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Hydrogen induced lattice expansion in 8/4 u.c. Mo/V superlattice

G. Reynaldsson[a,*], S. Olafsson[a], H.P. Gislason[a], G. Song[b], H. Zabel[b]

[a] *Science Institute, University of Iceland, Reyjavik, Iceland*
[b] *Ruhr-Universität Bochum, Fakultät für Physik und Astronomie, D-44780 Bochum, Germany*

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Abstract

The hydrogen-induced lattice expansion in highly strained quasi two-dimensional V layers embedded in a Mo/V 8/4 u.c. superlattice has been studied in the temperature range 140–300 °C. Comparison to lower strained V layers showed a strong dependency of the strain on the lattice expansion. For $c \leq 0.5$ the expansion was found to be lower than that for V-layers with lower initial strain. For $c > 0.5$ the expansion was increased indicating a change in site occupancy.

Keywords: Superlattices; Lattice expansion; Thermodynamics

Hydrogen-induced lattice expansion in two-dimensional superlattice structures has recently become of considerable interest. Examples of superlattices that have been studied include (001) oriented superlattices such as Mo/V 7/7 u.c. (unit cell) [1], $Mo_{0.5}V_{0.5}$/V 7/7 u.c. [2] and Fe/V 7/7 u.c. [3]. The initial strain in the vanadium layers is different in these superlattices. In the two former superlattices, the initial strain in the V layers is biaxial-expanded, but biaxial-compressed in the latest superlattice. The result is very different out-of-plane lattice expansion in the vanadium, which may be related to a different hydrogen site occupancy in the vanadium layers.

In this paper a Mo/V 8/4 u.c. superlattice is investigated, where the thickness ratio between the Mo and the V-layers creates a large initial strain in the vanadium layers. The in-plane strain may be estimated assuming coherent and dislocation-free superlattice and by considering the strain-energy density in the metal layers. These assumptions give the in-plane lattice parameters $a_{||} = 3.070$ Å for the $Mo_{0.5}V_{0.5/V}$ superlattices [2], $a_{||} = 3.11$ Å for the Mo/V 7/7 u.c. superlattice [1] and finally $a_{||} = 3.13$ Å for the Mo/V 8/4 u.c. superlattice studied here [4].

The Mo/V superlattice was grown on (001) oriented polished MgO substrate with a DC-magnetron sputtering at a sample temperature of 700°C and an argon sputtering pressure of $5 \cdot 10^{-3}$ mbar [5]. Low-angle X-ray scans showed well defined peaks indicating typical interfacial roughness of ±1.0 ML [6]. Measurements were performed at six different temperatures in the range 140 to 300 °C. For each isotherm the hydrogen pressure was increased from 0 to 730 mbar, stepwise.

A selection of X-ray diffractograms measured at 180°C is shown in Fig. 1. The main Bragg peak (002) moves towards lower 2θ value as the hydrogen pressure is increased. This shift originates from the out-of-plane expansion of the Mo/V superlattice when the hydrogen enters the vanadium layers. The intensity of the main bragg peak increases with the hydrogen pressure. The change in the intensity is followed by a corresponding decrease in the peak width, from a FWHM of 0.200° to 0.165±0.005° at maximum pressure.

From the main Bragg peak (002) the average Mo/V out-of-plane lattice parameter a_{avg} is obtained. Fig. 2 shows six expansion isotherms, where the average out-of-plane lattice parameter of the Mo/V superlattice is plotted as a function of the square root of the hydrogen loading pressure. The lattice parameter of the vanadium layers a_V is then determined from a_{avg} by the relation

$$a_{avg} = \frac{L_V a_V + L_{Mo} a_{Mo}}{L_V + L_{Mo}}. \tag{1}$$

Here a_{Mo} is the lattice parameter for Mo and $L_V = 4$ u.c.

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[*] Corresponding author.
E-mail address: grey@raunvis.hi.is (G. Reynaldsson).

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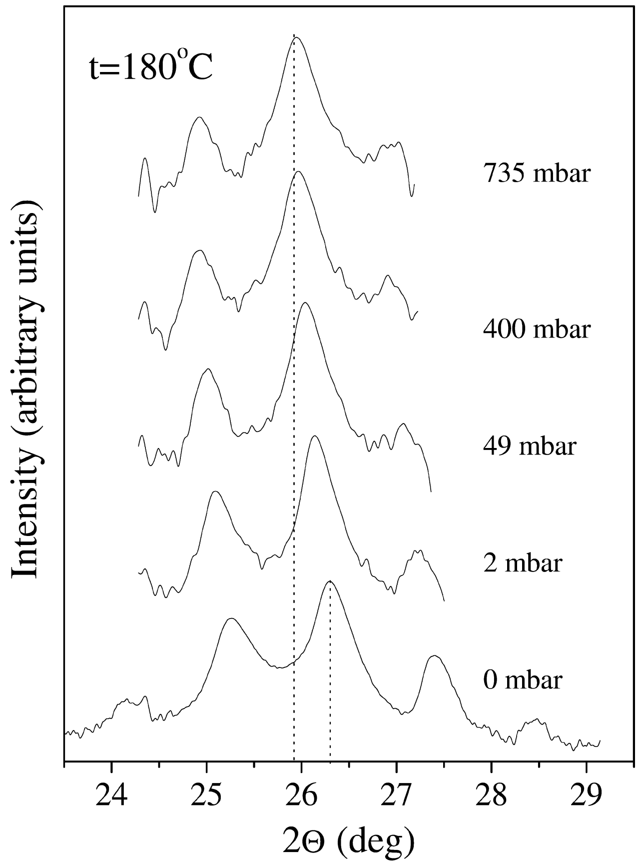

Fig. 1. A selection of X-ray diffractograms for the 8/4 u.c. Mo/V superlattice hydrogenated at pressures ranging from 0 to 735 mbar at $t = 180°C$. The increase in the out-of-plane lattice parameter due to the hydrogenation is reflected in a shift of the main Bragg peak (002) towards lower 2θ values.

and $L_{\mathrm{Mo}} = 8$ u.c. Fig. 3 shows a_{V} plotted as a function of the hydrogen concentration $c = \langle \mathrm{H/V} \rangle$.

The hydrogen concentration was determined through a resistance measurement which was performed parallel to the expansion measurements. The resistance change may be expressed by using a truncated power series of the H-concentration,

$$\Delta R(T,p)_{\mathrm{norm}} = f(c) = Ac^2 + Bc + C. \tag{2}$$

The constants A, B and C were determined for the concentration ranges, $c \leq 0.5$ and $c > 0.5$. For $c \leq 0.5$ the constants were determined through the conditions $f(0) = 0$, $f(0.5) = 1$ and $f'(0.5) \approx 0$, and for $c > 0.5$ through the conditions $f(0.5) = 1$, $f'(0.5) \approx 0$ and $f(0.8) = -1.5$. In the last condition the maximum concentration for bulk, $c = 0.8$, was used as a reference value [7] and $\Delta R(T,p)_{\mathrm{norm}} = -1.5$ is the lowest measured resistance change of the isotherms. From these two sets of conditions the parameters were determined,

$$\Delta R(T,p)_{\mathrm{norm}} = -4c^2 + 4c \quad \text{for } c \leq 0.5, \tag{3}$$

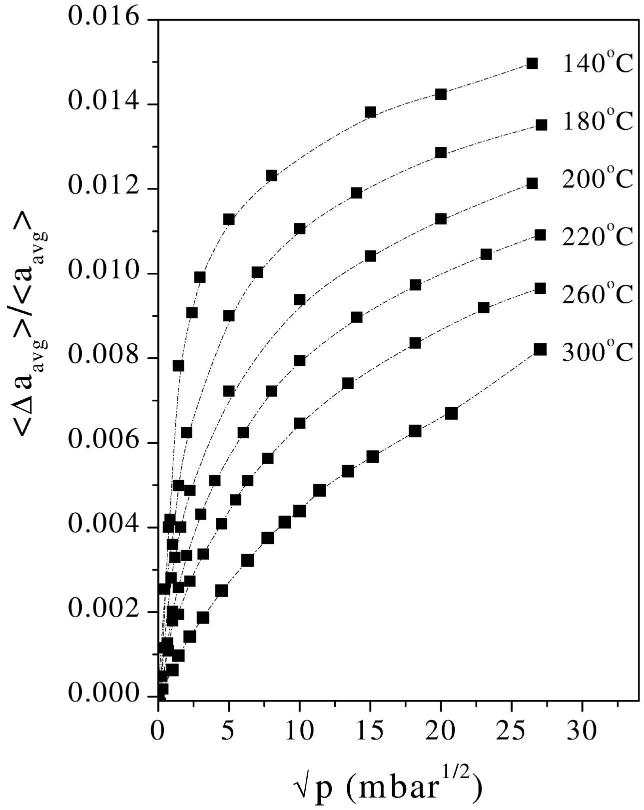

Fig. 2. Expansion isotherms showing the relative lattice expansion versus square root of the hydrogen pressure. The dotted lines are for showing the form of the isotherms more clearly.

$$\Delta R(T,p)_{\mathrm{norm}} = -28.3c^2 + 28.3c - 6.1 \quad \text{for } c > 0.5. \tag{4}$$

Using this calibration the expansion turns up to be linear with the hydrogen concentration c as appears in Fig. 3, where a_{V} is plotted as a function of c. This may be expressed with a linear equation

$$\Delta a_{\mathrm{V}} = k_z \cdot c, \tag{5}$$

where k_z is a one-dimensional lattice expansion coefficient. Two different k_z values are observed in the Mo/V 8/4 u.c. superlattice. For $c \leq 0.5$, k_z was found to be 0.09, while in the range $c > 0.5$ the expansion coefficient k_z increases to 0.29. This change in slope at higher concentrations originates partly from the introduced maximum concentration of $c = 0.8$ from V-bulk.

By noting in Fig. 3 that for each concentration value the expansion for each temperature is similar it may be concluded that the lattice expansion of the vanadium layers is temperature independent. This indicates that no phase change is observed over the whole temperature range at the same hydrogen concentration. From this we conclude that the vanadium layers are in the same phase regime in the temperature interval 140–300 °C.

The influence of the in-plane strain on the out-of-plane lattice expansion can now be seen in Fig. 3 by comparison

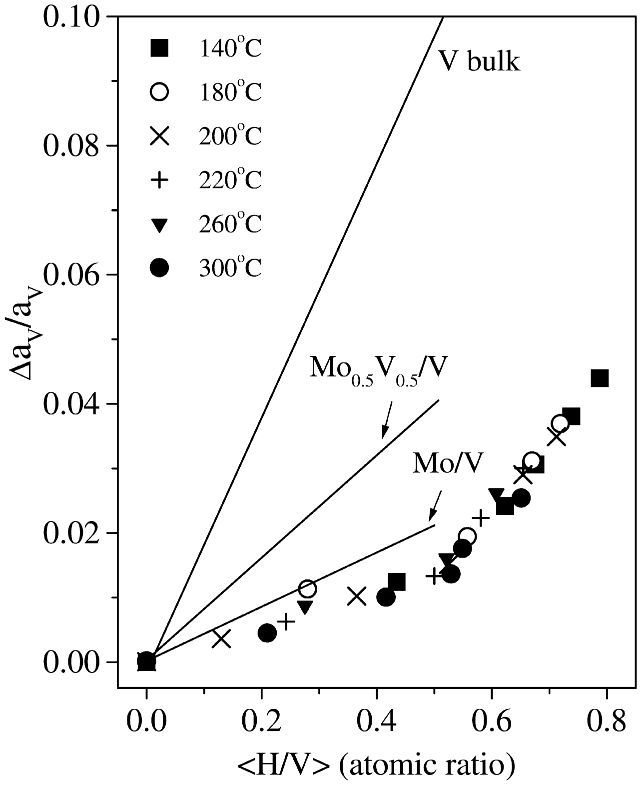

Fig. 3. Lattice expansion of the vanadium layers in the 8/4 u.c. Mo/V superlattice versus average hydrogen concentration $c = \langle H/V \rangle$. Shown is for comparison the expansion from the vanadium layers from $Mo_{0.5}V_{0.5}$/V 7/7 u.c. and Mo/V 7/7 u.c. superlattices and the vanadium bulk. What is noticeable is that the expansion decreases when the initial strain in the vanadium layers is increased.

to the result from $Mo_{0.5}V_{0.5}$/V 7/7 u.c. and Mo/V 7/7 u.c. superlattices [1,2]. The estimated in-plane strain for these superlattices for $c \leq 0.5$ are 1.7 and 3.0% and the lattice expansion coefficients $k = 0.24$ and 0.12. What is noticeable is that the expansion coefficient between the lowest and the largest strained superlattice differs by a factor of three. This is a very large difference considering that the difference in the in-plane lattice parameter is 1.8%.

Until now we have been discussing results from the out-of-plane lattice expansion a_V and the one-dimensional expansion coefficient. It is however more relevant to discuss the volume expansion as a function of the hydrogen concentration, where the volume is calculated as,

Table 1
The one-dimensional lattice expansion coefficients k_z, the estimated in-plane lattice parameters $a_{\|}$, the volume expansion coefficients k_{vol} and the initial volume V_0 in the absence of hydrogen for the Mo/V 4/8 u.c., Mo/V 7/7 u.c. and $Mo_{0.5}V_{0.5}$/V 7/7 u.c. superlattices and the V-bulk

	k_z	$a_{\|}$ (nm)	k_{vol}	V_0 (nm^{-3})
V-bulk	0.2	0.3030	0.018	0.0278
$Mo_{0.5}V_{0.5}$/V	0.08	0.3070	0.008	0.0286
Mo/V 7/7	0.04	0.3110	0.004	0.0293
Mo/V 8/4	0.03	0.3125	0.003	0.0296

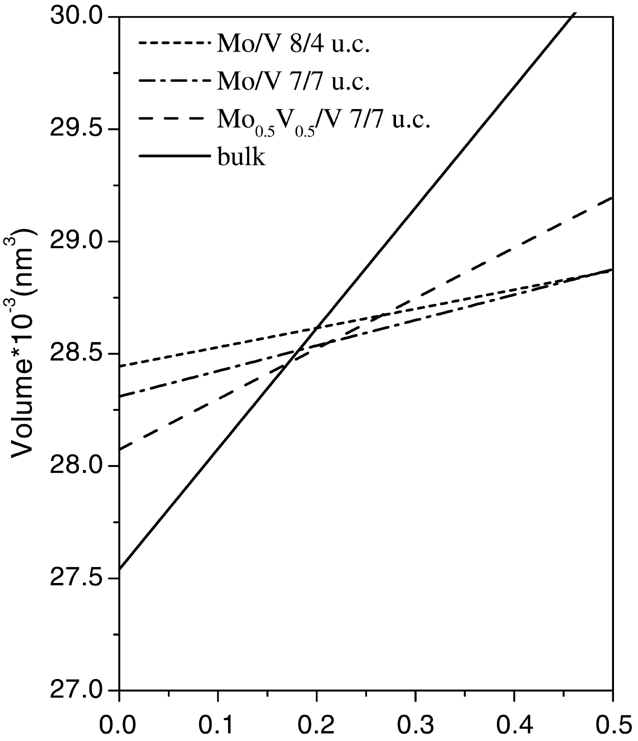

Fig. 4. The volume expansion as a function of the hydrogen concentration for V-bulk, $Mo_{0.5}V_{0.5}$/V 7/7 u.c., Mo/V 7/7 u.c. and Mo/V 8/4 u.c. superlattices.

$$V = V_0 + k_{vol} \cdot c. \tag{6}$$

V_0 is the initial volume in the absence of hydrogen and $k_{vol} = a_{\|}^2 \cdot k_z$ is the volume expansion coefficient which gives the expansion induced per hydrogen atom.

The values for V_0 and k_{vol} for the three superlattices and V-bulk are shown in Table 1 as well as the k_z values and the estimated in-plane lattice parameters $a_{\|}$. In Fig. 4 the result from Table 1 in combination with Eq. (6) is plotted. Apparently, the different initial in-plane strain affects the volume, which is not conserved. Initially the volume is larger for the strained V layers compared to V-bulk. Due to the lower expansion coefficients in Table 1 the excess in volume for the V layers in three superlattices for $c < 0.2$ compared to V-bulk is turned to a volume deficiency for $c > 0.2$. Although the results presented in Fig. 4 may be related to the interstitial sites the hydrogen is occupying this results is not sufficient to discuss the different types of interstitial sites. However, the sudden change in the slope in Fig. 3 for the vanadium layers for the Mo/V 8/4 u.c. superlattice at $c = 0.5$ points to an increase in the number of occupation of the O_z or T_z sites, which are mainly responsible for the out-of-plane expansion.

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