

The properties of pulsed laser deposited YH_2 films for switchable devices

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Abstract

In-situ deposited YH_2 films ranging from epitaxial to nanocrystalline were prepared by pulsed laser deposition (PLD). PLD has the advantage that the yttrium target acts as a hydrogen source. Comparing the switching behavior to that of MBE-grown, ex-situ loaded films, the PLD-films show a reduced optical and electrical contrast in switching, which is probably due to the formation of $\text{Y}(\text{OH})_3$. On the other hand, we found that in the nanocrystalline PLD-films the hysteresis in switching is absent. Moreover, these films have a smoother surface morphology. Both effects are important for the implementation of switchable rare earth hydride films in all-solid-state devices.

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1. Introduction

Smart windows will play an important role in reducing the energy consumption of buildings. Electrochromic materials such as WO_3 are already used in commercial energy saving windows [1]. Recently, Huiberts et al. [2] pointed out the relevance of rare earth (RE) hydrides for such applications. The advantage of the RE-hydrides is that they are much more reflecting than H_xWO_3 , when comparing both materials in their conducting metallic state. By tuning the hydrogen concentration in $\text{YH}_{2+\delta}$ one controls the reflection. Upon hydrogenation the metallic face-centered cubic YH_2 β -phase transforms into the semiconducting h.c.p. $\text{YH}_{3-\delta}$ γ -phase. The hydrogen concentration rather than the symmetry change is essential for the electronic transition [3,4]. The reversible metal–insulator transition is of high technological importance, especially if it can be driven within an all-solid-state device. Such a device consists of two electrodes with a switching layer, a storage layer and an electrolyte. The first demonstrator devices were prepared using sputtering to deposit the various (oxide and hydride) active layers [5,6]. As described in another paper in this issue [7] we found

that YH_2 films can be prepared in-situ by pulsed laser deposition (PLD). Here, we will compare the morphology and the optical and electrical switching properties of these films with MBE-deposited films. The latter films are deposited in the metallic h.c.p. α -phase and loaded ex-situ with hydrogen to form the f.c.c. β - and h.c.p. γ -phases. For an all-solid-state device in-situ deposition of YH_2 is essential. To prevent shortcuts in the insulating electrolyte the surface should be flat. In most applications, a hysteresis in the transition is to be avoided. We find that, although the PLD-films are promising in terms of surface flatness and hysteresis, the switching contrast is severely reduced. It remains to be investigated whether this is due only to the presence of some $\text{Y}(\text{OH})_3$ or that the microstructure (grain size) plays a role.

2. Experimental

Thin YH_2 films are grown in high vacuum (base pressure $<5 \cdot 10^{-8}$ mbar) by PLD using a pulse repetition frequency of 5 Hz and a fluence of 0.7 J/cm^2 . The Lambda Physik LPX 305i excimer laser, which has a pulse duration of 25 ns and a wavelength of 248 nm, is equipped with a beam homogenizer to obtain a spatially homogeneous spot. Epitaxial films are deposited on CaF_2 at a substrate temperature T_s between 400 and 600 °C. Nanocrystalline

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films are grown when depositing at room temperature on quartz (single crystalline) substrates. Epitaxial MBE grown Y films are deposited on CaF_2 at 700 °C at a base pressure of $6 \cdot 10^{-9}$ mbar. All films were covered with a 10 nm Pd cap layer to prevent the oxidation of the 100–300 nm films and to catalyze the hydrogen uptake.

The surface morphology is investigated using a Nano-scope III tapping mode atomic force microscopy (AFM) system. Simple gas switching experiments up to 100 mbar are performed in a vacuum chamber fitted with a LED-diode ($\lambda_0=635$ nm) and photodetector, while the resistivity is simultaneously recorded in a Van der Pauw geometry. Optical transmission and reflection spectra are recorded in a Bruker IFS 66/S spectrometer with a maximum pressure of 1 bar H_2 .

3. Results and discussion

3.1. Morphological and structural properties

The surface morphology of the PLD in-situ grown YH_2 films is quite different from that of MBE-grown epitaxial Y films, which are ex-situ loaded to the YH_2 phase. These ex-situ loaded thin films are characterized by flat crystalline regions with crystalline growth steps, separated by large platelike protrusions as shown in Fig. 1a. This triangular ridge pattern is the result of a special kind of twinning (the 111-direction being tilted by $\sim 90^\circ$ with respect to the main epitaxial orientation) due to compressive surface stresses during cooldown after deposition and subsequent YH_2 formation [8,9].

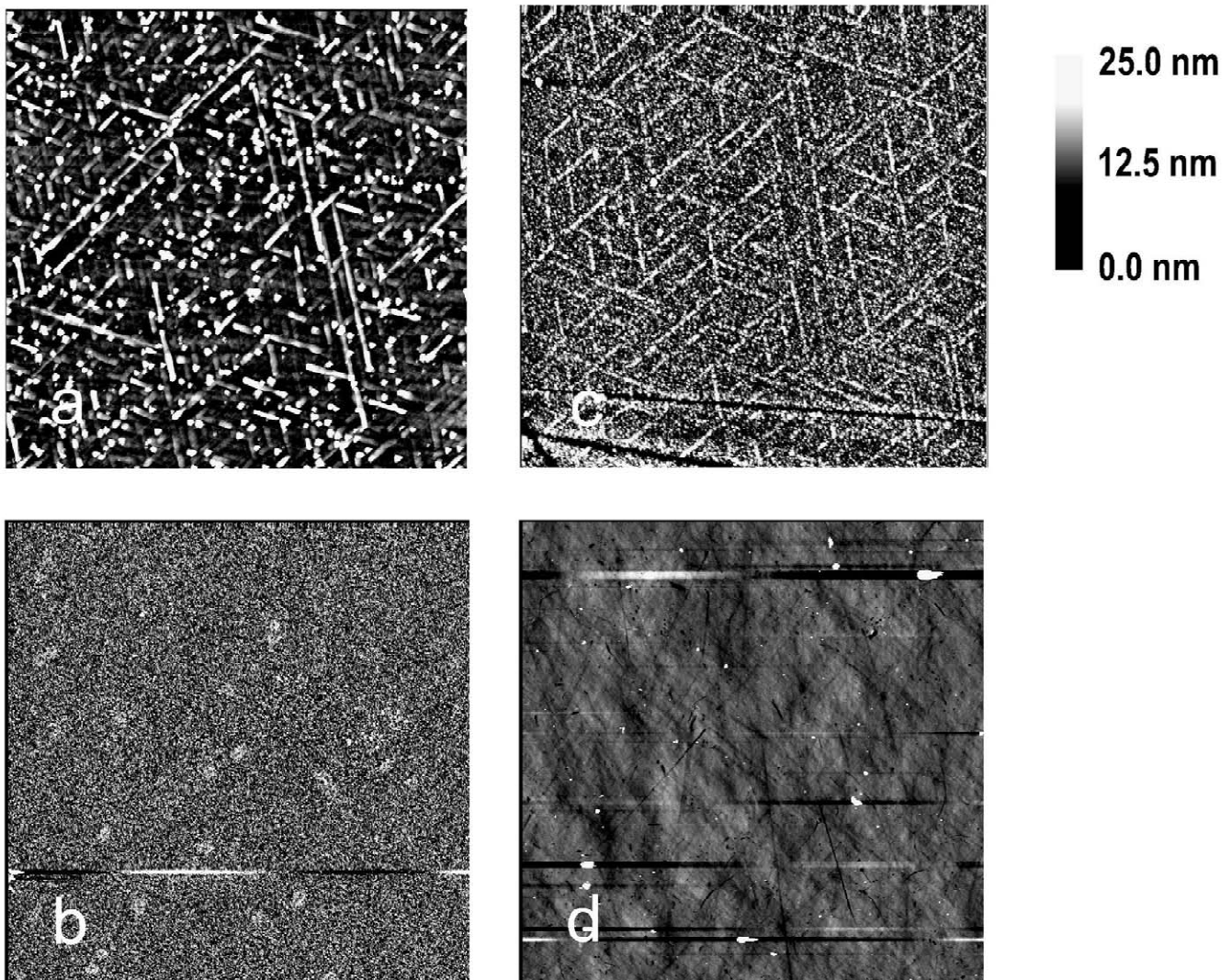


Fig. 1. AFM tapping micrographs of YH_2 films. All images have the same height scale and have the same size ($25 \times 25 \mu\text{m}$). (a) Ex-situ loaded epitaxial MBE film with typical ridge pattern. (b) In-situ grown epitaxial PLD film with typical morphology. (c) In-situ grown epitaxial PLD film. Ridges are uncommon (appear in less than 4% of the films) and consist of elevated grains. (d) In-situ grown nanocrystalline YH_2 film at room temperature on quartz. The surface has a flat and wavy appearance.

Epitaxial PLD grown YH_2 films are formed at much lower substrate temperatures compared to the MBE Y films (around 500 instead of 700 °C, respectively). As demonstrated in Fig. 1b these films are virtually particulate free. The grain size is around 30 nm, which precludes the observation of surface steps by AFM. Only in some irreproducible cases (in 4% of the films) we find something of a ridge structure (Fig. 1c). The ridge, however, is now an area where grains are protruded slightly above their surroundings. The absence of ridges is an advantage for devices since these surface protrusions could cause electrical shorts through the electrolyte layer. Nanocrystalline YH_2 films (Fig. 1d) deposited at room temperature on quartz substrates have the lowest surface roughness compared to epitaxial PLD and MBE films ($r_{\text{rms}}=0.6$ nm, $r_{\text{rms}}=4$ nm and $r_{\text{rms}}=1.8$ nm, respectively). These randomly oriented films have wavy surfaces without ever showing any ridge formation.

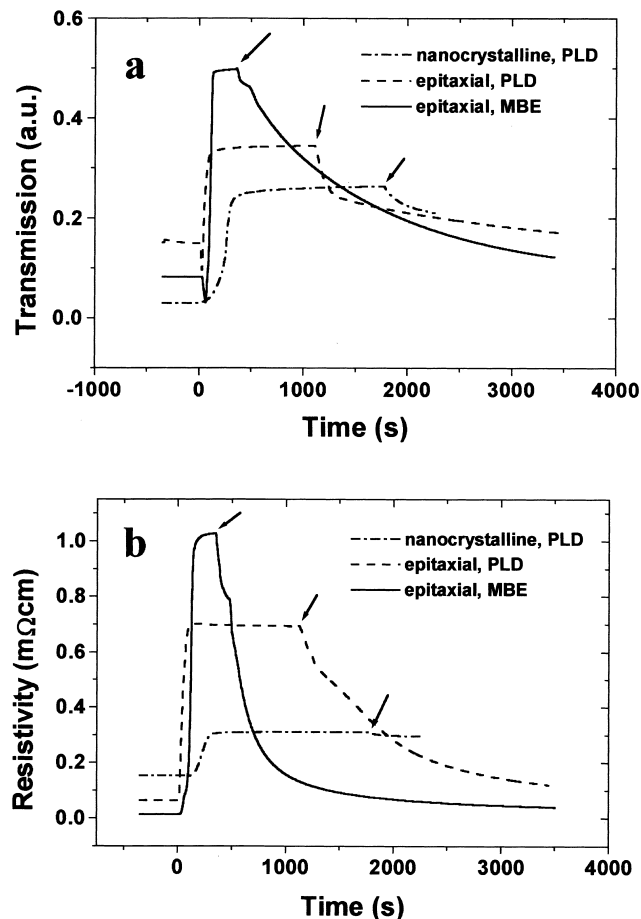


Fig. 2. Comparison of the switching behavior of in-situ grown PLD YH_2 films with ex-situ loaded MBE YH_2 films during loading and unloading to the YH_3 phase. Arrows indicate unloading. (a) Transmission at $\lambda=635$ nm. (b) Resistivity.

3.2. Switching properties

When comparing the optical properties during hydrogenation of the MBE-grown film with the PLD-grown films—both epitaxial and nanocrystalline—the MBE film has the largest change in transmission (see Fig. 2a). The epitaxial PLD film shows a relatively large transmission in the as-deposited state. In both epitaxial films the transmission first drops before it starts to rise. This corresponds to a commonly observed darkening within the dihydride phase upon loading. The dip is absent in nanocrystalline films.

As seen in Fig. 2b also the resistive transition shows a much wider dynamic range in the MBE films than in the PLD films. MBE films in the β -phase have a lower resistivity than the PLD deposited films. The change in resistivity is smallest for nanocrystalline films.

The same differences between PLD and MBE films in optical transmission are observed when plotting the whole spectrum (Fig. 3b compared to Fig. 2a). Additionally, the

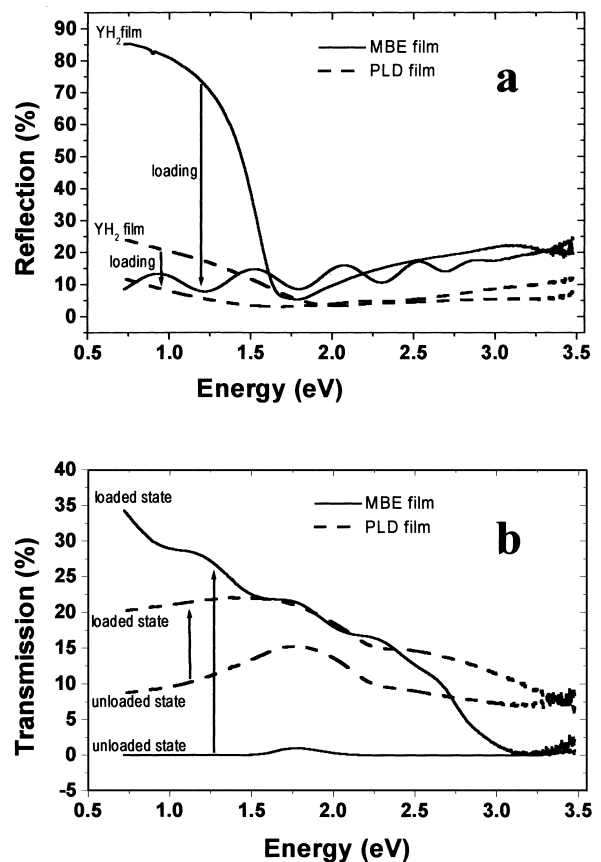


Fig. 3. Comparison of the optical properties over a side spectral range of the unloaded YH_2 and the loaded $\text{YH}_{3-\delta}$ phase for epitaxial PLD and MBE grown films. (a) Reflection. (b) Transmission. A shift in the band edge energy for the PLD film indicates the presence of secondary phases.

transmission in the loaded state extends to much larger photon energies in the PLD than in the MBE films. Moreover, the reflection shows a larger variation at the low photon energy region (NIR) for the MBE film than for the PLD film (Fig. 3a). These observations suggest the presence of impurity phases, like oxides and/or hydroxides [10]. Indeed, we observed a small amount of $Y(OH)_3$ as a secondary phase by X-ray diffraction measurements [7].

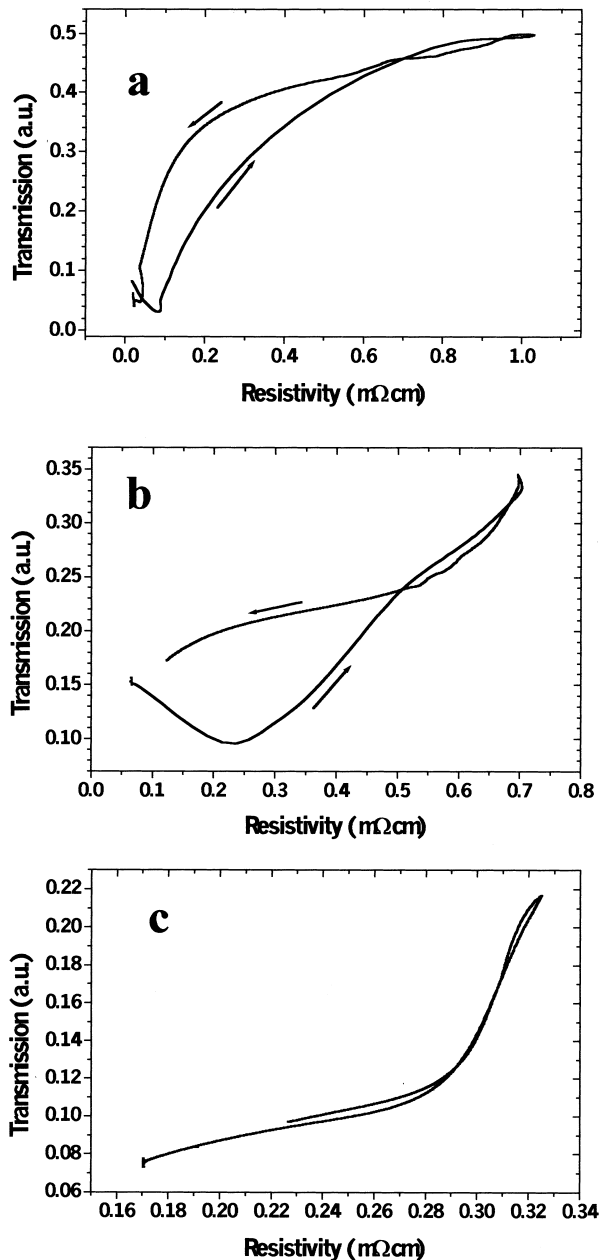


Fig. 4. Combining resistivity and transmission during loading and unloading reveals the presence or absence of hysteresis in switching. (a) Epitaxial MBE film. (b) Epitaxial PLD film. (c) Nanocrystalline PLD films. Only these films switch hysteresis free.

Combining the optical and resistive data one observes the remarkable absence of the hysteresis in the nanocrystalline PLD films (Fig. 4). The origin of hysteresis in epitaxial films was described by Remhof et al. [11]. Upon loading, first a dark β -phase ($YH_{2.1}$) is formed, while upon unloading the more transparent $YH_{1.9}$ -phase is formed. This is due to the different lattice expansion in the β - and γ -phases. Hysteresis is therefore not expected in the absence of a phase transition. Examining the nanocrystalline film in more detail, we find, in contrast to the epitaxial PLD films, that the c -axis remains almost constant during loading. Hence the film remains in the f.c.c.-phase during hydrogen loading. Apparently, the randomly oriented grains are too small to be transformed to the h.c.p.-phase. This might also affect the maximum hydrogen uptake and thereby the dynamic switching range. It appears that lattice expansion, phase transition, and grain size play an important role in the switching process.

4. Conclusions

PLD facilitates the formation of YH_2 films at very low hydrogen background pressures. PLD allows the formation of flat, ridge-free films. The nanocrystalline films formed at low substrate temperatures remain in the f.c.c. phase upon hydrogen loading. As a result, we do not observe a hysteresis in these films. Surface flatness and the absence of hysteresis are important features if these materials are to be incorporated in all-solid-state devices. However, the microstructure (secondary phases, grain size) influence the switching contrast of PLD deposited films.

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