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Surface and optical characterization of yttrium hydride films deposited on regular glass to be used as switchable mirrors

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Yttrium and palladium thin films deposited on glass have been characterized by means of XPS depth profiling, SEM, energy-dispersive x-ray spectroscopy and ultraviolet–visible spectroscopy. These films allow optical windows of variable transparency to be obtained based on the formation of yttrium hydride by hydrogenation, with the palladium film working as a barrier against yttrium oxidation but being permeable to hydrogen. The transformation of yttrium into its hydride is concomitant with a metal–semiconducting transition that changes the physical properties of the material, especially its optical behaviour: the transmittance in the visible range goes from 0% for the metallic state to 30–70% for the hydrogenated state. In this work, the preparation conditions of optical windows using low-cost regular glass as substrate have been optimized, both regarding the deposition and the hydrogenation. Uniform films free of impurities, such as oxygen and carbon, have been obtained under ultrahigh vacuum conditions of $\sim 10^{-7}$ Pa. Deposition has been performed by electron bombardment of the material, using palladium and yttrium of high purity. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: yttrium; palladium; thin films; switchable mirrors; metal hydrides

INTRODUCTION

Since the discovery of the drastic changes produced upon hydrogenation of yttrium and lanthanum regarding their electrical and optical properties,[1] intensive work has been devoted to the study of these compounds. When an yttrium film is hydrogenated a metal–insulator transition takes place, the yttrium hydrides becoming semiconducting and transparent to visible light. This phase transition is due to the hydrogenation of yttrium by a reaction of the type[2]

$$2\mathrm{Y} + x\mathrm{H}_2 \rightleftharpoons 2\,\mathrm{YH}_x\ (1 \leqslant x \leqslant 3) \qquad (1)$$

This reaction is reversible, and on diminishing the pressure of hydrogen the yttrium hydride becomes a metal again. This reversible reaction involves changes in all the physical properties of the material.[2] These materials have potential applications as optoelectronic devices: optical modulators, electronic circuits sensitive to the conditions of light, hydrogen sensors, windows of controllable transparency, etc.[3]

In this work we report on the surface properties of yttrium hydride thin films obtained by deposition of yttrium on a regular low-cost glass. Palladium is deposited on the yttrium film in order to prevent its oxidation (which could lead to the irreversible loss of variable transparency) while allowing hydrogenation of the film. We optimized the deposition and hydrogenation conditions of the samples in order to obtain good uniformity and a minimum contamination of oxygen and carbon impurities. For this purpose, ultrahigh vacuum (UHV) conditions were used during deposition. A new prototype device based on such films has also been proposed.

EXPERIMENTAL

Preparation of thin films

The films were prepared in a UHV chamber at a base pressure of 10^{-7} Pa. An ion gun (from the company Omicron) that uses argon of high purity (99.9999%) was employed for surface cleaning of the glass substrate; yttrium and palladium deposition was carried out using a Tectra electron-bombardment evaporator and the thickness was measured on a quartz-crystal microbalance. The tooling factor of the quartz balance was obtained *in situ* using well-known patterns.

Low-cost regular glass, previously cleaned in an ultrasound bath, was used as substrate. Once inside the UHV chamber the glass was cleaned by ion bombardment. This process also helps to improve notably the adherence of the

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first material deposited on the glass. Yttrium (99.9% purity) and palladium (99.95% purity) supplied by Goodfellow were used to produce the thin films. Both yttrium and palladium were deposited at a distance of no less than 0.3 m to ensure good homogeneity of the material flow and an evaporation speed of <0.1 nm s^{-1}.

Measurement equipment

Both SEM micrographs and energy-dispersive x-ray spectroscopy (EDXS) spectra were obtained with a Jeol JSM-6400 scanning electron microscope equipped with a Link Analytical System. The electron energy used was 20 keV.

The optical transmittance measurements were carried out using a Hewlett-Packard 8452A ultraviolet–visible spectroscopy (UV–VIS) spectrophotometer with a diode array, controlled by data acquisition software on a personal computer. The transmittance measurements were obtained in the wavelength range 190–820 nm. The equipment acquires each spectrum in $\sim$2 s. As a calibration target we used the clean atmosphere of the laboratory.

The XPS measurements and depth profiling were carried out with a PHI 5700 spectrometer (Physical Electronics, Eden Prairie, MN) using Mg Kα radiation (1253.6 eV) and Al Kα radiation (1486.6 eV) as excitation sources. Multiregion spectra were recorded at a 45° take-off angle with a concentric hemispherical energy electron analyser operating in the constant pass energy mode at 29.35 eV, using a 720 μm diameter area of analysis and depth profiling executed at 4 kV and 25 mA of Ar$^+$ emission current. Under these conditions, the sputter rate in a sample of tantalum oxide corresponds to 1 nm min^{-1}.

Hydrogenation system

The hydrogenation process was carried out by applying 3 atm of pure hydrogen for 3 h.

RESULTS AND DISCUSSION

Analysis by SEM and EDXS

The SEM observations of a 300 nm yttrium thin film covered with 15 nm of palladium show a very homogeneous aspect, except for the presence of white irregular protuberances randomly distributed on the surface. The EDXS analysis of these protuberances (Fig. 1) shows the presence of Si, Ca and O in addition to Pd and Y. A comparison with EDXS analysis of the glass substrate shows that these elements correspond to the calcium silicate of the glass. These protuberances are points of bad growth of the glass, recognizable with a 1000× optical microscope. The presence of Si, Ca and O suggests a lower thickness of the Pd and Y films in these areas.

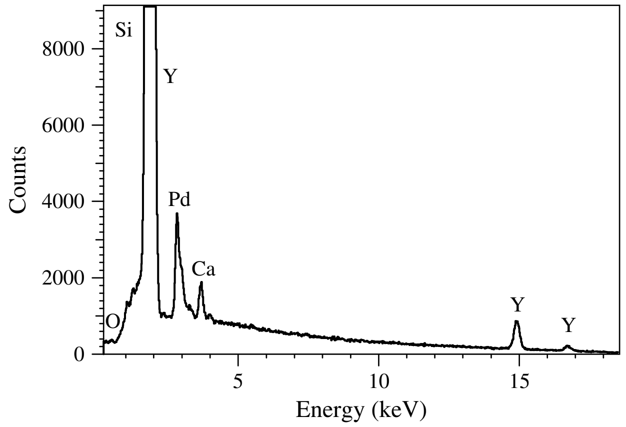

Figure 1. The EDXS spectrum of a white protuberance (see text).

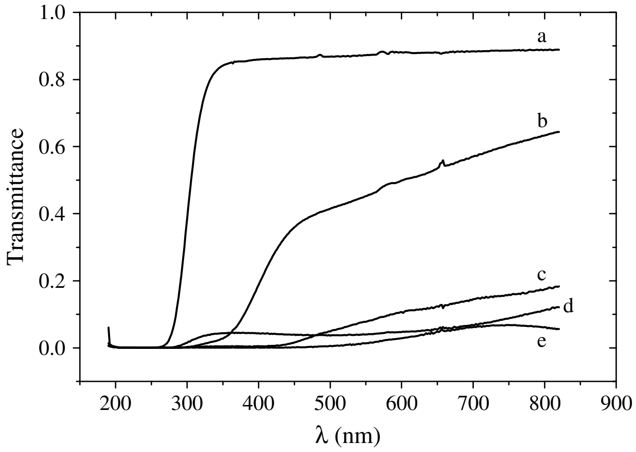

Figure 2. Transmittance for hydrogenated samples during 3 h at 3 atm: (a) glass basis; (b) 65 nm yttrium and 15 nm palladium; (c) 300 nm yttrium and 15 nm palladium; (d) 100 nm yttrium and 0 nm palladium; (e) 400 nm yttrium and 15 nm palladium.

Optical behaviour in UV–VIS

The transparency of the yttrium films is directly related to their degree of hydrogenation. Different studies were carried out for various yttrium and palladium thicknesses, measuring the optical transmittance after hydrogenating at 3 atm for 3 h. Figure 2 shows the transmittance results of the following samples: (a) the glass basis; (b) 65 nm yttrium and 15 nm palladium film; (c) 300 nm yttrium and 15 nm palladium; (d) 100 nm yttrium and no palladium film; (e) 400 nm yttrium and 15 nm palladium film. In all the spectra the glass substrate is included.

Case (b) shows the largest transmittance of $\sim$70% because the low thickness of this film allows complete saturation. The lowest transmittance therefore corresponds to spectrum (e) because the yttrium layer is much thicker. These results indicate that transparency can be reached with very thin layers of yttrium. However, yttrium layers of <50 nm are so thin that they have some transparency, even without hydrogenating.

Case (c) is one of the most efficient because there is a good proportion of yttrium and palladium, although their maximum transmittance is only 20%. Case (d) shows the transmittance of the sample with no palladium layer. The result (see Fig. 2) is indeed better than that of case (e). This indicates that it is possible to hydrogenate even through oxidized yttrium, although with very poor efficiency. This result is in disagreement with the studies published by den Broeder *et al.*,[4] because according to their work an oxidized yttrium layer with these characteristics would not allow the penetration of hydrogen.

Case (c) is selected to study the dehydrogenation of the sample. Figure 3 shows the transmittance spectra with time. Each spectrum diminishes with time and reaches total dehydrogenation (zero transmittance) in 15 900 s. While the sample is being dehydrogenated, the curves (Figs 3(c), (d) and (e)) present a maximum at ~700 nm due to different concentrations of YH_{3-x} ($0 \leqslant x \leqslant 3$) going through all the known non-stoichiometric phases.[5] These changes in transmittance agree with those reported in the literature.[6,7]

The hydrogenation and dehydrogenation reactions induced by a change of gas pressure have a very slow reaction rate and show hysteresis.[8] This is a handicap for developing fast optoelectronic devices from these films. At the moment, faster devices are designed based on other materials.[9] Nevertheless, the transition speed is adequate for other applications, such as the development of optical windows of variable transparency intended for manufacturing products.

Depth profiling by XPS

The XPS depth profile measurements determine the composition of the samples from surface to bulk. Figure 4 shows the depth profile of the sample with 25 nm palladium and 300 nm yttrium. First, from Fig. 4 we can see that the signal of palladium decreases while that of yttrium appears, indicating some interdiffusion. Carbon is only present at the topmost surface and is quickly removed, indicating no contamination during deposition. The oxygen signal has been fitted because the pd $3p_{3/2}$ peak at 533 eV drops inside the oxygen region. The curve of oxygen indicates that a tiny quantity is able to penetrate into the first monolayers of yttrium when palladium is on top.

An interesting result of this study is that yttrium oxide not only allows hydrogenation but can also retard dehydrogenation, allowing the sample to remain semitransparent for long periods. This is the case of the sample in Fig. 5(a). The oxygen region shows a contribution from a peak at ~530 eV, which is characteristic of Y_2O_3.[10] Although in the palladium region the peak is always in its elementary state of 335 eV, the yttrium region contains the contribution of at least three peaks (Fig. 5(b)). The first two peaks are located at ~157.5 and ~157 eV, respectively, and correspond to the formation of the hydride[11,12] and yttrium oxide,[10] whereas the third peak (~155.6 eV) corresponds to elementary yttrium.[13,14] Elementary yttrium appears because in UHV conditions the volatile hydrogen escapes, leaving the metal in the reduced state. The presence of hydrogen in this sample several days after hydrogenation suggests that yttrium oxide can hinder dehydrogenation.

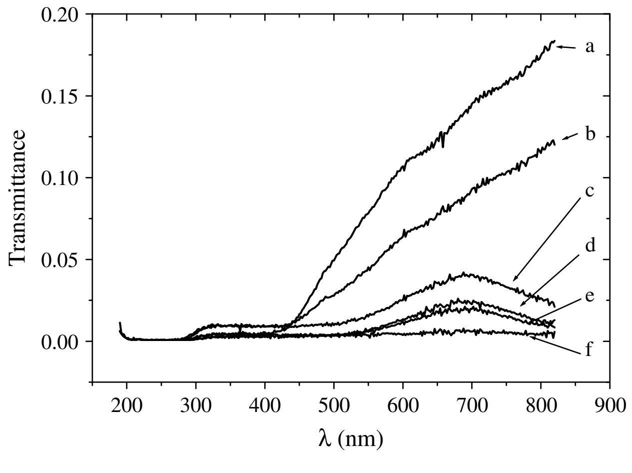

Figure 3. Transmittance spectra showing the dehydrogenation process of the film with 300 nm of yttrium and 15 nm of palladium: (a) 0 s; (b) 60 s; (c) 300 s; (d) 600 s; (e) 1200 s; (f) 15 900 s.

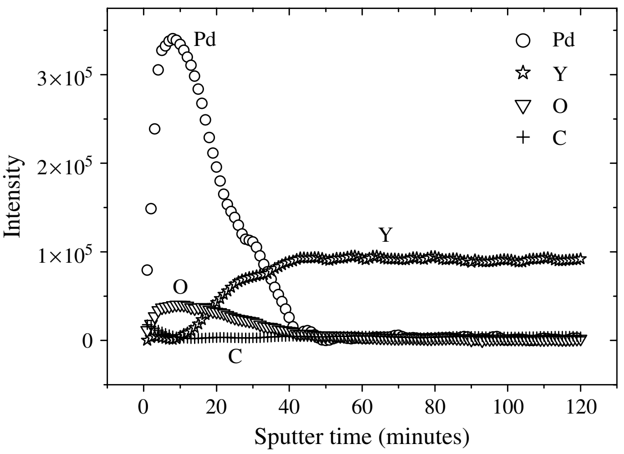

Figure 4. Depth profiling of the sample with 300 nm of yttrium protected with 25 nm of palladium.

Prototype

Some prototypes of variable transparency windows have been proposed in the literature[15,16] but none of them is of industrial application so far. One of the most promising prototypes is based on carrying out the hydrogenation and dehydrogenation processes electrochemically. A *'sandwich-like'* prototype has been developed recently (V. Parkhutik, personal communication, Universidad de Valencia, 2001) where an electrolytic solution is confined between an ITO (indium tin oxide) conducting glass and the yttrium and palladium sample. This prototype has the problem of destroying the layer of ITO after several hydrogenation and dehydrogenation cycles.

The prototype that we have developed is shown in Fig. 6. The hydrogenation and dehydrogenation processes are performed electrochemically by means of an appropriate cell without ITO. A 150 nm layer of yttrium is deposited on glass and recovered with a 15 nm layer of palladium. A second glass is recovered with a 15 nm layer of palladium. A frame of insulating material (polyvinylchloride) is appropriately placed to avoid ohmic contact, and an electrolytic solution of 0.01 M KOH is used.

By means of a 1.5 V simple battery, the yttrium film is hydrogenated or dehydrogenated. Dehydrogenation, characterized by the loss of film transparency, begins as soon as we invert the polarity of the battery. Electrochemical hydrogenation and dehydrogenation processes are much faster than those carried out with hydrogen pressure. The

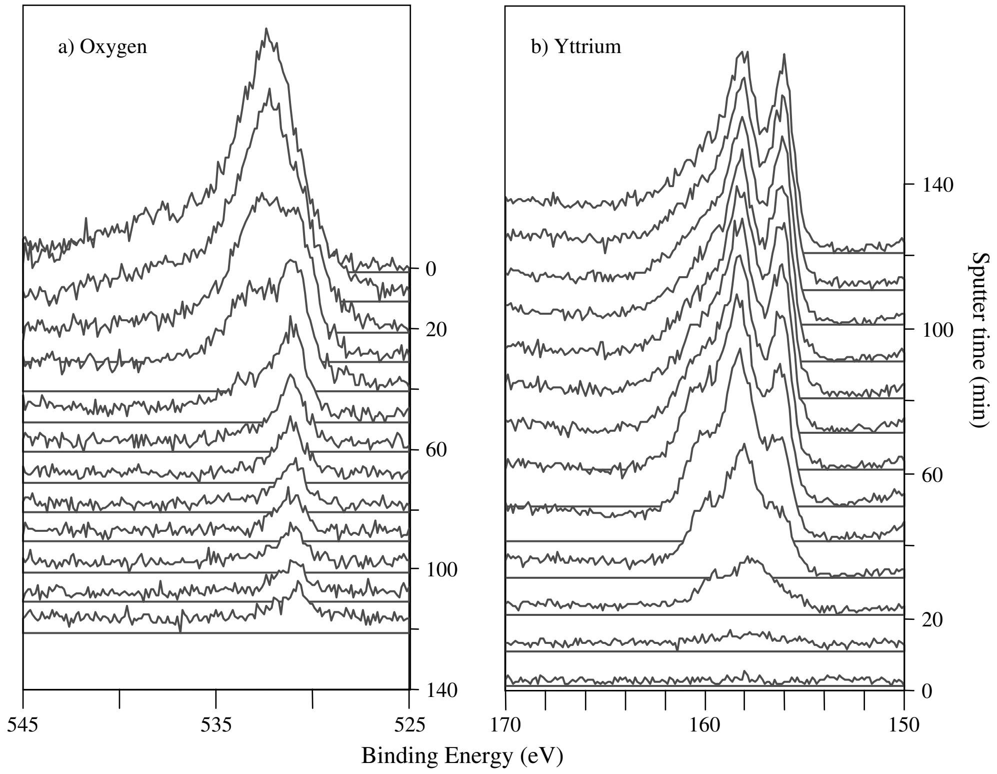

Figure 5. The XPS spectra corresponding to the depth profile of the sample with oxygen: (a) oxygen region; (b) yttrium region.

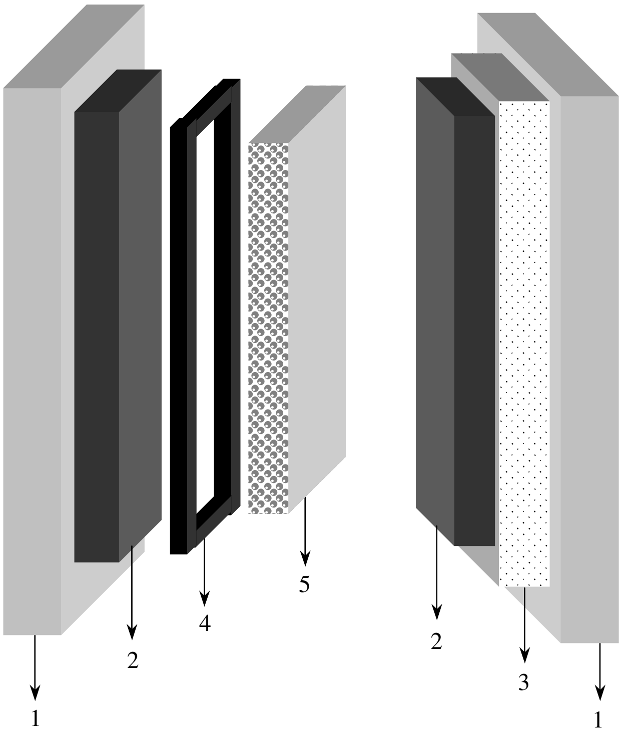

Figure 6. Cell prototype of optic window of variable transparency: (1) regular glass; (2) 15 nm of palladium; (3) 150 nm of yttrium; (4) chewed insulation; (5) electrolytic solution of 0.01 M KOH.

speed, however, is too low for high-speed optoelectronic devices. Also, the electrolytic solution of KOH is not the most appropriate for use over long periods of time because it deteriorates. Currently we are looking for a solid or gel electrolyte that can photoreact so that we do not need to use a battery for the prototype.

CONCLUSIONS

We have found interesting results using yttrium hydride, where the transparency has been corroborated using a low-cost regular glass substrate. This kind of system is perfectly suitable for developing optical windows of variable transparency. Such prototypes could be used in 'intelligent buildings' and low-frequency optoelectronic equipment.

The presence of yttrium oxide does not prevent hydrogenation, but if oxygen goes inside the yttrium thin film then it prevents the correct dehydrogenation process. Therefore, yttrium hydride thin films should be made in a UHV atmosphere with a pressure of $<10^{-7}$ Pa.

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REFERENCES

1. Huiberts JN, Griessen R, Rector JH, Wijngaarden RJ, Dekker JP, de Groot DG, Koeman NJ. *Nature* 1996; **380**: 231.
2. Griessen R, Huiberts JN, Kremers M, van Gogh ATM, Koeman NJ, Dekker JP, Notten PHL. *J. Alloy. Comp.* 1997; **253/254**: 44.
3. Joannopoulos JD, Meade RD, Winn JN. *Optical Processing of Information*. Princeton University Press: Princeton, NJ, 1996.
4. den Broeder FJA, van der Molen SJ, Kremers M, Huiberts JN, Nagengast DG, van Gogh ATM, Huisman WH, Koemaan NJ,

Dam B, Rector JH, Plota S, Haaksma M, Hanzer RMN, Jungblut RM, Duine PA, Griessen R. *Nature* 1998; **394**: 656.

5. Huiberts JN, Rector JH, Wijngaarden RJ, Jetten S, de Groot D, Dam B, Koeman NJ, Griessen R, Hjörvarsson B, Olafsson S, Cho YS. *J. Alloy. Comp.* 1996; **239**: 158.
6. Kremers M, Koeman NJ, Griessen R, Notten PHL, Tolboom R, Kelly PJ, Duine PA. *Phys. Rev. B.* 1998; **57**: 4943.
7. van Gogh ATM, Kooij ES, Griessen R. *Phys. Rev. Lett.* 1999; **83**: 4614.
8. Kooij ES, van Gogh ATM, Nagengast DG, Koeman NJ, Grissen R. *Phys. Rev. B* 2000; **62**: 10 088.
9. Griessen R. *Europhys. News* 2001; **March/April**: 41.
10. Reichl R, Gaukler KH. *Surf. Interface Anal.* 1990; **15**: 211.
11. Briggs D, Seah MP. Protocol Surface Analysis (2nd edn), vol. 1. John Willey: Chichester, 1983.
12. Fujimori A, Schlapbach L. *J. Phys. C* 1984; **17**: 341.
13. Baba Y, Sasaki TA. *Surf. Interface Anal.* 1984; **6**: 171.
14. Nyholm R, Matersson N. *J. Phys. C* 1980; **13**: 279.
15. Kooij ES, van Gogh ATM, Griessen R. *J. Electrochem. Soc.* 1999; **148**: 2990.
16. Armitage R, Rubin M, Richarson T, O'Brien N, Chen Y. *Appl. Phys. Lett.* 1999; **75**: 1863.