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Ag enhances optical and switching properties of gadolinium hydride films

E. Shalaan*, A.A. Al-Ghamdi

Physics Department, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

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ABSTRACT

An improvement of the optical properties of switchable mirrors is obtained by incorporating of silver (Ag) into the palladium (Pd) cap layer of nanocrystalline gadolinium hydride system Gd/GdH_3. Two methods for modification of Pd layer with Ag are employed. The first method is the forming of an AgPd binary alloy. The second method is the forming of Ag/Pd bilayer. In both cases the modification of the catalytic top layer of Pd with Ag gives higher transparency and better switching times. The optimal Ag layer thickness for the Gd/GdH_3 system is determined.

1. Introduction

Huilberts et al. [1] found, that thin films of YH_x exhibit reversible changes in their optical properties upon hydrogenation. By changing the hydrogen concentration x, these materials, and in fact almost all rare earth (RE) metals and RE based alloys [2–4], can be switched reversibly from metallic, reflective ($x \approx 2$) to semiconductor, transparent ($x \approx 3$), and therefore have a high technological potential [5,6].

The advantage of hydrides instead of transition metal oxides is the much higher optical reflectivity of the metallic films. The use of gadolinium hydride films (GdH_3) instead of (YH_3) shifts the absorption edge to lower wavelengths. Additionally this effect can be improved by the modification of the GdH_3 films by magnesium [2].

For the transformation of Gd to GdH_3 at room temperature, a catalytic material is necessary. Usually a top layer of palladium, Pd is used. Additionally, the Pd cap prevents the oxidation of the Gd film. But the Pd reduces the transparency of the film [7]. Unfortunately, the cap layer has to be rather thick. Thinner Pd film tends to form islands electrically separated by oxidize of active layer (e.g. gadolinium).

The palladium–silver system and its interaction with hydrogen have been investigated theoretically and experimentally dating back to about 40 years ago. From the study of the isothermal pressure–composition relationships of H_2 over the Pd–Ag system, Ag can form alloy with Pd at various atomic ratios. H_2 absorption of the alloy is generally lower than that of Pd, and the absorption amount is much more correlated to the partial pressure of H_2, especially at low hydrogen pressure where pure Pd cannot be used because of its large absorption of H_2, and absorption saturation even at low H_2 pressure around several tens of Torr. As a result, the palladium–silver alloy with a better mechanical strength can overcome the well-known problem of hydrogen embrittlement for pure Pd metal and the alloy system is expected to have a faster response. All these properties of the Pd–Ag system make it an attractive candidate as the catalyst and protective top layer of switchable mirror.

One of the aims of switchable mirror research is to optimize the cap layer properties. A catalytic cap film with better properties, with increased transparency and protection would be helpful. The incorporation of silver into the Pd film may be one possibility. We show here that a modified Pd cap layer with silver significantly improves the performance of metal–hydride switchable mirrors.

2. Material and methods

All the films were produced by rf sputtering technique. The production process was performed in a sputtering chamber with four target/sample positions. In this way, all the films which were necessary for the multilayer or alloy structure which should be aspired, can be produced in one single process. The gas composition at

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* Corresponding author. Tel.: +966 545949570; fax: +966 6901106.
E-mail address: eshalaan@yahoo.com (E. Shalaan).

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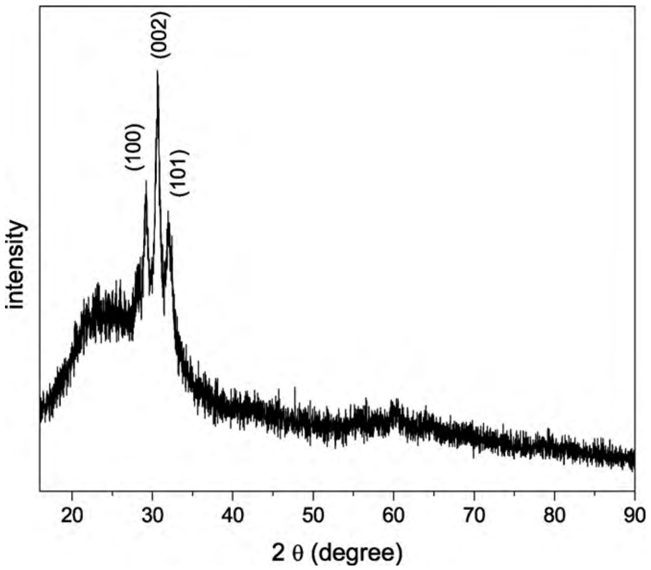

Fig. 1. XRD spectrum of Gd (400 nm) capped with Pd (15 nm) films on a glass, showing a (0 0 2)-preferential orientation.

the base pressure and during the sputtering process is controlled by a differentially pumped mass spectrometer. The thickness of the films is measured in situ by a microbalance. The base pressure in the sputtering chamber was 1×10^{-5} Pa. The oxygen partial pressure during sputtering was lower than the detection limit.

2.1. Film production

The nanocrystalline gadolinium films are deposited onto glass substrates in Ar atmosphere (4 Pa working pressure) at room temperature by use of Gd target with a purity of 99.999%. Three Gd films were prepared under identical conditions. All the films have the same thickness of $d = 400$ nm. Before exposing the films to the ambient, one Gd film is covered with a thin palladium cap layer of about 15 nm. The Pd film was grown at room temperature to prevent alloy formation with the gadolinium. The other two Gd films were reserved for capping with silver-modified Pd cap layer. For the production AgPd binary alloy cap layer, two target were used (Ag and Pd) with a purity of 99.99% each. These two target are sputtered simultaneously onto a prepared Gd film fixed on a rotating sample holder. The optimum PdAg alloy composition is 77 wt.% palladium and 23 wt.% silver.

2.2. Film characterization

Scanning electron microscope (SEM) and X-ray diffraction (XRD) were used to characterize the films. SEM pictures were received by use of a field emission microscope. The accelerating voltage was 10 kV. Room temperature XRD measurements were carried out using CuKα radiation in a X-ray diffractometer in the ($\theta - 2\theta$) geometry. The spectra of the films were scanned over the range of 20° to 120° (2θ), with a step rate of 0.02° (2θ) and a fixed counting time of 10 s for each step, in order to obtain spectra with sufficient signal-to-noise ratio.

2.3. Measurements of optical properties

The measurements of the optical, electrical, and switching properties were performed in a small gas-loading cell with optical windows and electrical leads. The films were hydrogenated to the trihydride phase, and this process was controlled by resistance measurements. The purity of H_2 was 99.9%. The transmission spectra (300–2500 nm) of GdH3 films were recorded with a double beam UV/vis/NIR spectrophotometer.

3. Results and discussions

The XRD spectrum of Gd films deposited onto glass at room temperature is shown in Fig. 1. The peak at about 31.13° refers to the (0 0 2) reflection of Gd lattice of hexagonal close-packed (hcp) structure. In addition, other diffraction peaks are visible in the XRD spectrum. One can see that, the grains in the films are preferentially oriented in (0 0 2) direction. This preferential orientation is very important for the possible application of the films, because in such films it is possible to reduce drastically the stress during loading the films with hydrogen. As shown by Pedersen et al. [8] 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 GPa. Dornheim et al. [9] 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.

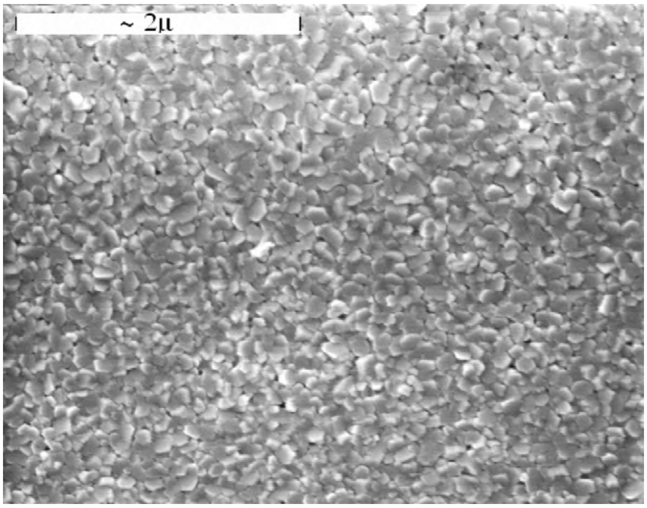

Fig. 2. SEM picture of a Gd metallic film (400 nm) on glass (i.e. before hydrogenation).

Figs. 2 and 3 show SEM pictures of Gd/Pd metallic film before and after hydrogenation, respectively. In Fig. 2 one can see the surface of a metallic Gd films before the loading with hydrogen gas, and Fig. 3 shows a film of GdH_3. In both cases the film is free of cracks. Further there is no evidence for plastic deformation [10].

Pure Pd is not attractive for practical applications because loading with hydrogen induces a structural phase transformation [11], which causes embrittlement over hydrogen loading and unloading cycles. By alloying Pd with Ag, the phase transition and the associated embrittlement can be suppressed [12]. For incorporating of Ag into Pd cap layer, two different methods are employed.

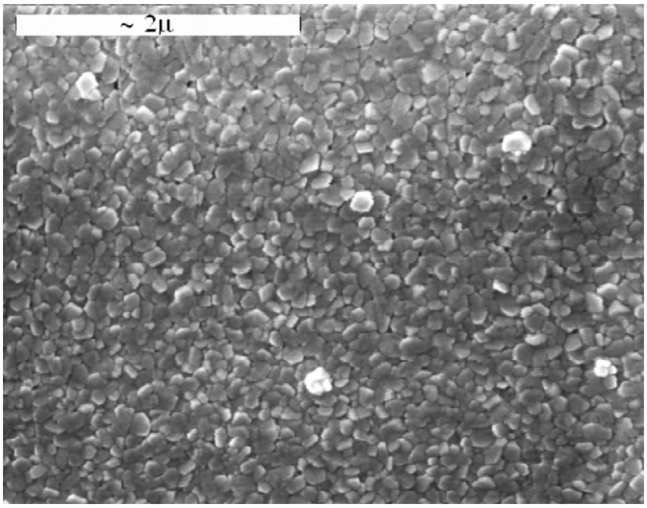

Fig. 3. SEM picture of a GdH_3 semiconducting film (400 nm) on glass (i.e. after hydrogenation).

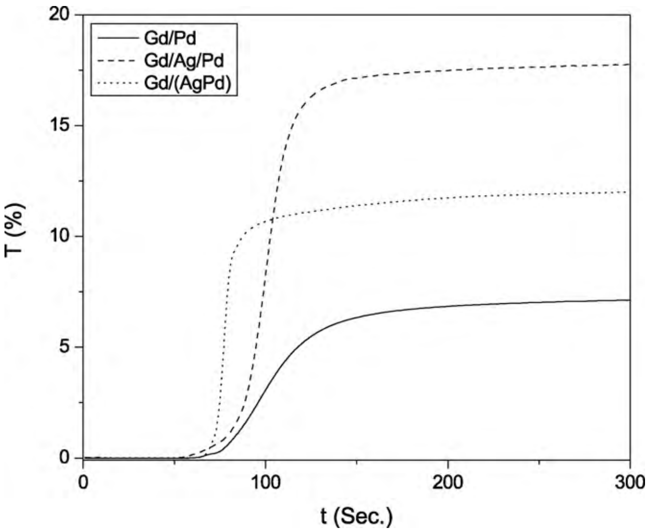

Fig. 4. Switching curves of Gd films (400 nm) with different catalytic top layers: Pd (15 nm), AgPd (30 nm) alloy (50% Ag and 50% Pd), and Ag/Pd bilayer (15 nm/15 nm) at a fixed wavelength (λ = 500 nm).

The first method is the forming of AgPd binary alloy. The second method is obtained by placing a thin Ag buffer layer between the Pd cap layer and the optically active, Gd layer, i.e. multilayer approach. In Fig. 4, a switching curve (the transmission at fixed wavelength (λ = 500 nm) was measured as a function of time, i.e. hydrogen concentration) of each type is shown in comparison with a pure Pd cap layer. In both cases an increase in the optical transmission and a decrease in the switching time can be seen, the switching time was taken as the time required attaining 90% of the maximum transmission value in trihydride state from the initial metal state.

Tailoring the optical properties of the RE materials to obtain a color-neutral state (constant transmittance in the visible range) has been one of the main goals in various research efforts [2,13,14]. However, from Fig. 5, one can note that, modification of the Pd top layer with Ag, improves the color neutrality (films with AgPd alloy and Ag/Pd bilayer has the most extended constant-transmission region). Thus, the use of modified Pd cap layer with Ag results in an all-around improvement in the switching characteristics of color neutrality, optical contrast and switching time. The transmission region is extended to the lower wavelength region (below 350 nm). In addition, the multilayer approach seems to be more suitable than alloy modification of Pd top layer with silver. In multilayer, the first contact layer with Gd film is a silver layer, the present of Ag layer prevents deteriorating effect of alloy formation at Gd–Pd interface, while in PdAg alloy some Pd atoms are in direct contact with Gd layer and hence the formation of Gd–Pd interface is not completely cancelled. In Figs. 7 and 8, the optical transmission and the switching time as a function of the Ag film thickness in the Ag/Pd multilayer are shown. The data indicate that at a constant Pd film thickness of about 15 nm, the optimal Ag film thickness is in the range of about 10 nm. The thickness of Ag layer is not allowed beyond a certain threshold for high transmittance in the visible. When the thickness of Ag layer is above 20 nm, high transmittance is hardly obtained. In addition, our experiments showed that the Ag films thinner than 10 nm were discontinuous island-shape films, which required a thicker Pd film for protective purpose. Thicker Pd film means high H_2 absorption, longer switching time, reducing total transmittance in hydrogenation state (reduced color neutrality).

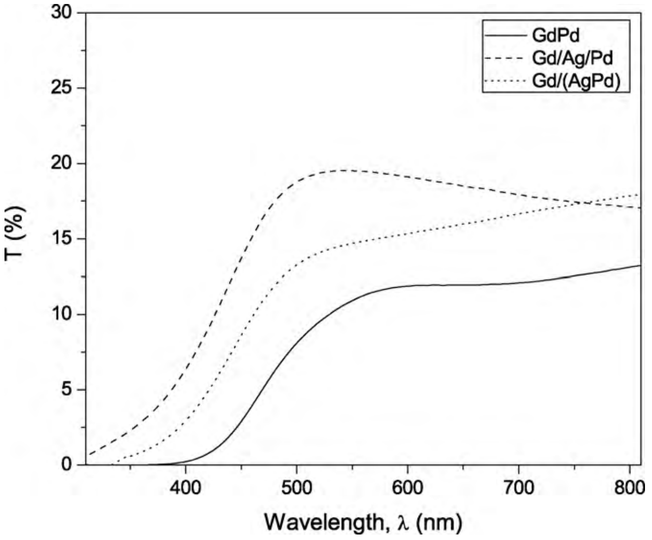

Fig. 5. Transmittance spectra of the hydrogenated Gd films with different catalytic top layers: Pd (15 nm), AgPd (30 nm) alloy (50% Ag, 50% Pd), and Ag/Pd (10 nm/15 nm) bilayer.

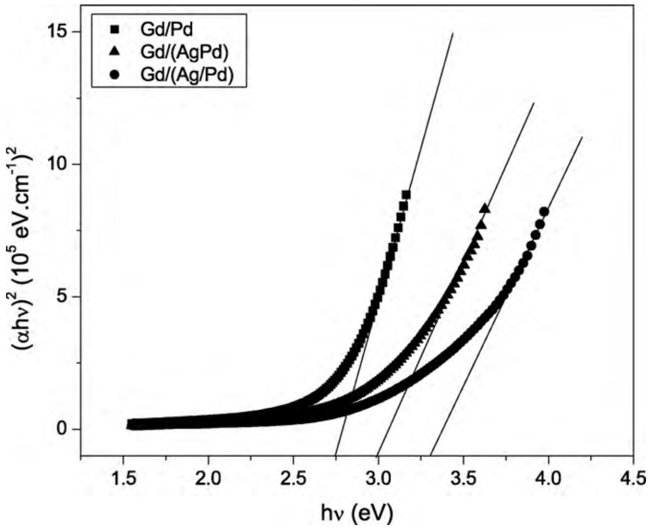

Fig. 6. Tauc's plots of the hydrogenated Gd films with different catalytic top layers: Pd (15 nm), AgPd (30 nm) alloy (50% Ag, 50% Pd), and Ag/Pd (10 nm/15 nm) bilayer.

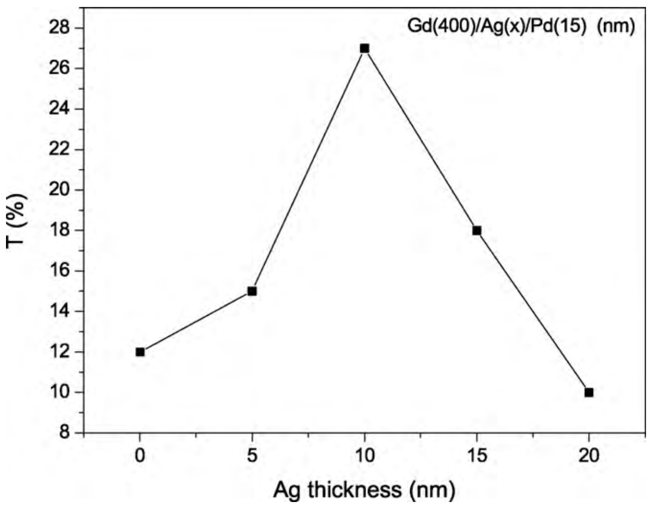

Fig. 7. Optical transmission as a function of the Ag thickness in the Ag/Pd bilayer (the transmission is measured at λ = 500 nm).

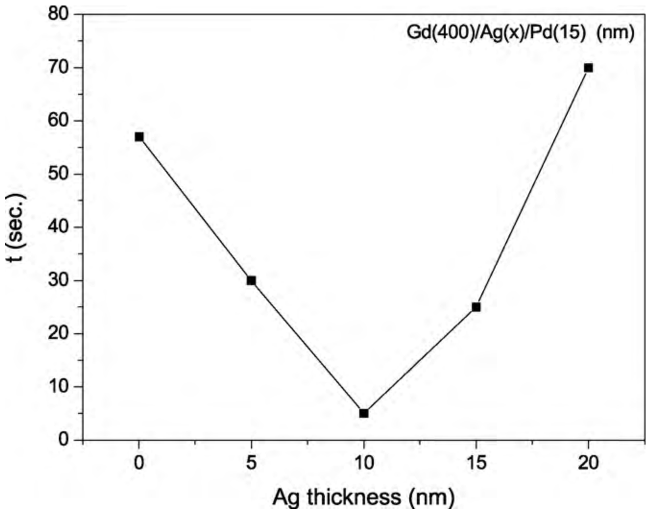

Fig. 8. Optical switching time as a function of the Ag thickness in the Ag/Pd bilayer (the transmission is measured at λ = 500 nm).

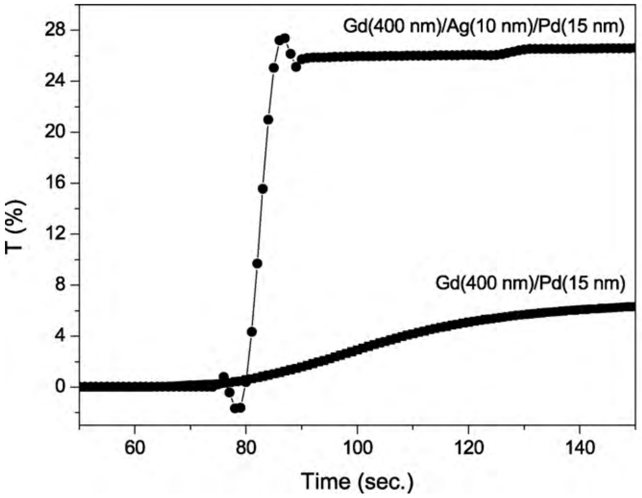

Fig. 9. Switching curves of Gd films with catalytic top layers of Ag/Pd (15 nm/10 nm) bilayer in comparison with Gd film with a pure Pd top layer at a fixed wavelength (λ = 500 nm).

Fig. 9 shows the switching curves of the Gd film with the Ag/Pd (10 nm/15 nm) bilayer as a top layer in comparison with a Gd film with a pure Pd (15 nm) cap layer.

Using the transmittance, reflectance, and thickness data of hydrogenated, Gd films with different cap layers and accounting for the transmittance and reflectance of Pd, Ag/Pd bilayer, and AgPd alloy, the optical absorption coefficient α of GdH_3 has been evaluated [15]. The best linear relationship is obtained for $(\alpha h\nu)^2$ versus $h\nu$ plots, shown in Fig. 6, indicating a directly allowed transition. The intercept of the linear fit to the abscissa at $\alpha = 0$ yields the optical absorption edge of 2.75 eV, 2.99 eV, and 3.30 eV for hydrogen loaded-samples with different cap layers; Pd, AgPd alloy, and Ag/Pd bilayer, respectively.

4. Conclusions

The modification of the catalytic top layer of Pd with Ag leads to a shift in the absorption edge to higher energy; more color neutrality, gives higher transparency and better switching time. In addition the observed improvement in color neutrality is due to the absence of a deteriorating effect of alloy formation at Gd–Pd interface. The switching characteristics of Gd samples can be further improved by optimizing the Pd over layer thickness as well as the thickness of Ag buffer layer.

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