Journal of Alloys and Compounds 404–406 (2005) 699–705

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Combinatorial method for the development of a catalyst promoting hydrogen uptake

A. Borgschulte*, W. Lohstroh, R.J. Westerwaal, H. Schreuders, J.H. Rector,
B. Dam, R. Griessen

Faculty of Sciences, Division of Physics and Astronomy, Vrije Universiteit De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

Received 7 September 2004; received in revised form 11 January 2005; accepted 18 January 2005

Abstract

A novel optical technique to measure catalytic activity for hydrogen sorption is presented. The catalytic activity of the noble metals of Pd, Ni, Cu and Ag is studied as function of pressure and temperature. The uptake rate is limited by chemisorption as deduced by modelling kinetics. An empirical relation between uptake rate and the measured activation energy is given. The catalytic activity of NbO_x is studied as a function of the oxygen concentration determined from electron spectroscopy. The measured activation energy depends strongly on the oxygen concentration and reaches a minimum of 0.6 eV at the highest oxygen content ($x = 2.5$, i.e. Nb_2O_5). Pure Nb does not display a significant catalytic efect.

Keywords: Hydrogen storage material; Thin films; Gas–solid interaction; Light absorption

1. Introduction

There is an enormous empirical knowledge about catalysis and catalysts. We know, for instance, that the kinetics of hydrogen sorption in Mg based storage devices is greatly enhanced by additives like transition metal oxides [1], while it was found that oxides on top of typical hydride forming metals (Mg, Y, etc.) strongly impede hydrogen absorption [2,3]. Sensors [4] and hydrogen switchable mirrors [5] use Pd as a catalytic caplayer, and usually Pt is used for hydrogen dissociation in fuel cell electrodes [6]. But in general, we do not know why [7]. One reason for this is that 'catalytic activity' is not a fundamental property of a material. In particular it depends on the surface properties of the catalyst, which are strongly influenced by external parameters like reaction gas purity etc. Moreover, the activity and selectivity hinge on the details of complex kinetic phenomena, often at spectroscopically elusive active sites. For finding general fundamental relations, it is mandatory to have an experimental method to reliably measure the catalytic activity for hydrogen sorption, and – at the same time – to probe the active sites by appropriate analysis methods. In this paper, we describe a novel method to determine the effect of catalysts on the kinetics of hydrogen sorption. The method uses an indicator layer, whose hydrogen uptake can be optically monitored [8]. The metallic indicator layer has a high affinity for hydrogen but is not able to absorb it directly due to its non-active oxide skin. This thin oxide layer does transport hydrogen to the optically active indicator layer, once the molecular hydrogen is dissociated [3] by a catalyst (e.g. Pd-clusters [9]). On this thin film system, various catalysts are deposited and their catalytic effect is studied as a function of composition, thickness, temperature and hydrogen pressure. The technique is extended to a combinatorial screening method by the use of large area thin film matrix samples with controlled gradients in local chemical composition of two or more constituents. The thin film approach opens the possibility to use well-established surface science techniques. As a demonstration of this technique we investigate the appropriate thermodynamic conditions for a fast sorption kinetics of noble metal catalysts. In addition, we study the role of oxygen in the NbO_x-catalyzed sorption process on microscopic scale by X-ray photoelectron spectroscopy.

---

[*] Corresponding author. Tel.: +31 20 4447924; fax: +31 20 4447992.
E-mail address: borg@nat.vu.nl (A. Borgschulte).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.01.137

2. Experiment

Polycrystalline Y, Pd, Ni, Cu, Ag and NbO_x films are grown using a dc sputtering system. The argon pressure is 10^2 mbar, the background pressure less than 10^{-7} mbar. NbO_x films are grown by reactive sputtering from a Nb target in an Ar/O atmosphere. The yttrium is surface-oxidized in air for 2 min. The surface composition of the films is determined by X-ray photoelectron spectroscopy (XPS). Experiments are performed in a VG ESCALAB 5 photoelectron spectrometer at a base pressure better than 10^{-9} mbar. The photoelectrons are excited by Mg Kα radiation (1253.6 eV). Yttrium films are used as indicator for the H concentration, as yttrium displays large optical changes upon hydrogen incorporation (see Ref. [5,8]). Pure yttrium and YH_x $x \leq 0.21$ (α-phase) are shiny metals. The dihydride YH_2 (β-phase) is also metallic, but has a weak transparency at a photon energy around 1.9 eV. The corresponding spectrum is shown in Fig. 1, the dihydride phase corresponds to the first maximum in the loading curve (at around 90 s in the inset of Fig. 1). YH_3 (γ-phase) is an insulator with a band gap of 2.68 eV [10] (Fig. 1). The time evolution of the optical changes of such yttrium samples is monitored with a CCD camera using a macro-objective. The sample is exposed to hydrogen in a loading cell with single-crystalline sapphire windows which withstand temperatures up to 300 °C in a hydrogen atmosphere at pressures up to 10 bar. The signal of the CCD camera is read out by a personal computer. The time evolution of the RGB signals during hydrogen ab/desorption for each pixel is analyzed by means of the dedicated image processing software eescan. The loading cell is placed in an oven to perform measurements at temperatures between room temperature and 300 °C. Camera and light source are placed outside the oven. The optical setup to measure catalytic activity is sketched in Fig. 2.

The time between the opening of the H_2 valve and the first maximum (corresponding to the infrared transparency window of the dihydride) is defined as the switching time of the film. We consider only the switching within the α- and β-phases, because the position of a maximum is better defined than the saturation level at the metal–insulator transition within the γ-phase. Additional reasons are thermodynamic considerations (see below). The switching time is a measure for the average hydrogen uptake of the yttrium film. However, it does not inform us about the progression of the kinetics. The transmission T increases exponentially with the formation of the β-phase (see Fig. 1). Therefore, the hydrogen absorption kinetics can mathematically be modelled by assuming a Lambert–Beer like law, a linear law for the change of the optical absorption Kd with hydrogen concentration x and a constant hydrogen flux $\dot{a}$ into the yttrium:

$$T = T_0\,\mathrm{e}^{-K(x)d}, \quad K(x) \propto -\dot{x} \tag{1}$$

Indeed, the logarithmic transmission functions in Fig. 3 are well fitted with a linear function within the mixed $\alpha + \beta$ state. The kinetics depends strongly on the particular surface modification, here the Pd- caplayer thickness (Fig. 3). For various thicknesses, the corresponding slopes $m = \mathrm{d}\ln T/\mathrm{d}t$ are plotted versus the reciprocal switching times 1τ (inset of Fig. 3). The resulting proportionality $\dot{x} \propto m$ proves a constant hydrogen flux over the whole absorption range. Therefore, the hydrogen flux is only determined by the properties of the thin film caplayer. The reciprocal value of τ as well as the logarithmic change of transmission can both be taken as a measure for the hydrogen uptake rate and thus as a measure of the catalytic activity of the caplayer. The analogousness of both methods was proven in Ref. [12]. Naturally, this behavior is only true, if the indicator layer (yttrium) fulfills particular conditions. The dissociation pressure of YH_2 has

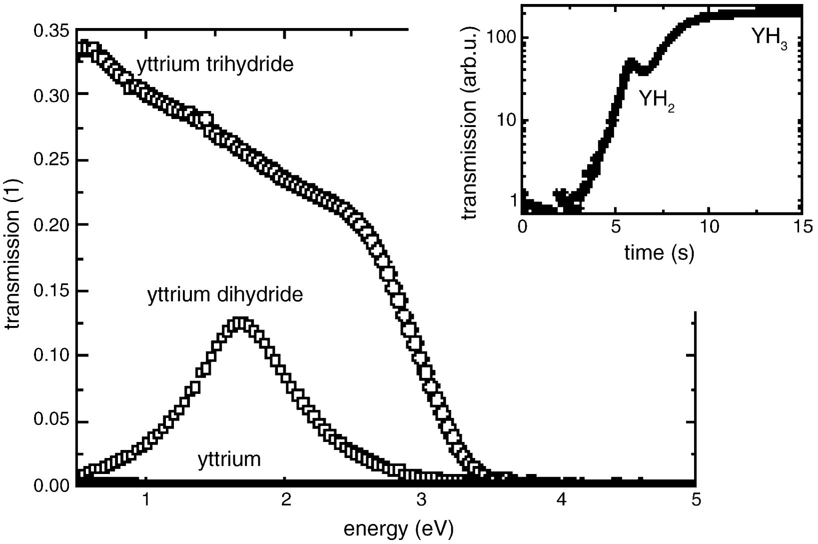

Fig. 1. Optical transmission spectra of a 100 nm yttrium film capped with 10 nm Pd. The inset shows the time evolution of the transmission in the integrated spectral range from 1 to 3.5 eV.

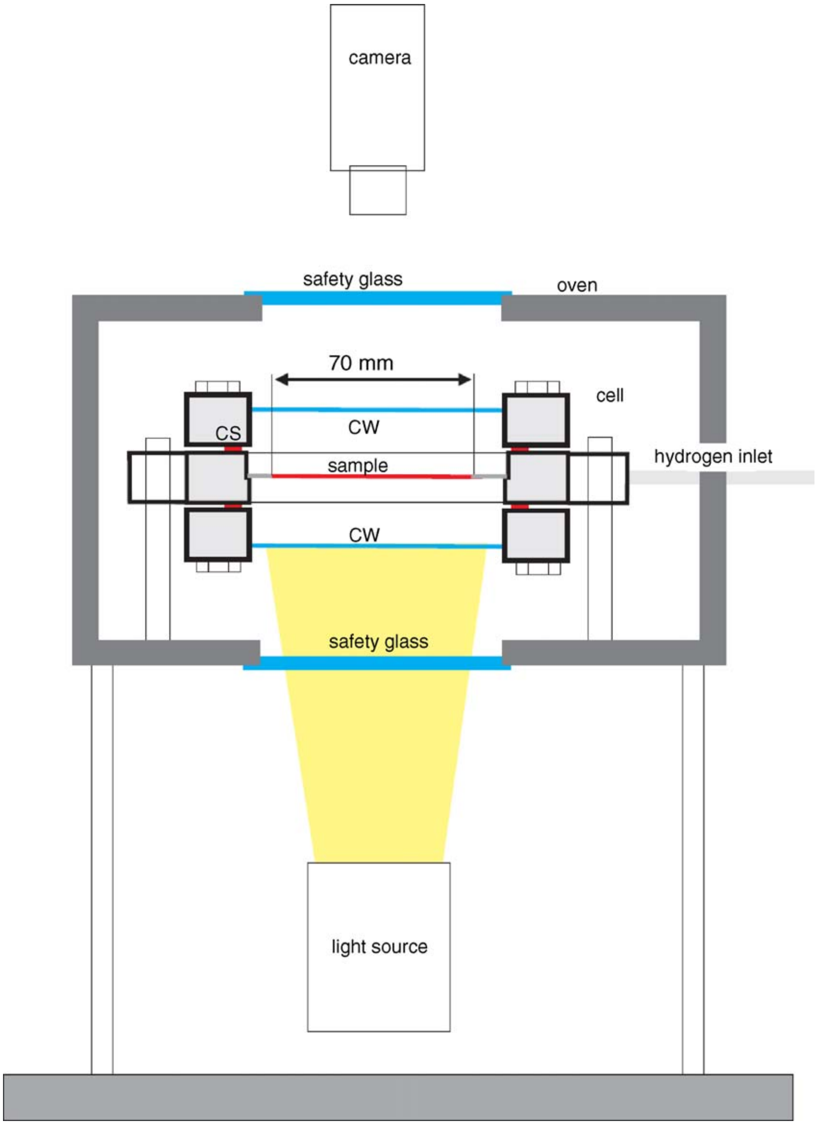

Fig. 2. Setup to measure optically hydrogen uptake of thin films. The hydrogen cell is setup by two CF100 sapphire single crystal windows (CW) withstanding 10 bar hydrogen and a CF100 stainless steel adapter flange with sample holder and temperature sensor. All used seals are made out of copper (CS) to avoid any contaminations at high temperature.

to be much lower than the used hydrogen pressure of 2 bar ($p_{\text{diss}} = 105$ Pa at 600 K [11]). This corresponds to the high heat of formation of -114 kJ/mol H of YH_2. Moreover, the diffusion within the yttrium has to be faster than the surface uptake rate. This is valid only in thin films. With a diffusion rate of $D = 3 \times 10^{-10}$ cm^2/s the time for hydrogen diffusing through 100 nm yttrium is $\tau = 0.3$ s [13], while a typical switching time is at least several seconds. A further condition for the use of a particular indicator material is that alloying or intermixing with the catalytic caplayer is avoided by, e.g. the formation of a chemically very stable but thin oxide skin. The hydrogen diffusion through this oxide should not be rate limiting [3]. From this it becomes clear that only a few hydride forming materials are suitable as an indicator, e.g. Y or Gd.

3. Results and discussion

In the following, we describe two typical systems to illustrate the indicator method. The optically measured hydrogen uptake kinetics for various noble elements is discussed in Section 3.1. Under real operating conditions one has to consider the effect of impurities, in particular oxygen. The importance of oxygen on the catalytic effect of Nb is described in Section 3.2. It also demonstrates the combinatorial ability of the indicator method.

3.1. Catalytic effect of noble metals

To shed light on the physical mechanism of the hydrogen absorption process, we study the kinetics as a function of the

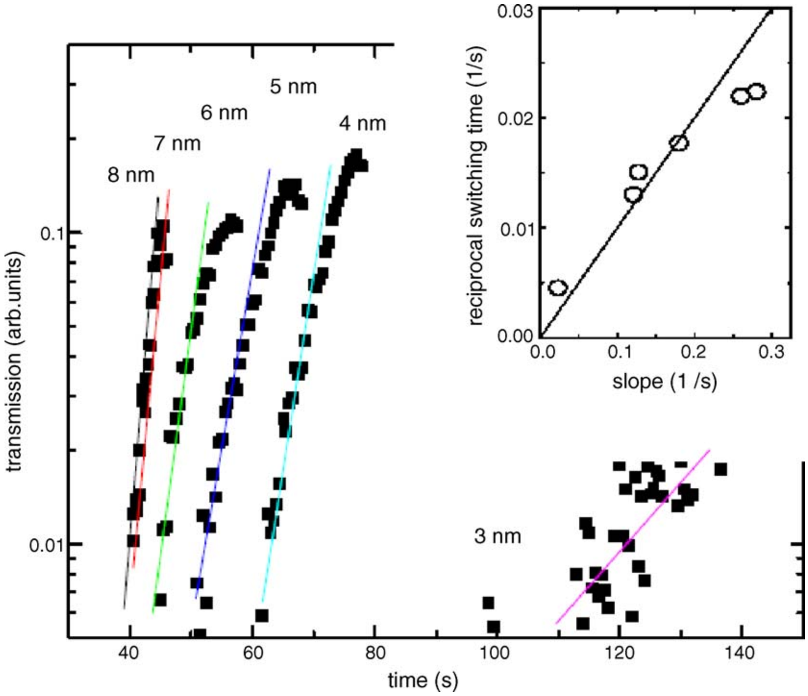

Fig. 3. Optical transmissions of a 100 nm yttrium film capped with various Pd-thicknesses during loading from the α- to the β-phase. The film is exposed to 2 bar hydrogen at 423 K at $t = 0$. Transmission values smaller than 0.005 have been removed (noise level of the camera). The inset compares the as-measured reciprocal switching time with the slope of the transmission curves.

external thermodynamic parameters pressure p and temperature T. From kinetic modelling we expect that:

(i) If dissociation is the rate determining step, the rate will be proportional to the physisorbed hydrogen [14]. Since the coverage with physisorbed hydrogen Θ_{ph} is small at room temperature, Θ_{ph} and therefore the total hydrogen absorption rate R is proportional to the hydrogen pressure [14]:

$$R \propto \Theta_{\mathrm{ph}} \propto p \qquad (2)$$

(ii) If the surface is not the rate limiting step, the driving force will be the thermodynamic potential difference between gaseous and dissolved hydrogen (quasi-equilibrium) [14] and $R \propto \sqrt{p}$

To distinguish between these two cases, the switching kinetics of Pd-capped yttrium film is studied as a function of H_2-pressure. For this, the switching time of the as-grown samples is measured at room temperature for various hydrogen pressures. The resulting rate, i.e. the reciprocal switching time, is a monotone function of the pressure (Fig. 4). The data points are well fitted by a linear function, i.e. chemisorption of hydrogen is the rate limiting step during hydrogen absorption. To investigate the temperature dependence of the hydrogen absorption process we determined the switching time of the as-grown samples at constant hydrogen pressure (2 bar) for various temperatures. The rates are plotted in an Arrhenius plot to determine an apparent activation energy E_A. This is shown in Fig. 5 for four noble metals Pd, Ni, Cu and Ag. As expected, Pd capped films display highest rates. The values are well fitted with a linear function from which an activation energy is calculated. However, the results are surprising in the following respect. The catalyst with the highest hydrogen absorption rate has the highest activation energy E_A, what is not expected for a true Arrhenius relation ($R \propto \exp(-E_A/(kT))$). The rates are better

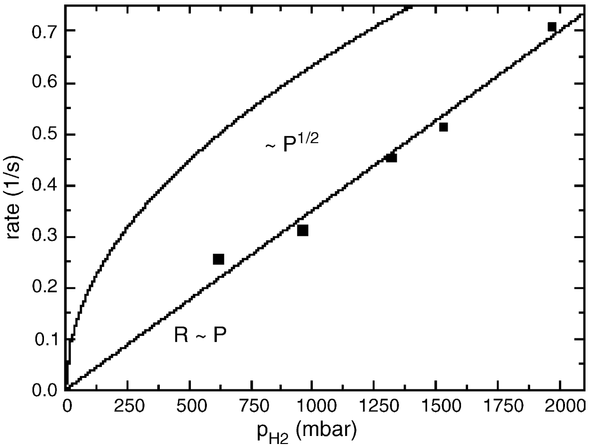

Fig. 4. Hydrogen absorption rate of Pd-capped yttrium film as a function of applied hydrogen pressure. The yttrium thickness is 150 nm, the Pd thickness 10 nm. The experimental data (squares) are compared to the chemisorption limited model (R/p) and the quasi-equilibrium model (R/pp).

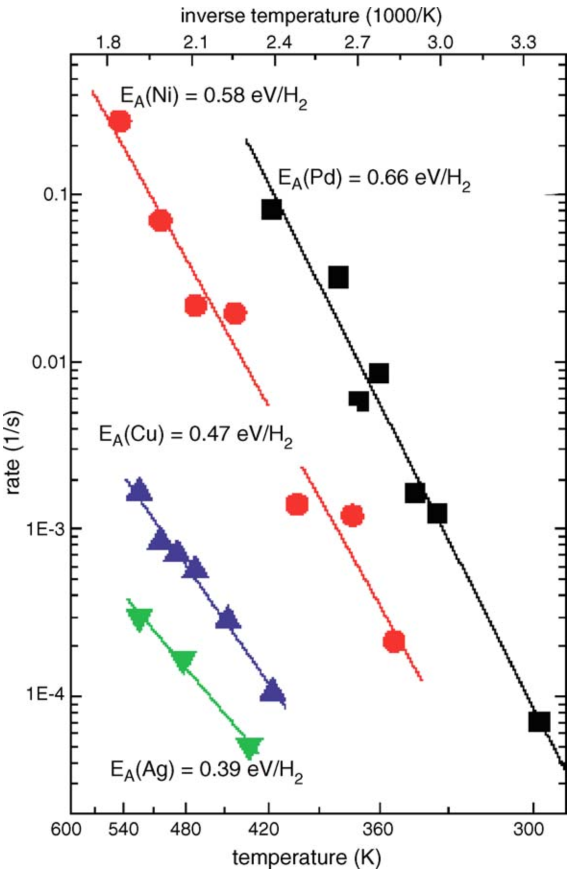

Fig. 5. Arrhenius plot of the hydrogen uptake rate of 130 nm yttrium films capped with the noble metals Pd, Ni, Cu and Ag at constant pressure (2 bar).

described by

$$R \propto p \exp\left(\frac{-E_{\mathrm{A}}}{kT} + \alpha\ E_{\mathrm{A}}\right) \qquad (3)$$

The factor $\alpha = 57.5\ 1\ \mathrm{eV}^{-1}$ is constant for all measured noble metals. From this, we conclude that two steps are involved in the process: one temperature dependent and one temperature independent step. A more detailed analysis will be published elsewhere.

3.2. Surface oxygen as catalytically active site for hydrogen sorption

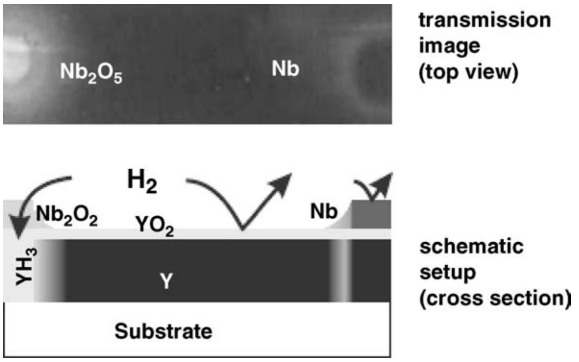

Fig. 6. Transmission image (top) of a yttrium film capped with a spot of 5 nm Nb_2O_5 and 5 nm surface-oxidized Nb after hydrogen exposure at 2 bar, 523 K for 1 h. Bright intensities display high transmission. The bottom image sketches the sample cross section after hydrogenation.

Using the indicator technique we probe the catalytic effect of both Nb_2O_5 and surface-oxidized Nb for hydrogen absorption in one experiment. Fig. 6 shows the transmission image of an yttrium film capped with a spot of 5 nm Nb_2O_5 and 5 nm surface-oxidized Nb after hydrogen exposure at 2 bar, 523 K for 1 h. The indicator film under the Nb_2O_5 film has absorbed hydrogen, evidence for a catalytic effect. The film under the thin Nb layer remains metallic; here, the hydrogen uptake is strongly reduced [17]. However, the spot displays a small halo. This effect is probably due to catalytically active Nb_2O_5, formed by total oxidation at the thin borders of the Nb. The observation fits well with that of Barkhordarian et al. [1], who observed an enhancement of the hydrogen sorption kinetics of Nb doped Mg after contamination with oxygen. To shed light on the effect of oxygen on the catalytic properties, we grow NbO_x layers, whose oxygen content varies locally on the sample (‘gradient samples’). The oxide gradient is realized by introducing 10^{-4} mbar oxygen through a tube towards one side of the 70 mm long sample during Nb sputtering at an argon pressure of 10^{-2} mbar. This leads to a locally higher partial oxygen pressure resulting in an oxygen gradient of the NbO_x over the entire sample [16]. Before depositing the oxide gradient, the indicator layer is deposited. Such a sample is exposed to 2 bar hydrogen and simultaneously the transmission is recorded as a function of time and position. In Fig. 7, a vertical linescan through the gray-scale image at a fixed position represents the optical transmission as a function of time at a given oxygen concentration. Thus, we are able to study the catalytic activity of the NbO_x-layer as a function of the oxygen content by measuring the evolution of the transmission. In first order, the change of $\ln T_{\mathrm{opt}}$ with time is a measure of the hydrogen uptake rate $R = \frac{\mathrm{d} \ln T_{\mathrm{opt}}}{\mathrm{d}t}$ (see Section 2). The temperature during hydrogen exposure is changed from $T_1 = 498$ K, $T_2 = 523$ K, $T_3 = 548$ K to $T_4 = 573$ K. The response of the gradient layer $R(T)$ depends strongly on the location, as shown in Fig. 7(b). The corresponding fitted slopes of $\mathrm{d} \ln T_{\mathrm{opt}}/\mathrm{d}t$ are plotted as a function of temperature in an Arrhenius plot, from which the activation energies as a function of the location are calculated. Obviously, the activation energy varies between 1.4 and 0.6 eV (≃62 kJ/mol). The value of 62 kJ/mol is in good agreement with the results in bulk desorption measurements of Nb_2O_5 doped Mg of Barkhordarian et al. [15]. This may be taken as an indication that identical phases and therefore mechanisms are present despite the different experimental setups. The location with lowest activation energy is that with the highest oxygen content as measured by XPS. This leads to the assumption that special sites on top of the surface are catalytically active, which are peculiar to the fully oxidized Nb_2O_5 surface.

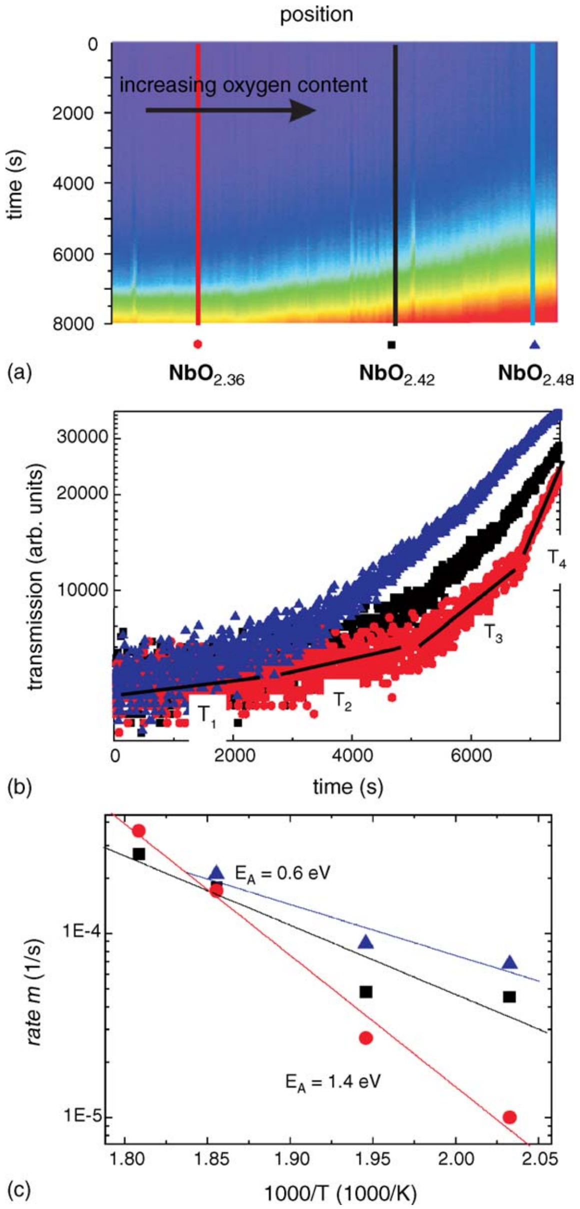

Fig. 7. (a) Transmission of a surface-oxidized yttrium sample capped with a 5 nm thick niobium oxide gradient during hydrogen exposure at 2 bar, as a function of location and time. The temperature is changed during composition from $T_1 = 498$ K, $T_2 = 523$ K, $T_3 = 548$ K to $T_4 = 573$ K. Bright intensities display high transmission. Three representative linescans at fixed positions are plotted for further analysis in (b). The slopes are plotted as a function of temperature in an Arrhenius plot (c), from which the corresponding activation energies are calculated. The oxygen concentration is measured by XPS.

4. Conclusions

We have presented a novel optical technique to measure the catalytic activity for hydrogen sorption. As a demonstration of the indicator technique we have investigated the hydrogen absorption catalyzed by various noble metals and metal oxide clusters deposited on the surface of the hydrogen absorbing metal. The catalytic activity of the noble metals of Pd, Ni, Cu and Ag is studied as function of pressure and temperature. The uptake rate is limited by chemisorption as deduced by modelling kinetics. An empirical relation between uptake rate and measured activation energy is given. A great advantage of our technique is the possibility to measure the hydrogen uptake rate on a sample that can be well characterized by standard surface science techniques. This made it possible to measure the amount of surface oxygen on NbO$_x$ by XPS. Using the indicator technique we probe the catalytic effect NbO$_x$. We find different that the activation energy for catalytic hydrogen absorption is large (≈1.4 eV) for an oxygen deficient surface and decreases with a decreasing amount of oxygen. It reaches a minimum of 0.6 eV at the highest oxygen content (Nb$_2$O$_5$). Pure Nb does not display a significant catalytic effect.

Acknowledgments

The authors are indebted to A. Züttel, University Fribourg, for supporting the XPS measurements. This work is financially supported by the Stichting voor Fundamenteel Onderzoek der Materie (FOM) and the Nederlandse Organisatie voorWetenschappelijk Onderzoek (NWO) through the ACTS program.

References

[1] G. Barkhordarian, T. Klassen, R. Bormann, Scr. Mater. 49 (2003) 213.
[2] E. Fromm, H. Uchida, J. Less-Common Met. 131 (1987) 1.
[3] L. Schlapbach, in: L. Schlapbach (Ed.), Hydrogen in Intermetallic Compounds II, Springer Verlag, Berlin, 1992.
[4] M. Eriksson, L.G. Ekedahl, J. Appl. Phys. 83 (1998) 3947.
[5] J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D.G. de Groot, N.J. Koeman, Nat. (Lond.) 380 (1996) 231.
[6] S.M. Haile, Mater. Today 6 (2003) 24.
[7] J.K. Norskov, T. Bligaard, A. Logadottir, S. Bahn, L.B. Hansen, M. Bollinger, H. Bengaard, B. Hammer, Z. Sljivancanin, M. Mavrikakis, Y. Xu, S. Dahl, C.J.H. Jacobsen, J. Catal. 209 (2002) 275278.
[8] A. Remhof, J.L.M. van Mechelen, N.J. Koeman, J.H. Rector, R.J. Wijngaarden, R. Griessen, Rev. Sci. Instrum. 74 (2003) 445;
see also F.J.A. den Broeder et al., Nat. (Lond.) 394 1998 656.
[9] A. Borgschulte, R.J. Westerwaal, J.H. Rector, B. Dam, R. Griessen, J. Schoenes, Phys. Rev. B 70 (2004) 155414.
[10] A.T.M. van Gogh, D.G. Nagengast, E.S. Kooij, N.J. Koeman, J.H. Rector, R. Griessen, C.F.J. Flipse, R.J.J.G.A.M. Smeets, Phys. Rev. B 63 (2001) 195105.
[11] R. Griessen, J.N. Huiberts, A.T.M. van Gogh, N.J. Koeman, J.P. Dekker, P.H.L. Notten, J. Alloys Compd. 253 (1997) 44.
[12] A. Borgschulte, R.J. Westerwaal, J.H. Rector, B. Dam, R. Griessen, Appl. Phys. Lett. 85 (2004) 4884.
[13] S.J. van der Molen, J.W.J. Kerssemakers, J.H. Rector, N.J. Koeman, B. Dam, R. Griessen, J. Appl. Phys. 86 (1999) 6107.

[14] M. Martin, C. Gommel, C. Borkhart, E. Fromm, J. Alloys Compd. 238 (1996) 193.
[15] G. Barkhordarian, T. Klassen, R. Bormann, J. Alloys Compd. 364 (2004) 242.
[16] R.C. Lee, C.R. Aita, J. Appl. Phys. 70 (1991) 2094.
[17] The metallic Nb film would have been thin enough to allow a sufficient transmission (approximately 5 nm), if the yttrium layer had become metallic.