Low-angle neutron and x-ray scattering of hydrogenated and deuterated Mo/V superlattices

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We present results from low-angle neutron and x-ray scattering experiments on hydrogen and deuterium loaded (001)-oriented single-crystal Mo/V superlattices. The individual Mo and V layer thicknesses in the samples were determined by simulations of the x-ray reflectivity curves. The intensity of the first-order neutron-diffraction peak for the hydrogenated sample is 31% larger than from the dehydrogenated sample. When deuterated, the intensity of the first-order peak is extremely small, only 0.5% of the dedeuterated sample. The distribution of hydrogen in the layers was derived by simulations of the neutron and the x-ray diffraction patterns. The results unambiguously demonstrate that the hydrogen isotopes are exclusively located in the V layers, but at the interfaces there is a region with reduced hydrogen concentration.

Low-angle neutron-scattering experiments have previously been used to investigate amorphous Si:H/Si:D,^{1,2} Si/Si:X (where X stands for a H-D mixture), and Si/Si:H/Si/Si:D multilayers.² In these studies the modulation of the scattering potential originated in the change in density and the concentration variation of the H isotopes in the as-produced samples. The use of metallic multilayers as neutron reflectors stimulated an investigation of NiH_y/TiH_x multilayers,³ in which the hydrogen was introduced during the growth of the samples. By annealing, the redistribution of hydrogen (leading to formation of Ni/TiH_x), and vacancy annihilation, the reflectivity contrast of the samples was found to be improved. Here we report on the changes in the low-angle neutron and x-ray scattering from Mo/V superlattices upon loading and unloading with hydrogen and deuterium. The experiments were performed to establish the distribution of the hydrogen isotopes in Mo/V superlattices. Furthermore, we will demonstrate that by loading samples, with hydrogen isotopes, the neutron-scattering potential of multilayers and superlattices can be modified. This feature can be used to finetune the intensity and the wavelength of a reflected neutron beam.

Growth of high-quality epitaxial (001) and (110) oriented Mo/V superlattices (SL) has been reported in the literature.⁴⁻⁷ Symmetric Mo/V superlattices, i.e., superlattices with equal Mo and V layer thicknesses, can be grown coherently with sharp interfaces up to a critical modulation wavelength Λ of 5 nm, corresponding to 16 ML in each SL layer. For asymmetric SL, the Λ range for coherent growth can be extended above $\Lambda=5$ nm. Above the critical limit, the V layers grow incoherently

in a three-dimensional fashion. For growth temperatures below 800 °C the variation of Λ is typically ± 1 ML, and is due to deviations from a perfect two-dimensional layer-by-layer growth and not from thermally induced intermixing.⁷ At higher temperatures, interdiffusion broadens the interfaces.

The Mo/V(001) superlattices used in this study were grown epitaxially on polished MgO(001) substrates ($10\times 10\times 0.5$ mm³) by dual target magnetron sputtering. The deposition system was equipped with two, 2-in.-diam, planar dc magnetron sources. After introduction, the substrates were annealed at 800 °C for 1 h, and thereafter the substrate temperature was lowered to the growth temperature of 700 °C. Two samples (labeled 1 and 2) were produced with a nominal layer thickness ratio L_V/L_{Mo} of 2/1 and modulation wavelength $\Lambda (=L_V+L_{Mo})=5.0$ nm. Prior to hydrogen (deuterium) loading, the samples were annealed in vacuum at 500 °C for 4 h to activate the H₂ (D₂) dissociation on the sample surface. After repeated flushing with purified H₂ (D₂), sample 1 was exposed to 1-bar H₂, and 2 to 1.4-bar D₂ at 225 °C for 24 h and thereafter rapidly cooled to room temperature under the same pressure. The D₂ pressure was higher to obtain the same fugacity at the surface. The samples were loaded to [H]/[V] and [D]/[V] ratios close to 1 (Ref. 8) to avoid isotope effects in the site occupancy,⁹ and to maximize the changes in the scattering potential. The heat of solution for H in bulk V is -0.30 eV/H (α -phase),⁹ whereas for bulk Mo, it is positive, 0.41 eV/H. The interstitial electron density in the host material is one of the most important properties determining the heat of solution for hydrogen in materials.¹⁰ When

Mo/V superlattices are grown epitaxially, the average lattice parameter perpendicular to the growth direction is increased in V and decreased in Mo, compared to their bulk values. The interstitial electron density will therefore be increased in Mo and decreased in V due to the volume changes associated with the strained structure. This implies even larger differences in the heat of solution for hydrogen in Mo and V. At moderate temperatures and pressures, the hydrogen content of Mo can therefore be expected to be negligible compared to that of V.

Conventional θ - 2θ x-ray diffraction (XRD) was carried out on the samples in the low-angle (reflectivity) region using a Philips Model (PW)1820 powder diffractometer with an accuracy of 001° in 2θ . The layer thicknesses (L_{Mo} and L_{V}) in each superlattice were determined by simulations of the reflectivity curves using the Philips GIXA code which uses full dynamical theory, taking care of multiple reflection, refraction, and absorption. Figure 1 shows x-ray reflectivity curves from sample 1 in the three stages of the experiment. The topmost curve in Fig. 1 is a simulation of the as-deposited film. The pattern from the as-deposited film shows many distinct but asymmetrically broadened superlattice peaks. After loading the sample with hydrogen, the superlattice satellites shifted towards the origin and the relative intensity of the third-order peak increased. The shift shows that the period Λ increased by 5.6% upon hydrogen loading. When the sample was dehydrogenated, Λ decreased by 6.2% and the relative intensity of the third peak decreased. The peak-to-background ratio in the reflectivity curves decreased by a factor of 0.1 when the sample was hydrogenated and did not recover when dehydrogenated. The results from the XRD analyses are summarized in

FIG. 1. Low-angle XRD data from sample 1 at all stages of the experiment. On top is the simulated diffraction pattern. The results from sample 2 are almost identical and are therefore not displayed.

TABLE I. Summary of results from the XRD analysis. The modulation wavelength refers to the experimentally determined value but the thickness of the layers is obtained from the GIXA simulations.

Identification	$\Lambda \pm \Delta\Lambda$ (nm)	L_{V} (nm)	L_{Mo} (nm)	$L_{\text{V}}/L_{\text{Mo}}$ (nm)
1, as deposited	4.98 ± 0.01	3.33	1.63	2.04
1, hydrogenated	5.26 ± 0.01	3.62	1.63	2.23
1, dehydrogenated	4.93 ± 0.01	3.32	1.62	2.05
2, as deposited	4.76 ± 0.01	3.18	1.58	2.01
2, deuterated	4.96 ± 0.01	3.43	1.57	2.19
2, dedeuterated	4.71 ± 0.01	3.17	1.56	2.03

Table I. In order to reproduce the asymmetric peak shapes in the simulations, a model with wedge-shaped layers had to be adopted. This is reasonable, as the samples were not rotated during the growth. From the simulations, it was found that the layer thicknesses varied by $\approx 10\%$ over the samples (a distance of 10 mm). Since the thickness variation of the constituents has opposite sign, the change in Λ across the samples will be less pronounced, and depends on the relative layer thicknesses. For example, when the average $L_{\text{V}}/L_{\text{Mo}} = 1$, there will be no variation in Λ and the peaks will be sharp and symmetric, but the even-order peaks will not be extinct as in an ideal structure. On the other hand, if $L_{\text{V}}/L_{\text{Mo}} \neq 1$, Λ will vary slightly across the sample, leading to asymmetric peaks, and at the positions for extinct peaks, double peaks will appear. This effect is clearly seen in the reflectivity curve from the as-deposited sample in Fig. 1. The experimentally determined layer thicknesses given throughout this work refers to the average values. The XRD results for sample 2 were qualitatively the same as for sample 1 (see Table I) and are therefore not displayed.

The reflectivity simulations demonstrated that all expansion in the growth direction occurred in the V layers and consequently implies the 5.6% hydrogen-induced expansion of Λ in sample 1, and 8.4% increase of the V layer thickness. Such an expansion alters the $L_{\text{V}}/L_{\text{Mo}}$ ratio from 2.04 to 2.22 and is seen in the experimental data as a relative intensity increase of the third-order satellite. The average lattice parameters in the growth direction ($\bar{c}$) and in the plane ($\bar{a}$) of the superlattices were determined by reciprocal space mapping (RSM) around the Mo/V (002) and (222) Bragg peaks using a Philips MRD diffractometer operated in the parallel-beam x-ray optics mode. $\bar{a}$ and $\bar{c}$ increased by 0.6% and 5%, respectively, upon hydrogenation. RSM showed no change in $\bar{a}$ after dehydrogenation. Bulk V has a bcc structure with a lattice parameter $a_0 = 0.302$ nm, which transforms upon hydrogenation to a tetragonal VH_x phase which has the lattice parameters $a = 0.300$ nm, $c = 0.330$ nm for $x = 0.5$ and $a = 0.304$ nm, $c = 0.342$ for $x = 0.9$.¹¹ This means that the VH_x lattice must be aligned with the c axis along the growth direction in order to account for the observed change in Λ . The lower peak-to-background ratio and the relaxation of Λ observed upon hydrogen cycling indicates that the lattice coherency strain was relaxed and the number of structural defects in the lattice increased.

The neutron experiments were performed at the triple

axis spectrometer, G43, at the Orphée reactor, Laboratoire Léon Brillouin in Saclay. The beam was collimated down to 30' for both the incident and the scattered beam. The neutron wavelength was 0.4245 nm, and the extension of the beam was larger than that of the sample. Thus the neutron-scattering data correspond to an average over the entire sample. All the experiments were performed at ambient temperature.

As the hydrogen isotopes are expected to be located exclusively in the vanadium layers, we can estimate the change in the relative intensity of the diffraction maxima imposed by the hydrogen and the deuterium loading. The intensity of the first-order peak in the low-angle neutron data can be approximated by $(\bar{b}_A - \bar{b}_B)^2$, using kinematic diffraction theory. $\bar{b}_A$ and $\bar{b}_B$ are the average coherent scattering amplitude densities of the layers *A* and *B*. The values of interest here are

$$b_{(\text{Mo})} = 4.41 \times 10^{10} \text{ cm}^{-2}, \quad b_{(\text{V})} = -0.360 \times 10^{10} \text{ cm}^{-2} \quad (\text{Ref. 12}),$$

$$b_{(\text{VH})} = -2.53 \times 10^{10} \text{ cm}^{-2}, \quad \bar{b}_{(\text{VD})} = 4.41 \times 10^{10} \text{ cm}^{-2}$$

(calculated using values from Ref. 12). If Mo does not absorb H, the introduction of hydrogen (forming VH) would lead to enhanced contrast, and hence larger intensity of the first-order maxima. On the other hand, the introduction of deuterium (forming VD) should lead to a featureless low-angle diffraction pattern, when no gradients in the D concentration are present in the V layers.

The neutron-diffraction results for both samples, loaded with the hydrogen isotopes as well as after dehydro-

genation, are presented in Fig. 2 and Table II. We chose to use the dehydrogenated samples as a reference, as the intensities of the hydrided and the dehydrided samples were the same in the XRD measurements. The distance between the superlattice peaks is found to be smaller in the hydrogenated sample compared to the dehydrogenated sample, consistent with the XRD results. The hydrogenated sample has 6.1% larger Λ than the dehydrogenated sample. Furthermore, the intensity of the first-order peak is enhanced by a factor 1.3. As stated above, this implies that the hydrogen is preferentially located in the V layers, in line with the XRD analysis and previous observations.^{8,13} When loaded with deuterium, the calculated Λ from the neutron-scattering data is found to be 5.3% larger, and the first-order peak in the diffraction pattern becomes extremely weak: only 0.5% as compared to the dedeuterated sample. The low intensity of the third-order peak in the unloaded samples is due to the approximate 2/1 thickness ratio of the constituents. Contrary to the XRD results, no enhancement of the third-order peak is observed in the neutron-scattering experiments of the hydrogenated sample. The shape of the diffraction pattern is almost the same for the loaded and the unloaded sample. In the deuterated sample, not only are the intensities affected, but the intensity ratios are completely different. The peak corresponding to the second-order maximum has the same intensity as both the first- and the third-order peaks. The coherent scattering amplitude for neutrons therefore does not reflect the same scattering profile as the x-ray scattering.

The thicknesses of the layers (L_{Mo} and L_{V}), determined by the GIXA analysis, were used as input parameters for simulations of the neutron-diffraction patterns at all stages of the experiments. Representative results are shown in Fig. 2, where the simulation of a dehydrogenated and the deuterated samples are displayed. Since the expansion of the V layer alters the $L_{\text{V}}/L_{\text{Mo}} = 2.04$ ratio to $L_{\text{V}}/L_{\text{Mo}} = 2.23$, the third-order satellite should be strongly enhanced upon hydrogenation, if the H were equally distributed in the V layers. A good correlation between the observed and the simulated intensities was obtained by including a 1–2-ML hydrogen-free interface region in V, in the simulations of the hydrogenated sample. With a larger interface region, the third-order peak became prominent. We were not able to reproduce the experimental results by the simulations with a constant hydrogen concentration throughout the vanadium layer. Upon deuterium loading, not only were the amplitudes of the peaks altered, but the intensity ratios were also dramatically affected. The intensity ratios of the first three peaks are found to be close to unity. From the

FIG. 2. Experimental and simulated neutron-diffraction patterns for samples 1 and 2. On top is the simulated pattern of the dehydrogenated sample using the results from the XRD analysis. The simulated curve for sample 2 is obtained with $[D]/[V] = 0$ in the first layer at the interface, $[D]/[V] = 0.5$ in the second layers, and $[D]/[V] = 1$ elsewhere.

TABLE II. Summary of results from the neutron-diffraction experiments.

Identification	Λ (nm)	I_1^a	I_2^a	I_3^a
1, hydrogenated	5.20 ± 0.02	500 ± 1	58.4 ± 0.5	
1, dehydrogenated	4.90 ± 0.02	381 ± 1	39.5 ± 0.4	
2, deuterated	4.95 ± 0.02	1.5 ± 0.2	1.5 ± 0.2	1 ± 0.2
2, dedeuterated	4.70 ± 0.02	298 ± 1	27.9 ± 0.3	

^aArbitrary units.

FIG. 3. Schematic illustration of a part of the scattering potentials for neutrons on (a) unloaded, (b) hydrogenated, and (c) deuterated Mo/V superlattices, and for x rays on (d) unloaded and (e) hydrogenated or deuterated Mo/V superlattices.

simulations we find that no second- or third-order maxima would be observed for the deuterated samples, if deuterium would be present throughout the V layers and $[D]/[V] \approx 1$. As for the hydrogenated sample, the simulations were consistent with a 1–2-ML-thick interface region in V. The simulated curve in Fig. 2 was obtained for a 1-ML deuterium-free V layer at the interface and with $[D]/[V]=0.5$ in the second monolayer and $[D]/[V]=1$ elsewhere. A schematic illustration of the deduced neutron and x-ray scattering potentials are shown in Fig. 3. The large coherent scattering amplitude of neutrons on H and D modifies both the contrast between layers as well as the scattering profile. This leads to larger intensities of the superlattice peaks in the case of hydrogen and completely different relative intensities in the case of deuterium. As a comparison, we display the deduced XRD scattering profiles. No change in the scattering intensity is expected, as the increase in the number of electrons in the V layers is compensated by the lattice expansion. The resulting changes in the x-ray scattering potentials are

therefore completely governed by the change in Λ .

Due to spillover of electrons from Mo to V layers, there is a region in V with enhanced electron density, which results in an increase in the heat of formation (less energetically favorable sites). The extension of this region was previously inferred to be 3 ML in V (≈ 0.45 nm), in the low concentration limit.⁸ These results were supported by first-principles calculations of the interstitial electron densities in Mo/V superlattices.¹⁴ As a consequence of this interface region, a new superstructure is formed in the Mo/V superlattices when loaded with the hydrogen isotopes. With increasing hydrogen content, the population of the interface region was found to be enhanced,⁸ which is consistent with the experimental results presented here. The V layer closest to the interface is expected to be almost hydrogen free. The second monolayer is presumably partially populated, due to phonon-assisted jumps from the interior toward the interface. Upon cooling, the population of the interface region should therefore diminish, and consequently the neutron-diffraction pattern would be altered. By measuring the diffraction pattern at different temperatures, it would be possible to make a quantitative analysis of the interface population.

The results unambiguously demonstrate that the hydrogen isotopes are exclusively located in the V layers, but at the interfaces there is a region with reduced hydrogen concentration. The results also demonstrate that the low-angle neutron-scattering intensity can be altered by changing the population of hydrogen isotopes in a sample. This feature can be used to accurately determine the concentration profile of hydrogen isotopes in multilayers and superlattices. Furthermore, as the loading of hydrogen isotopes can be performed in a reversible way, hydrogen isotopes can be used to finetune the neutron reflectivity of superlattices simply by changing the amount of hydrogen in the samples.

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