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Structural evolution and thermal stability of deuterated titanium thin films

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The thermal stability and structural evolution of titanium thin films deposited in a deuterium atmosphere were studied by x-ray diffraction (XRD), thermal-desorption spectroscopy (TDS), and differential scanning calorimetry. Samples deposited at a 423-K substrate temperature present the fcc CaF_2-like structure of δ-TiD_2. TDS experiments showed that deuterium thermal desorption follows a first-order kinetic characterized by a free activation energy of 1.63 ± 0.03 eV. When samples made of the fcc phase were submitted to thermal annealing at 723 K, XRD measurements revealed a crystalline transformation to the hcp α-Ti structure. These results indicate that the titanium deuteride decomposition is the rate-limiting process in deuterium desorption. Films deposited at 573- and 723-K substrate temperatures are made of deuterated α-Ti: for these samples deuterium desorption followed a second-order kinetics with a free activation energy of 1.53 ± 0.02 eV, and the rate-limiting process was the surface recombinative desorption of D atoms. [S0163-1829(98)04831-0]

I. INTRODUCTION

Due to the very high storage capacity of Ti for hydrogen isotopes, titanium and titanium alloys have in the past received considerable attention for various technological applications: titanium was proposed, for example, as a material for hydrogen storage and transportation,[1] as a getter pump for hydrogen isotopes in prototype fusion reactors,[2] and as a neutron energy moderator.[3] Bulk properties of the Ti-H_2 system have been widely studied, and consequently the phase diagram, thermodynamic functions, and transport properties are well characterized.[4]

Conversely, very little is known about the dynamics of hydrogen in titanium thin films, even if the system presents both fundamental and applicative interest as, for example, a supermirror for the transport of cold neutron beams.[5] Very few experimental studies on the interaction between hydrogen isotopes and titanium thin films are present in the scientific literature, and most of them are dedicated to the evaluation of the H_2 sticking coefficient,[6,7] in connection with the use of Ti as sublimation pump in high vacuum technology. These studies have revealed very unexpected and interesting aspects of the Ti-H_2 system. The hydrogen-titanium ratio in titanium hydrides does not normally exceed 2:1, the dihydride representing the limiting stoichiometry in the system: conversely, Badayal, Gellman, and Lambert[8] observed the formation of a hydride with TiH_3 composition when exposing evaporated titanium very thin films (e.g., monolayer) to gaseous hydrogen at 140 K. According to the Ti-H phase diagram, at room temperature, the α-Ti phase (hcp Ti with interstitially distributed H atoms) is stable for a H content less than 0.14 at. %, followed by a mixed $\alpha+\delta$ phase for H/Ti ratio less than 1.5 and finally by a single phase (δ-fcc titanium hydride) for a H/Ti ratio between 1.5 and 2: compositional measurements executed during the exposure of thin Ti films to H_2 at room temperature gave quite different results,[9] revealing an α-$\alpha+\delta$ boundary at 6-at. % H and an $\alpha+\delta$-δ boundary at 40-at. % H. Malinowsky[10] used Auger electron spectroscopy to study, through the analysis of the LVV and LMV Ti peaks, the deuteration process of Ti films and the decomposition of the resulting titanium deuteride: the author found that heating deuterated samples in vacuum with a linear temperature ramp of 0.34 K/s caused a complete deuteride decomposition much before the temperature of 680 K suggested by the phase diagram.

In a previous paper it was observed that, during *e*-gun evaporation of titanium thin films in a deuterium atmosphere, films with different crystalline structure could be obtained just by changing the substrate temperature:[11] keeping the Ti deposition rate fixed at 0.2 nm/s and the D_2 partial pressure at 10^{-4} torr, x-ray diffraction (XRD) revealed that, at a 423-K substrate temperature, substoichiometeric δ-TiH_x layers with the fcc CaF_2-like structure were produced, while at higher substrate temperature the resulting films were made of deuterated α-Ti. Elastic recoil detection analysis[11] (ERDA) revealed that the deuterium content of as-deposited samples decreases by increasing the substrate temperature during deposition: the deuterium concentration was between 30 and 35 at. % in the samples deposited at 423 K substrate temperature; it was lower than 6 at. % in the samples deposited at 573 K, and below the ERDA detection limit (~1 at. %) at 723 K.

This paper reports on a study of the structural evolution and thermal stability of titanium thin films deposited in a deuterium atmosphere that we carried out by XRD, thermal-desorption spectroscopy, and differential scanning calorimetry. In the first part of Sec. IV we present an analysis of deuterated α-Ti thin films, and the results are discussed with reference to literature data. In the second part of Sec. IV, the discussion focuses on the results pertinent to titanium deuteride thin films with the δ-TiH$_x$ structure. Here we study how the crystalline structure and the deuterium content of as-deposited samples influence thermal stability and structural evolution.

II. EXPERIMENT

Samples were prepared in a high vacuum stainless-steel chamber evacuated by turbomolecular pump: after one night pumping, the base pressure of the system was in the 10^{-6}-Pa range: in these vacuum conditions the dominant component among the residual gases is hydrogen (more than 90% of the residual pressure) due to the very low compression ratio of turbo pumps for this gas with respect to higher mass number gases.[12] Titanium thin films were deposited onto Si(100) wafers by electron-beam evaporation of Ti atoms in a deuterium atmosphere. Ti was evaporated from a titanium target (nominal purity $>99.99\%$) by e-gun at a deposition rate of 0.2 nm/s. During deposition, deuterium high-purity gas was supplied to the deposition chamber through a calibrated leak valve: the D_2 inlet flux was controlled to maintain the total pressure at 8.5×10^{-2} Pa. Films with different thicknesses (75, 150, and 300 nm) were deposited at substrate temperatures of 423, 573, and 723 K. A second set of samples was prepared with the same deposition conditions, but without deuterium in the deposition chamber. In the vacuum conditions used for the sample deposition, as evidenced by Rutherford backscattering (RBS) analysis (not reported here), bulk contaminant concentration was under a few at. % (RBS detection limit). In the following, films deposited in deuterium atmosphere will be called Ti:D films, while films deposited in a high vacuum conditions will be called Ti films. To study structural evolution and compositional changes, some of the samples were submitted to thermal annealing at 723 K in a UHV furnace (background pressure of 10^{-6} Pa during the process).

The deuterium content of the samples was measured by ERDA using a 1.6-MeV ^{4}He$^+$ beam, with a 10-nA current density at an incidence angle of 10°. A Si surface barrier detector was positioned at an angle of 150° relative to the incident beam direction, and was covered with a 9-μm-thick mylar foil, sufficient to stop all ^{4}He and heavier nuclei.

X-ray-diffraction patterns were collected by a high-resolution RIGAKU PMG-VH diffractometer, by using the traditional Bragg-Brentano geometry. The instrument was equipped with graphite bent crystal analyzer in the diffracted beam to cut background and K_β contributions from the Cu radiation produced at 40 kV and 45 mA.

The thermal stability of the deposited samples was studied by thermal-desorption spectroscopy (TDS) and differential scanning calorimetry (DSC). TDS measurements were performed in an UHV stainless-steel chamber pumped by vacuum ion pump and provided by quadrupole mass spectrometer;[13] the base pressure prior to the experiment was about 10^{-8} Pa. Experiments were carried out heating the sample with a linear temperature ramp of 0.07, 0.25, 0.50, and 1.0 K/s up to 750 K. DSC tests were done using a Perkin-Elmer Model 7/7 apparatus: a known mass of sample was placed in a covered W pan and ramped in temperature at a constant heating rate of 30 K/min in a flowing Ar atmosphere to avoid thermal noise related to oxidation reactions.

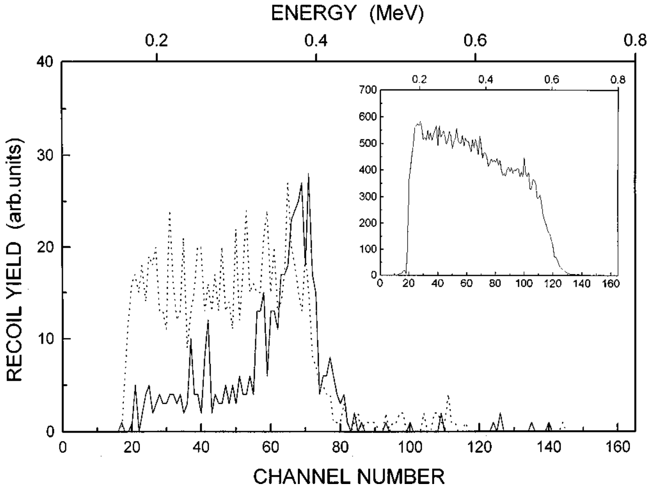

FIG. 1. Elastic recoil detection spectra samples deposited at 423 K: Ti:D after thermal annealing (dotted line) and as-deposited Ti (solid line). For comparison, the ERDA spectrum of the as-deposited Ti:D sample (Ref. 11) is reported in the inset.

III. RESULTS

A. Elastic recoil detection

The ERDA spectra of as-deposited samples were extensively presented in a previous paper.[11] Figure 1 shows the ERDA spectrum of the Ti:D sample deposited at 423 K after thermal annealing at 723 K (dotted line): for comparison, in the inset we show the spectrum of the as-deposited sample. As can be observed, deuterium is completely desorbed during the thermal process. A similar ERDA spectrum (not reported in the figure) was also observed studying deuterated samples deposited at a 573-K substrate temperature after thermal annealing. For comparison, Fig. 1 also reports the ERDA spectrum of the as-deposited Ti sample at 423 K (solid line).

B. X-ray diffraction

A detailed analysis of the XRD spectra of as-deposited Ti and of Ti:D films was also presented in a previous paper:[11] in the following we will show a comparison between the spectra of as-deposited samples and those of the same samples after thermal treatment. Figures 2 and 3 show the XRD pattern of Ti and Ti:D samples deposited on Si wafers: Ti deposited at 723 K [Fig. 2(a)] and 423 K [Fig. 2(b)], and Ti:D deposited at 723 K [Fig. 3(a)] and 423 K [Fig. 3(b)]. In all figures, the solid line represents the XRD pattern of the as-deposited sample, while the dashed line is the XRD pattern of the sample after thermal annealing at 723 K.

Generally it can be seen that as-deposited Ti samples exhibit the α-Ti diffraction peaks: (101) and (002) reflections and (100) and (002) reflections for samples deposited at 723 and 423 K, respectively. After thermal annealing the samples maintain the α-Ti structure. Films deposited at 723 K do not change their orientation [we can only observe a small shift in peak positions, mainly for the (002) line]; conversely, films

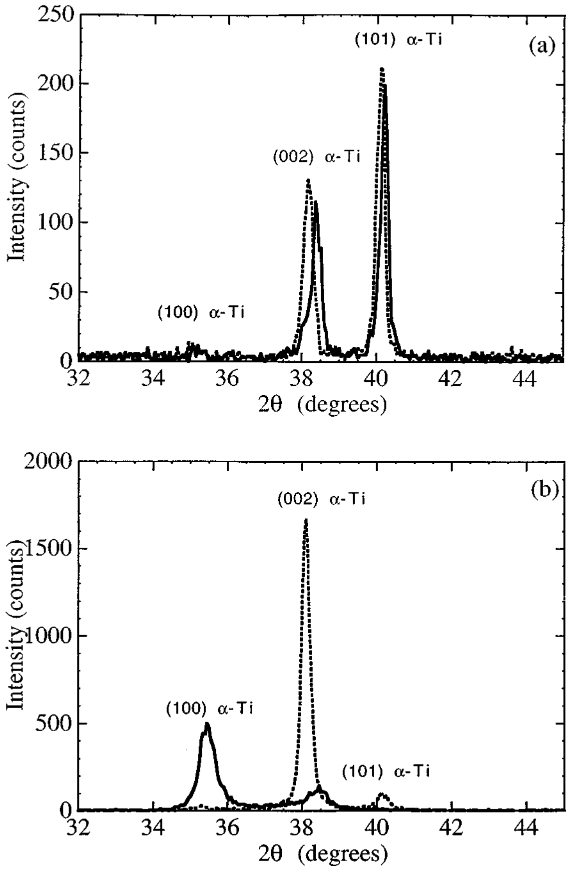

FIG. 2. XRD spectra of Ti samples deposited at 723 K (a) and 423 K (b): as-deposited sample (solid line); after thermal annealing (dashed line).

deposited at 423 K show recrystallization, with a clear change in orientation. The XRD pattern of the Ti:D sample deposited at 723 K is very similar to that of the Ti sample deposited at the same temperature: in both cases the (101) and (002) diffraction lines of the α-Ti phase are present; we can also observe that thermal annealing does not change grain orientation and the pattern is similar, except for a limited peak shift, as previously observed for the corresponding Ti sample.

The XRD pattern of the Ti:D deposited at 423 K exhibits a single broad line, which might be attributed to the α-Ti phase as well as the Ti deuteride phase.[14] A detailed texture analysis was necessary to understand the true structure;[11] pole figures at 35.15° and 40.54° revealed the fcc CaF_2-like structure of the δ-TiD_2 (titanium deuteride), which grew with a strong [111] orientation. During the thermal annealing at 723 K, samples underwent a phase transformation from a fcc TiD_2 to a hcp Ti structure with (101) and (002) orientations.

C. Thermal-desorption spectroscopy

TDS experiments were carried out by studying the evolution of the D_2 $(m/e=4)$ quadrupole mass spectrometer (QMS) signal during the temperature ramp. To compare the relative amounts of desorbed deuterium, after subtraction of the previously measured background level, the intensity of each signal was normalized with respect to the maximum value measured with the Ti:D sample deposited at 423 K: experimental errors were estimated from the mean value of the fluctuations in the $m/e=4$ QMS background level. Figure 4 shows the D_2 desorption flux pertinent to Ti:D samples deposited at 573 K (a) and 723 K (b); in these experiments the temperature ramp was fixed to 0.25 K/s. Figure 5 reports a typical TDS spectrum of Ti:D samples deposited at 423 K when the temperature ramp was fixed at 0.07 K/s (a), 0.25 K/s (b), 0.5 K/s (c), and 1.0 K/s (d). Figure 6 shows the TDS spectrum of Ti:D samples with different thickness, deposited at 423 K: 75 nm (a), 150 nm (b), and 300 nm (c).

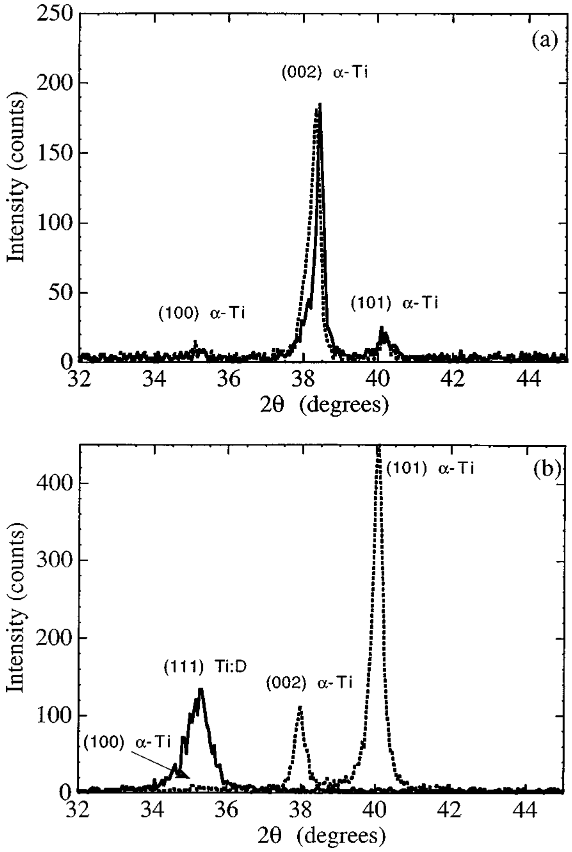

FIG. 3. XRD spectra of Ti:D samples deposited at 723 K (a) and 423 K (b): as-deposited sample (solid line); after thermal annealing (dashed line).

D. Differential scanning calorimetry

DSC scansions for samples deposited at 423 K are reported in Fig. 7 for Ti:D (a) and Ti (b) thin films. Both curves present a broad exothermic peak with a maximum in the 650–720-K temperature range. As shown in Fig. 7(c), no detectable DSC signal was observed with Ti samples deposited at a higher substrate temperature; the same occurs in the Ti:D samples.

IV. DISCUSSION

Titanium thin films deposition in a deuterium atmosphere at substrate temperatures of 573 and 723 K produced deuterated titanium layers with a hcp structure. When the deposited samples were subjected to a temperature ramp from room temperature up to 723 K, TDS measurements showed a deu-

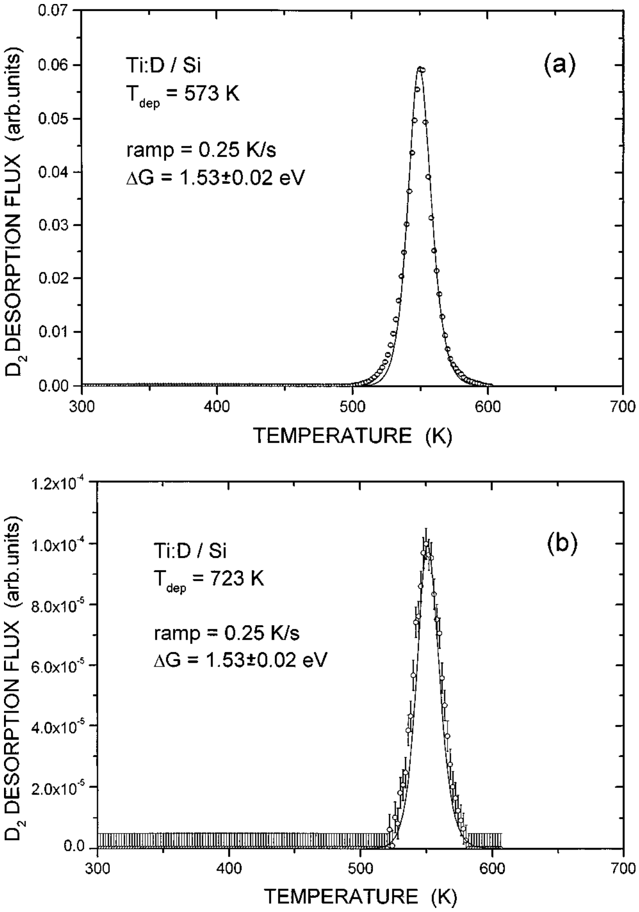

FIG. 4. Thermal-desorption spectrum of Ti:D samples deposited at 573 K (a) and 723 K (b). Experimental data are reported as open symbols with experimental errors; the solid line is a numerical fit of data based on Eq. (1).

terium effusion peak at ~550 K. XRD did not reveal any recrystallization of the deposited layers up to a temperature of 723 K, and no detectable DSC signal was observed. A simple model to analyze deuterium effusion considers the kinetics as governed by three processes: (a) release of deuterium atoms from the lattice site where they are contained, (b) atomic diffusion to the surface, and (c) recombinative desorption of the D atoms from the surface to the gas phase. Experimental investigations by proton magnetic resonance[15] and neutron diffraction[16] have shown that in deuterated α-Ti layers, hydrogen isotopes form an interstitial solid solution (H or D atoms occupy tetrahedral and octahedral sites in the hcp lattice); since the interstitial diffusion of light elements in metals is very fast, a simple order-of-magnitude estimate allows us to exclude the diffusion process as rate limiting in the desorption kinetics. Using published diffusion data of H diffusion in α-Ti,[17] we can estimate a characteristic diffusion time τ_{diff} by the random-walk expression $\tau_{\mathrm{diff}}=d^2/D_{\mathrm{diff}}$, where d is the film thickness and D_{diff} the diffusion constant: at 550 K, this gives a value of 10^{-3} s. The characteristic time for deuterium desorption T_p/β (in this expression, T_p is the temperature peak and β the heating ramp) is typically of 10^2 s in our experiments. While this estimate has only a qualitative meaning, it allows us to role out the deuterium diffusion as the rate-limiting process in the desorption kinetics.

When the desorption kinetics can be described as a singly activated process, the theory of absolute reaction rates provides a convenient framework to discuss our data.[18] This theory assumes that a deuterium atom must overcome an activation free energy barrier ΔG to be desorbed, this additional energy being supplied by thermal fluctuations. The frequency ν_0 at which this energy barrier is confronted by the atom is given by (K_bT/h), where T is the absolute temperature and h the Planck constant: therefore the frequency is 6.2×10^{12} s^{-1} at room temperature and 1.2×10^{13} s^{-1} at 600 K. The energy barrier is associated with a change in enthalpy ΔH and entropy ΔS by the relation $\Delta G=\Delta H-T\Delta S$; for a process of order n the equation describing the desorption rate is given by

$$R=-d(c/c_0)/dt=(K_bT/h)(1-c/c_0)^n\exp(\Delta S/K_b)$$
$$\times\exp(-\Delta H/K_bT), \tag{1}$$

where c_0 is the initial deuterium concentration (assumed uniform along film thickness), c the desorbed deuterium concentration, and n the order of the process, that is established by the shape of the desorption spectrum. The frequency ν_0 is often assumed as independent of the temperature and approximated by the Debye frequency ($\sim10^{13}$ s^{-1}): however, this approximation cannot completely account for the measured TDS data, having a simulated peak with a width much broader (~100 K) than that measured (~20 K). In Figs. 4(a) and 4(b), we report, together with the experimental points, a numerical modelling of desorption data for deuterated Ti samples based on Eq. (1) (straight line): the best fit was obtained for both samples by considering the desorption as a second order process ($n=2$) with $\Delta H=4.45$ eV and $\Delta S=5.31\times10^{-3}$ eV/K, equivalent to a free-energy barrier $\Delta G=1.53\pm0.02$ eV (the experimental desorption peak temperature is 550 ± 2 K). Second-order desorption processes have been observed very often when studying the release of light atoms forming diatomic molecules from solution in metals. They were generally interpreted by considering the recombinative desorption of gas atoms at the metal surface as the rate-limiting process,[19]

$$2\mathrm{D}_{\mathrm{surf}}\rightarrow\mathrm{D}_2(\mathrm{gas}).$$

When hydrogen is solubilized in metals in small concentrations (that is, when its solubility in the metal follows Sieverts' law) a theory developed by Pride and Titcomb[20] predicts an activation energy of desorption numerically equal to the heat of solution measured from equilibrium solubility. This prediction was experimentally confirmed by the authors studying the kinetics of evolution of hydrogen contained as a dilute solution in Nb in isothermal desorption experiments:[21] the measured value of the activation energy for the process was 67.56 ± 1.26 kJ/mol (0.70 ± 0.01 eV per molecule), very close to the value of 68.94 kJ/mol (0.71 eV per molecule) measured for the heat of solution.[22] As a second example, Ko and Schmidt[23] measured a value of 18 kcal/mol (0.78 eV per molecule) for the activation energy of hydrogen desorption from Ta in temperature ramp measurements at low heating

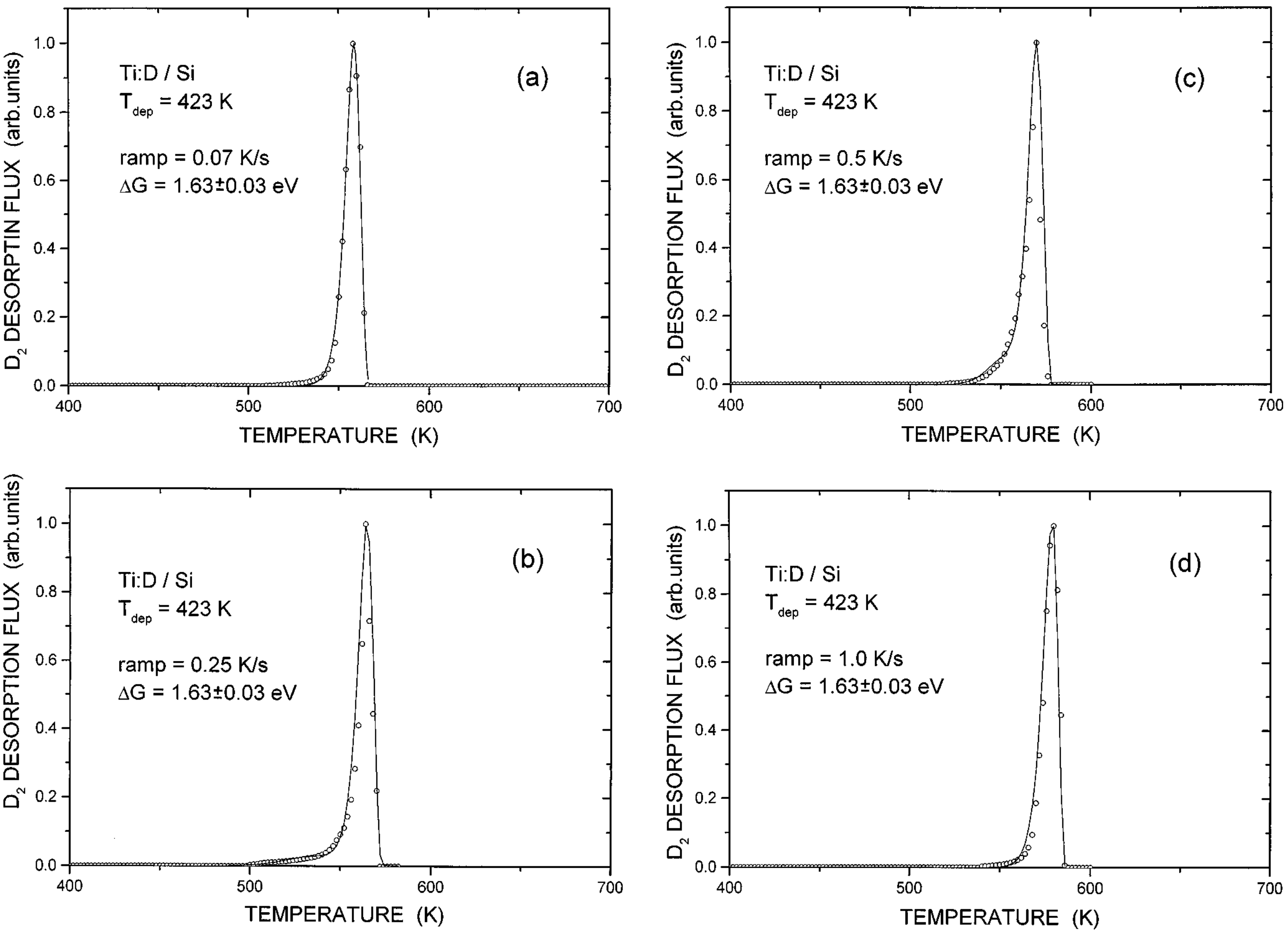

FIG. 5. Thermal-desorption spectrum of Ti:D samples, 150 nm thick, deposited at 423 K with different heating ramps: 0.07 (a), 0.25 (b), 0.5 (c), and 1.0 K/s (d).

rate: this value is very close to the solution energy of 17 kcal/mol (0.74 eV per molecule) measured by Pryde and Tsong[24] in pressure-composition experiments carried out in equilibrium conditions. Our result can be compared with measurement of H_2 absorption on clean Ti films: calorimetric measurements gave a heat of reaction of 35-kcal/mol H_2 equivalent to 1.52 eV per molecule;[9] this is in good agreement with the activation energy for effusion measured in this experiment.

RBS analyses carried out on Ti and Ti:D samples have revealed that the concentration of bulk contamination is lower than a few at. %, and thus that this probably does not influence the deuterium kinetics; on the other hand, it is known that an oxide layer readily forms on Ti during exposure to air. It is important thus to discuss the influence of this surface layer on deuterium effusion kinetics. Kasemo and Tornqvist[25] and Burrel and Armstrong[26] studied the effect of O and CO impurities on the hydriding/dehydriding process of titanium at room temperature. The authors observed that small amounts of oxygen on the Ti surface (~1 ML) only slightly reduce the absolute values of the adsorption/desorption rate without changing the kinetics with respect to a clean Ti surface. As observed by Brignolas, Bujar, and Bardollo,[27] the first two monolayers of oxygen adsorbed by Ti are incorporated below the surface, and thus Ti atoms remain at the surface; in these conditions the necessary hydrogen dissociation reaction may still occur. Conversely the authors observed that an oxide layer of sufficient thickness (at least ~1 nm thick) completely passivates the Ti surface against hydrogen absorption. The authors attributed this passivation effect to the absence of sites for H_2 molecular dissociation on the oxidized surface, and not to the formation of a diffusion barrier to hydrogen migration. This result was proved by showing that the evaporation of a small amount of fresh Ti onto the oxidized surface also restored the absorption capability of the material beneath the oxide layer. Coming back to our experiments, since we have measured an activation energy for deuterium desorption equal to the heat of solution measured by Wedler and Strothenk[9] on clean Ti films, we tentatively suggest that, even if present, the oxide layer does not influence the deuterium effusion kinetics, with the recombination of the D atoms possibly occurring at the interface between the thin surface oxide and the Ti layer.

It is interesting to compare some aspects of the deuterium effusion process from titanium studied in our experiment with the results obtained by Pick *et al.*[28] in a different metal-hydrogen system. These authors studied the hydrogen uptake and release form Nb by measuring the room-temperature conductivity of thin Nb foils exposed to H_2 gas, and analyzed their experimental results with the help of a very general model for the kinetics of hydrogen-metal systems developed in Ref. 29, which includes both surface and bulk effects,

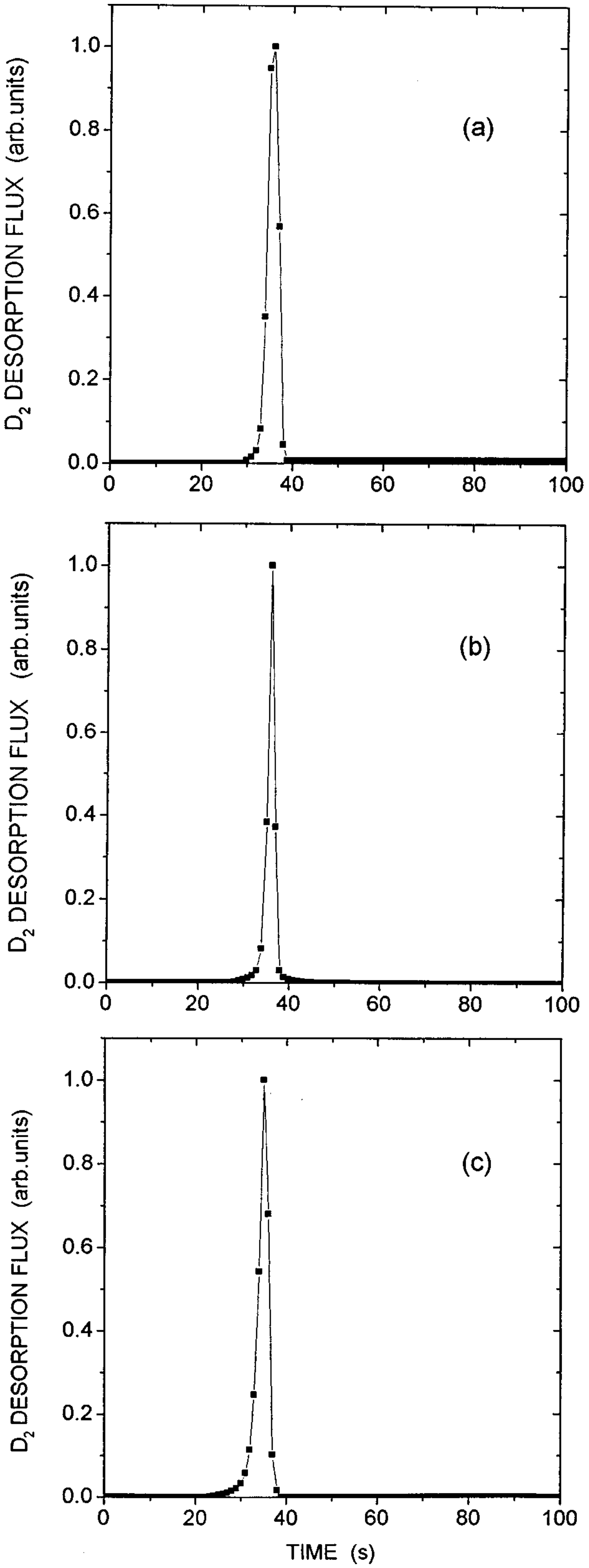

FIG. 6. Thermal-desorption spectra of Ti:D samples deposited at 423 K for three different thicknesses: 75 nm (a), 150 nm (b), and 300 nm (c). The heating ramp was 7 K/s.

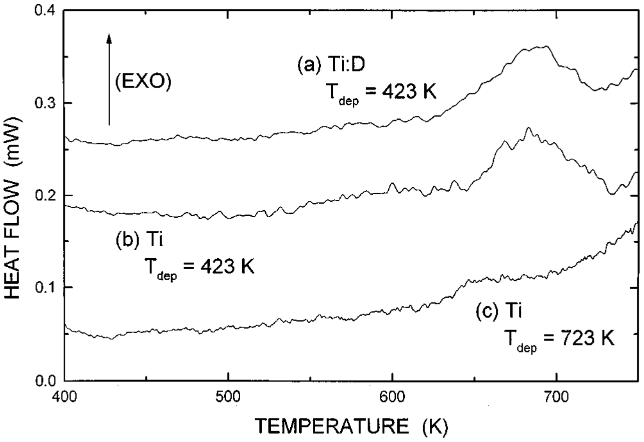

FIG. 7. Differential scanning calorimetry spectra of Ti:D samples deposited at 423 K (a), and Ti samples deposited at 423 K (b) and 723 K (c).

namely, the H_2(gas)↔2H(surf) process and the H(surf)↔H(bulk) process. The model suggests that hydrogen bulk concentration and surface coverage θ are in quasiequilibrium and, if the energy barrier E_A for migration of H atoms from the surface to the bulk is higher than the barrier E_B for the migration from the bulk to the surface, hydrogen accumulates at the Nb surface, so that when the bulk concentration is low (~1 at. %) the surface coverage is nearly 1. An important consequence of this surface effect is the slowing down of the adsorption (and desorption) rate which goes as $(1-\theta)^2$. It was in fact observed that if the difference between E_A and E_B can be made lower, for example by the deposition of a very thin Pd layer on the Nb surface, both the hydrogen uptake and release can be accelerated. From the surface energy models for the Ti-H_2 system proposed by Pick[30] and by Brown and Buxbaum,[31] a value of 7.1-kcal/mol H_2 can be obtained for E_A-E_B: this value is not much lower than the value of 8.5-kcal/mol H_2 pertinent to the Nb-H_2 system[28] and it cannot be excluded the occurrence of deuterium surface accumulation. But in this case, the surface coverage being $\theta \approx 1$ (as discussed above for the Nb-H system), we should expect a zeroth-order desorption kinetics instead of a second-order process,[23] as observed in our experiment.

Before discussing the results of TDS measurements carried out on deuterated samples deposited at 423 K, it is important to remember that deuterated α-Ti deposited at 573 and 723 K exhibited the same behavior as pure Ti samples deposited at the same temperature: considering XRD and DSC measurements after thermal annealing at 723 K, neither recrystallization of the α-Ti layers nor detectable DSC signals were observed.

The behavior of Ti films deposited in a deuterium atmosphere at a 423-K substrate temperature can be briefly described in this way: as-deposited samples have the fcc CaF_2 structure of titanium hydride with a (111) orientation. When submitted to a linear temperature ramp in the 300–723-K interval, the samples show (a) a very narrow deuterium effusion peak at 570 K in TDS measurements, (b) a crystallographic transformation from a fcc titanium hydride structure to a hcp Ti structure by XRD, and (c) a broad exothermic peak in the 620–723-K temperature range by DSC. We begin the second part of the discussion by analyzing the results of TDS experiments. Figures 5(a)–5(d) report, together with the experimental points, a numerical modelling of desorption data for titanium hydride samples based on Eq. (1) (straight line): in this case the best fit was obtained by considering the desorption spectra as the overlapping of two peaks: a first-order process $(n=1)$ with $\Delta H = 6.61$ eV and $\Delta S = 8.80 \times 10^{-3}$ eV/K, equivalent to a free-energy barrier $\Delta G = 1.63 \pm 0.03$ eV and a not completely resolved broad second-order peak $(n=2)$, with ΔH and ΔS values compatible with a free-energy variation ΔG of 1.5 eV. Taking into account the area of the two separated peaks, the deuterium content related to the second-order peak is about $\frac{1}{40}$ of the content related to the first-order one. The first peak, being characterized by a second-order process $(n=2)$, probably corresponds to the deuterium recombinative desorption from the surface of titanium deuteride layers. We can observe that the free-energy barrier ΔG pertinent to this release process, considering the experimental errors, is similar to the free-energy barrier measured with deuterated Ti samples: the fact that the desorption process from the surface of titanium is similar to the desorption process from the surface of titanium deuteride is not very surprising, the deposited fcc titanium deuteride films and deuterated hcp titanium films having the same surface geometry, presenting fcc (111) and hcp (002) lattice planes, respectively, which are equivalent.[32] As to the first-order peak, the recombination of deuterium atoms at the surface of the films can be ruled out as the rate-limiting process, as it would give a second-order peak as in the case of deuterated Ti films. Hydrogen diffusivity is a little bit lower in titanium hydride than in α-Ti:[33] using literature data, a diffusion time on the order of 10^{-2} s can be estimated, and, considering the same argument as in the case of deuterated Ti films, we can exclude deuterium transport from the bulk sites to the surface as the rate-limiting process in the deuterium desorption. The importance of diffusivity could be assessed by studying the deuterium desorption rate as a function of the sample thickness. In fact, if the diffusion process was the rate-limiting one, by doubling the sample thickness the effusion peak should translate to desorption times four times longer. Figure 6 shows the deuterium effusion peak from titanium deuteride thin films for three different thicknesses, namely, 75 (a), 150 (b), and 300 nm (c), using a 7-K/s heating rate: as can be observed, no shift is present. The process limiting the deuterium desorption rate is probably the release of deuterium atoms from the bulk site containing them, and this process physically takes place through the decomposition of the titanium deuteride layers: after deuteride decomposition, the resulting Ti layers are oversatured with deuterium (as shown by the Ti-H_2 phase diagram,[4] the maximum hydrogen solubility at temperatures near 570 K is lower than 7 at. %), and thus gas atoms are released very quickly. This decomposition has obviously occurred in correspondence to the effusion peak: (a) ERDA analysis of as-deposited and thermally treated samples have revealed that all deuterium atoms contained in the Ti layers were released in the thermal process; (b) TDS measurements revealed that the only D_2 effusion peak is in the 558–577-K temperature range, depending on the heating ramp; and (c) XRD measurements showed, in the analyzed temperature range, the occurrence of the phase transformation from fcc titanium deuteride to hcp titanium. It is important to remember that the thermal-desorption process is observed to occur with a narrow peak (~20 K) centered around 564 K, and that this temperature is in good agreement with the temperature of 573 K reported for the eutectoid reaction $\alpha + \delta \leftrightarrow \beta$ in the Ti-H_2 system.[4] The measured activation energy for desorption can be compared with values reported in literature for the heat of dissociation of TiD_x. Morton and Stark[34] measured the value of 22.5–22.7-kcal/mol D_2 for $x = 0.02-0.1$, which is 0.98 ± 0.01 eV per molecule; and 29–31-kcal/mol D_2 for $x = 0.1-1.8$, which is 1.30 ± 0.04 eV per molecule. Melkonian,[35] found a value of 40.25 kcal/mol, equivalent to 1.74 eV per molecule, for the heat of dissociation of the hydride in the two phase $\alpha + \delta$ region. This last value is comparable to the desorption activation energy measured in the present experiment.

DSC measurements of titanium deuteride thin films deposited at 423 K show a broad exothermic peak in the 620–723-K temperature range [Fig. 7(a)]. The temperature at which the onset of the DSC signal (620 K) is seen is much higher than the desorption temperatures of the titanium deuteride layers (564 K): therefore, the thermal release is not given by the decomposition of the titanium deuteride. Moreover, Fig. 7(b) shows that this thermal release is also observed when analyzing a Ti sample deposited at the same deposition temperature of 423 K. An order of magnitude for this energy release can be calculated: considering that the mass of the Ti film used for the DSC in Fig. 7(b) was 2×10^{-5} g, and given the area under Fig. 7(b) $(2 \times 10^{-3}$ J), an enthalpy variation $\Delta H \approx 10^2$ J/g is obtained, corresponding to a value of 5×10^{-2} eV per Ti atom. The observed thermal process can in principle be related to many different physical processes like recrystallization, structural relaxation of the deposited layers, or phase transitions. During thermal treatment, Ti samples deposited at 423 K change their (101)-(002) preferred orientation to the (100)-(002) one, as shown in Fig. 2(b). This recrystallization process does not take place during the thermal annealing of Ti samples deposited at higher substrate temperatures [see Fig. 2(a)], and accordingly no DSC signal is observed [Fig. 7(c)]. Bulk recrystallization in metal systems costs an energy of the order of 10^{-4} eV per metal atom,[36] that is two orders of magnitude lower than that observed. We suggest that the observed effect is connected with the structural relaxation of the Ti deposited layers occurring during the recrystallization process and involving the annealing of point or extended defects present in the disordered Ti lattice.[11] We have not been able to find similar results concerning thin metal films, but the current literature is rich in calorimetric studies concerning the crystallization and structural relaxation of silicon[37] and germanium films:[38] it has been observed that this process gives rise to a heat release equal to one-third of the heat of crystallization; that is, an energy release of the order of about 10^{-2} eV per atom, comparable with the DSC result of the present experiment.

V. CONCLUSIONS

The study of the thermal stability and structural evolution of deuterated titanium thin films produced by *e*-gun evaporation of titanium in a molecular D_2 atmosphere showed that the deposited layers present the fcc δ-TID_x fcc structure for 423-K substrate temperature, and are made of deuterated

α-Ti thin films (hcp structure) for higher temperature.

The deuterium desorption spectrum, measured during linear heating of deuterated α-Ti thin films, shows that D_2 effusion occurs through a second-order peak at 550 K, indicating recombinative desorption as the rate-limiting process in the deuterium effusion. Similar experiments carried out on δ-TiD$_x$ thin films have shown that D_2 effusion occurs produced a narrow (~20 K) first-order peak at 564 K related to the transformation of the deposited fcc layers to the hcp Ti structure. A weak exothermic signal was observed at higher temperature, in the 650–720-K interval, related to the structural relaxation of the titanium layers.

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