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Reversible loading of epitaxial Y(00.1) films with hydrogen

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Yttrium can be loaded with hydrogen up to high concentrations causing dramatic structural and electronic changes of the host lattice. We report on the reversibility of hydrogen loading in thin, monocrystalline Y films grown by molecular beam epitaxy on Nb/sapphire substrates. During hydrogen loading, the Y film undergoes structural transitions from the cubic dihydrid phase to the hexagonal trihydrid phase, while the structural coherence is maintained. The transition from YH_2 to YH_3 occurs at room temperature at a hydrogen pressure of 10 mbar and is completely reversible. [S0163-1829(97)51230-6]

Within the last decades hydrogen in metals and alloys has been studied in much detail.[1–3] Renewed interest in metal-hydrogen systems stems from interesting structural and functional properties which have recently been discerned in thin films and superlattices. Among those are giant lattice expansions caused by hydrogen in Mo/V (Ref. 4) superlattices, hydrogen induced changes of the exchange coupling in Fe/Nb superlattices,[5] and hydrogen governed switching of the optical properties in yttrium and lanthan-hydride thin films.[6] These results indicate clearly that hydrogen in metals is more than a structural ingredient and that it can be used as a functional agent in high technology materials. This development was only possible due to recent advances in thin-film deposition techniques and hydrogen loading capabilities.

At low hydrogen concentrations, the hydrogen in rare-earth (RE) metals can be described as a lattice gas. The metal lattice expands in proportion to the hydrogen concentration, while maintaining its structural and metallic properties (α phase). At higher concentrations, stable dihydrid (β) and trihydrid (γ) phases form. While most RE metals crystallize in the hcp structure, all dihydides of trivalent RE metals transform to CaF_2-like fcc structures. Apart from the divalent lanthanides and from the systems La-H, Ce-H, and Pr-H, all RE metals undergo a second phase transition at higher H concentrations to the hexagonal γ phase.

Up until recently most work on hydrogen in RE metals has been done using bulk or powder samples. Huiberts *et al.* investigated polycrystalline thin Y films under hydrogen loading. In the trihydrid phase, the formerly shiny metallic film becomes a transparent semiconductor with a direct band gap of 1.8 eV.[6] The optical changes are accompanied by a metal-insulator transition at hydrogen concentrations above 2.8. The polycrystalline film can reversibly be loaded with hydrogen and the switching time between a metallic reflecting mirror and a transparent film has dropped from several seconds to a fraction of a second.

The electronic structure of YH_{2+x} and LaH_{2+x} with switchable optical properties have recently been described by Ng *et al.*[7] in a local model assuming localized states centered at vacancies in the RE-H_3 structure. In another density-functional approach by Kelly *et al.*[8] small symmetry lowering displacements of the hydrogen atoms are required for driving the metal-insulator transition and for opening a large band gap. In both models the main challenge is to understand why only minute structural changes induced either by vacancies or by collective displacements cause dramatic optical switches. For a better understanding of the electronic properties it is therefore of utmost importance to prepare and study single-crystalline RE films with varying hydrogen concentration. Because of the structural phase transitions mentioned above, it is, however, not clear whether the once deposited epitaxial RE film would maintain its structural integrety up to $x=3$.

Here we report on our successful growth of epitaxial Y films by molecular beam epitaxial (MBE) methods and on hydrogen loading of these monocrystalline films with complete reversiblity up to high hydrogen concentrations. We have grown monocrystalline Y(00.1) films with a typical thicknesses of 50 nm by MBE using Al_2O_3 (11.0) substrates. The Y film is separated from the sapphire substrate by a Nb(110) buffer.

Hexagonal closed packed RE metals are known to grow epitaxially on Nb(110).[9] The epiaxial relation follows the Nishiama-Wassermann orientation, where the (10.0) axis of the RE is parallel to the $(\overline{1}\,\overline{1}0)$ axis of the Nb. In the special case of Y on Nb there is a 3:4 match, i.e., a supercell commensuration between the Y(10.0) distances of 0.316 nm and

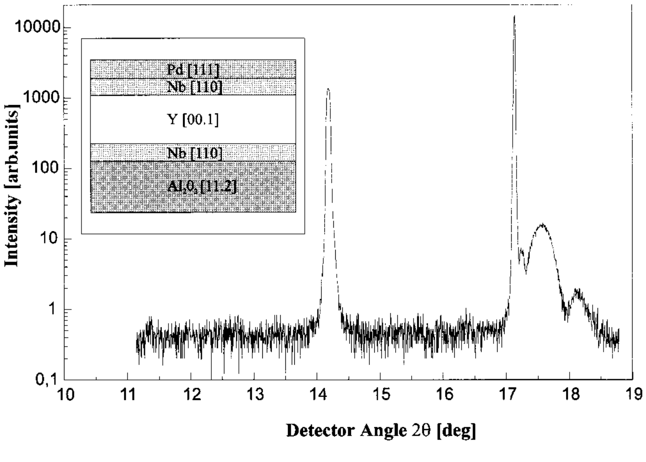

FIG. 1. Radial Bragg scan in the direction normal to the yttrium film after epitaxial growth. With increasing angle the Y(00.2) peak, the sapphire (11.0) peak, the Nb(110), and the Pd(111) reflection can be seen. The inset shows the sample architecture.

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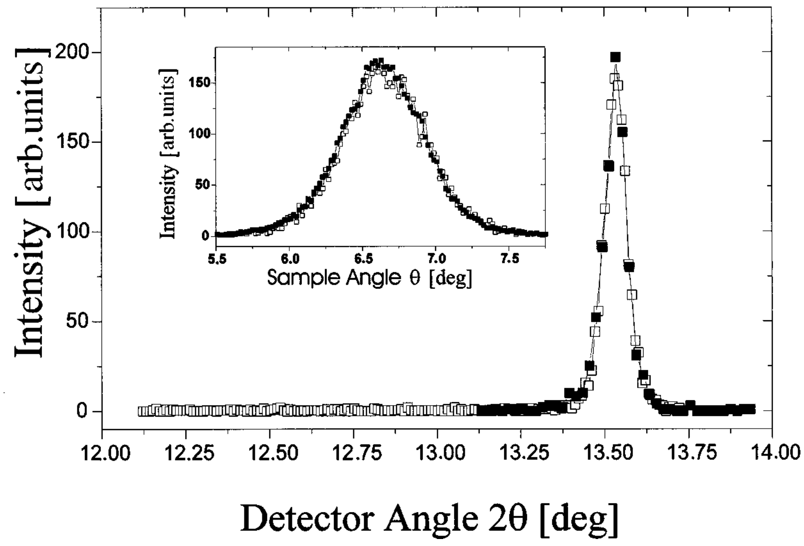

FIG. 2. Radial scans of the YH_2(111) reflection. Dark symbols refer to the first hydrogen loading, open symbols to the fifth cycle. The inset shows the corresponding rocking scans through the (111) reflection. Corresponding curves overlap, proving the total reversibility of the dihydrid phase.

the Nb($\bar{1}10$) distances of 0.234 nm. As the hydrides also form hexagonal basal planes with corresponding lattice spacings of 0.3184 nm (YH_2) and 0.3177 nm (YH_2), they should obey the same epitaxial relation.

To protect the Y film from oxidation and to dissociate the hydrogen molecules at the surface, the sample was covered with a 5-nm-thick palladium layer. Since palladium tends to form islands on yttrium, we deposited a second, 10-nm-thick niobium layer prior to the Pd growth to separate the yttrium from the palladium. The sample architecture is schematically shown in Fig. 1. The metal deposition was carried out in a Riber EVA 32 MBE machine under ultrahigh vacuum conditions (base pressure below 5×10^{-9} Pa). First the Nb buffer was deposited on the sapphire substrate at a temperature of 1200 K. During the yttrium deposition, the temperature was lowered to 850 K. The cap layers were added at room temperature. During the complete growth process, *in-situ* reflection high-energy electron diffraction was performed, confirming the excellent crystallinity of the sample.

Structural characterizations were performed via high angle x-ray scattering using $\mathrm{Mo}_{K_{\alpha1}}$ radiation of a fine focus x-ray tube, monochromated by a Si(111) reflection. For the *in situ* studies of the structural changes under hydrogen loading an x-ray furnace with Al windows was used. A Bayard-Alpert ion gauge and two capacitive transducers covering different pressure regimes allowed us to control the hydrogen pressure up to 10^5 Pa. Before hydrogen loading, the structure of the sample was determined by radial Bragg scans. Figure 1 shows successively with increasing angle the Y(00.2) peak, the sapphire (11.0) peak, the Nb(110), and the Pd(111) reflection, respectively.

Initially the Y(00.2) reflection has a longitudinal width of 0.07° and a transverse width of 0.1°. Its position refers to an out-of-plane lattice constant of 0.578 nm, which is about 1% larger than the bulk value of 0.573 nm, indicating initial hydrogen contamination. Hydrogen loading at room temperature up to YH_2 broadens the initially sharp transverse width to 0.65°. In radial scans, though, the Bragg peaks maintain their width and shape, indicating a constant coherence length. Simultaneously, the peak intensity drops by a factor of 6.5, conserving the integrated intensity under the Bragg peak. No additional diffuse scattering from structural disorder could be observed. From the peak position we deduce interatomic distances of 0.30 nm in the (111) direction, which matches perfectly with the value given in Ref. 10. Increasing the hydrogen pressure leads to the YH_3 phase. This phase transition takes place at 10 mbar. While the first transition is accompanied by a loss in the quality of crystal-

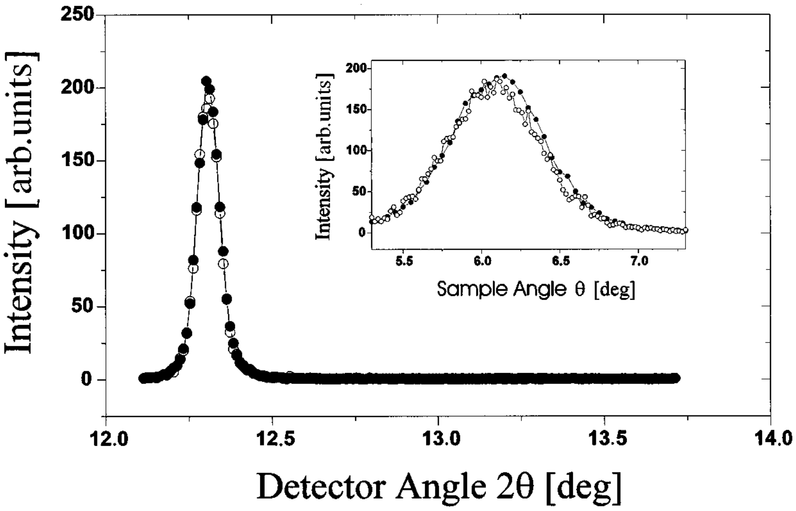

FIG. 3. Radial scans of the YH_3(00.2) reflection. The symbols are the same as in Fig. 2. The inset shows the corresponding rocking scans through the (00.2) reflection. As in the case of YH_2 corresponding curves overlap, proving the total reversibility of the trihydrid phase.

linity, the second transition causes no further change either of the width or of the shape of the x-ray peaks. The transition between the dihydrid phase and the trihydrid phase is completely reversible. The trihydrid exhibits a lattice parameter of 0.660 nm, which is slightly smaller than the value of 0.666 nm given in Ref. 10. We attribute this deviation by a substoichometric composition of the YH_3, where saturation is not yet achieved.

Expelling the hydrogen at 10^{-7} mbar and at 100 °C results again in the YH_2 phase. Even after several cycles, no loss in the structural coherence is observable. Figures 2 and 3 compare the radial scans and the rocking curves of the YH_2 (111) reflections and the YH_3 (00.2) reflections in the first and in the fifth cycle, respectively. Within the statistics, the corresponding curves overlap perfectly.

The time needed to form the trihydrid is governed by the external hydrogen pressure, i.e., the amount of hydrogen offered. At 10 mbar the transition takes about 1 h, whereas it takes typically 15 min at 250 mbar. During this time, a coexistence of both phases can be observed. Once the dihydrid has been formed, it is possible to switch reversibly between YH_2 and YH_3 without further loss of structural coherence by control of external hydrogen pressure and temperature. We also investigated the tunable optical properties of the material. The sample switches from shiny reflecting in the metallic dihydid phase to the transparent trihydrid phase, as expected.

In conclusion, we have grown epitaxial Y films on sapphire substrate using a Nb buffer layer. The Y film was covered with a Nb layer for oxidation protection and an additional Pd layer to enhance the diffusivity of hydrogen into the Y film. Using this layer arrangement we observed a complete reversibility of the hydrogen loading between the YH_2 and the YH_3 phase. While the mosaicity of the film increases, the structural coherence length along the direction parallel to the film normal remains constant. Using single-crystalline epitaxially grown films has two major advantages over polycrystalline films. First, they are easier to protect against oxidation by a thin epitaxially grown caplayer. Second, they allow one to determine precisely the positions of the hydrogen atoms in the yttrium lattice at high concentration, an information urgently required to perform accurate band-structure calculations. Work in this direction is in progress.

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