing Sc concentration.

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2. Experimental

$Y_{1-z}Sc_z$ alloy rods were made by arc melting stoichiometric mixtures of 99.9% Y and Sc. Arc melting was performed in an inert-gas, zirconium-gettered chamber and verified by pre and post mass measurements. $Y_{1-z}Sc_z$ polycrystalline films of 100 nm thickness (monitored using calibrated crystal oscillators during evaporation) were electron-beam evaporated onto 1×1 cm^2 glass substrates at room temperature in a vacuum of 10^{-8} Torr. A capping layer of 10 nm palladium (Pd) was deposited over the alloy films to prevent oxidation and to catalyze hydrogen gas (H_2) dissociation and absorption into the rare-earth layer.

The transition from yttrium dihydride to trihydride occurs in seconds at 1 atmosphere of hydrogen. In order to study the transition more closely, films were loaded with ultra-high purity hydrogen using an MKS Baratron partial-pressure, mass-flow-controlled manifold. The controller is capable of mixing 0.1% H_2 in argon which slows the YH_2 to YH_3 transition to approximately 1 h. The gas flow was directed through a reflection grating optical transmission spectrometer ($1.29\leq\hbar\omega\leq3.65$ eV). A background intensity spectrum, I_0, was measured prior to each hydrogen loading, and the transmittance calculated as

$$T(\omega)=\frac{I_T(\omega)}{I_0(\omega)}, \tag{1}$$

where $I_T(\omega)$ are the spectra measured during hydrogen loading. Simultaneous in-line, 4-contact, electrical resistivity measurements are made using a 1–2 mm sectioned region of the film outside of the spectrometer beam. Electrical transport properties will be reported after future temperature-dependent measurements. Hydrogen concentration was not measured in this study. The term *fully loaded* is used to denote hydrogen saturation at 1 atm H_2 and room temperature.

The crystal structure of the as-deposited films was characterized by $\theta-2\theta$ X-ray diffraction (XRD) scans using a Philips diffractometer. The films were scanned at 0.05° increments for 3–7 s integration times over the angular range $10°\leq2\theta\leq70°$. The pure metals have hexagonal (hcp) lattice structure, while ScH, ScH_2, and YH_2 are cubic (fcc) [14].

3. Results and discussion

In Fig. 1, the alloy composition dependence of the lattice constants a and c is shown. The trend is a linear decrease in both lattice parameters with increasing z. The resulting total decrease in cell volume ($V_{\mathrm{cell}}=3\sqrt{3}a^2c/2$) is ~38%. For $z\leq0.20$, we find larger cell parameters than expected. This is due to hydrogen incorporation during evaporation. By linearly fitting literature values of a and c of YH_x for $0\leq x\leq0.3$, we calculate an initial hydrogen concentration of $x=0.30\pm0.05$. However, when $z>0.20$, the resulting lattice is smaller than expected possibly due to presence of the cubic ScH phase. The Sc hcp (100) and (002) reflections have close angular correspondence to the fcc (111) and (100) ones, respectively. Because the grains are small, the width of XRD peaks is on the order of separation of these two peaks (1–2°) which may cause unidentifiable overlap of the two phases. For example, observed angular widths of ~1° correspond to a particle size of 0.1 μm. Preliminary measurements show grain sizes do not vary significantly after hydrogen loading.

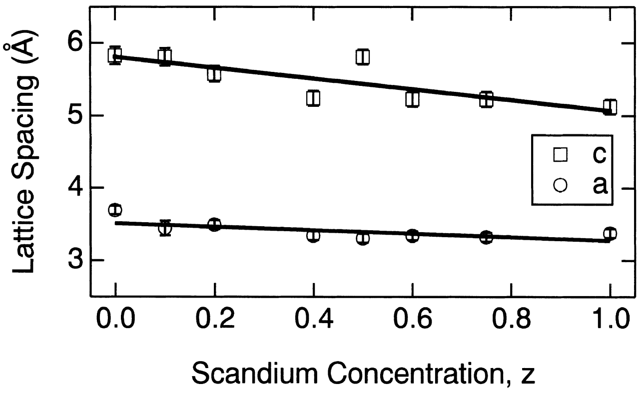

Fig. 1. Compositional dependence of the cell lattice parameters a and c for the $Y_{1-z}Sc_z$ system in as-deposited films.

Optical transmittance measurements for $z\leq0.10$ show dramatic optical switching properties commensurate with previous results for YH_x [2]. Fig. 2 exhibits optical spectra (uncorrected for the Pd over layer) as a function of hydrogen loading time for the alloys Y, $Y_{0.90}Sc_{0.10}$, and $Y_{0.80}Sc_{0.20}$. The three spectra are set to approximately the same vertical scale. The maximum transmittance for pure Y and $Y_{0.90}Sc_{0.10}$ (Figs. 2a and 2b, respectively) is approximately 0.10. However, we find that for $z\geq0.20$ (Fig. 2c) the trihydride transmittance is heavily suppressed. This is more apparent if one looks at the change in transmittance from the dihydride state. The films are allowed to desorb hydrogen in flowing argon or in air for approximately 24 h after the initial hydrogen loading; the resulting material is a stable phase very near the dihydride state ($Y_{1-z}Sc_zH_{2\pm\delta}$). The spectra in Fig. 3 verify this state with the well known dihydride transmission peak seen in the initial spectrum near $\hbar\omega=1.8$ eV [1,2]. It can be seen in Fig. 3 that the transmittance increase for Y (Fig. 3a) due to loading between YH_2 and YH_3 is a factor of 3 or greater than that for $Y_{0.80}Sc_{0.20}$ (Fig. 3b) and a factor of 12 greater than for Sc (Fig. 3c). Other alloys with $z\geq0.20$ exhibit similar transmittance spectra to those of Figs. 3b and 3c. We compare the transmittance at 1.51 eV for unloaded and fully loaded films of various alloys in Fig. 4. This energy is the mean dihydride maximum for all alloys. For alloys with $z\geq0.15$, the transmittance is largely suppressed and behaves as a dihydride with maximum transmittance at

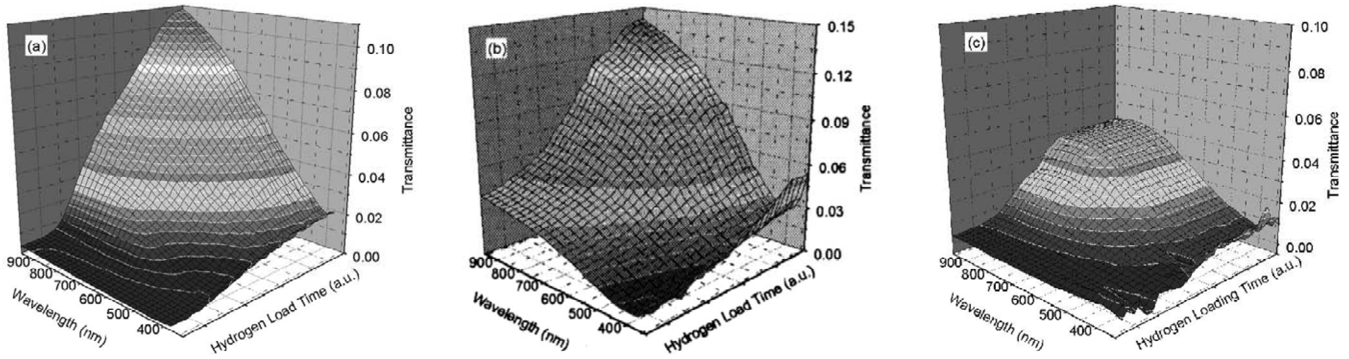

Fig. 2. Optical transmittance spectra as a function of hydrogen loading time (in arbitrary units) starting from as-deposited films of (a) Y, (b) $Y_{0.90}Sc_{0.10}$, and (c) $Y_{0.80}Sc_{0.20}$. The scale is the same for all three figures; the loss in optical switching capability is evident for $z=0.20$. The full loading time scale is typically 1–2 h.

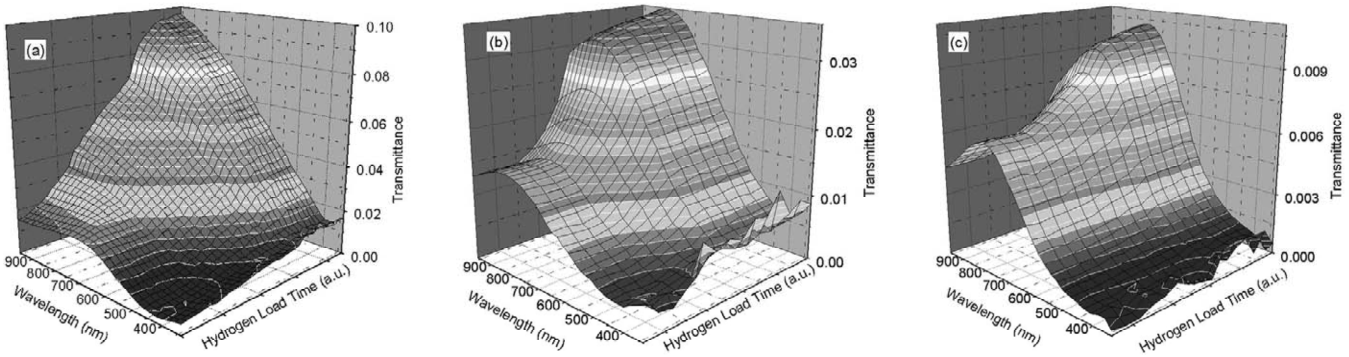

Fig. 3. Optical transmittance spectra as a function of hydrogen loading time (in arbitrary units) starting from unloaded films (near $x=2$) of (a) YH_x. (b) $Y_{0.80}Sc_{0.20}H_x$, and (c) ScH_x.

wavelengths less than 960 nm ($\hbar\omega > 1.29$ eV). When $z \geq 0.15$, the transmittance decreases rather monotonically with the exception of $z = 0.50$, possibly due to atomic disorder or phase separation. The difference between loaded and unloaded transmittance for Y is $\Delta T(\omega)=0.067$, where for $Y_{0.80}Sc_{0.20}$ $\Delta T(\omega)=0.025$ and Sc $\Delta T(\omega)=0.0056$. It is not surprising that $z=0.15$ is a trihydride limiting composition. At this composition, each octahedral hydrogen may have at least one Sc nearest neighbor, likely reducing the octahedral filling needed for optical switching. To make more evident the suppression of optical transmittance, the spectra of fully loaded films for various $Y_{1-z}Sc_z$ alloys are displayed in Fig. 5a and the dihydride spectra are shown in Fig. 5b. Similar to what is seen for $La_{1-z}Y_z$ alloys, there is significant quenching of this transparency window. Comparing the energy of maximum transmittance in Fig. 6, one sees that the behavior of the fully loaded films approaches that of the unloaded ($x \sim 2$) films for increasing z. This convergence occurs primarily above $z = 0.15$.

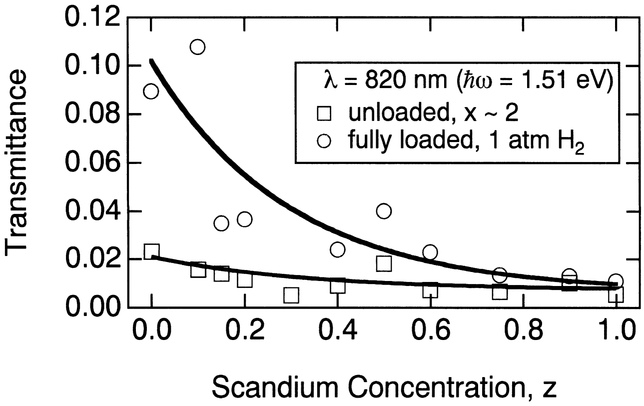

Fig. 4. Transmittance at $\hbar\omega=1.51$ eV as a function of Sc concentration, z. The amount of transmittance for fully loaded films approaches that of unloaded films (near $x=2$) with increasing z indicating a loss of octahedral sites for trihydride formation. The lines are shown to guide the eye. The scatter in the data may be due to atomic disorder effects.

Large disorder effects due to alloying have been found in the electrical transport properties of $La_{1-z}Y_z$ [6]. The change in optical properties of the $Y_{1-z}Sc_z$ system is probably due to reduction of the unit cell volume [13]. Up to the dihydride phase, hydrogen in yttrium and lanthanum primarily fills the tetrahedral sites where it is highly localized. Typically up to $x = 2$ only a few atomic percent of hydrogen locate in octahedral sites, which have higher mobility than tetrahedral sites [15]. Because the transition occurs beyond the dihydride phase when octahedral sites become significantly occupied, it is assumed that this filling is responsible for the optical transition. The quench-

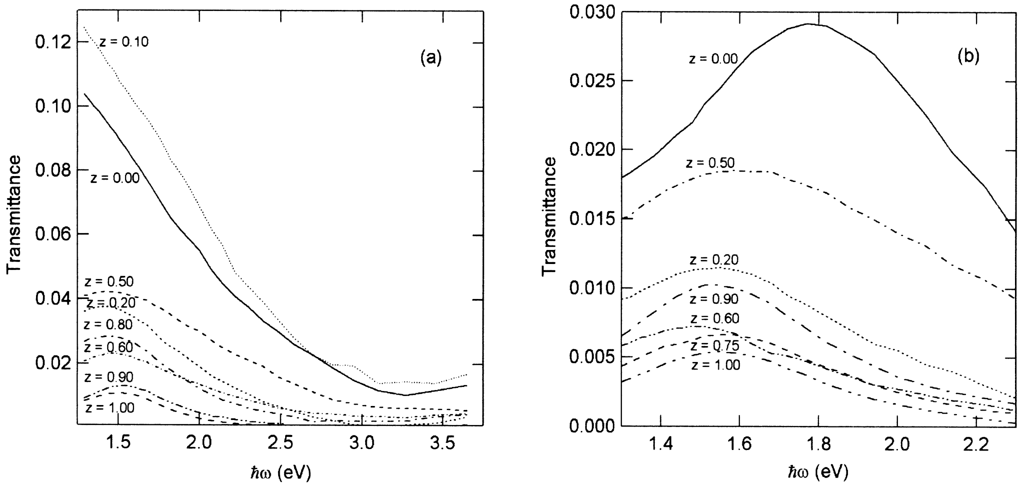

Fig. 5. (a) Fully hydrogen loaded and (b) unloaded (near $x=2$) film optical spectra showing transmittance maxima dependence on alloy composition.

ing of the optical transmittance is most likely due to the sudden loss of available octahedral sites caused by the reduction of lattice dimensions. It is interesting to note that the unit cell volume we measure for $Y_{0.80}Sc_{0.20}$ (176.63 Å^3) is equal to the unit cell volume of lutetium ($V_{Lu}=$ 176.64 Å^3), the largest known rare-earth element that does not form a trihydride.

4. Conclusions

The sudden loss of octahedral site occupancy as a function of Sc concentration in $Y_{1-z}Sc_zH_x$ causes the suppression of the optical switching properties seen in metal-trihydrides. Substitution of Sc for Y indicates that there is a minimum cell volume for trihydride forming rare-earth metals around 177 Å^3. Further study of the alloy phase diagram for the transition region $0.10<z<0.20$ is underway. In addition it will be interesting to characterize the switching processes, i.e. whether the mechanism is similar to trihydride-forming alloys or like that of compounds of one trihydride- and one dihydride-forming metal. We intend to investigate this and other possibilities in the future.

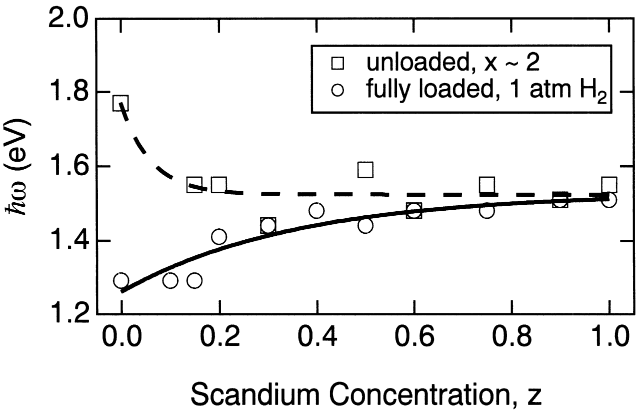

Fig. 6. Energy of maximum transmittance (for the range $1.29\leq\hbar\omega\leq3.65$ eV) as a function of Sc concentration, z. The transparency energy of the fully loaded films approaches that of the unloaded films (near $x=2$) as z increases. The lines are shown to guide the eye. The scatter in the data may be due to atomic disorder effects.

Acknowledgements

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