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Research Article

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Study of Surface Morphology of Palladium Overlayer on Switchable Samarium Hydride Thin Films

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Abstract

A reversible metal-to-semiconductor transition was attained in samarium thin films covered with several thicknesses of palladium (Pd) coating during *in-situ* hydrogen loading by applying normal pressure of hydrogen gas at ambient temperature. The electrical change is followed by extreme variations in optical properties in the visible range, where the metallic gray color of samarium thin films switched to golden greenish tinge transparent films upon hydrogen absorption. The thickness of Pd overlayer shows a decisive role in this switching phenomena and we have studied the effect of Pd overlayer thickness using electrical, optical and scanning electron microscopy (SEM) measurements. Electrical measurements reveal that Pd overlayer on samarium films is discontinuous only for thicknesses of less than 3 nm. SEM studies indicate significant changes in surface morphology of Pd overlayer as a function of its thicknesses. The micrographs reveal a gradual variation in the average size of the spherical crystallites with increasing thickness of Pd overlayer. Cracking of Pd grains has been observed on hydrogenation if the underlying samarium film thickness is >100 nm. Results of electrical and optical changes upon hydrogenation/dehydrogenation are presented.

Keywords

Metal hydrides, Palladium, Switching, Surface morphology, Thin film

Introduction

There has been a great interest of scientific community in rare earth metal hydrides. These materials have been investigated since several decades due to their application in hydrogen sensing [1]. Most of the rare earth metals form dihydrides with fluorite type structure except europium and ytterbium (that has orthorhombic dihydrides). Further these metal also easily absorb hydrogen to form trihydrides, whereas light rare earths (La, Ce, Pr, and Nd) form trihydrides, with no change in structure, by merely filling octahedral sites with hydrogen atoms. The heavy rare earth (Sm, Tm, Tb, Gd, Dy, Lu, Ho, and Er) hydrides transform to a hexagonal structure before reaching the composition REH3 though initially filling the octahedral sites of these heavy rare-earths with hydrogen atoms [2]. Due to the similarity of their hydriding characteristics, scandium and yttrium are treated along with the rare-earth elements.

The complete study of electrical and optical properties of rare earth metal bulk samples was long hindered by the fact that rare earth in its trihydride form fell apart into powders. This obstacle might be solved by making thin films of these materials as was reported by Huiberts et al. [3]. Typically, 500 nm thick films of yttrium were vacuum evaporated onto transparent insulating substrates and then covered with a thin (5 - 20 nm) Pd overlayer.

The Pd overlayer acts as catalyst to break hydrogen molecule into atomic form and further it gives shield to the underneath layer against oxidation. It also improves the hydrogen sticking coefficient during hydrogen absorption and desorption. Hydrogen diffuses into the rare earth film both by vertical and lateral diffusion though the rate of lateral diffusion in Pd covered films is much smaller than that of the vertical diffusion. The stoichiometric YH_3 was possible to produce by making a thin film of 500 nm and capped it with Pd overlayer. The metal to insulator transition was observed when Pd capped yttrium thin film exposed to hydrogen. Similar transitions were reported in thin LaHx films [4]. Due to their metal to insulator transition, these rare earth metal thin film has found applications in hydrogen sensor, smart windows, and electrochromic devices. These wide range of applications has triggered a large-scale investigation in this type of thin films [5-7]. Hydrogenation of these so called "switchable mirrors" can be accomplished either by gas phase hydrogen loading or by electrochemical hydrogen loading in a suitable electrolyte solution [8-11].

While going through the literature, it was found that a very little attention was given to samarium. Hence this lack of information in literature about samarium thin films makes a great scope of the present study. We have, therefore, selected samarium metal for the current study.

Experimentation

The physical vapor deposition i.e., resistive heating evaporation method was used to deposit the thin films in high vacuum. The materials were obtained from STREM, USA with 99.9% purity. The glass slides were used as substrate to deposit thin films. The glass substrate was cleaned by rubbing soapy cotton followed by ultrasonication several time in DI water and then acetone. The *in-situ* electrical measurement was done when Pd capped samarium thin were exposed to hydrogen gas. For that, aluminum contact was deposited on the two edges (each 2 mm x 2 mm) of these glass substrates. The electrical contact was made using copper wire on to the aluminum contact. The samarium and Pd was kept into two tungsten boat in resistive heating evaporation system. Both boats were placed proportionally with respect to the glass substrate kept at a distance of 150 mm from the boats. A pre-calibrated quartz crystal was fixed at same height as substrate that was needed to control the deposition rate and monitor the thickness of the deposited thin films. The rate of deposition was kept constant at 1.0 nm/s. A high vacuum of about 2.6 x 10^{-4} Pa was created in the chamber before evaporation of samarium and Pd. A mechanical shutter was used to fully cover one of the boats when other was used for evaporation. The thin film of samarium was deposited on substrate followed by the deposition of Pd overlayer. The deposited thin films were then taken immediately to confirm the thickness using a surface profiler (Talystep-Tayler-Hobson, UK). The Pd capped samarium thin film then again kept into the chamber for *in-situ* hydrogen loading. Hydrogen gas with purity of 99.99%, Indian Oxygen was used for this purpose. The thin film sample were then exposed to a constant hydrogen gas pressure of PH_2 = 1.105 x 10^5 Pa. The hydrogen gas introduced in to the vacuum chamber through one of the feedthrough using a needle valve in a controlled way. Unloading of hydrogen from sample was done by eliminating a H_2 gas by utilizing the rotary pump. The two-probe method was used to monitor the change in the resistance *in-situ* as a function of time using a programmable Keithley electrometer (Model-617).

Ultraviolet-Visible spectrophotometer (Hitachi-330) in the range of 350 - 850 nm was used to investigate the optical properties of the deposited thin film. The changes in surface morphology of the films as function of overlayer thickness was studied by using SEM (LEO 435VP).

Results and Discussion

Table 1 lists the initial (Ri) and saturation (Rs) value of resistance for three identically deposited samarium films of thickness of 55.0 nm each, but coated with Pd overlayers of dissimilar thickness of 10, 6, and 2.5 nm. It is clear that the magnitude of N defined as the ratio Rs/Ri is maximum when the Pd thickness is 2.5 nm. To examine this behavior, we examined the surface morphology of these films.

Figure 1a and figure 1b show the SEM images of two films with Pd thicknesses of 10 nm and 2.5 nm coated on samarium films of thickness 55 nm. Pd films on samarium deposit via the island growth. In figure 1a we can see the discontinuous distribution of Pd spherical crystallites, the average size of the crystallites being about 0.5 μm. The average size of these

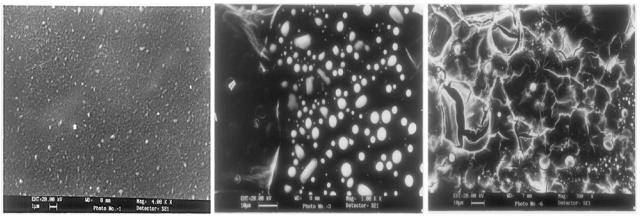

Figure 1: Surface morphology on hydrogenation of samarium hydride film (thickness 55 nm) covered with Pd overlayer of **(a)** thickness 2.5 nm, **(b)** thickness 10 nm, and **(c)** thickness 10 nm.

Table 1: Change in resistance, response, and recovery time of Pd capped samarium films on hydrogenation.

Pd thickness	Initial value of resistance (Ri)	Final value of resistance (Rs)	Ratio	Response time (ts)	Recovery time (tr)
nm	ohm	ohm	N = Rs/Ri	s	s
10	50	550	11	17	677
6	52	745	14.3	25	781
2.5	64	20,000	312.5	1680	2000

crystallites is about 0.5 μm for a Pd film of thickness 10 nm. It is clear that at very low thickness ~2.5 nm, the Pd film on the surface of samarium films is discontinuous. With increase in thickness of Pd overlayer, the islands start to coalesce and at a particular thickness, the Pd film becomes continuous.

The reason for the different values of N in table 1. can thus be explained as follows. When the Pd layer thickness is 2.5 nm, the Pd film is electrically discontinuous and therefore the resistance measured is that of $SmH_{3-\delta}$. In the other two cases, however we are actually measuring the resistance of a parallel sequence of SmH_x and PdH_x (it is to be noted that PdH_x is also metallic). Since the amount of monoatomic hydrogen increases with the increase in Pd surface area the decreased response time ts (the response time ts normally taken as the 90% of the saturation value) and recovery time tr (recovery time tr is taken as the resistance to fall up to 30% of its saturation value of the resistance of SmH_X films on unloading) with increase in Pd overlayer thickness is on expected lines. Figure 1c shows the surface morphology for a samarium film (thickness 80 nm) coated with 10 nm of Pd overlayer. It indicates the cracking of samarium films. We have found cracks if the samarium film thickness is >60 nm, irrespective of the Pd layer thickness. Increase in samarium thickness beyond 60 nm leads to a more drastic effect. The stresses built up due to H-H interaction are so large that they lead to peeling off the films. This is because an increase in samarium thickness leads to an increased H-H repulsive interaction and a decreased effect of the clamping of the substrate to film.

In set of figure 2 shows change in resistance with time on exposure of two samarium films of thickness of 55 nm each and capped with two different thickness of Pd overlayers of 6 and 10 nm to hydrogen gas. Depending upon the thickness of Pd overlayer, a minimum resistance of film attained within 3 to 5 s of contact to hydrogen. This lowest state of resistance is a confirmation of the achieving dihydride stage. Further exposure to hydrogen atmosphere leads to a sharp elevation in resistance followed by saturation in resistance, depending on the thickness of Pd overlayer. This saturation state normally correspond to the approximately trihydride state $SmH_{3-\delta}$. The saturation condition attainment is denoted by point A in all of the curves in figure 2 and the part AB correspond to the almost saturated value of resistance. Figure 3 shows the change in resistance with time for a 2.5 nm thick Pd overlayer, Since both the response and the recovery times in this case were found to be very high therefore such thicknesses was not used to study transition between metal and insulator. As stated prior, the hydrogen desorption was done by evacuating the chamber utilizing a rotary pump. In figure 2, the part B to C denotes the reduction in resistance on desorption of hydrogen from the samples. Successive absorption of hydrogen (C to D) and desorption of hydrogen (D to E) phases are also illustrated in figure 2. The tr are found to be more than the corresponding ts. Comparable the ts, the tr also depend on Pd cap layer thickness and found to rises with reduction in thickness of Pd overlayer which clearly suggest that the switching behavior among the di- and tri-hydride phase is better in the sample that has higher thickness of Pd overlayer [11].

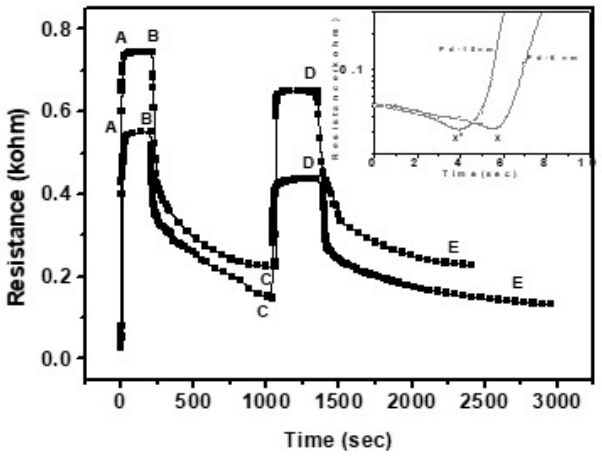

Figure 2: Change in resistance on hydrogen absorption and desorption (PH_2 = 1.01 x 10^5 Pa) of samarium film (55 nm) covered with different thickness of Pd films **(a)** 6 nm and **(b)** 10 nm as a function of time at room temperature. Inset (X – highly conducting state).

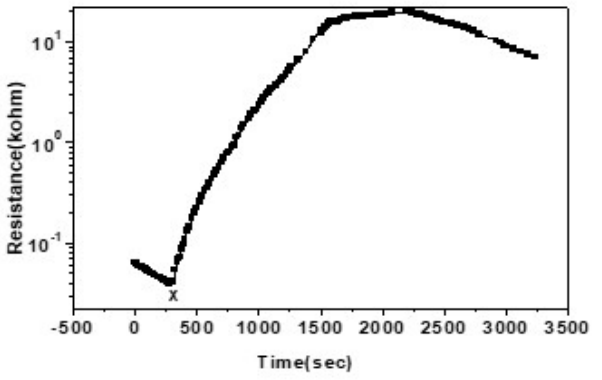

Figure 3: Resistance change during hydrogen absorption and desorption (PH_2 = 1.0 x 10^5 Pa) for 55 nm samarium film coated with 2.5 nm Pd film at room temperature. X – highly conducting state.

It might be noted that hydrogen if introduced in chamber at a very high rate, leads to cracking and peeling off of samarium film even when samarium thickness is < 6 nm. This is because the more quick is the hydrogen absorption, the larger is the degree of cracking. Similar observations have been reported for bulk hydrides [12]. In this study, the problem of cracking of thin film on loading was solved by introducing hydrogen at a controlled rate (25 ml/min) with a needle valve into the chamber. The sufficiently low absorption rate of hydrogen into the films result in relieving of the stress induced due to lattice distortion on absorption of hydrogen by self-annealing ability of the metal. It is to be noted that the heat is released during the reaction between samarium and hydrogen, it is called a exothermic process.

As observed visually, the color of fully transparent glass chamber was converted to metallic gray on samarium evaporation in reflection mode and looks almost opaque in transmittance mode. After depositing Pd overlayer and subsequent hydrogenation, the color of samarium films saturated with hydrogen converted to a golden greenish

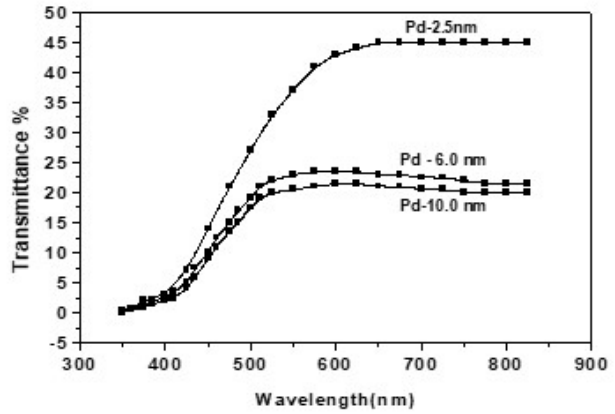

Figure 4: Change in transmittance as a function of wavelength for samarium hydride film coated with different thicknesses of Pd overlayer.

color when seen in the transmission mode. Further removing of hydrogen from the film using rotary pump the color of samarium dihydride changes from golden greenish to dark brown. Figure 3 shows the spectral dependence of T for hydrogen-saturated films coated with Pd layer of various thickness. Influence of metallic nature of thin Pd films is clearly visible in the magnitude of the transmittance of the films, which decreases with increases in thickness of Pd cap layer (Figure 4).

Conclusion

In the conclusion, we show the SEM studies carried out to support the electrical measurement. From the SEM images and electrical measurement, we can conclude that the Pd films deposited on samarium films of typical thickness 55 nm are electrically discontinuous only if the Pd thickness is < 3.0 nm. Correct magnitude of the resistance of Sm:$H_{3-\delta}$ films can only be obtained by using a discontinuous Pd overlayer. Furthermore, it was concluded that by control of rate of hydrogen uptake the cracking of samarium thin film on hydrogenation can be controlled. However, the cracking of samarium film having thickness more than 60 nm on hydrogenation was observed. Hence, to avoid the cracking and study the switching in SmH_x thin films, the optimized thickness of 55 nm of samarium thin film was used. The presented study might be useful in designing the hydrogen sensors with a very good response and recovery time with optimized parameters based on extraordinary material i.e., samarium.

Acknowledgements

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Conflict of Interest

None.

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