

Generation and detection of H electrodiffusion waves

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Hydrogen electrodiffusion waves are forced oscillations of the H concentration within a host metal, driven by an electric field. Simulations show that they suffer less from the drawbacks of ordinary diffusion waves such as heavy damping. H in Y/V bilayers fulfills all the requirements to generate and to detect H electrodiffusion waves. We demonstrate the possibility to spatially modulate the H concentration in a thin V film and to drive H “pulses” via an applied electric field. The electric field is also used to control the hydrogen uptake of the sample. We visualize the temporal and spatial evolution of the H distribution in the V film using the switchable mirror material YH_x as an optical hydrogen indicator. © 2003 American Institute of Physics. [DOI: 10.1063/1.1518569]

Diffusion waves arise from forced oscillations of diffusing particles. Denoting the particle density as c and the diffusivity as D , one-dimensional diffusion waves are mathematically described as solutions of the diffusion equation

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} \right), \quad (1)$$

in which $c(x,t)$ varies as $c(0,t) = \sin(\omega t)$ at the origin. Examples are oscillating temperature such as the temperature profile of the earth resulting from the seasonal temperature variation¹ or diffuse photon density waves in a turbid medium.² Reviews on diffusion waves together with examples of their technological applications have been published by Yodh³ and by Mandelis.⁴

In this article, we describe a simple technique to generate and to visualize hydrogen diffusion waves in thin metallic films. It is a further development of the optical method presented by Den Broeder *et al.*⁵ to monitor the *lateral* migration of hydrogen in Y, exploiting the intrinsic concentration dependent optical properties of the Y–H system.⁶ Electromigration studies on thin film YH_x samples demonstrated that H in Y behaves like a negatively charged particle,^{5,7} opening the possibility to work with *electrodiffusion waves*. In the presence of a static electric field E a charged particle experiences an additional force, leading to electrodiffusion waves which are solutions of a modified diffusion equation:

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} \right) - \frac{\partial}{\partial c} \left[\frac{eZED}{\partial \mu / \partial c} \right] \frac{\partial c}{\partial x}, \quad (2)$$

where eZ denotes the effective charge of the particle, and μ is the chemical potential of H in the metal. The prefactor of the linear term of Eq. (2),

$$v(c) = \frac{\partial}{\partial c} \left[\frac{eZED}{\partial \mu / \partial c} \right], \quad (3)$$

has the dimension of a velocity. Electrodiffusion waves may exist at all frequencies and suffer less from damping than ordinary diffusion waves, which typically damp out within one wavelength.

In order to investigate diffusion waves, we need to work in a concentration regime in which (i) the hydrogen concentration can be varied continuous and reversible and (ii) in which the optical properties depend strongly on the hydrogen concentration. Recently, Van der Molen *et al.*⁸ succeeded in creating a single “pulse” of H vacancies *within* the $\text{YH}_{3-\delta}$ phase. In the presence of an electric field, the vacancy distribution does not only spread out with time, but also moves with the electric field. For a study of electrodiffusion waves, $\text{YH}_{3-\delta}$ is not ideal because of its rather small diffusion coefficient ($D = 10^{-8} \text{ cm}^2/\text{s}$) and of its strongly concentration dependent electrical resistivity. However, a thin layer of Y deposited on top of H absorbing thin films such as V, can advantageously be used to visualize H migration in the covered transition metal layer.⁹

In order to study the analogies (or dissimilarities) between diffusion fronts (and waves) with their optical counterparts, heterostructures with locally varying diffusion constants have to be realized. In other words, it is essential to create interfaces between regions of different diffusivities to realize planar objects such as “lenses” or “prisms” to investigate the refraction and reflection of diffusion waves.

We demonstrate here the feasibility to use the hydrogen switchable mirror material YH_x both as an indicator to monitor H electromigration and as an agent to control hydrogen diffusion in a thin V film. Furthermore, we show a possibility to induce a spatial modulation of the H concentration in the V film and to visualize this modulation by means of the optical indicator method. Additionally, we present a suitable sample design allowing one to control the H uptake of the sample via an applied voltage.

The samples are prepared using electron-gun evaporation in an ultrahigh vacuum system (background pressure $< 10^{-9}$ mbar). The sample design, together with the result of a hydrogen gas-phase loading, is displayed in Fig. 1. A typi-

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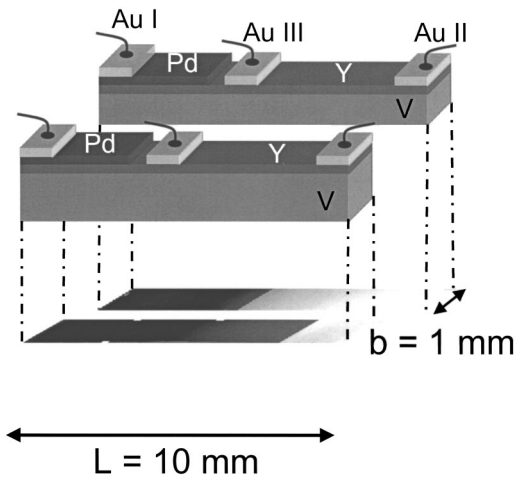


FIG. 1. Schematic sample design. Yttrium-covered (50 nm) vanadium stripes of various thickness are deposited onto an amorphous-SiO₂ substrate. The stripes are partially covered with a Pd cap layer (10 nm) to enable gas-phase H loading. Via the three gold contacts (labeled Au I, Au II, and Au III), the sample is electrically connected to the outside world. Lower panel: Photographs of two samples loaded in a hydrogen atmosphere ($p_{\text{H}_2} = 1$ mbar and $T = 473$ K). The composite V/Y stripes take up H via the Pd layer, which is located on the left-hand side of the sample. 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 YH₂ phase, which appears dark in reflection. The upper V film has a thickness of 50 nm, the lower of 100 nm. Note the influence of the V thickness on the position of the YH₂ front in the indicator.

cal sample is a V stripe of length $L = 10$ mm, width $b = 1$ mm, and thickness between $d = 50$ – 500 nm. The samples are covered with a 50 nm thick Y layer as an optical indicator for hydrogen diffusion. One end of the combined V/Y stripe is covered *in situ* with a 10 nm thick Pd cap layer to enable H loading. Finally, three gold stripes (thickness 200 nm) are evaporated perpendicular to the Y/V stripe. They serve as electrodes and are connected to the outside world. Two of the electrodes are located at the ends of the Y/V bilayer (electrodes I and II), electrode I partially covers the Pd stripe. The third electrode (electrode III) is placed 1 mm away from the Pd stripe. For a more detailed description of the deposition parameters and the structural characteristics of the sample, we refer to Ref. 9. Hydrogen is introduced into the sample via gas-phase loading. The gas loading cell and the experimental setup have been described earlier.^{5,10}

In the following, we describe two different experiments. First, we demonstrate the optical indicator in a gas-phase loading experiment and show how the local diffusivity can be controlled. Later, we discuss the possibilities of combining the optical indicator with electromigration.

Exposed to hydrogen the Y underneath the Pd immediately starts absorbing hydrogen, quickly reaching equilibrium in the transparent YH_{3- δ} phase. Further hydrogen uptake is achieved by lateral hydrogen diffusion since H uptake can not occur via the passivating, natural yttrium oxide layer. The lateral migration of hydrogen in Y away from the Pd-covered region can easily be monitored optically, as different yttrium-hydride phases are formed at different hydrogen concentrations, exhibiting characteristic optical properties.^{6,11} Figure 1 depicts below the schematical sample

design two vanadium samples of 50 nm and 100 nm thickness. The images are recorded after an exposure of 3 h in a hydrogen atmosphere of 1 mbar at 473 K. The front separating the α from the β phase is clearly identified from a discontinuous change in reflection. Note that the progress of the front depends on the V/Y thickness ratio. As a thicker V film can transport more H, the front advances faster in the Y layer covering the thicker V sample. We have shown earlier that the thickness dependence of the front can be used to (i) measure the diffusion coefficient in V and (ii) to locally engineer the effective diffusivity of the sample by varying the local V thickness.⁹ Thus, planar structures such as straight or curved interfaces separating areas of different effective diffusivities are possible, as well as more complex structures such as lenses or prisms. Using these kind of structures, investigations on the refraction and reflectionlike behavior of H diffusion fronts and waves will become possible.

In the presence of an electric current ($j = 8 \times 10^4$ A/cm²) from the Pd-covered part (electrode I, +) to the opposite end of the sample (electrode II, -), the front accelerates until after a short time (few seconds), it progresses with a constant speed of 1.85 $\mu\text{m/s}$. Compared to electromigration in *pure* YH_x (Refs. 5 and 7), there are two striking differences. First, the sign of the effective charge of the migrating H impurities. Unlike H in pure Y, in the composite V/Y layers investigated here, hydrogen behaves as a *positive* particle, as in pure bulk vanadium.^{12,13} Second, the velocity of the β -front is orders of magnitudes higher in the composite V/Y layers. As the velocity of the front $v \propto D$ [see Eq. (3)], this results from the much higher diffusivity of H in V than in Y. These two differences clearly demonstrate that what we observe here is an intrinsic property of the V layer itself. The Y layer indeed acts as an indicator for the H migrating through the V. Despite the fact that H has different effective charges in both materials (Y and V), the optical indicator method to study H diffusion in transition metals can be extended to the study of H electromigration in transition metals.

The cathode acts as a hydrogen attractor. More hydrogen is transported to the cathode than away from it. Consequently, H piles up locally until the hydrogen concentration reaches the highest possible level (YH₃ in the indicator). This high concentration can be clearly identified via the distinct optical properties of the indicator, which lead to a bright blue appearance in reflection. As H is still transported to the cathode, a *H traffic jam* forms. Just as in ordinary traffic jams, there is a high-density region close to a bottleneck, whose tail (in our case, the front separating the blue high concentration γ phase from the darker β phase) moves opposite to the incoming hydrogen.¹⁴ Reversing the current at this stage of the experiment leads to a repulsion of H from electrode II (the former cathode, now the anode), resulting in a rapidly growing H depletion zone. The depletion zone can be clearly identified via the change in color of the indicator that reverses to its original, dihydride phase. Consequently, a high H concentration region is formed, that moves toward the cathode (electrode I). Figure 2 depicts how this experiment can be used to generate a traveling hydrogen pulse. Each of the four photographs covers a 3×0.1 mm² area of

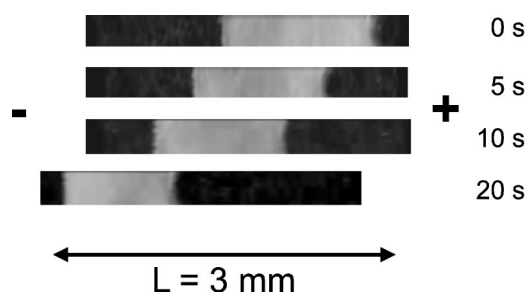


FIG. 2. A traveling hydrogen block wave. Each of the four photographs depicts a $3 \times 0.1 \text{ mm}^2$ area of the sample. In the presence of an electric current ($j = 8 \times 10^4 \text{ A/cm}^2$), the high concentration area, which can be identified by its bright color, moves towards the cathode. The first picture (labeled 0 s) shows the situation a few seconds after the pulse has been generated. The other photos are recorded 5, 10, and 20 s later.

the sample. The first picture (labeled “0 s”) shows the situation a few seconds after the current has been reversed. The other photographs are recorded at 5, 10, and 20 s. The high concentration area has a bright color. This experiment demonstrates nicely the possibility to generate a hydrogen block wave and to move it via an applied electric field.

The effective charge of H in V can also be used to control the H uptake in the sample. As long as electrode I acts as an anode and electrode II as a cathode, H entering the sample via the Pd stripe is driven into the sample toward the cathode. If we now connect electrode III, which is just in front of the Pd stripe, instead of electrode I with the positive pole of the current source, no additional H passes this electrode. Only those H ions already present between electrode II and III continue to move in the direction of the cathode (electrode II). In other words, the electrical potential of electrode III can be used as a “hydrogen valve” to control the H uptake of the sample without varying the external H pressure.

Summarizing, we have demonstrated that Y/V bilayers are very promising candidates to study hydrogen electrodiffusion waves *optically*. The switchable mirror material YH_x can be used as an optical hydrogen indicator to visualize the

(electro) migration of H in transition metals such as V. Furthermore the applied electric field allows one to spatially modulate the H concentration in a thin V film, to drive H pulses and to control the hydrogen uptake of the sample. The high diffusion coefficient of H in V makes it possible to study electrodiffusion waves over relatively large distances of up to 1 cm.

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