Finite size effects: deuterium diffusion in nm thick vanadium layers

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Abstract

We investigate the effect of finite size on the chemical diffusion of deuterium in extremely thin V(001) layers. A five fold increase in the diffusion coefficient is observed at concentrations around 0.2 [D/V], when the thickness of the V is decreased from 28 to 14 atomic layers (≈2–4.2 nm). The size dependent deuterium–deuterium interaction energy is argued to be the root of the observed changes as the diffusion rates are similar at low concentrations. The results demonstrate the feasibility of using finite-size effects to enhance the chemical diffusion of light interstitials in solids. We discuss the general applicability of these effects to other systems.

1. Introduction

A fundamental understanding of the physics of hydrogen migration in metals and alloys is essential since kinetic properties, such as diffusion and dissociation rates, are essential engineering criteria for the viability of metal hydrides in a future hydrogen economy [1]. Many metal hydrides, MgH2 being a prime example, offer great storage capacity of hydrogen yet suffer from poor kinetics of uptake and release. In contrast, vanadium offers less favourable gravimetric storage capacity, but exhibits one of the fastest diffusion rates of hydrogen in the classical hydrides, comparable to the mobility of liquid water molecules at room temperature. There is a large ongoing effort involving influencing both thermodynamic and kinetic properties by finite-size or nano-scaling [2–4]. However, investigations of finite size effects on diffusion are scarce. There are multiple effects that may influence the chemical diffusion in an unpredictable and uncontrollable way, when changing the extension of the hydrogen absorbing materials. This includes, for example, changes in the surface to volume ratio, defect density, crystal symmetry, microstructure, cycling effects, as well as strain. Therefore, it is of large value to have access to model systems, where all but one identified contribution can be kept constant. This can be achieved by the use of single-crystal metallic superlattices which can be grown with a high structural quality and controllable strain state [5, 6]. Furthermore, the crystalline quality and interface sharpness of metallic superlattices can be maintained for different thicknesses of the layers, when the strain state is the same. This can for example be achieved by keeping the thickness ratio of the layers (L_A / L_B) constant, as illustrated by a number of authors [6, 7]. We also note that these superlattices can be loaded and unloaded hundreds of times without any structural degradation [8], and we can therefore exclude irreversible influences from grain boundaries and microstructure. Hence the platform provided by these materials is ideal for investigations which require a high degree of reversibility and reproducibility, such as the diffusion measurements described here.

Measuring hydrogen diffusion in thin films is challenging, but can be achieved, for instance, by making use of optical indicator layers [9, 10]. However it is highly desirable to have access to the spatial concentration profiles of hydrogen in the host material itself as a function of time as described by Pálsson [11]. This technique has been applied recently to the diffusion of hydrogen in 50 nm vanadium films, where the activation energy was found to change profoundly with concentration, that was linked to a change in site occupancy, even though the measurements were performed above the known phase boundaries [12]. When combining two materials in the form of a superlattice, one can choose the spatial modulation of the absorption potential by the choice of composition, and the spatial distribution of hydrogen concentration is decided by the difference of the absorption potential in the composition. Nb/Ta superlattices [13, 14] show a weak modulation in the hydrogen
concentration due to the similarity of the free electron density of the elements. As a contrast to this, the use of molybdenum or iron in combination with vanadium will result in a strong modulation of the hydrogen density in the superlattices [15]. For example, hydrogen is absorbed exothermically in vanadium, while it is endothermic in iron [16]. As a consequence, the hydrogen is solely absorbed in the vanadium layers in a wide temperature range [17–20] and Fe/V superlattices can be used as a model system for investigations of the finite size effects. This approach has been used for e.g. investigations of finite size effects on the thermodynamics of absorption [17] as well as the influence of strain on the diffusion rate of H in extremely thin V(001) layers at low concentration [21]. Here we present results of deuterium diffusion measured in a wide concentration and temperature range for Fe/V428 (n = 2, 3, 4) superlattices. We will demonstrate large finite size effects on the diffusion rate, originating from finite size induced changes in the D–D interaction.

2. Experimental details

2.1. Sample preparation

The single crystal Fe/Vn (n = 2, 3, 4) superlattices used for the study were grown on MgO (001) substrate with magnetron sputtering as described in [5, 6, 22]. The purity of the V and Fe targets is 99.95% and the size of the MgO (001) substrate is 1 × 1 × 0.1 cm³. The thickness of the vanadium and iron layers are 7n and n monolayers, with n equal to 2, 3 and 4. The superlattices consist of 23 (n = 2), 15 (n = 3), 11 (n = 4) bi-layers of Fe and V layers, with one additional V layer as illustrated e.g. for FeV428 (n = 4) superlattice in figure 1. The repetition of the layer sequence is used to improve the accuracy of the measurement as well as to allow detailed structural analysis of the samples. 7 nm thick palladium was deposited on top of the vanadium layers in order to catalyze the dissociation of hydrogen molecules into hydrogen atoms. In addition, the palladium protects the vanadium from oxidation. A 10 nm thick amorphous Al₂O₃ film is deposited on top of the samples, leaving two 0.1 cm wide stripes of palladium open at both ends for hydrogen to enter and subsequently diffuse along the [110] axis in the vanadium layers. The epixial relation between film and substrate is Fe/V(001) || MgO(001) and Fe/V[100] || MgO[110] [5]. A schematic illustration of the similar superlattices can be found in [23]. They were characterised by x-ray reflectivity and diffraction as described in [6, 8]. Briefly they are fully coherent throughout the total thickness of the samples and with an in-plane coherence length of several hundred nm [6].

2.2. Concentration profile determination

After inserting the sample, the chamber was baked for 2 d, reaching a base pressure of low 10⁻⁶ mbar. As the sample is exposed to an atmosphere of deuterium molecules (D₂), they can spontaneously dissociate on the uncoated palladium surface and migrate into the sample (see the inset of figure 1). This gives rise to a high deuterium concentration under these areas, which acts as a source in the diffusion experiments.

The deuterium concentration can be calculated from changes in the transmitted light intensity using [17, 24]

\[ c = \alpha \ln \left( \frac{I(c)}{I(0)} \right) \]  

(1)

\( \alpha \) is a scaling factor; \( I(c) \) is the light transmission after hydrogenation; \( I(0) \) is the light transmission in the absence of hydrogen (D). The lateral resolution of the optical system is 10 μm, and the wavelength used is 625 nm. Representative concentration profiles obtained from the measurements are illustrated in figure 1.
2.3. Determination of diffusion constants
The diffusion constants were extracted from the concentration profiles, as described in [12]. Briefly, Fick’s second law
\[
\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D_c \frac{\partial c}{\partial x} \right)
\]
is used to describe the diffusion process. The samples can be treated as a semi-infinite system within the given time frame. One can integrate both sides of the equation from \(x\) to \(L\) and obtain
\[
\int_x^L \frac{\partial c(x, t)}{\partial t} \, dx = D_c \frac{\partial c(x, t)}{\partial x} \bigg|_{x=L}^{t=L},
\]
the boundary condition is
\[
\frac{\partial c(x, t)}{\partial x} \bigg|_{x=L} = 0.
\]
The concentration dependent \(D_c\) from the profiles \(c(x)\) can be extracted at constant times \(t\) by this integration method given by:
\[
D_c = -\left[ \int_x^L \frac{\partial c(x, t)}{\partial t} \, dx \right] \left[ \frac{\partial c(x, t)}{\partial x} \right]_{x=L}^{t=L}.
\]
The analysis of the data is restricted to the times for which the actual boundary and initial conditions hold [12]. Empirically we have found that this holds for the concentration profiles in the range from \(x = 0\) to \(x = L = 0.2\) cm for \(t \leq 200\) s using the approach described here. The deuterium diffusion coefficients \(D_c\) as a function of position and time are obtained from equation (5) using numerical methods. This involves smoothing the concentration profiles in order to reduce the noise in the data (here an 11 point 2nd order Savitzky–Golay filter was used for the profiles). The final diffusion coefficients are obtained as the average value of the diffusion coefficients from the different deuterium concentration profiles in the time window 0–200 s, at the corresponding concentration \(c\). Here the concentration range is divided into intervals of width of \(\Delta c = 0.01\) [D/V]. More details can be found in reference [12].

If the \(D_c\) is independent of concentration, the analytic solution of Fick’s law is given by
\[
c(x, t) = c_0 \sum_{k=1}^{\infty} \left[ \text{erfc} \left( \frac{2(k-1)L + x}{2\sqrt{D_c t}} \right) + \text{erfc} \left( \frac{2kL - x}{2\sqrt{D_c t}} \right) \right] (-1)^{k-1}
\]
for our boundary and initial condition from \(x = 0\) to \(x = L = 0.4\) cm throughout the time range (\(t \leq 1500\) s) of diffusion [21]. This function fits concentration profiles of hydrogen diffusion in metals very well at \(c \leq 0.05\) [D/V] [21], which is used to extract the deuterium diffusion coefficients at low concentration in the current study.

3. Results and discussion
3.1. Concentration dependence of hydrogen diffusion
The deuterium concentration profiles as a function of time were determined for all the superlattices in the temperature range 383–523 K, as for example illustrated in figure 1 for \(\text{Fe}_4/\text{V}_{25}\). From this data we extract the concentration dependent diffusion in a single experiment, as described above and illustrated in figure 2. The diffusion constants are therefore extracted under identical external conditions of temperature and applied deuterium pressure. As seen in figure 2, a clear minimum in the chemical diffusion coefficients is obtained. The observed trend is consistent with that in both bulk and thin films of vanadium [12, 25]. At low concentrations, the diffusion coefficients for the \(\text{Fe}_n/\text{V}_{25}(n = 2, 3, 4)\) superlattices approach the same value, which is consistent with the absence of finite size effects of the chemical diffusion in the low concentration limit [23]. We note a marked departure of the diffusion rate values between the three superlattices as the concentration is increased above 0.1 [D/V]. We denote the observed minimum diffusion value as \(D_m\) for later reference.

To ascertain the mechanism behind these finite-size effects, we examine the full expression for the chemical diffusion [16, 26]
\[
D_c(c, T) = \frac{D_0(c) e}{H(c) k_B T} \frac{\partial \mu(c, T)}{\partial c} \exp \left( \frac{-E_a}{k_B T} \right)
\]
where \(H(c)\) is Haven’s ratio, \(D_0(c)\) is the Arrhenius prefactor, \(E_a\) is the activation energy, \(k_B\) is Boltzmann’s constant, and \(\mu\) is the chemical potential. Multiplying by the temperature and taking the natural logarithm of both sides yields:
We can now identify possible roots to the finite size effects using equation (8), as illustrated in figure 3 where we display $\ln [T D_{cm}(c, T)]$ as a function of $1/T$. A linear dependence is observed, whereby we conclude that the temperature dependence of the derivative of the chemical potential must be weak. We see directly from figure 3 that the slopes and consequently the activation energy is the same for all the samples. Fitting of equation (8) to the data was therefore done with a common value for the activation energy and the product $Y = \frac{c \partial \mu}{\partial c} D_0(c) / H_R(c)$, these fitting parameters are summarised in table 1. Since there is no difference in the chemical diffusion at different thickness of vanadium for low concentration range, we conclude that there is no intrinsic finite-size dependence to the prefactor $D_0(c)$ and Haven’s ratio $H_R(c)$. If we assume that these quantities do not change strongly with thickness at higher concentrations, the changes in the diffusion rate (around 0.2 [D/V]) would need to originate from the changes in $\frac{c \partial \mu}{\partial c}$. This finding is in line with the obtained
changes for H in thin V(001) layers, where the interaction energy was found to decrease with the inverse thickness of the layers \[17\].

A simple model for the chemical potential in metal hydrides that can be used to capture these effects is \[17, 27\]

\[
\mu = u_0 - uc + k_B T \ln \left( \frac{c}{r - c} \right),
\]

(9)

where $u_0$ is the binding energy, $u$ the interaction energy and $r$ the maximum concentration. Xin et al \[17\] found that the critical temperature ($T_c$) scales linearly with the inverse thickness in similar superlattices which also holds for the interaction energy in the mean field approximation, whence $u \rightarrow u(L)$. Taking the derivative of the chemical potential in this model yields:

\[
\frac{\partial \mu}{\partial \xi} = -u(L) + k_B T \frac{r}{c(r - c)}.
\]

(10)

Thus, when the interaction energy $u$ is the dominating contribution to the changes in equation (10), the $\frac{\partial \mu}{\partial \xi}$ should scale with the inverse thickness of the layers. The essence of this analysis is illustrated in figure 4, the changes in the product $Y$, which is related to $\frac{\partial \mu}{\partial \xi}$ and chemical diffusion of deuterium, are well captured by the assumed inverse thickness dependence which supports the interpretation provided above. At first sight one might expect a negative slope as in equation (10), however a closer look at Xin’s expression \[17\] shows that the sign is reversed in the thickness dependence. Hence the present interpretation also captures the sign of the changes, which lends further credence of this model.

4. Conclusions

We conclude that the profound (factor of 5) increase in the chemical diffusion constant arises from changes in the chemical potential and its derivative when changing the thickness of the vanadium layer from 28 to 14 monolayers. These changes (chemical potential and its derivative) arise from finite size effects, where the absence of neighbours at the interfaces reduces the effective attractive elastic interaction. We are also able to separate out the effects of strain and pure finite size, as the superlattices considered in this work are tuned to have the same strain state when the thickness is altered. The results highlight the large influence of the interaction between light interstitials on their chemical diffusion in condensed matter. The results from this study could aid the understanding that underpins the improvement of kinetics of uptake and release in hydrogen based storage materials and batteries. These results can be generalised in that any mechanism, such as finite size or doping, that modifies the phase diagram due to a change in the interaction energy (and subsequently manifested in a change in the thermodynamic factor), will also cause a concomitant change in the kinetic properties, as clearly demonstrated here in the case of hydrogen diffusion in thin vanadium layers.

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