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Switchable mirrors for visualization and control of hydrogen diffusion in transition metals

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We show that the switchable mirror material YH_x can be used both as an indicator to monitor and as an agent to control hydrogen diffusion in thin films. The applicability of the optical-indicator technique is demonstrated for VH_x thin films. The diffusion coefficient is typically $10^{-5} \text{ cm}^2/\text{s}$ at concentrations around 0.7 H/V at temperatures between 373 and 473 K. Deposition of a layer of Y on V makes it also possible to tune the effective hydrogen mobility via the V/Y thickness ratio. This can be used for investigation of hydrogen diffusion waves in laterally structured objects.

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One of the striking properties of hydrogen in metals is its large mobility. Already at room temperature the H diffusion coefficient can be as high as $10^{-5} \text{ cm}^2/\text{s}$, i.e., a value almost comparable to diffusion in liquids. A review of experimental data and techniques used so far to measure hydrogen diffusivity in bulk samples is given by Alefeld and Völkl.¹ Most of these methods are not applicable to thin films as they are either hampered by the influence of the substrate (e.g., in Gorsky effect) or by the rather small volume of the film (e.g. in quasielastic neutron scattering). Consequently, relatively little is known about hydrogen diffusion in thin metallic films and multilayers. The understanding and manipulation of hydrogen transport through films is, however, important for the control and optimization of coatings and thin-film devices such as hydrogen detectors,^{2,3} metal-hydride switchable mirrors^{4,5} or tunable magnetical elements.^{6,7} Recently den Broeder *et al.*⁸ presented an optical method to monitor the lateral migration of hydrogen in Y, exploiting the intrinsic concentration dependent optical properties of the Y-H system.⁹ Especially the progression of the boundaries separating the various stable hydride phases can easily be detected as discontinuities in the optical contrast.

The main purpose of this communication is to demonstrate that visualization of H diffusion is also possible for hydrogen in opaque transition-metal films. More specifically (i) we demonstrate the feasibility to use a thin layer of Y as an optical indicator to visualize the lateral H migration in thin films of vanadium, (ii) we show that the mobility of the phase boundaries in a composite film (e.g., V/Y) can be tuned through the sample/indicator thickness ratio, and (iii) we determine quantitatively the H-diffusion coefficient in a vanadium film by means of our optical indicator method.

The samples are prepared by means of e-gun evaporation in an ultrahigh vacuum system (background pressure $< 10^{-9}$ mbar). A typical sample consists of a V stripe of length $L = 10$ mm, width $b = 1$ mm, and thickness $25 \text{ nm} < d_s < 250$ nm. Usually 11 stripes of various thickness d_s are deposited onto one, polished amorphous quartz substrate. The V stripes are covered with a thin layer of yttrium as an optical indicator for hydrogen diffusion. Indicator thicknesses $10 \text{ nm} < d_l < 50$ nm are examined. One end of each of the combined V/Y stripes is covered *in situ* with a 10-nm-thick Pd cap layer as indicated in Fig. 1. The thicknesses of the metallic layers are monitored *in situ* by means of a water-

cooled quartz microbalance during deposition and are checked *ex situ* by profilometry and by Rutherford backscattering (RBS). Furthermore, RBS is used to characterize the chemical composition of the metallic stripes and to detect eventual alloy formation at the interfaces. The RBS spectra show well-defined layers, no intermixing at the interfaces, and no chemical impurities. The thickness of the natural oxide layer that forms in ambient air on the uncovered part of the yttrium layer is determined to be 15 nm.

The gas loading cell and the experimental setup have been described earlier.^{8,10} At $t = 0$ a sample assembly (consisting here of 11 individual V/Y stripes) is exposed to hydrogen. As described by Den Broeder *et al.*,⁸ the Y underneath the Pd immediately starts absorbing hydrogen, and forms the transparent $\text{YH}_{3-\delta}$ phase. Further hydrogen uptake is achieved by lateral hydrogen diffusion mainly through vanadium, since H uptake cannot occur via the superficially oxidized Y. The lateral migration of hydrogen in vanadium away from the Pd-covered region can easily be monitored optically in the Y indicator layer as the various yttrium hydride phases formed at different hydrogen concentrations, exhibit characteristic optical properties.^{9,11} For example, the front corresponding to the coexisting α and β phases is clearly identified as a discontinuous change in transmission and reflection.⁸ In Y, the phase boundary of the hcp α -phase is $c_{\alpha, \text{max}} = 0.2 \text{ H/Y}$ and that of the fcc β -phase is $c_{\beta, \text{min}} = 1.9 \text{ H/Y}$, thus Δc_l

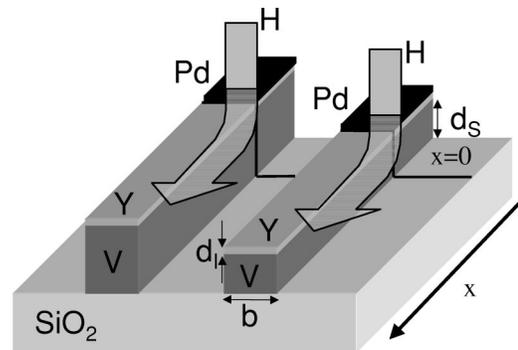


FIG. 1. Schematic sample design. Yttrium-covered vanadium stripes ($1 \times 10 \text{ mm}^2$) of thickness 25–125 nm are deposited onto an α - SiO_2 substrate ($15 \times 10 \times 0.53 \text{ mm}^3$). The stripes are partially covered with a Pd cap layer to enable gas phase H loading. In the actual sample series there are 11 stripes.

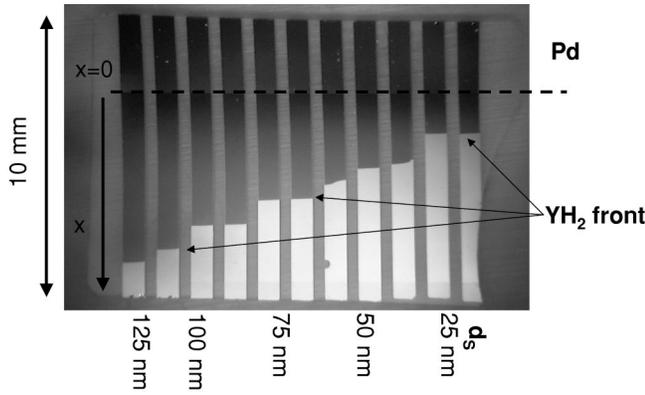


FIG. 2. Photography of an 11 stripe sample loaded in a hydrogen atmosphere ($p_{H_2}=1$ mbar, $T=473$ K) for 10^4 s. The 11 composite V/Y stripes take up H via the Pd layer, which is located at the upper part of the photo. Lateral H migration occurs along the stripes, away from the Pd-covered part. Within the indicator layer (Y layer), the presence of H leads to the formation of the YH_2 phase, which appears blue in reflection. Note the influence of the V thickness on the mobility of the YH_2 front in the indicator. The thickness of the V stripes decreases from 125 nm to 25 nm from left to right. The 2nd, 7th, and the 9th stripe have a nonconstant V thickness.

$=c_{\beta,\min}-c_{\alpha,\max}=1.7$ H/Y.^{11,12} In the following we call this optical feature the “ β -front” or simply *the front* and its position x_f .

Figure 2 depicts a snapshot at $t=10^4$ s after the 11-stripe-sample assembly was exposed to a hydrogen atmosphere of 1 mbar at $T=473$ K. The Pd-covered parts, where the hydrogen enters the samples and the lateral diffusion starts, is at the top of the photo. The optical discontinuity within the indicator corresponds to the boundary between the silvery gray low concentration α - $YH_{0.2}$ phase and the blue (in reflection) dihydride phase β - $YH_{1.9}$. The results in Fig. 2 do not only show that the progression of H in V is easily followed through the optical appearance of the indicator layer, but also that the front mobility can be tuned through the ratio of the sample (V) and the indicator (Y) thicknesses. Note the pronounced thickness dependence of the front mobility $K=x_f^2/t$. The thickness of the stripes in Fig. 2 decreases from left to right from 125 nm to 25 nm. All the stripes are covered with 50-nm Y. Oxidation reduces the *effective* Y thickness down to 35 nm. The thickness of the Pd cover in the upper part of the stripes is 10 nm for all the 11 stripes. Systematic measurements, in which the temperature, the sample thickness, and the indicator thickness are varied, show that the mobilities exhibit an Arrhenius behavior (for a given sample thickness). At a given temperature the mobility increases with increasing d_S/d_I , i.e., in a thick sample covered by a thin indicator the front progresses faster than in a thin sample covered by a thick indicator.

We show now that the hydrogen-diffusion coefficient can be determined from experimental results of the type shown in Fig. 2. For this we note that below the Pd clayer the hydrogen concentration c_{S0} in the sample is in thermodynamical equilibrium with the surrounding H_2 atmosphere. We choose the coordinate system such that the direction of

diffusion is in the positive x direction. The reservoir-sample interface lies at $x=0$ and $c_S(x=0)=c_{S0}$. The concentration $c_S(x,t)$ is determined by the diffusion equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right). \quad (1)$$

Since (i) the enthalpy of hydrogen solution in the indicator (here Y) is much more negative than in the sample (here V) and (ii) the diffusion constant D in the sample (V) is orders of magnitude larger than in the indicator (Y), all the hydrogen flows via the sample into the indicator. This creates a diffusion front at $x=x_f$ that is experimentally found to move as $x_f^2=Kt$. The H atoms crossing in the time interval δt , the cross section $d_S b$ at x_f are used (i) to move the front by δx_f and (ii) to fill the overlaying indicator up to a concentration of 1.9 H/Y. In this way $c_f d_S b \delta x_f$ hydrogen atoms are accommodated in the sample and $\Delta c_I d_I b \delta x_f$ in the indicator. As long as the indicator is still in the dilute YH_x α -phase it takes up all the hydrogen from the underlying sample. There is essentially no difference in position between the position of the front in the indicator and the sharp drop of concentration in the sample at x_f . Conservation of the number of particles leads to

$$j_f b d_S \delta t = b (\Delta c_I d_I + c_f d_S) \delta x_f, \quad (2)$$

where $j_f = -D_f (dc_S/dx)|_f$ is the flux of H atoms at the front through the sample. Assuming a concentration independent D , the solution of Eq. (1) with $c_S(0,t)=c_{S0}$ and the boundary condition Eq. (2) is

$$c_S(x,t) = c_{S0} - \alpha \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right). \quad (3)$$

As the concentration c_f at the front is given by

$$c_f \equiv c_S(x_f,t) = c_{S0} - \alpha \operatorname{erf} \left(\frac{\sqrt{K}/2}{\sqrt{D}} \right), \quad (4)$$

we obtain from Eqs. (2) and (3)

$$\frac{d_I}{d_S} = \frac{2\alpha\sqrt{D}}{\Delta c_I \sqrt{\pi K} e^{K/4D}} + \frac{\alpha}{\Delta c_I} \operatorname{erf} \left(\frac{\sqrt{K}}{2\sqrt{D}} \right) - \frac{c_{S0}}{\Delta c_I}. \quad (5)$$

In an experiment d_I , d_S , Δc_I , and K are known. The diffusion coefficient D , the parameter α , and the equilibrium concentration c_{S0} can be extracted from measurements of K as a function of d_I/d_S . The experimental data for two different sets of experiments (each of them for five values of d_I/d_S), are represented in Fig. 3 together with their respective fits. We obtain a hydrogen-diffusion coefficient in vanadium $D_V = 1.2 \times 10^{-5}$ cm²/s and an equilibrium concentration $c_{S0} = 0.62$ H/V at 473 K and at $p_{H_2}=1$ mbar. At $T=373$ K and $p_{H_2}=1$ bar the measured values are $D_V = 0.67 \times 10^{-5}$ cm²/s and $c_{S0} = 0.83$ H/V.

For a discussion of these results we assume first that the phase diagram of H in V films is the same as for bulk VH_x . Then our results at $T=473$ K pertain to the α - VH_x phase in which H occupies randomly tetrahedral sites in the bcc V lost lattice. Our results at $T=373$ K, on the other hand, corre-

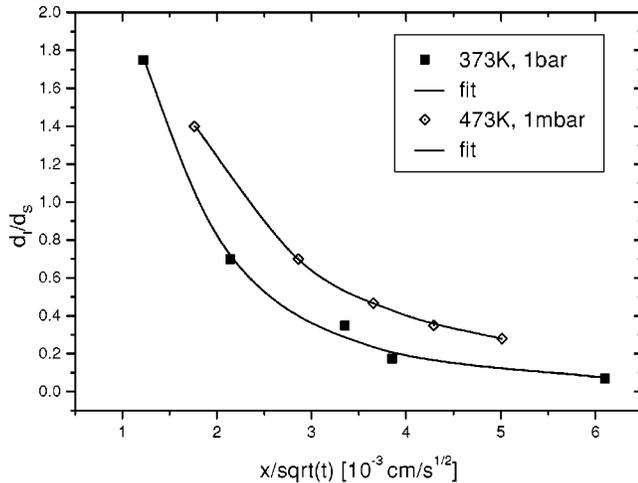


FIG. 3. Hydrogen front mobility K in the yttrium indicator ($\sqrt{K} = x_f/\sqrt{t}$) versus sample thickness ratio (d_f/d_s) together with the respective fits according to Eq. (5). The fits yield a hydrogen-diffusion coefficient in V of $D_V = 1.2 \times 10^{-5} \text{ cm}^2/\text{s}$, and a H concentration $c_{S0} = 0.62 \text{ H/V}$ at $T = 473 \text{ K}$ and $p_{H_2} = 1 \text{ mbar}$ (upper curve). At $T = 373 \text{ K}$ and $p_{H_2} = 1 \text{ bar}$ the corresponding values are $D_V = 0.67 \times 10^{-5} \text{ cm}^2/\text{s}$ and $c_{S0} = 0.83 \text{ H/V}$.

spond to the β_2 -phase that exists for temperatures between 293 and 463 K at hydrogen concentrations between 0.45 and 0.83 H/V. The β_2 -phase is separated from the cubic CaF_2 -like VH_2 phase by a large miscibility gap.¹³

We consider now our data at 473 K. Recently, solubility isotherms of thin-film V-H samples within the α -phase have been studied by Andersson *et al.*¹⁴ Within the investigated thickness range $50 < d_S < 100 \text{ nm}$, no pronounced thickness dependence of the isotherms could be observed. The equilibrium hydrogen concentrations depend strongly on p_{H_2} and T in the pressure range of $p_{H_2} = 0.5\text{--}50 \text{ mbar}$ and at temperatures between 450 and 500 K. In the case of our measurements at $T = 473 \text{ K}$ and $p_{H_2} = 1 \text{ mbar}$, this makes a direct comparison difficult. However, within experimental uncertainties, the measured value of $c_{S0} = 0.62 \text{ H/V}$ is consistent with the data published by Andersson *et al.*

Apart from the equilibrium concentration at given hydrogen pressures, the *slope* of a solubility isotherm yields the derivative of the chemical potential with respect to the hydrogen concentration $\partial\mu/\partial c_S$. The *macroscopic diffusion coefficient* D , investigated here, is related to the *tracer diffusion coefficient* D_t via $D/D_t = (c_S/k_B T)(\partial\mu/\partial c_S)$. Nuclear magnetic resonance (NMR) experiments on bulk vanadium show a monotonic decrease of D_t with increasing hydrogen concentration c_S from $D_t = 2 \times 10^{-4} \text{ cm}^2/\text{s}$ at $c_S = 0.02 \text{ H/V}$ down to $D_t = 2 \times 10^{-5} \text{ cm}^2/\text{s}$ at $c_S = 0.68 \text{ H/V}$.¹⁵ The slope of the 473 K solubility isotherm¹⁴ at $c_S = 0.62 \text{ H/V}$ yields $(c_S/k_B T)(\partial\mu/\partial c_S) \approx 3$, leading to a diffusion coefficient of $D = 6 \times 10^{-5} \text{ cm}^2/\text{s}$, comparable with our value of $D = 1.2 \times 10^{-5} \text{ cm}^2/\text{s}$. Again, a comparison between samples prepared by different techniques, leading to different grain sizes, stress states, impurities etc., hampers a direct comparison.

Let us now focus on the results at $T = 373 \text{ K}$ and $p_{H_2} = 1 \text{ bar}$. Even though the phase diagram for bulk V-H may deviate markedly from that for thin films and nanocrystalline samples,^{14,16} under the condition of 1 bar and 373 K we expect our V samples to be in the saturated β_2 -phase. For bulk samples this phase boundary lies at 0.82 H/V and is essentially temperature independent between room temperature and 373 K. The H-rich γ -phase cannot be reached at 373 K without applying high pressures (ca. 50 bar), so we exclude the presence of this phase in our samples.¹³

Orimo *et al.*¹⁶ report a modification of the β_2 - γ phase boundary in the V-H system within nanometer-scale V grains. They conclude that the β_2 - γ phase boundary decreases from 0.82 H/V for 80-nm grains down to 0.67 H/V for 10-nm grains. By using NMR techniques, the same authors measured a hydrogen jump rate of $\nu_{300 \text{ K}} = 10^9 \text{ s}^{-1}$ at 300 K in 80-nm-sized V grains with $c_S = 0.82 \text{ H/V}$. Using an activation energy of 240 meV,^{16,17} we obtain a jump rate $\nu_{373 \text{ K}} = 6 \times 10^9 \text{ s}^{-1}$ at 373 K. Together with a jump length of 0.15 nm, the distance between two interstitial sites, this results in a tracer diffusion coefficient of $D_t = 2.3 \times 10^{-7} \text{ cm}^2/\text{s}$. Compared with our measured $D = 0.67 \times 10^{-5} \text{ cm}^2/\text{s}$ this implies $D/D_t = (c_S/k_B T)(\partial\mu/\partial c_S) = 29$. This value is consistent with the steepness of the 373 K solubility isotherm near the β_2 - γ phase boundary.¹³

In conclusion, we have demonstrated that thin layers of YH_x can be used as indicators to visualize hydrogen migration in opaque transition metals such as vanadium. In addition, our optical method allows measuring the equilibrium concentration in the material under investigation and its macroscopic diffusion coefficient. In principle, our technique is applicable to any material that can be coated with a switchable metal-hydride mirror material as long as (i) its H-diffusion coefficient is higher than the one of the indicator and (ii) its hydrogen affinity is low compared to the hydrogen affinity of the indicator. Furthermore, by varying the sample/indicator thickness ratio the effective mobility of the hydrogen front in the indicator layer can be tuned over a wide range. In principle, D can be varied at room temperature by four orders of magnitude between the extreme values of H in Y (typically $10^{-9} \text{ cm}^2/\text{s}$) and H in V (typically $10^{-5} \text{ cm}^2/\text{s}$). In a patterned thin film this opens the opportunity to locally vary the mobility of the front and to investigate hydrogen diffusion waves.¹⁸ Future investigations will include refractionlike and reflectionlike phenomena at interfaces separating areas of different effective diffusivities.¹⁹

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