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Electrochemical kinetics of hydrogen intercalation in gadolinium switchable mirrors

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Potential-step experiments on gadolinium thin-film electrodes provide current and optical transmission transients, whose time constants are related to effective hydrogen diffusion coefficients according to a standard diffusion model. The diffusion coefficients and switching kinetics depend on temperature, hydrogen concentration, potential, and film thickness. A thickness dependence of the kinetics is observed in which the diffusion coefficient and optical switching time are linearly dependent. © 2003 American Institute of Physics. [DOI: 10.1063/1.1606863]

I. INTRODUCTION

Electrochromic material research was extended in 1996 to a class of smart optical materials: the metal hydride switchable mirror.¹ The switchable mirrors consisted of thin yttrium and rare-earth metal films, that showed a reversible optical change on going from the dihydride to the trihydride state. However, the films were yellow in transmission, which led to a search for color-neutral switchable mirrors. Color neutrality was achieved by alloying the rare earths with magnesium.^{2,3} More recent research showed that thin films containing magnesium alloyed with other metals also exhibit an optical transition upon hydrogen intercalation.^{4,5} A solid-state device based on the gadolinium magnesium alloy has been shown to switch with speeds in the minute range.⁶

The switching time, which is technologically very important, is typically of the order of seconds in gas-phase experiments.^{1,7} Van der Molen *et al.*⁷ determined mobility coefficients from lateral hydrogen diffusion underneath the oxide layer of an yttrium thin film by optical inspection. The lateral mobility coefficients were compared to switching times in thickness-dependent experiments on yttrium matrix samples. The interpretation of these results was complicated by the fact that the morphology of the film depends on the film thickness. A difference between the layer structure normal and parallel to the sample surface therefore raises the question as to how the switching time and the diffusion coefficient normal to the sample surface are related.

Experiments on the rare-earth switchable mirrors are usually performed with a cap layer of palladium which acts as a catalyst for hydrogenation and protects the film from oxidation. Hydrogen can be introduced from the gas phase,¹ chemically with NaBH₄,⁸ and electrochemically⁹ according to the reactions¹⁰



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Electrochemical loading has the advantage that the concentration of hydrogen in the film can be controlled accurately. The adsorbed hydrogen diffuses into the material; the hydrogen/metal atomic ratio in the film, x , is proportional to the charge transferred in reaction (1a).¹¹

In the present work electrochemical potential-step experiments provide information about the kinetics of the switching process. The transmission and current were studied as a function of time after a potential step. It is shown that both transients are directly related to hydrogen diffusion, normal to the sample surface. These kinetic experiments, performed as a function of temperature, hydrogen concentration, film thickness, and applied potential, provide insight into the nature of optical switching.

II. EXPERIMENT

The active layers were 57, 100, 200, 300, and 400 nm thick, polycrystalline gadolinium films top-coated with a thin palladium layer (nominal thickness 10 nm), deposited on an indium–tin–oxide (ITO) coated glass substrate. The active film covered only part of the ITO surface to allow a back contact to the film via the ITO.¹² To ensure good adhesion of the gadolinium, a 0.5 nm thick magnesium layer was evaporated onto the ITO. The layers were deposited by evaporation at 10⁻⁷ mbar base pressure. A platinum lead was fixed with silver glue (2400 Circuit Works Conductive Epoxy, Agar Scientific) on the free ITO, and both the lead and the ITO were protected from the solution by Apiezon wax. The active surface area was 1.2 cm².

A two-compartment electrochemical glass cell was used for the measurements. The working electrode was positioned together with a Hg/HgO reference electrode in one compartment and a platinum counter electrode was placed in the other compartment. All potentials are given with respect to Hg/HgO. Argon gas was bubbled through both chambers. The glass cell had windows on both sides through which we could illuminate the sample and measure transmission with a diode laser (Vector, 670 nm) and a standard photodiode. All electrochemical experiments were performed in a 1 M KOH solution at room temperature, unless otherwise stated. A

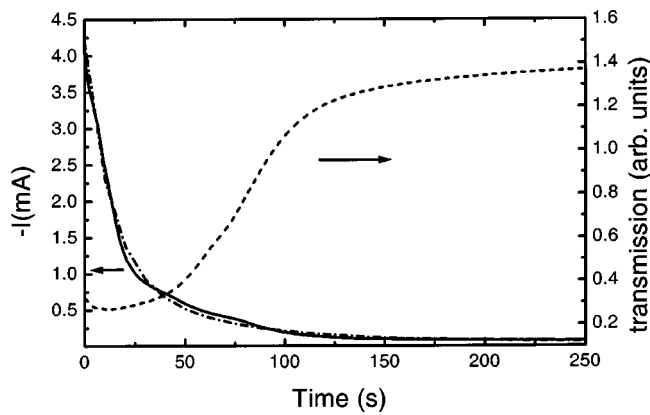


FIG. 1. Transient of the current (solid line) with fit (dashed-dotted line) and the transmission (dashed line) of a gadolinium thin film after a potential step from 0.2 to -0.95 V.

potentiostat/galvanostat [EG&G Princeton Applied Research (PAR 273A)] was computer controlled by in-house programs (LabView).

III. RESULTS AND DISCUSSION

The gadolinium samples were first galvanostatically “loaded” to the trihydride state. Unloading of the sample to a metal/hydrogen ratio close to two is possible at positive potential. The current and transmission transients were recorded simultaneously after a step from 0.2 V to a negative potential. At 0.2 V the sample is in the unloaded state ($\text{GdH}_{1.8}$). In Fig. 1 typical transients in the long-time domain are shown. In the first seconds a fast decay of the current is clear. The slight initial decrease of the transmission is caused by an optical window^{9,11} at around $x=2$, which is the starting point for the transients. Van Gogh *et al.*¹³ explain this feature by a screening of the plasma energy and a low interband absorption coefficient, leading to lower absorption. A much slower decay in the current transient is accompanied by the main optical change, as can be seen from the transmission in Fig. 1. The transmission increases until the hydrogen concentration is uniformly distributed within the film and the electrochemical potential corresponds to the applied potential. The current reaches a low steady-state value which corresponds to the hydrogen evolution reaction. The current transients can be fitted with a double exponential function, using five parameters; pre-exponential terms A_1 and A_2 , time constants τ_1 and τ_2 and I_0 , the steady-state current

$$I(t) = I_0 + A_1 \exp\left[-\frac{t}{\tau_1}\right] + A_2 \exp\left[-\frac{t}{\tau_2}\right]. \quad (2)$$

This exponential current decay suggests an analogy with results obtained previously by Wen *et al.*¹⁴ In this study lithium was intercalated in a lithium–aluminum alloy as a charge-storage material. A relation between the fit parameters for the current decay and a diffusion coefficient was derived with a simple model. The system is considered to consist of two parallel plates; one side (the substrate) is not permeable to the intercalating species while the concentration at the other side (the film/solution interface) is constant. Before the potential step, the lithium concentration in the film is uni-

form and constant. Solving Fick’s diffusion equations¹⁵ and taking first order terms, Wen *et al.*¹⁴ have shown that the time dependence of the current is given by

$$I(t) = FS\Delta C \left[\frac{D}{\pi t}\right]^{1/2} \quad t < L^2/D, \quad (3a)$$

$$I(t) = \frac{2FSD\Delta C}{L} \cdot \exp\left[\frac{-D\pi^2 t}{4L^2}\right] \quad t > L^2/D, \quad (3b)$$

where D is the diffusion coefficient, L the film thickness, F the Faraday constant, S the active surface area, and ΔC the difference between the concentration before and after the potential step. The exponential decay of the current found for $t > L^2/D$, corresponds to the time at which the intercalating species has reached the impermeable side of the film. This model enables us to relate the decay times from our results to a hydrogen diffusion coefficient.

The double-exponential decay can be explained by the two structural phases involved in the reversible dihydride to trihydride transition. In the hydrogen concentration range $x = 1.8$ – 2.3 the β phase exists.¹⁶ From $x = 2.3$ to $x = 2.9$ a β and γ phase coexist (miscibility gap). For $x > 2.9$ the single γ phase remains.¹⁶ The dihydride β -phase has an fcc structure, while the trihydride γ phase has a hcp structure.¹⁷ During switching the hydrogen concentration passes through the range corresponding to the β phase and the $\beta\gamma$ coexistence range in which the diffusion coefficients are expected to be different. The concentration range corresponding to the β phase fills up first; the β – γ transition is subsequently completed to give a single γ phase. The total charge of the fast exponential decay is typically 37% of the total deloading charge. Comparing this result with the β phase concentration range of about 40% in the phase diagram of the gadolinium hydride, we therefore conclude that the fast decay very likely corresponds to the concentration range of the β phase with a higher diffusion coefficient. The slow decay is then related to the β to γ transformation in the $\beta\gamma$ coexistence range.

Each phase should show both the square root and an exponential dependence of the current on time. With two phases there are consequently four time domains. The former includes a square root and exponential current decay. This fast square root current decay corresponds to time domains, which are not detectable with the current setup. The fast exponential decay overlaps with the “square root decay” of the slow process, and is probably masked by it; this complicates the interpretation of the first current decay process. Therefore the analysis in this article will be focused mainly on the exponential current decay of the slow process, which determines optical switching.

On the basis of the experimentally determined diffusion coefficients, we can conclude that the condition $t > L^2/D$ is not valid for the entire time range of the transient. However, Montella¹⁸ has shown that for $t \geq 0.23 \cdot L^2/D$ the error made will be $\leq 1\%$.

The diffusion coefficients for the slow process can be obtained from the fit of Fig. 1; the values range from 10^{-12} to $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ depending on film temperature, concentration, potential, and thickness. The corresponding value for the fast process is 1 order of magnitude larger. Hydrogen

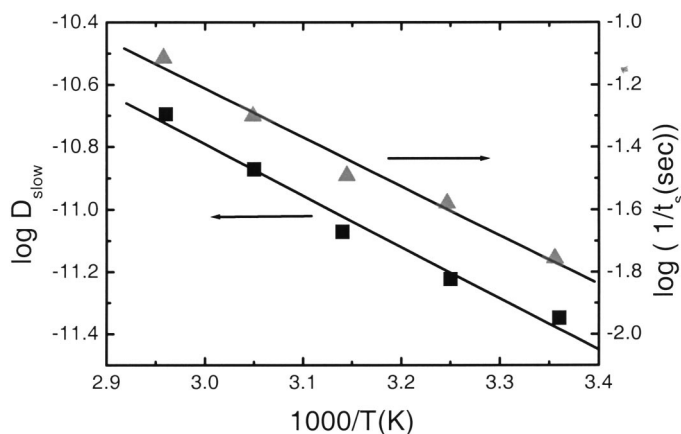


FIG. 2. Arrhenius plots of the diffusion coefficient and the reciprocal switching time for the slow process in a 200 nm film determined from the exponent in the exponential current decay fit.

diffusion coefficients have not been reported for the β and γ phases of gadolinium hydride. The values for the related material yttrium, also measured on a switchable mirror, are of the same order of magnitude. From the yttrium hydride diffusion coefficient parameters provided by Majer *et al.*¹⁹ from powder nuclear magnetic resonance (NMR) experiments in the β phase we calculate a diffusion coefficient of $10^{-11} \text{ cm}^2 \text{ s}^{-1}$ which is close to our values for the gadolinium thin film.

A. Temperature dependence

In Fig. 2, the logarithm of the diffusion coefficient for the slow process, derived from the exponent [Eq. (4)], is shown as a function of the reciprocal temperature. The straight line clearly indicates an Arrhenius dependence. The diffusion coefficient for the slow process ranges from 4.5×10^{-12} to $2.0 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ in a temperature interval from 25 to 65 °C; the corresponding activation energy is 0.32 eV. The fast decay gives a activation energy of approximately 0.29 eV. Our values are similar to those reported for yttrium thin films; these gas-phase experiments on films, loaded by lateral hydrogen transport, provide an activation energy of 0.37 eV for the $\beta\gamma$ transition.²⁰

Assuming free diffusion through the entire film, a certain minimum charge must be passed (e.g., a % of the charge needed to fully load the sample) before the film becomes transparent. It can be shown that the expected switching time t_D is related to the diffusion coefficient according to

$$t_D \propto \frac{L^2}{D}. \quad (4)$$

We define the measured switching time t_s as the maximum of the derivative of the transmission with respect to time. The relation between t_D and t_s is an unknown function but assumed to be independent of external parameters. Therefore $t_s = \eta t_D$, in which η is a constant. In Fig. 2 the reciprocal switching time is plotted as a function of the reciprocal temperature. From the slope we calculate an activation energy of 0.29 eV. The markedly good agreement between the activation energies independently determined from the current and

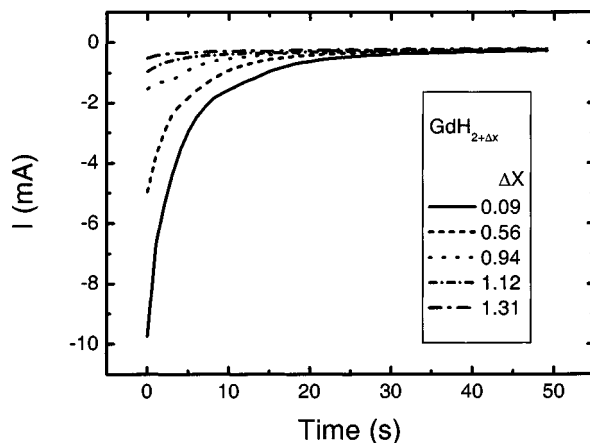


FIG. 3. Current transients measured after addition to a 100 nm film of different amounts of hydrogen Δx . Δx is indicated in the inset.

transmission transients and the good agreement of the activation energies with literature values for hydrogen diffusion in yttrium thin films, is strong evidence for diffusion-limited kinetics.

B. Concentration dependence

In practical systems the effective diffusion coefficient can in principle depend on the concentration of the diffusing species.¹⁵ After a large potential step this concentration may change considerably. Crank and Park²¹ have shown that a concentration dependent diffusion coefficient can be obtained by averaging over the concentration range; this approach is independent of the nature of the concentration dependence. If in our case the diffusion coefficient depends on the hydrogen content of the film, then this should be clear in experiments in which the film is first preloaded (above $x = 2$) before the potential step experiment is performed. Partial loading of the sample prior to the potential step will provide a diffusion coefficient which is averaged over a shorter concentration range, thus corresponding to higher concentrations. Current transients measured after addition of a fraction of the possible loadable hydrogen concentration, are shown in Fig. 3. The first exponential decay clearly disappears. After introduction of $\Delta x \geq 0.2$ the transient can be fitted with a single exponential function. Subsequent addition of hydrogen before the potential step leads to a further decrease of the current density in the transients. The corresponding diffusion coefficients for the slow decay are shown in Fig. 4. The diffusion coefficient increases from 3.2×10^{-12} to $6.9 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ with increasing hydrogen concentration. Since this concentration-dependent diffusion coefficient is determined by the average diffusion coefficient, taken over a decreasing concentration domain, we can conclude that the diffusion coefficient must be increasing with increasing hydrogen content. The diffusion coefficient usually decreases at higher concentrations of the diffusing species due to blocking.²² However, a change in electronic structure at higher hydrogen concentrations, as is apparent from the optical change, could give rise to a lower diffusion barrier.²³ The optical switching time also decreases after introduction of hydrogen in the film before the potential step,

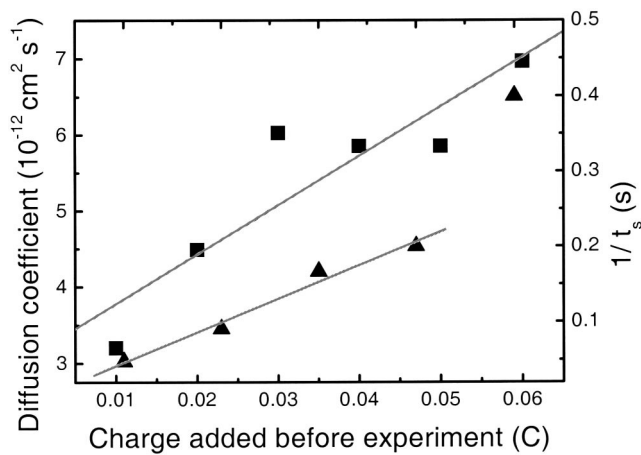


FIG. 4. Diffusion coefficients calculated from the current transients shown in Fig. 3 (squares), and the reciprocal switching time (triangles, right axis) of the film as a function of the added hydrogen Δx , intercalated before the potential step.

as shown in Fig. 4. A linear dependence of the reciprocal switching time on added charge is apparent for the first four points. After $\Delta x = 0.8$ the switching time could not be established accurately, since the transparency is almost complete before the potential step is applied.

C. Potential dependence

In Fig. 5 the effective diffusion coefficient related to the slow process is plotted as a function of the applied potential of the potential-step experiments. The diffusion coefficient increases from 1.4×10^{-11} to $1.3 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ in the potential range from -0.91 to -1.2 V. The switching time decreases from a 100 to 10 s with decreasing potential. The reciprocal switching time as shown in Fig. 5 is also clearly linearly dependent on the potential. The linear dependence of both the reciprocal switching time and the diffusion coefficient on the potential are an indication that the switching is determined by diffusion.

The potential at the sample corresponds, via the Nernst equation, to an equivalent hydrogen pressure p_{H_2} ²⁴

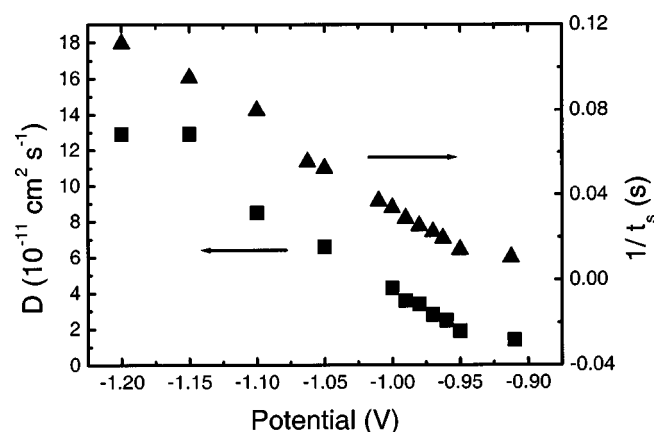


FIG. 5. The potential dependence of the diffusion coefficient and the reciprocal switching time (calculated from the maximum of the derivative of the transmission with respect to time) of a 400 nm film.

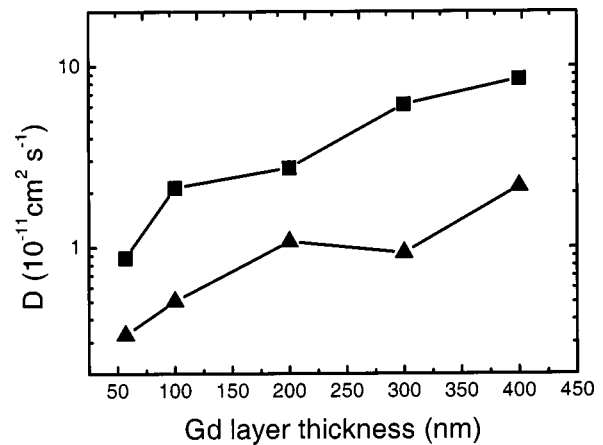


FIG. 6. Diffusion coefficients as a function of film thickness for two applied potentials: 1.0 V (squares) and -1.1 V (triangles).

$$p_{\text{H}_2} = \exp \left[- (E_e + 0.926) \frac{nF}{RT} \right]. \quad (5)$$

Here, F is the Faraday constant, R the universal gas constant, T the temperature, and n the number of electrons involved in the hydrogen evolution reaction ($n=2$). The hydrogen pressure is expressed in bar. Equation (5) is only valid for equilibrium. During a potential step experiment an overpotential component will influence this direct relation between the potential and pressure. A dependence of the switching time on the hydrogen pressure in epitaxial yttrium thin films has been reported by Remhof *et al.*²⁵ in gas phase experiments. Assuming that the production of adsorbed hydrogen according to Eq. 1(a) is not limited by the applied potential, it is therefore likely that the electrochemically applied equivalent hydrogen pressure also influences the effective hydrogen diffusion coefficient. From the isotherm of gadolinium²⁶ we know that the pressure and concentration are directly related. It is therefore also possible that the potential dependence is indirectly a concentration dependence.

D. Thickness dependence

In Fig. 6 the diffusion coefficient is shown as a function of film thickness for two potentials. For the potential step to -1.0 V the diffusion coefficient increases from 3.2×10^{-12} to $2.1 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ as the thickness is increased from 57 to 400 nm. The diffusion coefficient for the potential step to -1.1 V is higher, as expected from the potential-dependent measurements, but shows the same trend with increasing thickness. It is known that for thin metal films hydrogen diffusion coefficients can depend on the film thickness.²⁷ The upward trend in our results is in agreement with the increase of the mobility coefficient for lateral hydrogen diffusion with increasing thickness as reported for yttrium films by Van der Molen *et al.*⁷ In the same study the morphology was shown to depend on the film thickness. This is confirmed by an AFM study on our gadolinium films. In Fig. 7 the increasing grain size of films with increasing thickness is apparent. It is therefore likely that the diffusion coefficient is determined by the morphology of the film. The effect of morphology may

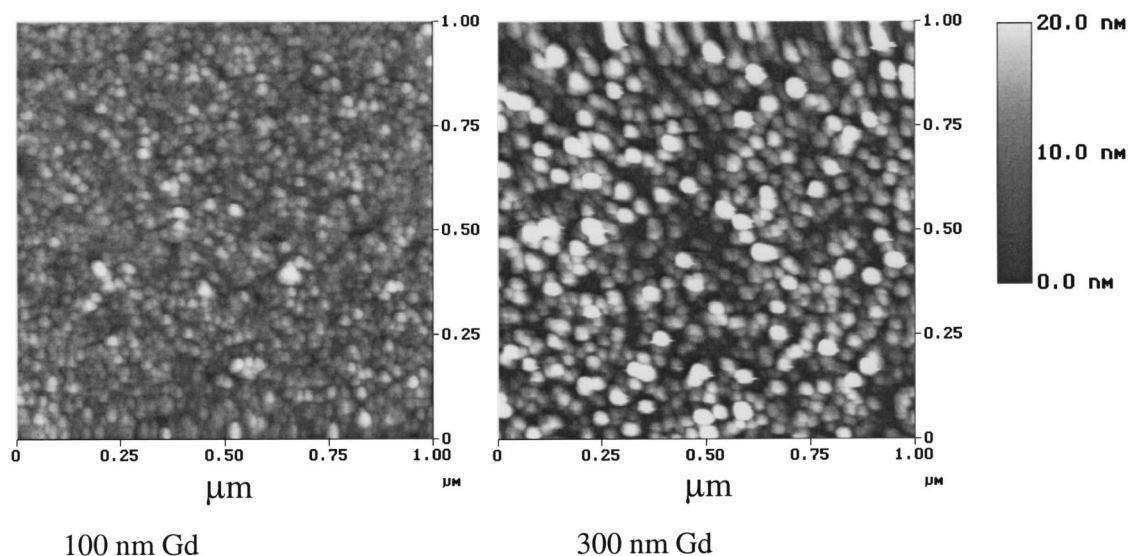


FIG. 7. The surface morphology as recorded by AFM for a 100 nm (A) and a 300 nm (B) gadolinium film.

be different for lateral or normal diffusion; in both cases the switching time does not show the L^2 dependence expected from Eq. (4) (see Fig. 8).

A surface-limited process, either at the palladium surface or the palladium–gadolinium interface, should result in a switching time which is independent of the film morphology; only the surface process should affect the kinetics. Since the geometric area and properties of the surface are unlikely to be influenced much by the internal structure of the film we do not expect a dependence of a surface limited process on the morphology. The switching time should then be linearly dependent on the film thickness, since only the size of the “reservoir” matters. From the clear nonlinear dependence of the switching time we conclude that switching limited by a surface process can be excluded.

In a diffusion-controlled process, an indication of the switching time can be obtained from Eq. (4). In Fig. 9 the diffusion coefficient is shown as a function of the reciprocal switching time. A linear relation between of L^2/t_s and D is found, which is not dependent on the film thickness; the

slope of this linear plot, or prefactor, is determined by η which relates the optical absorption coefficient to the concentration profile within the film. If the optical switching is completely diffusion limited, the prefactor should have the same value for all thickness-dependent experiments. From this information we conclude that a dependence of the diffusion coefficient on the morphology directly influences the optical switching time, but the diffusion process and the switching time remain strongly correlated.

In Fig. 10 the logarithm of the diffusion coefficient is plotted as a function of the logarithm of the reciprocal switching time, for the results obtained at various temperatures, concentrations and potentials. It is clear that the data points lie about a straight line, like the results of Fig. 9. The different relative positions of the data points from different experiments are the result of the different film thickness used in these experiments. A difference of the prefactor for these experiments would translate in an upward or downward shift of the points. The results of Fig. 10 show that the strong correlation between current decay and optical switching time

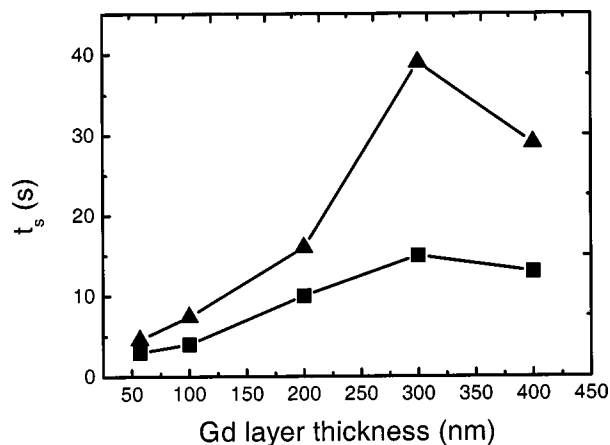


FIG. 8. The reciprocal switching time as a function of film thickness for two applied potentials: -1.0 V (squares) and -1.1 V (triangles).

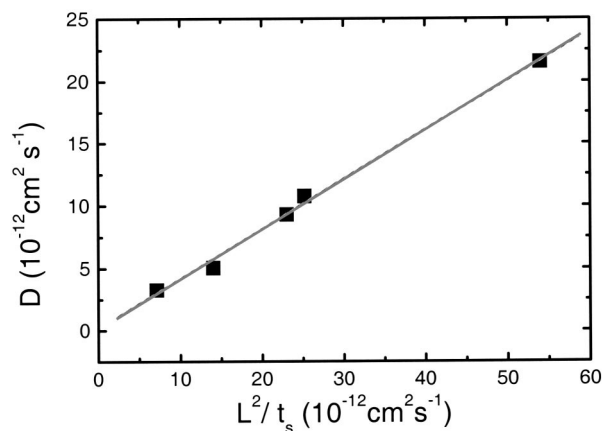


FIG. 9. The diffusion coefficient as a function of L^2/t_{switch} for the films of different thickness.

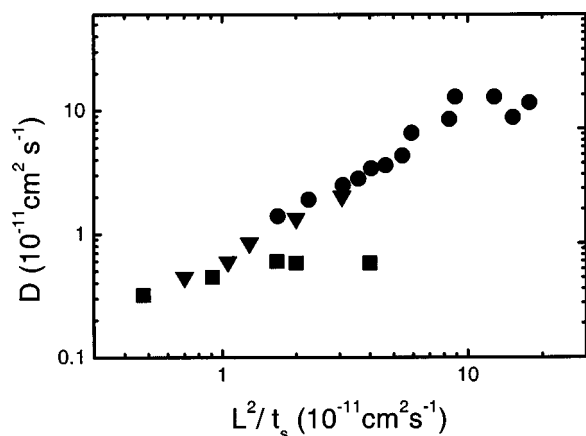


FIG. 10. The diffusion coefficient determined from the current transient as a function of the reciprocal switching time. The experimental results for different temperatures (triangles), concentrations (squares) and potentials (dots) are shown.

is independent of temperature and potential. The first two points of the concentration dependent results (filled squares) lie on the straight line. The deviation of the remaining points is explained by a dependence on concentration of the function that relates the transmission and concentration.

E. Comparison with literature

In the experiments of Den Broeder *et al.*²⁰ involving lateral diffusion, the $\beta\gamma$ phase boundary is visible as a transmission discontinuity, which moves with a $t^{1/2}$ dependence. Since the film is very thin, formation of a phase boundary during loading normal to the surface is unlikely due to the limited time. For much thicker films a phase boundary model could relate the diffusion coefficient to the switching time.

Typical electrochemical switching times are in the order of 10 s for a potential stepped to around -1.1 V. More negative potentials will only result in hydrogen gas development. Gas phase experiments on yttrium switchable mirrors at 1 bar hydrogen pressure show similar switching times. Van der Molen *et al.*⁷ reported a switching time of 3 s for a 200 nm yttrium film. Huijberts *et al.*¹ measured a switching time of 70 s for a 500 nm yttrium film. Therefore a fundamental difference in switching kinetics for gas phase and electrochemical loading seems unlikely.

IV. CONCLUSIONS

We show that a simple diffusion model describes consistently the switching kinetics of a gadolinium thin film upon hydrogenation. The time constants of the current and transmission transients are directly related to the diffusion coefficient, pertaining to the reversible loading of the gadolinium film. Two time domains are attributed to the different structural phases involved in the transition from the dihydride to the trihydride state. There is a clear dependence of the switching time and diffusion coefficient on temperature, potential, concentration, and film thickness. The measured activation energies correspond well with literature values for

similar materials. A significant increase of the diffusion coefficient with increasing hydrogen concentration and decreasing applied potential is found. A thickness dependence of the switching time and diffusion coefficient is also clear. The nonlinear dependence of the switching time on the film thickness indicates the role of diffusion limited kinetics in optical switching.

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- ¹J. N. Huijberts, R. Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot, and N. J. Koeman, *Nature (London)* **380**, 231 (1996).
- ²P. van der Sluis, M. Ouwkerk, and P. A. Duine, *Appl. Phys. Lett.* **70**, 3356 (1997).
- ³D. G. Nagengast, A. T. M. van Gogh, E. S. Kooij, B. Dam, and R. Griessen, *Appl. Phys. Lett.* **75**, 2050 (1999).
- ⁴T. J. Richardson, J. L. Slack, R. D. Armitage, R. Kostecki, B. Farangis, and M. D. Rubin, *Appl. Phys. Lett.* **78**, 3047 (2001).
- ⁵T. J. Richardson, J. L. Slack, B. Farangis, and M. D. Rubin, *Appl. Phys. Lett.* **80**, 1349 (2002).
- ⁶P. van der Sluis and V. M. M. Mercier, *Electrochim. Acta* **46**, 2167 (2001).
- ⁷S. J. van der Molen, J. W. J. Kerssemakers, J. H. Rector, N. J. Koeman, B. Dam, and R. Griessen, *J. Appl. Phys.* **86**, 6107 (1999).
- ⁸P. van der Sluis, *Electrochim. Acta* **44**, 3063 (1999).
- ⁹P. H. L. Notten, M. Kremers, and R. Griessen, *J. Electrochem. Soc.* **143**, 3348 (1996).
- ¹⁰J. O'M. Bockris, J. McBreen, and L. Nanis, *J. Electrochem. Soc.* **112**, 1025 (1965).
- ¹¹E. S. Kooij, A. T. M. van Gogh, and R. Griessen, *J. Electrochem. Soc.* **146**, 2990 (1999).
- ¹²M. Di Vece, P. van der Sluis, A.-M. Janner, and J. J. Kelly, *J. Electrochem. Soc.* **148**, G576 (2001).
- ¹³A. T. M. van Gogh, D. G. Nagengast, E. S. Kooij, N. J. Koeman, J. H. Rector, and R. Griessen, *Phys. Rev. B* **63**, 195105 (2001).
- ¹⁴C. J. Wen, B. A. Boukamp, and R. A. Huggins, *J. Electrochem. Soc.* **126**, 2258 (1979).
- ¹⁵J. Crank, *The Mathematics of Diffusion*, 2nd ed. (Oxford University Press, New York, 1999).
- ¹⁶W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, *Metal Hydrides* (Academic, New York, 1968), Chap. 10.
- ¹⁷*Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (North Holland, Amsterdam, 1979), Vol. 20, Chap. 20.
- ¹⁸C. Montella, *J. Electroanal. Chem.* **518**, 61 (2002).
- ¹⁹G. Majer, U. Kaess, and R. G. Barnes, *Phys. Rev. Lett.* **83**, 340 (1999).
- ²⁰F. J. A. den Broeder *et al.*, *Nature (London)* **394**, 656 (1998).
- ²¹J. Crank and G. S. Park, *Trans. Faraday Soc.* **45**, 240 (1949).
- ²²H. C. Bauer, J. Volkl, J. Tretkowski, and G. Alefeld, *Z. Phys. B* **29**, 17 (1978).
- ²³G. Majer, J. Gottwald, D. T. Peterson, and R. G. Barnes, *J. Alloys Compd.* **330–332**, 438 (2002).
- ²⁴M. Kremers, N. J. Koeman, R. Griessen, P. H. L. Notten, R. Tolboom, P. J. Kelly, and P. A. Duine, *Phys. Rev. B* **57**, 4943 (1998).
- ²⁵A. Remhof, G. Song, K. Theis-Brohl, and H. Zabel, *Phys. Rev. B* **56**, R2897 (1997).
- ²⁶M. Di Vece, S. J. M. Zevenhuizen, and J. J. Kelly, *Appl. Phys. Lett.* **81**, 1213 (2002).
- ²⁷Y. Li and Y. T. Cheng, *Int. J. Hydrogen Energy* **21**, 281 (1996).