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Hydrogen-vanadium system in thin films: Effect of film thickness

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The absorption of hydrogen in thin V(001) films under pressures of $1-10^5$ Pa H_2 and at temperatures between 350 and 530 K was studied as a function of film thickness between 50 and 5 nm using *in situ* electrical resistivity measurements. The critical temperatures for the order-disorder transitions taking place in the V-H system are decreased with decreasing film thickness. At 370 K, the high-concentration (ε-VH) phase disappears as the thickness of the film is reduced from 50 to 10 nm and the low-concentration (β-V_2H) phase follows when the film thickness is further decreased to 5 nm. The difference in solubility at 530 K of H in the α phase of V films down to 10 nm is small but it increases for lower temperatures. At low concentrations the heat of solution in the 10 nm film is somewhat lower than in the bulk, but around $H/V=0.07$, the values of ΔH_H in the film approach those of the bulk. The values of ΔS_H^{nc} of the film are rather close to those of the bulk. Significant difference is found in the pressure-resistivity isotherms above the maximum of the residual resistivity, ΔR_{max}. For the 10 nm film, in contrast to the 50 nm film, a minimum is located just beyond ΔR_{max} for the whole temperature range but the difference between the maximum and minimum starts to decrease above 420 K. This results in, by extrapolation, the vanishing of the maximum around 520 K. We suggest that this phenomenon is the result of an $Oz \rightarrow T$ transition due to a final size effect. This transition means additional randomly distributed interstitial sites available for the H atoms in the lattice of the V film leading to a continuous increase in the residual resistivity with H concentration.

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I. INTRODUCTION

The thermodynamic and kinetic properties of hydrogen-absorbing metals and alloys may be significantly affected by reducing the dimensionality of the absorbing system. This is true for nanoparticles (three dimensional), nanotubes (two dimensional), and thin films (one dimensional). Understanding this effect is important for hydrogen storage and device applications as well as of fundamental interest. For thin vanadium films the absorption of hydrogen has been studied in the past by several researchers in comparison with that of vanadium bulk.[1–3] Papathanassopoulos and Wenzl have found that 500 nm vanadium films grown by chemical vapor deposition and covered with Pd cap can be used as samples with bulk properties regarding the thermodynamics of hydrogen reaction with the metal.[1] Andersson *et al.*[2] have measured the hydrogen-absorption isotherms in Pd-capped 100 and 50 nm vanadium (001) films using hydrogen-induced resistivity changes. No thickness dependence has been observed and both films have demonstrated bulklike behavior. In a previous work[3] we have studied the thermodynamics and hydrogen-induced structural changes in a 50 nm vanadium (001) film using x-ray diffraction and reflection and resistivity measurement. The bulklike $\alpha \rightarrow \beta$ and the $\beta \rightarrow \varepsilon$ phase transitions[4] were clearly identified in the film and the plateau pressures were almost identical to those of bulk vanadium. It is clear from the experimental results that down to 50 nm the interaction of vanadium film with hydrogen shows many of bulk vanadium features. Thus, to observe the effect of thickness on the V-H thermodynamics it is necessary to further reduce the film thickness.

There are at least three correlated effects which can modify the V-H thermodynamics as the film thickness is decreased. (1) The strain field induced by the mismatch between a metallic layer clamped to a rigid substrate.[5,6] At low hydrogen concentrations, the lattice of the clamped film can expand only in the out-of-plane direction, i.e., normal to the substrate surface.[7] The H-induced lattice expansion thereby provides stresses which may be very large at high H concentrations.[8] This effect is important for the case of Nb.[8,9] However, in contrast to niobium and tantalum in which the tetrahedral (T) sites of the bcc lattice are preferred for H occupation, in vanadium thin films occupation of the Oz sites is favored, even for the α phase since the expansion of the lattice is facilitated along the z axis.[3,10] As a result, in V(100)-oriented thin films the in-plane biaxial stress will be significantly smaller than in Nb and Ta. Indeed, Nb-H isotherms of films thicker than 500 nm were found to deviate from the bulk isotherms[8,11,12] whereas V(001) film as thin as 50 nm has demonstrated bulklike behavior.[2,3]

(2) *The final size effect.* As the thickness of the film is decreased differences in structure and energy may occur between sites in the xy plane and along the z axis. For example, in FeV multilayers the H atoms dissolved in the vanadium layers are initially directed to sites in the xy plane. Only when all the allowed sites in the xy plane are filled the sites along the z axis start being accommodated.[13,14] This effect results in a change in the H-H interaction within the V layers from attractive to repulsive.

(3) *Interface effects.* Near the interface between H absorbing and the nonabsorbing metals modifications of the H absorption properties may occur. For example, in MoV (Ref. 15) and FeV (Ref. 13) superlattices, depletion zones of H interstitials were found. These zones were few atomic layers (1–3) thick. This phenomenon was interpreted to result from a charge transfer between the metals. The significance of this effect increases as the film thickness is decreased.

In the present work we show the effect of reducing the film thickness of V(001) layer on the thermodynamics and structure of the V-H system. As mentioned above, it has been shown that V(001) single layers 50 nm thick or higher, grown on MgO substrate, either directly[2] or with a buffer iron layer[3] demonstrate a bulklike behavior. In this work the thermodynamics of H absorption (and desorption) from thinner V films are studied and the results are compared to those of bulk V. The results are interpreted on the basis of the effects discussed above.

II. EXPERIMENTAL

Vanadium film (001) oriented and 10 nm thick was grown on polished MgO(001) single-crystal substrate in a DCA 4 sources dc-magnetron sputter system. The deposition was carried out from V (99.7%) target using 2 mbar purified (99.9999%) Ar as sputtering gas onto a $10\times10\ \text{mm}^2$ single-crystal MgO(001) substrate held at 300 °C. The growth rate was 0.1391 Å/s. After cooling to room temperature, the film was covered with a 5 nm Pd cap in order to facilitate hydrogen loading and to protect against oxidation.[1] Additional 5 nm film was grown with iron buffer layers below and above the V layer and palladium cap using dc magnetron sputtering from separate Fe (of 99.95% purity) and Pd (of 99.95% purity) targets.

The samples are mounted on a ceramic sample holder with four tungsten springs arranged in a four-point probe set up. The resistivity of the sample is measured using a dc reversal technique; A Keithly 2400 Sourcemeter produces a square modulated current and the voltage drop over the sample is monitored by a Keithly 2182 nanovoltmeter which is phase locked to the sourcemeter. The temperature at the sample's surface is measured using Chromel-Alumel thermocouple with precision of ±0.1 K. The sample holder is placed in a quartz tube connected to a Sieverts apparatus pumped by Turbo molecular 250 l/s pump. All parts of the system are UHV compatible. The base pressure of the sample's reactor is 10^{-7} Pa, following a baking out at 423 K. The partial pressures of all the residual gases, beside hydrogen as determined by a RGA (residual gas analyzer) is less than 10^{-9} Pa. A heating jacket is mounted on the quartz tube and the temperature is controlled using a Eurotherm 2408 PID controller. Hydrogen gas, 99.9998% pure is further purified using a West Associates ULTRAPURE gas purifier and stored in a $MmNi_5$ metal hydride bed from which it is supplied using a controlled heater. Four Leybold capacitance pressure gauges are used to monitor the pressure in the reaction: 1, 100, and 1000 Torr and 20 bar. The data from the pressure gauges is acquired simultaneously using a Keithly 2000 DMM.

The resistivity, temperature and pressure of the sample were simultaneously measured starting from the moment it was mounted and the cell sealed. The changes were followed during evacuating the cell down to the base pressure and heating the sample up to 520 K. The exposure to hydrogen started after the resistivity has been stabilized for several hours (usually overnight). This indicated that no significant oxidation of the sample was taking place in the chamber even at the highest temperature used. After each absorption-desorption cycle the hydrogen was removed by heating the sample to 520 K under vacuum. No significant changes in resistivity of the hydrogen-free sample were detected following the experiments.

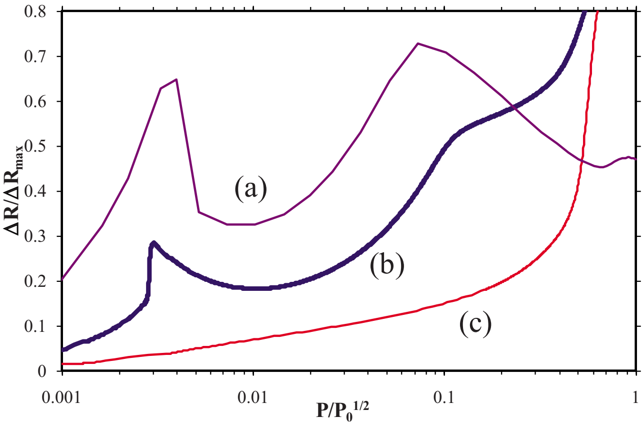

FIG. 1. (Color online) Resistivity-pressure isotherms of V(001) films at 370 K; (a) 50 nm film; (b) 10 nm film; and (c) 5 nm film.

III. RESULTS AND DISCUSSION

A. Effect of film thickness on the order-disorder transitions in the V-H system

It has been shown previously that the special structure of the V(100)-oriented thin film facilitates the bulklike order-disorder reversible transitions without degradation of the film.[3] These transitions can be seen in the resistivity-pressure isotherms below the critical temperature, around 470 K for the β and ε-VH phase formations.[4] This is well demonstrated in Fig. 1(a) showing the changes in ΔR as a function of the hydrogen pressure (and concentration) for the 50 nm V(001) film at 370 K. The initial increase in ΔR with the H pressure is a result of H dissolution in the V α phase. Hydrogen atoms occupy interstitial sites in the V lattice serving as scattering centers for electrons, thus increasing the residual resistivity. In the bulk the tetrahedral (T) sites are occupied, but in V(001) films on MgO substrate, due to the orientation and the initial strain the octahedral Oz_1 sites are preferred. The first maximum of Fig. 1(a) is the point at which the β-$VH_{0.5}$ phase is starting. Since this phase is an ordered structure it will reduce ΔR. In the two-phase region ΔR continue to decrease until at the first minimum the β phase complete its formation. Further increase in the H pressure leads to dissolution in the β-$VH_{0.5}$ phase of H atoms occupying mostly the Oz_2 sites in a random way and thus increasing ΔR again.

A second maximum is observed when half of the Oz_2 sites are occupied (at around $H/V=0.75$). A similar behavior of the excess resistivity was found for Ta wire exposed to hydrogen.[16] X-ray diffraction (XRD) measurements[3] show that in contrast to the first maximum the decrease in ΔR beyond the second maximum in the 50 nm film at this temperature is not associated with the formation of separated ε-VH phase. For the bulk, in the phase diagram based on DTA data[4] the ε-VH phase exists above around $H/V=0.65$, but p-c-T isotherms in the range $0<H/V<0.8$ (Ref. 4) show inclined plateaus similar to our XRD isotherm around this concentration indicating a single phase region. Additional minimum followed by a small maximum at the high pressure side of Fig. 1(a) are observed for the 50 nm film but cannot be identified in the phase diagram of bulk vanadium. A more detailed account of this spectrum can be found in our previous work.[3]

Figure 1(b) shows the resistivity-pressure isotherm for the 10 nm film. Comparing Figs. 1(a) and 1(b) the most important effect of reducing the film thickness from 50 to 10 nm are the changes beyond the first minimum: the second maximum is replaced by an inflection point and no second minimum is observed. It seems as the system is above the critical temperature for the ε-VH phase formation (in which all the Oz sites are occupied). Thus, the effect of decreasing the film thickness from 50 to 10 nm is to decrease this critical temperature.

The resistivity-pressure isotherm for the 5 nm film is shown in Fig. 1(c). Here, the trend of decreasing the critical temperature is extended to the β-$VH_{0.5}$ phase formation represented by the first maximum and minimum of Fig. 1(a). There is no maximum observed over the whole pressure range for this film which means that no ordered structure is formed at the working temperature. The steep increase at the high pressure side of the curve is due to the formation of PdH hydride originating in the 5 nm Pd cap on the film as proved by a hysteresis loop (not shown in the figure).

Thus, it is concluded that the critical temperatures for the order-disorder transitions taking place in the V-H system which manifest themselves by multiple maxima-minima in the resistivity-pressure isotherms are decreased with decreasing film thickness. The high-concentration (ε-VH) phase is more sensitive to the film thickness than the low-concentration (β-VH) phase. At 370 K the high-concentration transition disappears as the thickness of the film is reduced from 50 to 10 nm, and the low-concentration transition disappears as the thickness reduced from 10 to 5 nm.

B. Relation between the residual resistivity and the H concentration

In Fig. 2 the resistivity-pressure isotherms of the 10 nm vanadium (001) film are compared with those of the 50 nm film. For both films a maximum in the excess resistivity, $\Delta R_{\max}$, is observed. The pressure associated with $\Delta R_{\max}$ for the 10 nm film is somewhat lower than for the 50 nm film. Under higher pressures beyond that of $\Delta R_{\max}$ more significant differences between the two films are observed. In particular, the 10 nm film exhibits a minimum in the excess resistivity immediately beyond the maximum. Such a minimum is not observed for the 50 nm film above the critical temperature. Above the minimum the change in the resistivity of the 10 nm film is opposite to the trend of change for the 50 nm film, namely, it increases for the 10 nm film and decreases for the thicker films.[2,3]

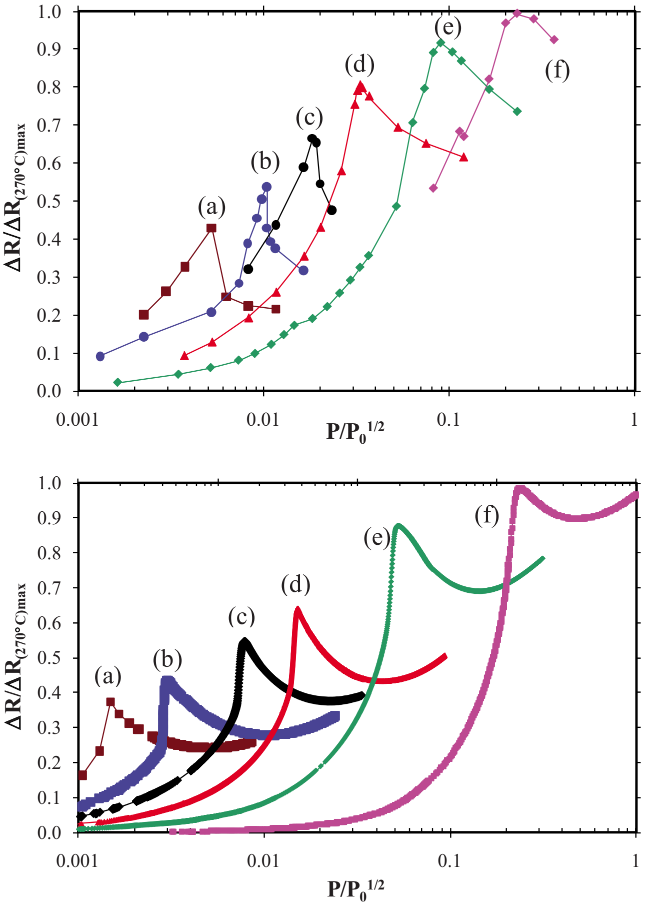

FIG. 2. (Color online) Resistivity-pressure isotherms (partial) of V(001) films. Upper graph: 50 nm film (a) 380 K; (b) 400 K; (c) 420 K; (d) 440 K; (e) 480 K; and (f) 530 K. Lower graph: 10 nm film (a) 350 K; (b) 373 K; (c) 400 K; (d) 423 K; (e) 473 K; and (f) 523 K.

The resistivity-pressure isotherms cannot be used directly for thermodynamic analysis. They must be converted into composition-pressure isotherms. In fact, the difficulty to determine the hydrogen concentration makes the interpretation of results for nanosized systems so complicated. However, at relatively low H concentrations the relation between the excess resistivity and the concentration, x, expressed as [H/V], is given by the modified Nordheim equation[16]

$$\Delta R = Kx(n-x), \tag{1}$$

where n is a limiting concentration which depends on the geometry of metal lattice and the type of site occupied, and K is a constant. Using Eq. (1) the concentration, x, can be expressed as

$$x = n/2 - n/2(1-\Delta R/\Delta R_{\max})^{1/2}, \tag{2}$$

where $\Delta R_{\max}=K(n/2)^2$. For temperatures above the critical temperature, T_c, the concentration at $\Delta R_{\max}$ is $n/2$. Theoretically, $\Delta R_{\max}$ is temperature independent. This has been shown experimentally for tantalum wires.[16] To obtain the concentration from Eq. (2), the values of n and $\Delta R_{\max}$ should be evaluated. In theory, for the ε-VH phase there is a total of one octahedral (Oz) site available per metal atom ($n=1$).[4] Experimentally, the value of n is lower than 1. Since the 50 nm film demonstrates a bulklike behavior,[2,3] we have compared the curve of $\ln P(\Delta R_{\max})^{1/2}$ vs $1/T$ where $P(\Delta R_{\max})$ is the pressure at which $\Delta R = \Delta R_{\max}$ of the 50 nm film, with curves of ln $P(x)^{1/2}$ vs $1/T$ measured for different x values in bulk samples.[4] The curve of $\Delta R_{\max}(T)$ was found to overlap perfectly the curve associated with H/V=0.4 in the bulk. This corresponds to a value of $n=0.8$. Assigning the correct value for n prevents an erroneous expansion of the plateau region toward high hydrogen concentrations found for films.[2]

It has been found experimentally for thin vanadium films[2] that at the vicinity of the critical temperature $\Delta R_{\max}$ has slightly parabolic temperature dependence. Thus the value of $\Delta R_{\max}$ can be found from the temperature dependence of $\Delta R_{\max}(T)$. Extrapolation of our experimental results for the 10 nm film using parabolic fit we found that around 540 K $\Delta R_{\max}$ achieves it maximum value. Now that n and $\Delta R_{\max}$ are known the hydrogen concentration can be calculated using Eq. (2).

C. Infinite dilution solubility range

At sufficiently low hydrogen concentrations the solubility of hydrogen in the metal is proportional to the square root of the pressure (Sieverts law)[17]

$$(P_{\mathrm{H}_2}/P_0)^{1/2} = K_s(T)x, \tag{3}$$

where P_0 is a reference pressure, usually taken as 1 bar. According to this relation, applicable only at low concentrations, $K_s(T)$ is the dimensionless temperature-dependent Sievert's constant.

The theoretical interpretation for Eq. (3) is based on the assumption that under thermal equilibrium condition the chemical potentials of the H atom in the gas phase and in the metallic solid solution are equal. The H_2 gas chemical potential is proportional to the gas pressure logarithm, $\ell\mathrm{n}(P_{\mathrm{H}_2})$. On the other hand, the chemical potential of the solid solution includes an ideal configurational term given approximately by—$RT\ell\mathrm{n}[x/(n-x)]$,[18] where n is the number of interstices available for an H atom per a metal atom in the lattice. In theory the configurational n is identical to that given in Eq. (1). Equating these terms yields the equation relating H pressure and concentration

$$\ell\mathrm{n}(P_{\mathrm{H}_2}/P_0)^{1/2} - \ell\mathrm{n}(x/(n-x)) = \Delta\mu_{\mathrm{H}}^0/RT = \Delta H_{\mathrm{H}}/RT - \Delta S_{\mathrm{H}}^{\mathrm{nc}}/R, \tag{4}$$

where $\Delta\mu_{\mathrm{H}}^0 = \Delta H_{\mathrm{H}} - T\Delta S_{\mathrm{H}}^{\mathrm{nc}}$ is the Gibbs free-energy change for solution. ΔH_{H} is the heat (enthalpy) of solution and $\Delta S_{\mathrm{H}}^{\mathrm{nc}}$ is the nonconfigurational entropy of solution referred to the H_2 gas under pressure P_0 and temperature T. Using the low-concentration condition $x \ll n$, the Sievert's constant from Eq. (3) can be substituted in Eq. (4) to yield

$$R\ell\mathrm{n}K_s(T) = \Delta H_{\mathrm{H}(x\to 0)}/T - [\Delta S_{\mathrm{H}(x\to 0)}^{\mathrm{nc}} + R\ell\mathrm{n}(n)]. \tag{5}$$

Thus, from the temperature dependence of the solubility constant, the enthalpy and entropy of H solution at infinite dilution can be obtained. It should be noticed that if n, for the vanadium-group hydrides, is taken incorrectly to be unity, then $\Delta S_{\mathrm{H}(x\to 0)}^{\mathrm{nc}}$ obtained from Eq. (5) will contain a configurational contribution $R\ell\mathrm{n}(n)$.

In Fig. 3 the solubilities of hydrogen in the 50 and 10 nm films are compared for two different temperatures. It is evident that at this region the behavior of both films follows Sieverts relation, Eq. (3). The results shown in Fig. 3 show that the hydrogen solubility in the thinner, 10 nm film is lower than in the 50 nm film, namely, the effect of decreasing the film thickness is to decrease the hydrogen solubility. Also, it is seen that the effect of thickness is larger at the lower temperatures. We have also measured H solubilities for the 5 nm film. It seems that the solubility decreases dramatically between 10 and 5 nm. However, due to the decrease in the H absorption by the vanadium 5 nm film, the effect of H absorption of the Pd 5 nm cap on the residual resistivity of the film interferes with that of the vanadium (see Fig. 1). Therefore, the results for the 5 nm film are not shown in Fig. 3. In Fig. 4 the temperature dependence of K_s in the form of van't Hoff relation is compared for the films and for the bulk metal. According to Eq. (5), ΔH_{H} and $\Delta S_{\mathrm{H}}^{\mathrm{nc}} + R\ell\mathrm{n}(n)$ of the infinite diluted solution can be obtained from the slope and the intercept of the linear dependence of $\ell\mathrm{n}(K_s)$ vs $1/T$ curves, respectively. The results for the different samples are summarized in Table I, arranged in order of decreasing heat of solution.

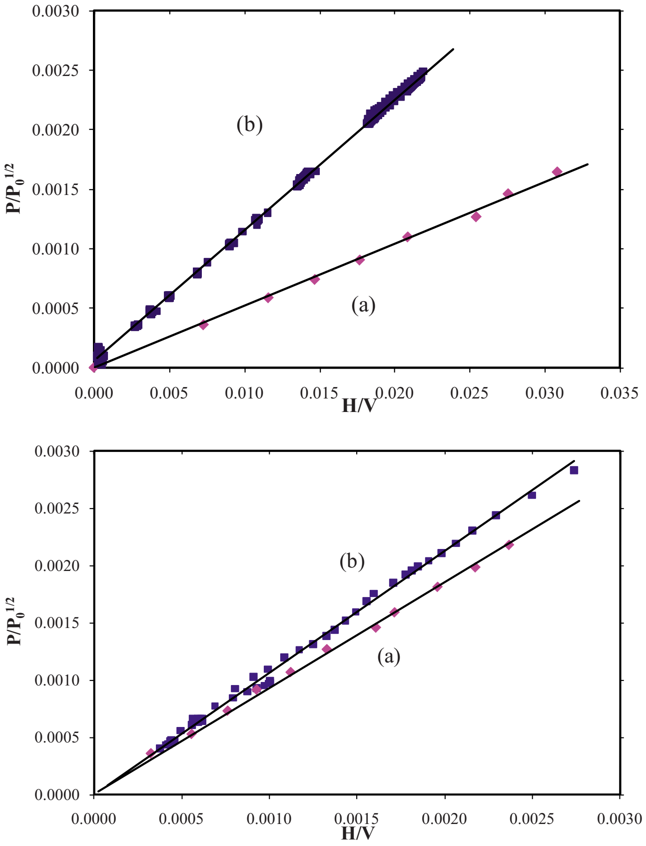

FIG. 3. (Color online) Solubility curves of hydrogen in vanadium thin films. Upper graph: 400 K (a) 50nm film; (b) 10 nm film. Lower graph: (a) 50nm film at 530 K; (b) 10 nm film at 523 K.

It is shown in the table that the heat of solution of hydrogen in the Oz sites of the 50 nm film is a little more negative compared with that of hydrogen in the T sites of the bulk. Namely, the energies of the H atom in an Oz site of the film and in a T site of the bulk are comparable. The lower heat of solution for the 10 nm film compared to the 50 nm film is

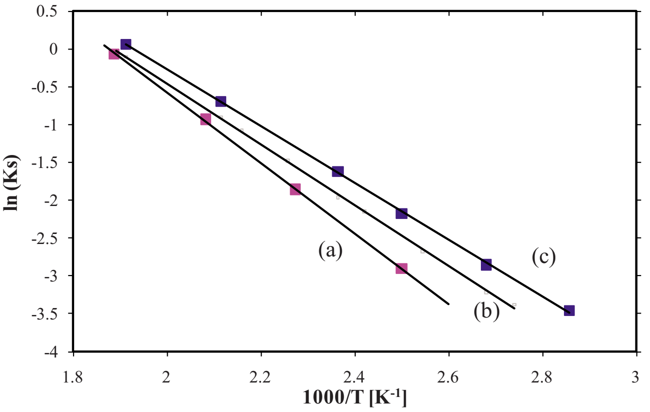

FIG. 4. (Color online) The temperature dependence of the Sieverts constant of (a) 50 nm V film; (b) bulk vanadium (Ref. 19); and (c) 10 nm V film.

probably the result of the final size effect described in Sec. I. The difference in the type of sites occupied by H atoms in the 50 nm film and in the bulk may account also for the difference between the values of ΔS_H for the two structures. The Oz sites which are preferred for occupation in the film[3] yield $n=1$ compared to the bulk in which the occupied sites are mostly the tetrahedral with $n=6$. This will contribute $1.8(=\ln 6/1)$ to ΔS_H for the 50 nm film. However, considering the error in measuring ΔS_H this small difference may be insignificant. For the 10 nm film ΔS_H is less negative than for the 50 nm film which means the value of n is higher. The higher n and lower heat of solution indicate that the effect of reducing the thickness of the film from 50 to 10 nm is to decrease the energetic difference between the tetrahedral and octahedral sites for the infinitely diluted solution.

D. Hydrogen solubility at higher concentrations

The heat of solution and the nonconfigurational entropy of solution are generally concentration dependent as a result of interactions between hydrogen atoms.[17] Equation (4) can be used to determine the values of ΔH_H and ΔS_H^{nc} as a function of x. This is done by plotting $\ell n(P_{H_2}/P_0)^{1/2}$ as a function of $1/T$ for a specified x. The slope and intercept of each curve are used to calculate ΔH_H and $\Delta S_H = \Delta S_H^{nc} - R\ell n[x/(n-x)]$ as a function of x.

The dependencies of ΔH_H and ΔS_H^{nc} on hydrogen concentration for the 10 nm film are shown in Fig. 5 in comparison with bulk vanadium. The concentration range is limited to the part below the excess resistivity maximum for which Eq. (2) is valid. The relatively large error bars are a result of some temperature dependence of the thermodynamic constants which contribute nonlinearity to Eq. (4).[17] In general, there is only a slight difference between the thermodynamic parameters of the film and the bulk. At low concentrations the heat of solution in the film is somewhat lower than in the bulk, but when the attractive H-H interaction become important, above around $H/V=0.07$, the values of ΔH_H in the film approach those of the bulk. The values of ΔS_H^{nc} of the film are rather close to those of the bulk. In conclusion, for the 10 nm film, the thermodynamic parameters ΔH_H and ΔS_H^{nc} at the low-concentration range are comparable to those of the bulk, like in the infinitely diluted case.

TABLE I. Enthalpy (heat) and entropy of H solution at infinite dilution for vanadium. The results for the bulk are average of literature data.

Structure	50 nm film	Bulk (Ref. 4)	10 nm film
ΔH_H (kJ mol^{-1})	−39	-32 ± 1	−31
$\Delta S_H^{nc}+R\ell n(n)$ [J deg^{-1}(mol H)$^{-1}$]	−72	-64 ± 7	−60

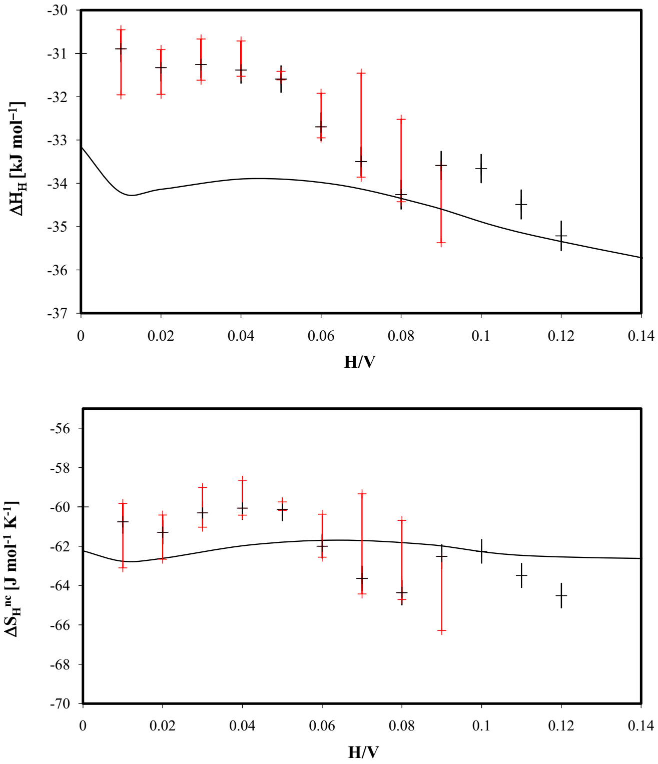

FIG. 5. (Color online) The dependence of the enthalpy of solution (upper graph) and of the nonconfigurational entropy of solution (lower graph) on the hydrogen concentration, for the 10 nm film. The solid lines, for bulk vanadium, are taken from Ref. 19.

E. Excess resistivity at high concentrations of hydrogen

As shown in the preceding sections the hydrogen-solubility properties of vanadium below the excess resistivity maximum are not extensively modified by decreasing the film thickness down to 10 nm. Above ΔR_{max}, however, there are significant differences between the 10 nm and the thicker (50 nm and above) films both below (Sec. III A) and above (Sec. III B) the critical temperature. More specific, for the 50 nm film below the critical temperature the changes in ΔR as a function of the hydrogen pressure (and concentration) indicate changes in ordering of the H atoms in the vanadium lattice in accordance with the bulk V-H phase diagram,[3] as discussed in Sec. III A. Above the critical temperature there is only a single maximum left corresponding to the occupa-

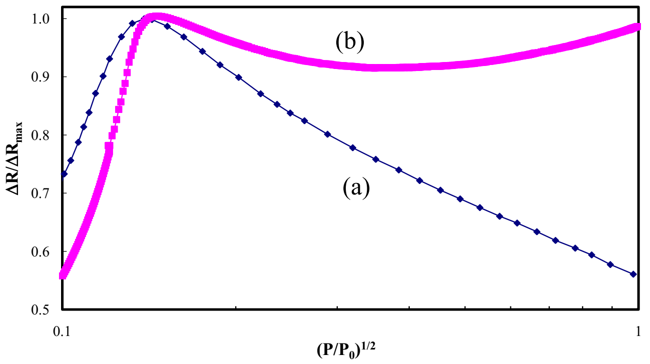

FIG. 6. (Color online) The effect of film thickness on the resistivity-pressure isotherms of vanadium above the critical temperature for the ε phase formation: (a) 50 nm film at 523 K (Ref. 2); (b) 10 nm film at 513 K.

tion of half of the Oz sites available for H atoms, and all the additional maxima and minima of the 50 nm film disappear. Beyond this maximum the excess resistivity decreases. It should be noticed that for the bulk vanadium above the critical temperature only tetrahedral sites are available for the H atoms. For occupation of the T sites, in contrast to Oz sites, no maximum should be observed around $H/V=0.5$ since no ordered structure will be formed at $H/V=1$. In Fig. 6 the resistivity-pressure isotherms at around 520 K are compared for the 50 and 10 nm vanadium films. This temperature is well above the bulk critical temperature for the ε phase transition in the bulk.[4] Up to the maximum in resistivity both samples exhibit a similar behavior. It is worth noting that the maxima of both samples are located at exactly the same pressure, indicating the same H/V concentration. Beyond the maximum, however, the curves of the two samples are significantly different. The excess resistivity of the 50 nm film, Fig. 6(a), decreases with increasing pressure as the hydrogen concentration approaches a value of $H/V=1$ up to at least 1 bar. Since the bulk V pressure-composition isotherm at this temperature shows a very small change in concentration between 1 and 50 bar (between $0.6<H/V<0.7$)[20] it is predicted that a broad minimum in the residual resistivity will be observed up to about 50 bar.

For the 10 nm film, on the other hand, under similar P and T conditions a shallow minimum, independent of the bulk critical temperature, is observed immediately beyond the maximum under a pressure which is much lower than 1 bar, as demonstrated in Fig. 6(b). This pattern of sharp maximum followed by a relatively broad minimum is kept along the whole temperature range as shown in Fig. 2 (the lower graph). Thus, no effect of the bulk critical temperature is observed on the pressure-resistivity isotherms of the 10 nm film in contrast to the 50 nm film which reveals a bulklike behavior.

The minimum of the excess resistivity in the 10 nm film cannot be attributed to the complete occupation of the Oz sites in the vanadium lattice like in the case of the 50 nm film. There are several reasons for this statement. First, the value of the minimum is too high, especially at the higher temperatures, as seen in Fig. 6. This point will be discussed separately below. Second, the ratio between the pressures associated with the maximum of the excess resistivity and the minimum which follows decreases a little with increasing temperature but it is almost constant below 400 K. This means that the amount of H absorbed between the maximum and the minimum is almost constant. The proximity to the maximum indicates that this amount is relatively small, much less than needed to complete the occupation of the Oz sites. Also the relatively low pressures and high temperatures in which the minimum takes place eliminate the option for VH formation. Thus, it seems that the origin of the minimum associated with the 10 nm film, at least above the critical temperature, is different than that of the 50 nm film.

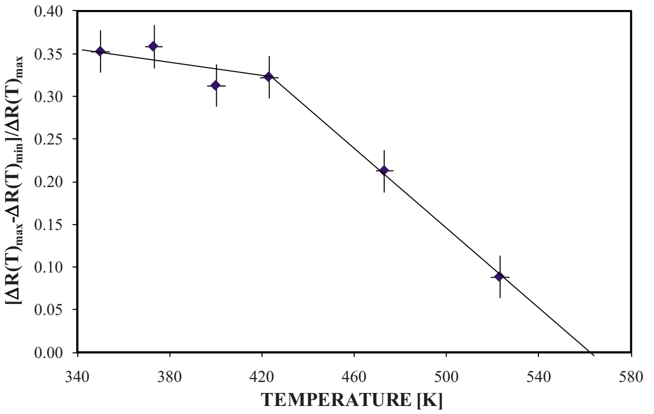

FIG. 7. (Color online) The change in the relative difference between the maximum and the minimum excess resistivity as a function of temperature in the 10 nm vanadium film. The linear line above 420 K indicates, by extrapolation, that around 560 K the difference is vanished.

We have further investigated the relation between the minimum and the maximum of the residual resistivity in the 10 nm film. It can be seen in Fig. 2 that the value of the minimum resistivity approaches that of the maximum at the higher temperatures. In Fig. 7 the relative difference between the maximum and the minimum of the excess resistivity is plotted as a function of temperature.

It is evident from the figure that 420 K is a point of change. Up to this temperature there is only a slight decrease in the difference between the maximum and minimum. Actually, it is almost independent of temperature with a value approximately one third of the maximum. However, above this temperature the difference decreases significantly with increasing temperature. By extrapolation it is expected that at around 560 K the difference between the maximum and the minimum will decrease to zero so that the maximum and minimum will disappear. Since this phenomenon is unique for the 10 nm film and is absent in the 50 nm film it can be attributed to the effect of reducing the film thickness.

To account for this phenomenon it should be noticed that above the critical temperature there is an essential difference between the H solid solution of the 50 nm V(001) film in which the Oz sites are occupied, and that of the bulk in which the tetrahedral sites are occupied. If T sites are to be occupied in the film no maximum will be observed at $H/V=0.5$ because no ordered structure will be formed at $H/V=1$. We suggest that up to the resistivity maximum at around

H/V=0.5, H atoms in both, the 50 and 10 nm films occupy Oz sites above the critical temperature. However, at higher concentration the two films act differently; whereas in the 50 nm film H atoms continue to occupy the Oz sites, in the 10 nm film tetrahedral sites become available for H atoms occupation. A similar behavior is encountered in the V-D bulk system for which at $x=0.51$ a $\beta \rightarrow \alpha$ order-disorder transition takes place at 406 K.[21] In nuclear-density maps obtained for temperatures just below the transition temperature a maximum has been found at the T sites neighboring the Oz_2 sites simultaneously with a decrease in the nuclear density of the Oz_1 sites.[22] Due to the final size effect in the 10 nm film such T sites may be preferred to an Oz_2 site located along the z axis right above an occupied Oz_1 site. Similar order-disorder transitions are found also for the V-H bulk system.[21] The introduction of H atoms into T sites leads to an increase in the value of n in Eq. (1). Under this condition the additional H atoms absorbed in the V lattice do not bring the system toward the ordered structure in which all the Oz sites are filled. Instead, the H atoms now occupy sites in a random way, resulting in additional scattering centers and thus increase ΔR. A similar view has been already suggested by Pryde and Tsong who derived Eq. (1) for the Ta-H system.[16] The equation was applied only for the low hydrogen concentration region up to the maximum of the excess resistivity. They claimed that it is unsafe to assume that the equation continues to hold at higher concentration and temperatures since extra tetrahedral sites may become available which would correspond to an increase in the value of n. In the Ta-H system the ordered TaH structure is based on tetrahedral sites occupation whereas in the V-H system mostly octahedral sites are occupied.

Thus, decreasing the V(001) film thickness from 50 to 10 nm induces transition from Oz to T occupation by H atoms at elevated temperatures. The process starts at 420 K above H/V=0.5. Increasing the temperature decreases the H concentration for the transition until at 560 K the transition takes place below H/V=0.5 and no maximum is observed in the residual resistivity vs concentration curve. It follows that for films thinner than 10 nm there will be no maximum observed in the residual resistivity vs H concentration curve even at lower temperatures. This phenomenon may account for the absence of residual resistivity maxima in the ultrathin V layers of Fe/V multilayer structures.[23] The availability of additional interstitial sites for high concentration of hydrogen for the film with reduced dimension leads to an increase in the hydrogen terminal solubility in the film. Such a behavior is not limited solely to thin films; significant increase in the hydrogen solubility has been also measured for nanocrystalline Pd (Ref. 24) and it can be, at least partly, explained on the basis of the same mechanism. Thus, the results of the present work can be applied to nanoparticles in general.

IV. SUMMARY AND CONCLUSIONS

We have studied hydrogen absorption in V(001) thin films deposited on MgO substrates under pressures up to 1 bar and temperatures between 350 and 530 K using *in situ* resistivity measurements in purpose to elucidate the effects of reducing the film thickness below 50 nm on the properties of the V-H system. It has been shown previously that a 50 nm film exhibit bulk properties.

In the low-concentration range where hydrogen is dissolved in the V α phase the effect of reducing the film thickness down to 10 nm is relatively small; the solubility decreases slightly at 400 K. The difference between the solubilities increases as the temperature is decreased. The heat of solution of the thinner film at infinite diluted solution is lower: 31 kJ mol^{-1} and 39 kJ mol^{-1} for the 10 nm and the 50 nm films, respectively (32 kJ mol^{-1} for the bulk). But above H/V=0.07 they tend to converge. Also the difference in the entropy of solution is small. There are indications that between 10 and 5 nm the effect is much larger and the decrease in the hydrogen solubility is significant but this point is not shown in detail in the present work.

Much larger effects are found for the high-concentration range. There are two important thickness-dependent phenomena in this range. The critical temperatures of the order-disorder transitions taking place in the V(bulk)-H system decrease with decreasing of the film thickness. Thus, reducing the film thickness from 50 to 10 nm leads to a decrease of the critical temperature associated with the formation of the ordered ε-VH structure, 430 K, down to lower temperature below 350 K. For a 5 nm film both, the β-$VH_{0.5}$ and ε-VH ordered structures are not observed above 350 K. the second thickness-dependent effect observed at the high-concentration range is a $Oz \rightarrow T$ transition which increases the number of sites available for hydrogen occupation in the vanadium lattice with decreasing film thickness. This change leads to gradual decrease in the difference between the maximum of the residual resistivity and the minimum that follows it until, by extrapolation, at 520 K the maximum disappears. This leads to the conclusion that the distinction between the Oz and T sites in V(001) films decreases with film thickness.

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