

Optical properties of YH_x ($0 \leq x \leq 2.1$) thin films

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Abstract

Thin single-crystalline films of YH_x have been prepared by molecular beam epitaxy in a hydrogen atmosphere, thus avoiding the usual Pd capping layer. Near-normal incidence reflectivity and ellipticity measurements have been performed in the photon energy range from 1.2 meV to 5 eV and 1 to 10 eV, respectively. With increasing H concentration but $x \leq 2$, the absorption decreases below 2 eV and stronger structures develop above 2 eV. For $x > 2$, an additional peak is found in the infrared showing a pronounced x and temperature ($4 \text{ K} \leq T \leq 295 \text{ K}$) dependence. Its behavior is discussed in terms of an order–disorder transition of hydrogen atoms.

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1. Introduction

Ever since the discovery of the switchable mirrors in 1996 [1], a precise determination of the optical properties of the hydrogenated metal film was hindered by the (Pd) capping layer needed to prevent oxidation and to dissociate molecular into atomic hydrogen for loading the metal. Several attempts were made to unravel the optical functions of the switchable mirrors by using multilayer theories for the sample consisting of substrate, switchable mirror and capping layer [2,3]. However, since the optical properties of the capping layer depend on its hydrogen content, its morphology and the morphology of the switching film, this procedure leads only to approximate values. This has recently been demonstrated by showing that fits of measurements from the substrate side give other values than from the capping layer side [3]. In the transparent and weakly absorbing region, the problem can be solved by preparing switchable mirrors of different thicknesses with the same capping layer and dividing the transmitted intensities [4]. In the intermediate and more strongly absorbing region,

however, reflectivity measurements are imperative and the above mentioned difficulties arise. To circumvent these difficulties, the metallic capping layer must be substituted by some non absorbing film. One thought is to replace it by an ion conductor like non stoichiometric CaF_2 allowing the diffusion of hydrogen through this film. We performed such an experiment, but could not effectively load the Y switchable mirror. Therefore, we decided to renounce to the external loading and switching and to load the film in situ. For this, yttrium was evaporated in our MBE system [5] in the presence of atomic hydrogen. Since the electron gun can only be operated at gas pressures below some 10^{-6} Torr, the hydrogen content of the films was restricted to values $x \leq 2.1$. After exposure to air, a largely transparent yttrium oxide layer forms at the surface and prevents a deterioration of the YH_x film.

2. Results and discussion

Three different spectrometers were used. In the far infrared near-normal incidence, reflectivity spectra were recorded with a Bruker 113v Fourier transform spectrom-

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eter covering the photon energy range from about 1 meV to 1.2 eV. A helium cryostat reduces somewhat the low energy limit, but allows measurements down to 4 K. From 1 to 4.5 eV, a home made ellipsometer was used to determine the real and imaginary parts of the complex dielectric function $\varepsilon = \varepsilon_1 - i\varepsilon_2$. For higher photon energies up to 9.5 eV, a similar polarizer–sample–analyzer (PSA) ellipsometer at the BESSY II synchrotron in Berlin was used. From the ellipsometric data, the reflectivity was computed and combined with the direct reflectivity measurements to obtain the full reflectivity spectra. These spectra were fitted with 1 Drude and up to 9 Lorentz oscillators.

2.1. YH_x with $0 \leq x \leq 0.24$

For hydrogen partial pressures $p(H)$ below 2.0×10^{-6} mbar during evaporation of Y onto CaF_2 substrates yttrium hydride in the α^* phase forms. In this phase, hydrogen is dissolved in the closed packed hexagonal structure of Y occupying tetrahedral sites. Thin films at $p(H)$ of 0, 1.5 and 2.0×10^{-6} mbar have been grown and the reflectivity has been determined from 10 meV to 9 eV. The behavior of all the films is metallic with large reflectivity values below 0.5 eV. In contrast to the behavior below 0.5 eV, near 1 eV the reflectivity of the hydrogenated films is higher and above 3 eV shifts of structures appear. For a quantitative analysis, the optical conductivity spectra are presented. Fig. 1 displays such spectra which have been obtained by fitting the reflectivity spectra with Drude and Lorentz oscillators for YH_x and the optical constants of CaF_2 . One recognizes now that the increase of the reflectivity near 1 eV is due to additional and/or shifted transitions. In addition, the plasma energies derived from the Drude terms decrease from 10.16 to 8.73 to 8.50 eV going from $p(H) = 0$ to 1.5 to 2.0×10^{-6} mbar, respectively. Both variations together indicate a lowering of the Fermi energy (E_F), as expected if hydrogen enters as H^- ion in the metal and withdraws electrons from the conduction band formed by 4d and 5s electrons of yttrium. At the same time, a bonding state between Y-5s and the two H-1s and an antibonding combination of the two hydrogen 1s wavefunctions forms [6]. While the former state is expected to have a binding energy of several eV, the binding energy of the latter is smaller and depends sensitively upon the H–H distance. As was calculated by Gupta [6] for transition metal dihydrides, the antibonding state overlaps with the metal d-bands. Thus, we attribute the large peak between 1 and 3 eV for the hydrogenated Y films to transitions from those H-1s antibonding states into empty Y-5s states as well as to transitions of the remaining Y-5s and Y-4d electrons into states above E_F . The pure Y film, of course, has also transitions of 5s and 4d electrons, but the antibonding band is missing, explaining the less structured spectrum for $p(H) = 0$. For the Y-5s and H-1s bonding state, the calculation of Gupta for ZrH_2 predicts a three times larger binding energy than for the antibonding state

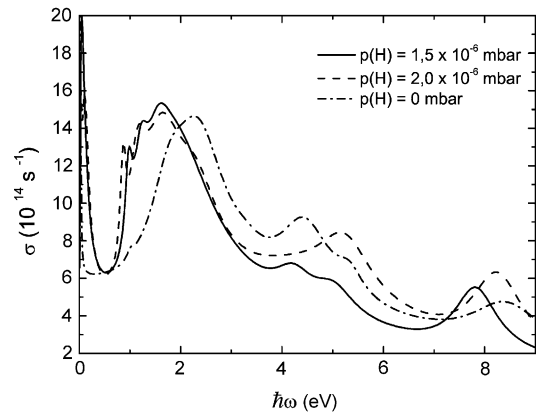


Fig. 1. The optical conductivity at room temperature for two yttrium films of 100 nm thickness grown under different hydrogen pressures and for a pure yttrium film with a thickness of 200 nm.

[6]. Thus, we attribute the structures observed between 4 and 6 eV to transitions from these states into empty states above E_F .

2.2. YH_x with $2.0 \leq x \leq 2.1$

As shown by X-ray diffractometry, Y films prepared under hydrogen partial pressures $p(H)$ of 3.5×10^{-6} mbar belong to the cubic β - YH_x phase which is known to exist for x ranging from 1.8 to 2.1 [7]. The lattice parameter for the film prepared at $p(H) = 3.5 \times 10^{-6}$ mbar is 5.218 ± 0.005 Å which is slightly larger than the values reported for bulk [8] and Pd-capped films [9]. For this film and a second film grown at $p(H) = 4.5 \times 10^{-6}$ mbar, the same type of reflectivity and ellipsometry measurements as discussed in the previous section have been performed. The plasma energy decreases to around 3 eV indicating a substantial diminution of the free carrier concentration. Above 2 eV, two prominent peaks occur which in the reflectivity spectra are located near 3 eV and between 5 and 6 eV. These peaks and the corresponding peaks in the optical conductivity are again assigned to transitions from the bonding and antibonding states generated by hydrogen and from Y states. Here, we like to concentrate on changes appearing in the far infrared. For this purpose, Fig. 2 shows the optical conductivity spectra on a logarithmic energy scale. We find a prominent peak below 0.1 eV which shifts to slightly higher energy with increasing $p(H)$, becomes stronger and narrows. In addition, this peak which has not been observed before, displays a striking temperature dependence. Fig. 3 shows optical conductivity spectra in the relevant energy range at different temperatures for the film grown at $p(H) = 4.5 \times 10^{-6}$ mbar. One recognizes that the peak decreases and shifts to lower photon energy with decreasing temperature. Eventually, it disappears between 160 and 230 K. This temperature range is very close to the 200–250 K range in which Daou and Vajda [10] found anomalies in the electrical resistivity of bulk sam-

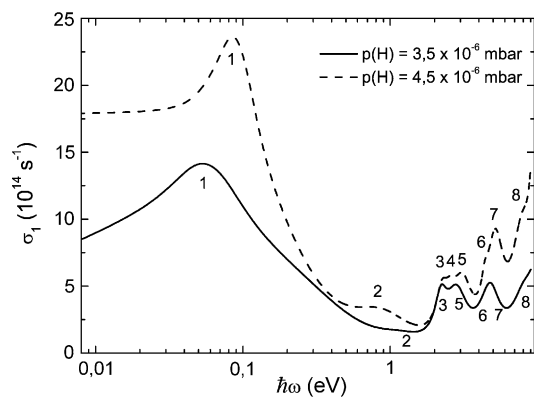


Fig. 2. Optical conductivity spectra for two 100 nm thick yttrium films grown under higher hydrogen pressure than in Fig. 1.

ples and which they attributed to order–disorder transitions within the octahedral hydrogen sublattice. We have also performed resistivity measurements on our films and plotting the temperature derivative of the resistivity versus temperature $d\rho/dT$, we also find anomalies of $d\rho/dT$. For the film grown at $p(\text{H}) = 3.5 \times 10^{-6}$ mbar, $d\rho/dT$ displays a maximum near 160 K in agreement with the results for bulk samples with $x \cong 2.05$ [10]. This has been attributed to a short range ordering of the H-sublattice as consequence of the occupation of octahedral sites which starts at $x = 2$. For the film grown at $p(\text{H}) = 3.5 \times 10^{-6}$ mbar, $d\rho/dT$ increases monotonically up to 240 K and displays structures above this temperature. These structures have been associated with long range ordering of hydrogen atoms on octahedral sites and were reported to occur in bulk samples for $2.085 \leq x \leq 2.1$ [10]. The transition from the ordered low-temperature phase to the disordered high-temperature phase is related to a metal–insulator (M–S) transition, due to the collapse of a delocalized H-impurity band near E_{F} . This model is parent to the proposal of Shinar et al. [11] for LaH_x with $2.80 \leq x \leq 2.90$. The authors determined the resistivity from Q factor measure-

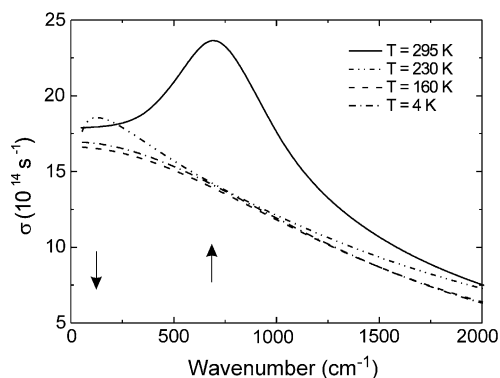


Fig. 3. Optical conductivity spectra in the far infrared for the yttrium film grown under a hydrogen pressure of 4.5×10^{-6} mbar for different temperatures between 4 and 295 K.

ments on coarse powder LaH_x samples and found narrow and sharp peaks between 220 and 260 K with thermally activated resistivities above the transition. This metal–insulator transition occurring, contrary to the usual situation, with increasing temperature is attributed to a collapse of a delocalized band at E_{F} , associated with the superlattice of octahedral H-vacancies. The main difference between the two models is that the former starts from the dihydride and assumes a H-impurity band, while the latter starts from the trihydride and considers a H-vacancy band. Since the dihydride is a metal and the trihydride is an insulator, the experimental situation is much clearer in the latter case and one might interpret the changes of $d\rho/dT$ in the former case as a precursor of the real M–S transition. Both groups of authors derive activation energies. Daou and Vajda derive a value of 18 meV for $x = 2.095$ [10], while Shinar et al. find an increase of the activation energy from 18 to 140 meV when x increases from 2.80 to 2.90 [11]. It is tempting to associate our optical peaks (Fig. 2) at 55 and 85 meV for $p(\text{H}) = 3.5 \times 10^{-6}$ mbar and 4.5×10^{-6} mbar, respectively, appearing at a similar temperature as the order–disorder transition with these activation energies. The corresponding gap should be twice the activation energy, placing our peak values well in the expected range.

In conclusion, we have reported the first optical measurements on YH_x films having no metallic capping layer. This allows us a more precise determination of the optical properties in general and opens the way to a study of the properties in the energy range of intermediate absorption. As a first striking result, the observation of an optical transition in the infrared is presented for the β -phase which is discussed in terms of the order–disorder transition and which is seen as a precursor of the metal–insulator transition for larger x .

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