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Journal of Alloys and Compounds 356–357 (2003) 526–529

Journal of ALLOYS AND COMPOUNDS

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In situ preparation of YH_2 thin films by PLD for switchable devices

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Received 4 September 2002; accepted 15 November 2002

Abstract

We prepared epitaxial YH_2 films on (111) CaF_2 by pulsed laser deposition (PLD) from a metallic yttrium target. Without adding any reactive hydrogen, the dihydride is formed in situ due to the hydrogen evolving from the metallic target which contains ~7 at% H. Upon pulsed laser irradiation, the target acts as a pulsed source of both yttrium and hydrogen. The increased hydrogen content of the film as compared to the target is explained to be due to diffusion assisted preferential ablation of hydrogen. Due to this deposition process the hydrogen load on the deposition system is minimized, which is important in view of the fabrication of hydride/oxide stacks for all-solid-state switchable mirror devices. Furthermore, the preparation of both nanocrystalline and epitaxial YH_2 films shows the versatility of the PLD process.

Keywords: Thin films; X-ray diffraction; Vapour deposition

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1. Introduction

In 1996, Huiberts et al. [1] discovered that YH_x and LaH_x show spectacular reversible optical changes when loaded from the dihydride to the trihydride phase. Since the transition is reversible at room temperature this switchable mirror is of technological importance, especially if all-solid-state devices can be made.

Sputtering has been used to deposit the various (oxide and hydride) active layers of such a device [2,3]. Alternatively, we use pulsed laser deposition (PLD) to manufacture switchable devices. This flexible deposition technique is ideally suited to explore the materials aspects of these complicated heterostructures. As a first step we report here on the in situ deposition of YH_2 by PLD. We find that PLD has several important advantages. First of all, even when using metallic yttrium targets, we can deposit YH_2 (β-phase) films in situ without adding any hydrogen gas. Hydrogen dissolved in the metallic (α-phase) yttrium target provides for the necessary hydrogen. The background hydrogen pressure during this deposition process is only 10^{-7} mbar. Secondly, when keeping the substrate at room temperature, *nanocrystalline* dihydride films can be formed. Thus, using PLD, we can investigate the effect of the microstructure on the switching properties.

In this paper we discuss the deposition and the structural aspects of PLD YH_2 films. In a subsequent paper we will focus on the switching and optical properties of these films.

2. Experimental

Thin YH_2 films are grown in high vacuum (base pressure $<5\times10^{-8}$ mbar) by PLD, using a Lambda Physik LPX 305i excimer laser, which has a pulse duration of 25 ns and a wavelength of 248 nm. To minimize the formation of particulates a fluence of 0.7 $J\,cm^{-2}$ was used. At a laser pulse repetition frequency of 5 Hz we obtain a deposition rate of about 0.1 $nm\,s^{-1}$. Epitaxial films were deposited on CaF_2 at substrate temperatures (T_s) between 400 and 600 °C. Nanocrystalline films were deposited on SiO_2 at room temperature. A Pd cap layer of typically 10 nm is deposited at room temperature to prevent the oxidation of the 100–300 nm films and to catalyze the hydrogen uptake.

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doi:10.1016/S0925-8388(03)00117-8

X-ray diffraction measurements using the Cu Kα radiation (λ=1.54 nm) were performed on a Bruker D8 diffractometer. For rest gas analysis (RGA) we used a VSW mass analyst quadrupole mass spectrometer.

3. Results and discussion

3.1. The deposition process

Pulsed laser deposition from a yttrium target typically leads to an increase in background pressure. From the RGA, we learn that the hydrogen partial pressure increases to 10^{-7} mbar, while all other gases remain at least one order of magnitude lower in pressure. Especially, the oxidizing gases such as O_2 and H_2O remain well below the 5×10^{-8} mbar level. The hydrogen evolves from the metallic (α-phase) yttrium target in which some hydrogen is dissolved. As the *c*-axis length of yttrium in the α-phase depends linearly on the hydrogen content, we could estimate from the XRD spectrum that the hydrogen content of the target is around 7 at% hydrogen (Fig. 1).

To investigate the hydrogen evolution from the target, we measured the hydrogen (mass=2) signal of the mass spectrometer as a function of time and fluence, at a laser repetition frequency of 5 shots per second. The amount of hydrogen increases with the laser fluence up to F=0.6 J cm^{-2}. Also the amount of hydrogen increases steadily with time up to this fluence (Fig. 2). At higher fluences the hydrogen pressure has a maximum in time. Apparently, the hydrogen depletion of the yttrium target surface occurs only when F>0.6 J cm^{-2}.

Note, that during the actual deposition process we *rotate* the target, creating a circular track of laser ablation imprints on the target. As a result, the time between two ablation events at the same target position increases from 0.2 to 4 s. In the latter case, we find a steady increase in hydrogen pressure with time during deposition, even at our standard deposition fluence of 0.7 J cm^{-2}, indicating a critical recovery time between 0.2 and 4 s.

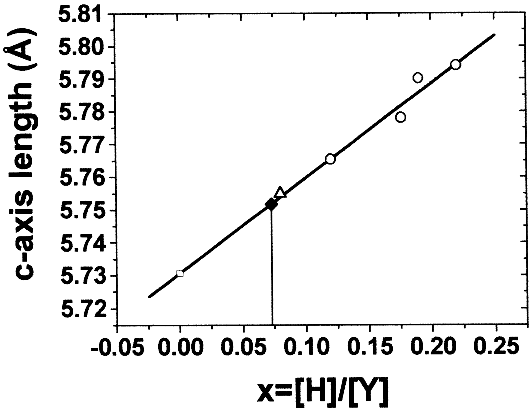

Fig. 1. Determination of the hydrogen content of the yttrium target from the *c*-axis length. Open circles are data from Ref. [4], the open triangles from Ref. [5], the open squares from Ref. [6], while the filled diamonds represents our measurement.

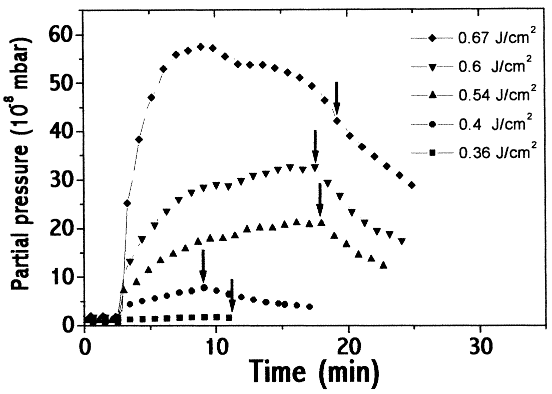

Fig. 2. Time and fluence dependence of the hydrogen pressure during ablation. The RGA is positioned approximately 12 cm away from the plume. Arrows indicate when the ablation was halted. In this experiment, the target is stationary, as opposed to rotation during actual deposition.

If the laser plasma is allowed to condense on a CaF_2 substrate heated to 400–600 °C we obtain an epitaxial YH_2 film. The X-ray spectrum only shows the 111 and higher order reflections of the YH_2 phase (Fig. 3a). Metallic yttrium was not found. Around 26° we find proof for the presence of a small amount of $Y(OH)_3$. A texture measurement (a phi–psi scan with 2θ fixed at the 111 reflection of YH_2) showed the six-fold arrangement of symmetry equivalent 111-reflections (two sets of 111-reflections appear due to twinning [7]), which confirms the epitaxial nature of the YH_2 film (Fig. 3b). Nanocrystalline films were obtained when depositing at room temperature on a quartz substrate (Fig. 3c). Texture measurements show a very broad band of symmetry equivalent 111-reflections, indicating that these YH_2 films are randomly oriented with only a slight preference for a 111-surface orientation. Though we again expect the presence of some $Y(OH)_3$, it could not be identified in the XR spectrum.

Although the plateau pressure of YH_2 is of the order of 10^{-25} mbar, the direct formation of YH_2 is not trivial. To deposit YH_2 films under similar conditions in, for example, MBE, elaborate hydrogen purification and conditioning of the vacuum system are needed [8]. The fact that YH_2 is nevertheless formed in a relatively dirty PLD system, is either due to the pulsed nature of the PLD process, or due to the formation of atomic hydrogen. Although atomic hydrogen is the most likely ablation product, in our RGA analysis the H/H_2 ratio never exceeded 10%, not even when the ion-source of the mass spectrometer was positioned just above the ablation plume. Hence, we have no evidence that *atomic* hydrogen plays a role in the deposition process. We conclude therefore that the simultaneous pulsed supply of highly kinetic Y and H_2 is responsible for the YH_2 formation. For the all-solid-state switchable mirror device the reduced reactive gas load in

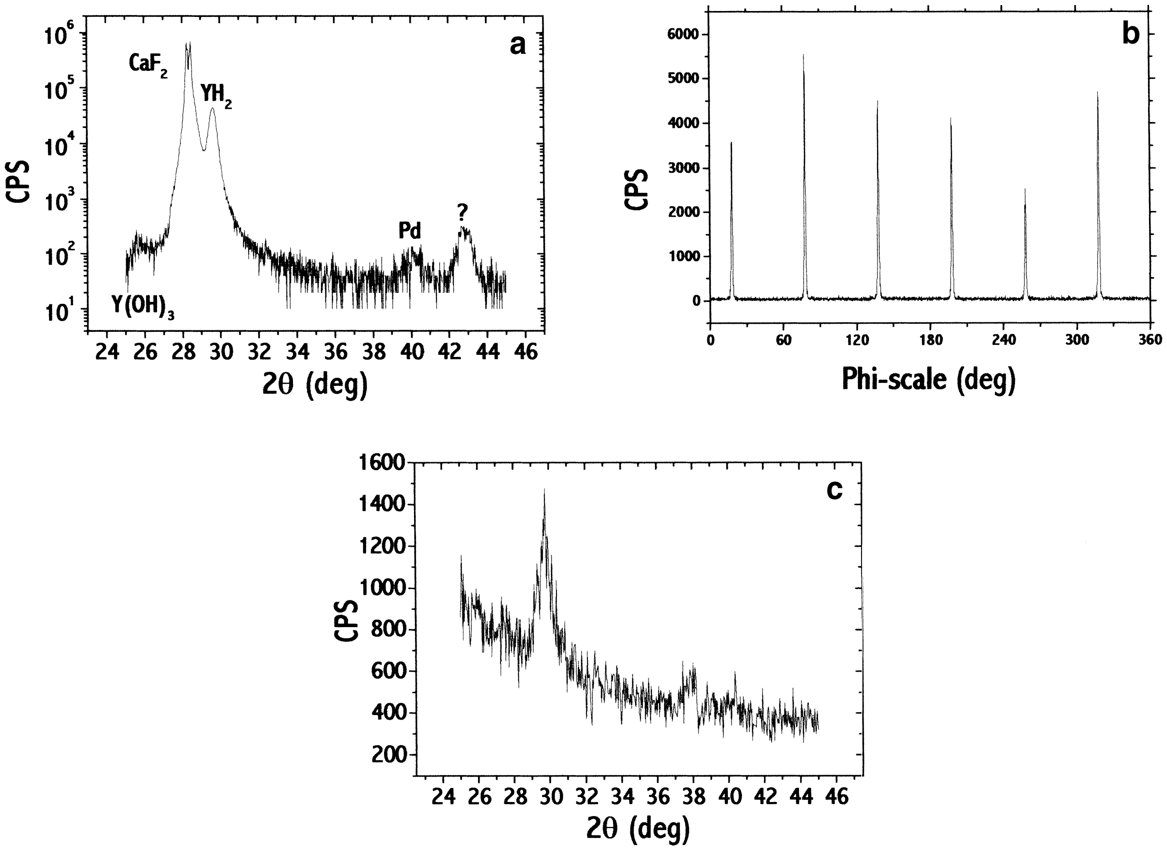

Fig. 3. (a) XRD θ–2θ scan of YH_2 film on CaF_2 showing the preferential 111-orientation of the f.c.c. structure. (b) Texture analysis of the 111-reflection of the same film showing the six symmetry equivalent 111-directions, confirming the epitaxial (albeit twinned) nature of the YH_2 films. (c) XRD θ–2θ scan of a nanocrystalline YH_2 film deposited at room temperature on quartz.

hydride PLD is an advantage. In these switchable devices, metal and oxide functional layers have to be deposited subsequently. In order to prevent cross-contamination and a quick change of reactive gases, the deposition system should have a decent pumping capacity and the reactive gas load should be minimized.

3.2. Diffusion assisted preferential hydrogen ablation

PLD is well-known for its ability to deposit congruent films from complex targets. However, as we explained elsewhere, at low fluences target surface processes may preclude such congruent deposition [9]. A non-stoichiometric ablation process may be maintained through a continuous supply towards the target surface by diffusion of the target component which is preferentially ablated. As the diffusion of hydrogen is very fast, we propose to explain the incongruent deposition along similar lines. To explain the hydrogen enrichment of PLD yttrium films we need to assume two things: (1) preferential ablation of the hydrogen during laser irradiation of the target and (2) sufficient hydrogen diffusion towards the target surface between two laser pulses.

If there is a strong preference to withdraw H from the $YH_{0.07}$ target during ablation, a H concentration gradient will set in. The concentration gradient is a driving force for diffusion towards the target surface. The mean diffusion length of the hydrogen during one laser pulse is roughly $\lambda = \sqrt{D_{\mathrm{H,m}} \cdot \tau} = 110$ nm, in which $D_{\mathrm{H,m}}$ is the diffusion coefficient of hydrogen in the molten yttrium ($=5\times10^{-3}$ $\mathrm{cm}^2\ \mathrm{s}^{-1}$) and τ is the duration of the laser pulse ($=25$ ns). At 0.7 J cm^{-2} one laser pulse ablates 3 nm away from the yttrium target (as determined by measuring the weight of the target before and after deposition). Hence, the number of hydrogen atoms leaving the target per shot is ~37 times larger than the number of H atoms present in the 3-nm layer of yttrium. This may well explain the ~29-fold increase in hydrogen concentration from film to target. Note, that PLD is not a simple evaporation process. The laser induced plasma formation is several orders of magnitude faster than the evaporation rate. We, therefore, assume that hydrogen only evolves from the target during laser irradiation and that the evaporation of hydrogen from the target after the laser pulse is negligible.

After the laser pulse, the surface area of the yttrium target is depleted in hydrogen. Diffusion towards the surface from underlying layers will take place between the laser pulses. The very small volume heated by the laser beam quickly cools as soon as the laser pulse has stopped. If the time between the laser pulses is to short for the target to recover, the amount of hydrogen desorbed will decrease in the following laser pulses. We observe such depletion effects when the time between two laser pulses is decreased from 4 to 0.2 s. This diffusion time leads to average hydrogen diffusion coefficient between $2.5\times 10^{-12} < D_{H,Y} < 1.25\times 10^{-10}$ cm^2 s^{-1}, which would correspond to a local average target temperature between 300 and 350 K [10]. Hence, it appears that the fast target cooldown after each laser shot is the limiting factor to replenish the target surface.

We conclude that the incongruent deposition of YH_2 is due to a preferential ablation of hydrogen, which is assisted by a hydrogen diffusion. During the laser shot, fast diffusion towards the ablating surface maintains the hydrogen desorption rate. Between the laser shots, sub-surface target depletion is replenished by low temperature hydrogen diffusion.

4. Conclusions

PLD facilitates the in situ formation of YH_2 films at low hydrogen background pressures. The deposition process is extremely incongruent. Due to diffusion assisted preferential ablation this incongruent deposition process can be maintained. Crucial is the replenishment of the target between the shots. The PLD process has the advantage that a complicated hydrogen purification is unnecessary. Moreover, the gasload during deposition is minimal, which is beneficial for the fabrication of hetero-structures consisting of metal, hydride and oxide functional layers.

The in situ growth process allows us to study the switching behaviour as a function of the crystallinity. Depending on the substrate temperature, the crystallinity of the film ranges from epitaxial ($T_s = 500$ °C) to nanocrystalline (T_s = room temperature). Unfortunately, the PLD hydride films still contain some oxygen. As we will show in a subsequent paper both the crystallinity and the oxygen content are relevant to the switching process [11].

Acknowledgements

This work is part of the research program of FOM (Fundamenteel Onderzoek der Materie) which is financially supported by NWO (Nederlands Wetenschappelijk Onderzoek).

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