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Influence of biaxial strain on thermodynamical properties of hydrogen in (001) oriented Mo/V superlattices

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Abstract

The influence of the strain state on the thermodynamics of hydrogen in quasi-two-dimensional V layers embedded in three Mo/V superlattices is reported in the temperature range 140–300 °C. The enthalpy change in the two lower strained V layers was found to be low in the low concentration range and approached the disordered V bulk value through an attractive hydrogen–hydrogen (H–H) interaction. For the most strained V layer the enthalpy change was larger in the low concentration range and decreased with a repulsive H–H interaction. The entropy change for the hydrogen in the V layers in the three superlattices was found to be much higher than that for V bulk and approached the bulk β-phase value. This indicates a less energetically favourable interstitial site for the hydrogen to occupy.

Keywords: Superlattices; Resistance; Thermodynamics

Hydrogen interactions in two-dimensional superlattice structures have recently become of considerable interest. Example of superlattices that have been studied include Nb/W(110) [1] and Mo/V superlattices [1,2]. By examining superlattices with different Mo/V thickness ratios, where the V layer thickness is held fixed, the influence of the initial strain in the V layers on the hydrogen interaction can be studied. In this paper this influence is studied for three Mo/V superlattices with Mo/V thickness ratios 1/4, 3/4 and 4/4 unit cell (u.c.). The thinnest Mo layers creates therefore the lowest initial strain in the V layers and the thickest Mo layers the largest strain. The in-plane strain (x–y plane) may be estimated by assuming the superlattices to be coherent and dislocation free and by considering the strain energy density in the metal layers. These assumptions give the following in-plane mutual lattice parameter for the Mo/V 1/4, 3/4 and 4/4 u.c. superlattices: $a_{||} = 0.3065$, 0.3100 and 0.3110 nm.

The three Mo/V superlattices were grown epitaxially on (001) oriented polished MgO substrate using DC-magnetron sputtering at an argon gas pressure of 5×10^{-3} mbar at 700 °C. The Mo/V 1/4 u.c. superlattice was grown with the repeat distance $\Lambda = 1.65$ nm with V layer thickness of $L_V = 1.23$ nm and Mo thickness of $L_{Mo} = 0.42$ nm, the Mo/V 3/4 u.c. superlattice with a repeat distance $\Lambda = 2.0$ nm with $L_V = 1.16$ nm and $L_{Mo} = 0.84$ nm and Mo/V 4/4 u.c. superlattice with a repeat distance $\Lambda = 2.45$ nm with $L_V = 1.18$ nm and $L_{Mo} = 1.27$ nm. Finally all the samples were covered with a 5–10-nm thick Pd layer. High- and low-angle XRD diffractograms of the samples showed constant period Λ throughout the superlattices. Well-defined peaks in the low-angle indicated a typical interfacial roughness of ±1.0 monolayer (ML) [4]. The resistance of the samples was measured with a four-point probe technique [2] using a lock-in amplifier and by applying 1 mA AC current and measuring the voltage drop. Measurements were performed at five different temperatures, in the range 200–300 °C. At each temperature, the equilibrium between the hydrogen gas pressure and the resistance was measured in steps up to 1000 mbar. By repeating these measurements for different temperatures $p - \Delta R/\Delta R_{max} - T$ isotherms were obtained.

Fig. 1 shows a collection of such isotherms for the three superlattices, where the $\Delta R/\Delta R_{max}$ is the normalized change in resistance due to the hydrogen uptake, which is used as a measure of the hydrogen concentration in the metal. Here ΔR_{max} is the maximum change in the resistance value for each isotherm. All isotherms show similar behavior, a monotonic increase until the maximum value is

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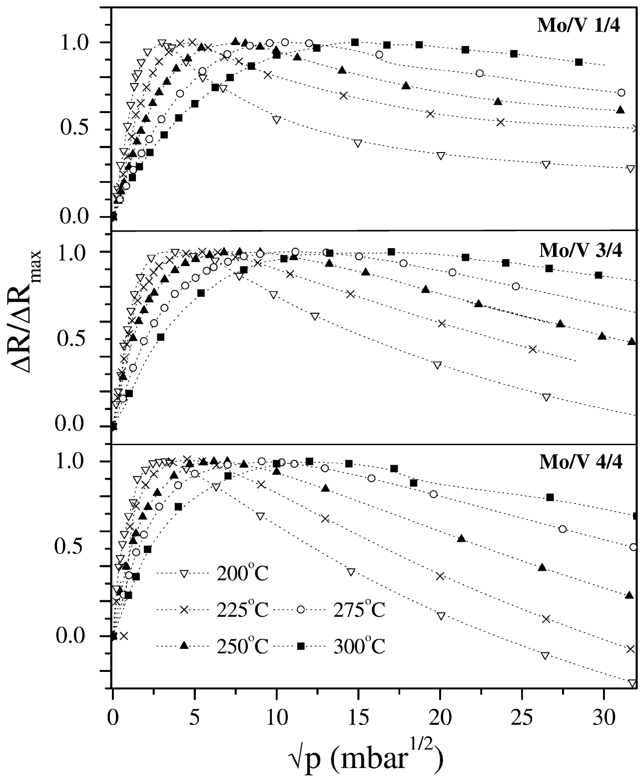

Fig. 1. Isotherms for the superlattices Mo/V 1/4, 1/4 and 4/4 u.c. Shown is the normalized resistance change versus the square root of the hydrogen pressure.

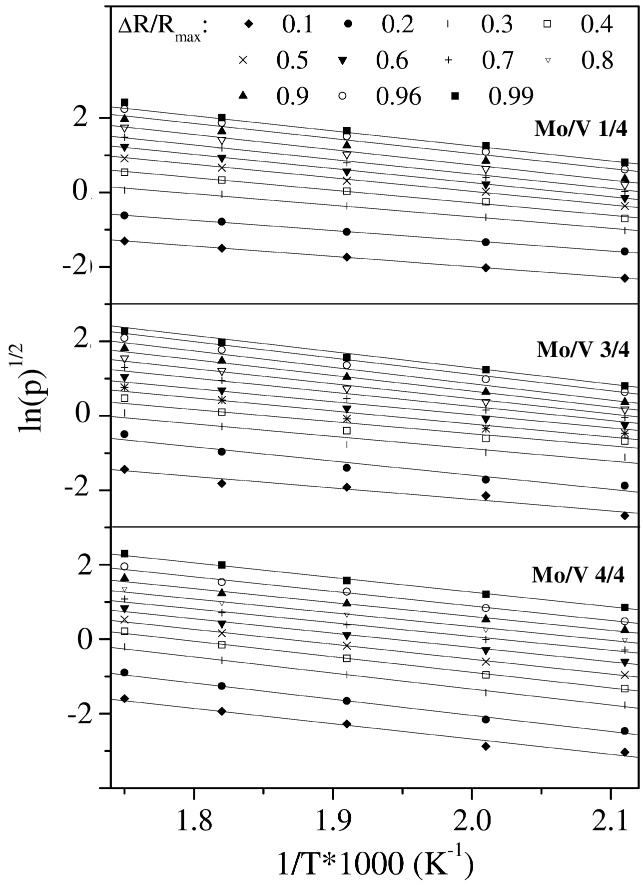

Fig. 2. Selection of Van't Hoff plots for the Mo/V 1/4, 3/4 and 4/4 u.c. superlattices.

reached, and then a subsequent decrease at higher pressure, in accordance to the model developed by Pryde and Tsong [5]

$$\frac{\Delta R}{\Delta R_{\max}} = Kc(n - c) \tag{1}$$

The model gives the relation between the normalized resistance change $\Delta R/\Delta R_{\max}$ and the hydrogen concentration $c = \langle \mathrm{H/V} \rangle$. K is a constant depending on the relation between c and $\Delta R/\Delta R_{\max}$ and n the number of hydrogen atoms per metal atom. Here $\Delta R/\Delta R_{\max} = 1$ corresponds to hydrogen concentration $c = 0.5$ [2], which gives $K = 4$ when $n = 1$. Eq. (1) can therefore be used to calibrate the measured resistance values to the hydrogen concentration. This relation is well obeyed for $c \leq 0.5$.

Each point in Fig. 1 represent an equilibrium between the dissolved hydrogen and the external hydrogen pressure, which can be described with the Van't Hoff relation [3]. Fig. 2 shows a selection of such Van't Hoff plots for the isotherms as a function of the hydrogen concentration for all samples. The enthalpy change ΔH_{H} and the entropy change ΔS_{H} obtained from the Van't Hoff plots is plotted in Figs. 3 and 4 in the region $0 < c \leq 0.45$.

Generally for the three superlattices a certain trend can be seen in both ΔH_{H} and ΔS_{H} compared to the V bulk [6]. In the low-concentration limit ($c \to 0$) in Fig. 3 the increasing strain in the V layers for the Mo/V 1/4, 3/4 and 4/4 u.c. superlattices increases the volume of the vanadium and therefore lowers the electron density. As a result the enthalpy change ΔH_{H} of the hydrogen increases ($|\Delta H_{\mathrm{H}}|$ is larger) with increasing strain in the V layers in accordance to the effective medium theory [7]. It is surprising how low ΔH_{H} is for the Mo/V 1/4 u.c. superlattice, which consists of a large part of vanadium only, compared to V bulk and the Mo/V 7/7 u.c. superlattice [2]. This points to the role of interface effects and increased charge transfer from the highly strained Mo layers to the V layers, which mostly affect the two nearest monolayers to the V layers [8]. Here the V layers are only 4 u.c., or 8 ML in total, so half of the atomic V monolayers are affected by the Mo layers. These results indicate that interface effects are increased when the number of Mo monolayers are decreased. As that occurs the compressive strain in the Mo layers is increased, which could result in stronger charge transfer over to the V-layer and hence stronger interface effect. This may be the reason for the shift in the enthalpy curves for the Mo/V 1/4 and 3/4 u.c. superlattices over the whole concentration range. Similarly, the large ΔH_{H} for the Mo/V 4/4 u.c. superlattice could be argued through lower charge transfer compared to the

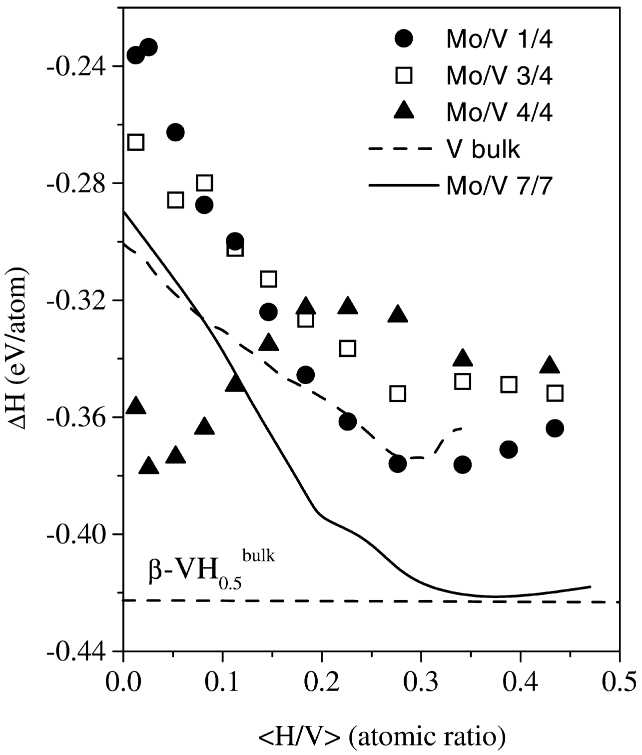

Fig. 3. Enthalpy change for the Mo/V 1/4, 3/4 and 4/4 u.c. superlattices.

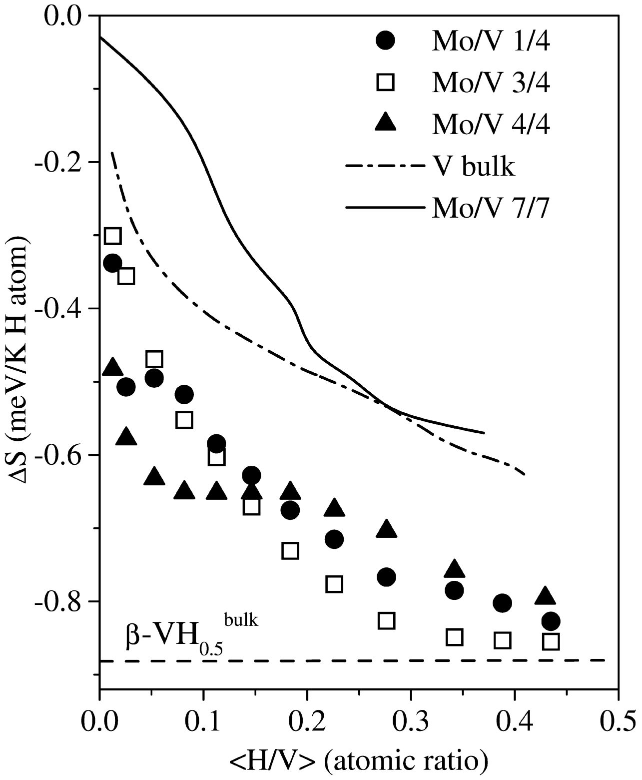

Fig. 4. Entropy change for the Mo/V 1/4, 3/4 and 4/4 u.c. superlattices.

Mo/V 1/4 and 3/4 u.c. superlattices, i.e. a decrease in the electron density corresponding to an increase in the binding energy.

As the hydrogen concentration increases ΔH_{H} changes due to an H–H interaction ($u_{\mathrm{H-H}}$). For the Mo/V 1/4 and 3/4 u.c. superlattices ΔH_{H} approaches bulk behaviour with an attractive $u_{\mathrm{H-H}}$ up to $c \approx 0.27$. For the Mo/V 4/4 u.c. superlattice $u_{\mathrm{H-H}}$ is repulsive up to $c \approx 0.17$, zero in the range $c = 0.17$–0.25 and becomes attractive for $c > 0.25$. This completely different behaviour is interesting considering that due to the similar initial strain in the V layers as in the Mo/V 7/7 u.c. superlattice one would expect to see a similar behaviour. Such a behaviour has been observed in Nb layers embedded in Nb/W(110) superlattices, where $u_{\mathrm{H-H}}$ was turned from being attractive to repulsive by increasing the strain in the Nb layers [1]. The difference between the Mo/V 7/7 and 4/4 u.c. superlattices is probably a result of a reduced thickness of the V layers. Here it is important to take into account the thickness of the interface region at the interfaces of the metal layers in the superlattices that does not dissolve hydrogen to the same extent as at the interior region. In the Fe/V superlattice this thickness was found to be 3 ML V at the interface [9]. According to this, the thickness of the interior region of the 8 ML thick V layers is 2 ML thick, while the interior thickness in the Mo/V 7/7 u.c. superlattice would be 8 ML. In general, the effect of increasing the strain state is firstly a blocking of the O_z sites (decrease in the out-of-plane lattice parameter), which makes T_{xy} sites more energetically favourable, and secondly increasing the localization of the O_x and O_y sites (increase in the in-plane lattice parameter). If we focus on Mo/V 4/4 u.c. superlattice where the strain is largest, the O_x and O_y could be well localized, making the T_{yz} and T_{xz} less energetically favourable. Due to the thickness of the V layers, this would likely extend over the whole high absorbing H-interior. The result is that the site occupation of hydrogen is such that out-of-plane expansion is reduced and the interaction is in the plane. Due to the elastic boundary conditions between the V and the Mo layers it follows that $u_{\mathrm{H-H}}$ is repulsive [10]. The strong localization of the O_x and O_y in the Mo/V 4/4 u.c. superlattice would be followed with a lower number of interstitial sites and therefore a large ΔS_{H} as shown in Fig. 4. For the lower strained V layers the localization of the O_x and O_y decreases making the T_{yz} and T_{xz} sites more energetically favourable. This enables an expansion out-of-the plane which is seen in the attractive $u_{\mathrm{H-H}}$. The increase in T_{yz} and T_{xz} sites is reflect in the decrease in ΔS_{H} by moving from the Mo/V 3/4 u.c. to Mo/V 1/4 u.c. superlattice.

At higher concentration ranges ΔS_{H} approaches the ordered V bulk β-phase, while the enthalpy change is close to that of the disordered V bulk phase. A similar result was observed in Nb layers in the Nb/W(110) superlattices [1]. This may be an intermediate situation for the vanadium–hydrogen system, since the expected in-plane lattice parameter of the superlattice $a = 0.306$ nm is quite different from the bulk β-phase lattice parameter $a = 0.300$ nm.

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