Hydrogen-Induced Strain Modulation in Nb-Ta Superlattices

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We report the first observation of a hydrogen-induced strain modulation in a metal superlattice due to interstitially dissolved atomic hydrogen. The intensities of the x-ray satellites from this strained Nb-Ta superlattice depend on temperature. This leads to a Curie-Weiss behavior for a H concentration modulation and can be explained in terms of a simple modulated lattice-gas model. In addition, we have found that the solubility of H in these thin Nb-Ta films is dramatically increased from what would be expected for bulk Nb or Ta.

Bulk quantities of Nb and Ta are known to be good absorbers of hydrogen. The absorbed hydrogen atoms occupy interstitial tetrahedral sites of the bcc host lattice causing a lattice expansion proportional to the dissolved hydrogen concentration.[1] When the host metal consists of an artificial chemical modulation (i.e., a metal superlattice of alternating thin Nb and Ta layers) we anticipate the presence of a modulation in the thermodynamic potential for an absorbed hydrogen atom. This will generate a corresponding modulation in both the hydrogen concentration and in the associated lattice expansion. In this Letter we report the first observation of such an induced hydrogen density modulation in a metal superlattice. In addition, our experiments indicate that the solubility of H in thin Nb-Ta films is greatly increased over that which would be expected from either of these metals in their bulk form. This system provides not only an opportunity to understand a new hydrogen-metal system but also a unique way to strain a superlattice in a controllable, continuous manner.

The x-ray study reported here has been performed on Nb-Ta superlattices having a modulation periodicity of $\Lambda = 20$ Å and a total thickness of 2500 Å. These films are grown by molecular beam epitaxy[2] along the [110] direction of the bcc metal lattice and are deposited on sapphire substrates of [11$\bar{2}$0] orientation. The x-ray scattering results were obtained with a double-axis spectrometer using MoK$_\alpha$ characteristic radiation off of a flat (111) Si single-crystal monochromator. Each Fourier component of the chemical modulation exhibits itself in the x-ray diffraction pattern by the appearance of two (+ s and − s) "satellite" reflections, one on each side of the average bcc reciprocal lattice point and separated by a distance equal to that of the Fourier wave vector ($k_s = 2\pi s/\Lambda$). X-ray scans of the samples used in this study typically reveal three to four Fourier components. In the hydrogen-free superlattice we find that the + s and − s satellite reflections have equal intensity, indicating that Nb and Ta layers have identical lattice parameters throughout the structure. This lattice parameter is the same as for bulk Nb and

Ta (which have essentially the same lattice constant). We have also measured reflections of the bcc reciprocal lattice which are not along the [110] growth direction and have found x-ray peak widths comparable to those of the (110) and (220) reflections, thereby assuring us that the samples are truly three-dimensional crystals.

Hydrogen loading of the superlattice was accomplished *in situ* using a high-vacuum x-ray furnace. The superlattice was first heated to 400 °C (a temperature at which no interdiffusion could occur) in a vacuum of better than 10^{-6} Torr before introducing highly purified hydrogen from a Pd cell. Upon the presence of the hydrogen, one expects two obvious changes to occur in the x-ray diffraction. First, since the lattice expands, we will see a shift in the positions of all reflections to lower angles. Secondly, the induced strain modulation will cause an asymmetry in the intensities for the pair (± s) of satellite reflections. The x rays scattered from both a strain wave and a composition wave will interfere to give the following intensities for the satellites (± s) about a Bragg reflection of the average bcc lattice[3]:

$$I_\pm \propto [\eta \mp \epsilon(\Lambda/d \pm 1)]^2; \qquad (1)$$

η is the amplitude of the atomic scattering factor modulation arising from the artificial chemical modulation with periodicity Λ and ϵ is the amplitude of the strain modulation which alters the [110] interplanar spacing, d. Here ϵ is assumed positive when the atomic species with the larger electron density has the larger interplanar spacing.

Figure 1 shows that the intensities of the $s = \pm 1$ satellite reflections for a 20-Å Nb-Ta superlattice containing a constant hydrogen concentration ($c = 0.32$ H/metal) are temperature dependent. Figure 2 shows that the strain, calculated from the data in Fig. 1 according to Eq. (1), is inversely proportional to the temperature. By assuming a linear strain-concentration relationship, this result implies the existence of a hydrogen-concentration fluctuation exhibiting a Curie-Weiss behavior. In the temperature range con-
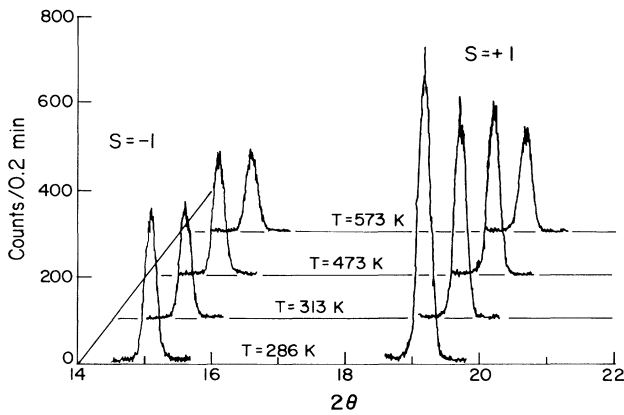
FIG. 1. X-ray scans of the ± 1 satellite reflections of a 20-Å Nb-Ta superlattice with 32% hydrogen concentration. The relative intensities change with temperature as a result of changes in the relative concentrations of hydrogen in the two materials.
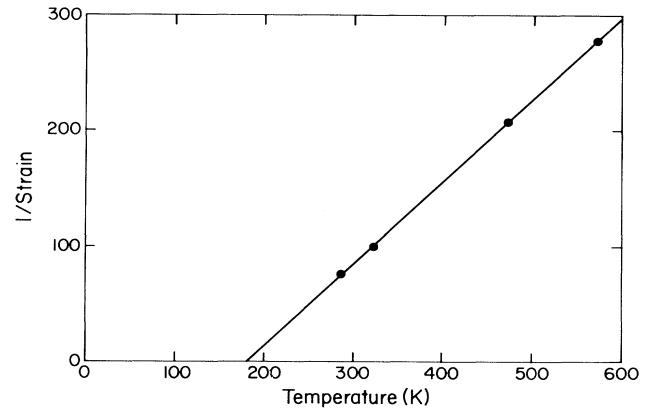

FIG. 2. The amplitude of the strain modulation was calculated from the data in Fig. 1 with use of Eq. (1). Since the strain is linearly related to the hydrogen concentration, this plot demonstrates that the amplitude of the hydrogen concentration modulation has Curie-Weiss behavior.

sidered here (13 to 300 °C) we have found no evidence for a phase separation due to a lattice-gas transition or hydride formation. Phase separations would have been observed for bulk Nb and Ta at these temperatures and concentration.

A starting point to understand this behavior should begin with a mean-field lattice gas model, since it is known[4] that this model can explain many of the observed features in bulk H-metal systems. The potential energy for the dissolved hydrogen in this model consists of two terms: (1) the interaction of a H atom with the metal and (2) the effective H-H interaction, which is mediated by the elastic distortion field of the host lattice.[5] The Helmholtz free energy is equal to the above potential energy minus a term due to the entropy of mixing.

As a result of the artificial chemical modulation of the host superlattice, a lattice gas model must contain spacially varying interaction energies and H concentration. We may calculate locally a chemical potential as outlined above. By introducing the Fourier transform for all spacially varying quantities and requiring that the chemical potential is everywhere constant, we then obtain a simple relationship between the Fourier components of the potentials and the H concentration provided that the amplitudes of the H modulation are small. A similar procedure has been carried out for the problem of concentration waves as a precursor to order-disorder transformations in solid solution systems.[6] The above treatment leads to two equations relating these Fourier components:

$$\mu_0 = U(0) + c(0)J(0) - k_B T \ln\frac{1-c(0)}{c(0)} \quad (\mathbf{k}=0), \tag{2}$$

$$c(\mathbf{k}) = c(0)[1-c(0)]\frac{-U(\mathbf{k})}{k_B T + c(0)[1-c(0)]J(\mathbf{k})} \quad (\mathbf{k}\neq 0). \tag{3}$$

Here, U, J, and c are the Fourier transforms (with wave vector $\mathbf{k}$) of H-metal binding energy, H-H interaction energy, and the H/metal concentration, respectively. The first equation describes the average properties of the system and is important when considering the solubility of hydrogen and the lattice-gas transition. The second equation results from the spatially varying properties of the host. Notice that for attractive binding and interaction energies both U and J are negative. Since $c(\mathbf{k})$ is assumed to be proportional to the strain, Fig. 2 and Eq. (3) describe a Curie-Weiss behavior for the H concentration modulation. Equation (3) predicts a phase transition at $T = c(0) \times [1-c(0)] \times J(\mathbf{k})/k_B$ for each $\mathbf{k}$. It is not possible to

predict a single transition temperature or the symmetry of an ordered phase based on the data from one Fourier component alone. A reasonable guess would be that the ordered phase follows the chemical modulation of the superlattice with the onset of the transition at about 180 K, the temperature extrapolated to in Fig. 2. Future experiments would need to verify this.

In order to determine an absolute concentration of hydrogen from the lattice expansion, it is necessary to assume a specific relation between strain and concentration. At present, such a relation is not available. However, we have measured the thermal expansion of the superlattice to be 7.2×10^{-6} K^{-1} which is essen-
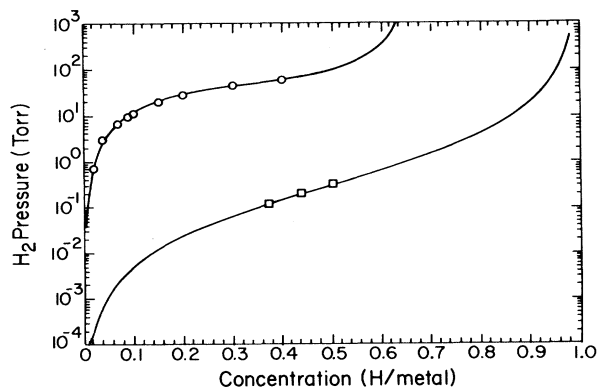
FIG. 3. Our measured solubility isotherm is plotted at 400 °C for a 20-Å Nb-Ta superlattice (squares) and compared with an isotherm for bulk Nb (circles) replotted from the literature (Ref. 8) at the same temperature. The solid lines are a least-squares fit to Eq. (2).

tially the same as for bulk Nb and Ta.[7] This is an indication that the elastic properties of the superlattice are similar to the bulk metals. Also, since the linearity of the strain-concentration relationship holds to high H concentrations for a large variety of metals and metal alloys with surprisingly close values for their coefficient of expansion,[1] we assume that the superlattice has a coefficient of expansion of 0.000 55 per percent H/metal which is the average of 0.000 58 and 0.000 52 per percent H/metal for Nb and Ta, respectively. With the same expansion coefficient for both the Nb and Ta layers, Fig. 1 indicates that the Nb absorbs more hydrogen than the Ta since the $s = +1$ satellite has more intensity than the $s = -1$. This is consistent with the known isotherms[8] for bulk Nb and Ta which show hydrogen to be more soluble in Nb than in Ta.

When loading a superlattice with hydrogen we have noticed that a small hydrogen gas pressure results in a relatively large concentration in the sample. Motivated by this observation we set out to measure a solubility isotherm. An accurate measurement is complicated by an oxide layer which forms on the sample surface and inhibits the flow of hydrogen into the sample. While this effect was very useful in the Curie-Weiss measurement where constant concentration is desired, it limits the number of data points obtainable in a solubility measurement. Figure 3 shows our pressure-concentration isotherm measured at 400 °C for a 20-Å Nb-Ta superlattice. Notice especially the logarithmic scale and the comparison to an isotherm at the same temperature for bulk Nb replotted from the literature.[8] The H concentration was determined from the average lattice expansion as measured by x-ray diffraction.

The solid lines in Fig. 3 are based upon a least-squares fit to Eq. (2) where μ_0 is taken to be one-half the chemical potential for molecular hydrogen gas[9]

minus the disassociation energy of the molecule. From these two fits we can estimate that the H-metal binding energy is 0.23 ± 0.05 eV more attractive in the superlattice than in bulk Nb. The lattice-gas critical temperature $[T_c = J(0)/4]$ for the superlattice is estimated to be 60 K. However, this value may be off by as much as 100 K since T_c is much more sensitive than the binding energy to the curvature of the isotherm which is clearly underdetermined due to the limited number of data points.

In a recent experiment, Bakker et al.[10] have shown that hydrogen in thin films of palladium on a quartz substrate has a lower critical temperature than in bulk Pd. They concluded that the lowering of T_c resulted from the elastic constraints placed on the film by the substrate. It is well known[5] that the H-H interaction will be repulsive for a sample which is "clamped" at all surfaces. Besides the lowering of T_c, they also observed that the H-metal binding energy became more attractive. The sum of the changes in these two interactions resulted in practically no change in the overall solubility. Our measurements show a more dramatic change in these two interactions with the consequence of yielding a large increase in the solubility. Since the solubility is driven by the average properties of the superlattice [Eq. (2)] we conclude by analogy with the thin film Pd-H system that the increased solubility of H in the superlattice is a result of the thin-film–substrate coupling.

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