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THE PHASE DIAGRAM OF HYDROGEN IN ULTRA THIN FILMS

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ABSTRACT

In this paper, we discuss changes in the phase diagram of hydrogen in both bilayer (i.e. 200-2000 Å Nb/ 100 Å Pd on glass) and multilayer configurations. Comparison of x-ray diffraction, electrical resistivity and volumetric measurements of the films before and after hydrogen charging indicate that the phase equilibria between a correlated (high concentration) and a dilute phase of hydrogen in Nb is not sensitive to the number of layers in the films. On the other hand, the experimental methods show different behavior for 200 Å thick Nb films and thicker (>400 Å) Nb layers. The diffraction results also show that, while charging with hydrogen, the Nb layers mainly expand along the surface normal of the films, while the Pd layers expand in all directions equally, and transform to the bulk α' phase.

INTRODUCTION

The absorption of hydrogen by thin metal films has been emphasized in many recent studies[1-4]. One reason for this interest is that the metal-hydrogen interaction is sensitive to the macroscopic geometry of the metal[5]. Thus, the phase diagram of thin films is greatly modified from that of the bulk. For example in thin Nb films[1-4] a suppression of the hydride β phase is observed. In a recent study[6], we demonstrated a new method for mapping the metal-hydrogen phase diagram of thin Nb films using volumetric measurements, together with four-probe resistivity data[6]. The Nb films were deposited on glass and were capped with Pd. The Pd layer protects the Nb from oxidizing, increases hydrogen dissociation and binds hydrogen less strongly to the surface which allows rapid absorption into the bulk[7]. The phase diagram of these films was found to be influenced by the degree of clamping of the film to the substrate at the interface and also by the nanostructure of the Nb. We attributed to the apparent relaxation of the strain field during hydrogen charging to grain boundaries in the films. In this study we will show that there are similarities between bilayer and multilayer Nb/Pd structures. The similarities are a consequence of the fast diffusion of hydrogen in these films, which leads to a constant chemical potential of the hydrogen throughout the films. On the other hand, we will also show how the thickness of the layers, controls the hydrogen-hydrogen correlations.

THE EXPERIMENT

The sample preparation procedures are described elsewhere[6]. Bilayer and multilayer of Nb and Pd films (200-2000 Å Nb/ 100 Å Pd) were dc magnetron sputtered on acid washed glass pieces (1"× 1"). After being deposited, the films were exposed to the atmosphere. The impurity level of the films was estimated to be of less than 1 atomic %[6] of oxygen or other gases. X-ray measurement were performed on beamline X22A at the National Synchrotron Light Source with 10 KeV x-rays. A standard four circle geometry was used allowing the determination of lattice constant expansion both perpendicular and parallel to the film surface in the reflection geometry. The asymmetry of the expansion in the two directions during hydrogen uptake will be discussed

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below. X-ray diffraction showed that both the Pd and Nb films grow with a preferred cyrstallographic orientation parallel to the substrate (for Nb it is [110] planes, and for Pd the [111] planes). The particle size was found to be ~70 Å for the 200 Å Nb films. The particle size increases with film thickness from 70 to ~150 Å for films going from 200 to 2000 Å thickness. The size of the particles was found to be about the same both perpendicular and parallel to the plane of the substrate. X-ray data also show no preferred rotational orientation of the particles in the plane of the film. Repeated cycling of the films with hydrogen decreased the particle size by ~20% and also stabilized the film's resistivity.

For the volumetric and resistivity measurements a small hydrogen uptake chamber (27.3 cm^3) equipped with a pressure transducer (MKS type 122A) was used. The resistivity measurements were made using a standard four probe technique[6]. The resistivity method was done only for Pd/Nb films charged in low hydrogen pressure (<~8 Torr, i. e. Fig. 3). In this case, the hydrogen is concentrated almost totally in the Nb layers. This is due to the different chemical potential dependencies of hydrogen in Pd and Nb. At higher pressures the Pd layers were filled with significant amount of hydrogen, and one must use techniques which are capable in measuring the concentration in both the Pd and Nb layers. At these pressures (i.e. Figs. 1 and 2), we used x-ray diffraction, assuming the bulk relations between hydrogen concentration and lattice volume expansion[8] . This estimate may be in error by as much as 20% when used for thin films[9].

RESULTS AND DISCUSSION

a. X-ray Scattering Results : In Fig.1 we show x-ray θ:2θ scans for an 800 Å Nb layer capped with 100 Å of Pd. The scans are taken in the c-axis configuration and show that the lattice of this thin film expands perpendicular to the film surface by up to 8% with an expansion in the plane of the film of less than 0.5 % in each direction. This gives a volume expansion (ΔV) of about 10% which corresponds to a [H/Nb] ratio of about 0.70[8]. The Pd lattice, on the other hand, expands symmetrically up to 4%, yielding a volume expansion of 12% and a corresponding hydrogen concentration of about 0.64. The difference between the modes of Nb and Pd expansion may be due to the lattice mismatch between Nb and Pd. Figure 1, also shows that at first the hydrogen discharges from the Pd (two lower scans in Figure 1). We then observe a shift in the Nb[110] direction. At lower hydrogen concentration, the Nb[110] splits into two peaks (see scans 5-8 from the bottom of Fig 1). Each one of the peaks remains at almost the same position, but the ratio between the peaks intensity varies with hydrogen concentration[6]. The coexistence of the two peaks represents a mixed phase region in the Nb between a low density phase and a higher density phase. At lower hydrogen concentrations (top most scan in Figure 1), the higher density phase is consumed, and only the lower density phase survives. The X-ray diffraction curves of films with multilayers of Nb/Pd with the same thickness were similar to that of the bilayers (not shown). Figures 2 a,b demonstrate the evolution of the Nb[110] and Pd[111] X-ray peaks while hydrogen discharges from a 3 × (100 Å Pd / 200 Å Nb) film, which was initially charged at an external pressure of 250 Torr. In this case the results were also similar to those measured with a single layer of 100 Å Pd / 200 Å Nb (Apart from the better signal to noise in the multilayer structure) . Figure 2 also demonstrate the effect of recycling with hydrogen charging and discharging with hydrogen. Curve 2 (i) was taken before any charging with hydrogen. A clear shift to lower angles of both the Pd and Nb is observed in curve (h) after charging and discharging. These shifts are associated with relaxation process[9]. Quantitatively, Figure 2 a, shows the same trends as Figure 1. In Figures 1 and 2 a it can be seen that hydrogen leaves the Pd first (see dotted lines in figure 1). During this initial time the Nb[110] peaks move only slightly with values of the lattice constant reflecting that the Nb still contains large amounts of hydrogen.

The mixed phase region is also manifested in figure 2. The main difference between Figures 1 and 2a is the width of the x-ray peaks. In the case of Figure 2, the peaks are broader, and therefore it is harder to resolve the various peaks from each other. This is a result of the smaller particle size for the 200 Å Nb films compared to the 800 Å Nb films. Figure 2 a,b also show the expansion of the Pd lattice, which expands equally in all directions by 4%. In the Pd layer, the hydrogen goes to the bulk α' phase, while in the Nb, the hydrogen high density phase is completely different from that of the bulk.

One can conclude the following about the dependence of the chemical potential on the hydrogen concentration in the two layers: We start from a film which is under a hydrogen pressure of 250 Torr. The chemical potential μ of the hydrogen in the gaseous phase is high enough to charge the Nb to a concentration of $c\sim0.7$ and the Pd to $c\sim0.64$. At this chemical potential value the slope of $\mu(c)$ of both the Nb and the Pd is extremely high, and therefore the hydrogen concentration in the two metals is not sensitive to the hydrogen pressure. As we get down to hydrogen pressures of ~10 Torr the slope of $\mu(c)$ of the Pd becomes small, while that of the Nb is still high. Decreasing the hydrogen pressure at these levels hardly affects the hydrogen concentration in the Nb, but changes dramatically that of the Pd. When hydrogen is pumped and air is introduced to the film, the Nb layers are still filled with hydrogen. At this stage the hydrogen in the film is far from equilibrium with the hydrogen in the air, but the hydrogen is in quasi equilibrium in the film. For that reason, the hydrogen concentration is the same in all Nb layers. The desorption of hydrogen is not limited by interface or bulk diffusion but is determined by the

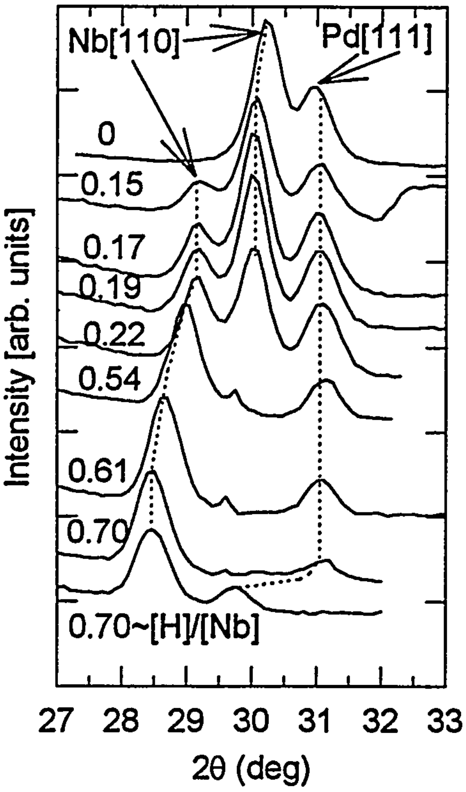

Figure 1: X-ray θ:2θ scans of a 100 Å Pd / 800 Å Nb film. The **q** vector is directed to the normal of the film surface. The lower scan was taken when the film was under hydrogen pressure of 250 Torr, and each one of the other scans was taken at a different time, after a film charged with hydrogen was exposed to air. The numbers associated with each scan present the calculated hydrogen concentration of hydrogen in the Nb layer. The concentration of hydrogen in the Pd layer is 0.61in the lower scan, and 0.00 at the rest of the scans.

surface barrier to associate with oxygen into water. As the hydrogen discharges, $\mu(c)$ decreases until it becomes almost[6] constant in the mixed phase region. When hydrogen is discharged farther into the low density phase, $\mu(c)$ continues to decrease until it gets to $-\infty$ when hydrogen is completely discharged.

B. Transport Measurements. The above picture can be tested also by measuring the film resistance while charging and discharging with hydrogen. Figure 3 shows the dependence of the resistivity as a function of hydrogen concentration with film thickness. The curves were made while the films were charged under a hydrogen pressure of ~3 Torr. The different curves $(R-R_0)/R_0$ were multiplied by a variable factor to align their initial slopes. It is clear that the behavior of the 400 Å Nb thick film resembles that of the 800 Å and the 2000 Å film more than that of the 200 Å film. In thicker films, the resistivity tends to bend over more then in the thinner films. We argue that the bending over starts at concentrations at which the hydrogen-hydrogen correlations are significant[6]. In thicker films the hydrogen-hydrogen elastic interactions are stronger and closer to the bulk, and thus hydrogen atoms are more correlated. Figure 3 also confirms the similarities between bilayer and multilayer films. Our experience with a variety of films showed that the curves of almost all the films with equal thickness look alike, apart from films with thickness

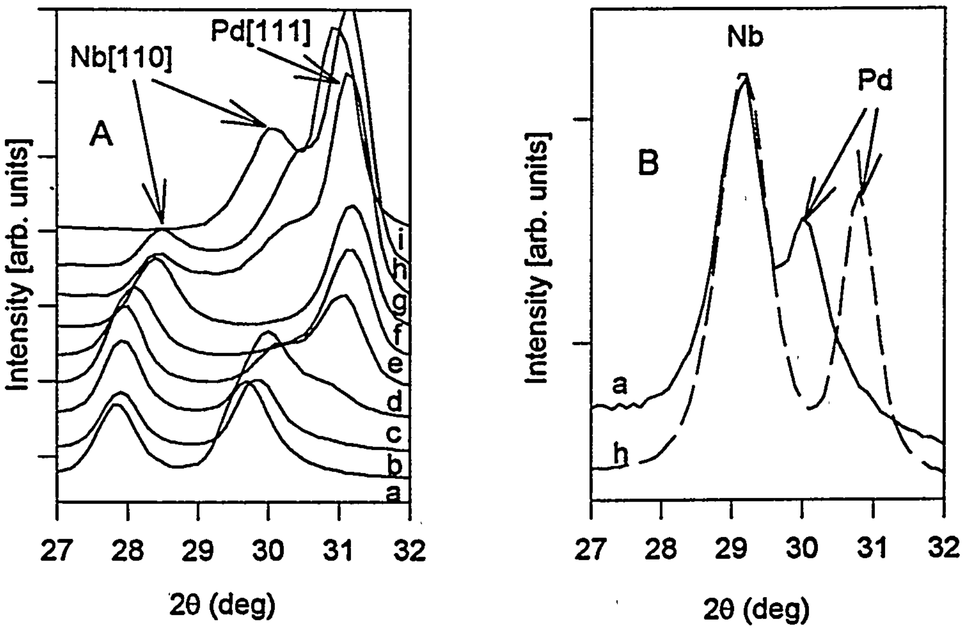

Figure 2: X-ray θ:2θ scans of a 3×(100 Å Pd / 200 Å Nb) film. In 2 a. 'q' is directed to the normal of the film surface, and in 2 b. the angle between 'q' and the surface normal is 85°. In scans 'a' the film was kept under hydrogen pressure of 250 Torr, and in scans 'b' and 'c' the hydrogen was leaking out slowly of the X-ray chamber. The rest of the scan were taken at a different time, after the film was exposed to air. The estimated concentration of hydrogen in these scans is : [H]/[Nb]= 0.7, 0.682, 0.664, 0.616, 0.513, 0.032, 0.004, 0 for a, b, c, d, e, f, g, h, i correspondingly, and [H]/[Pd]= 0.61, 0.56, 0.29, 0.06, 0.01, 0.00, 0.00, 0.00, 0.00 for a, b, c, d, e, f, g, h, i correspondingly. Curve 'i' was taken on a virgin film, before any exposure to hydrogen.

varying between 300 Å to 500 Å. These films may have curves resembling either the curve for the 200 Å Nb film (fig. 3) or the 2000 Å Nb film. We believe that the parameter controlling the dependence of the hydrogen properties with film thickness, is the ratio between the film thickness and particle size, although this has not been measured in detail. When this parameter exceeds unity, the dependence of hydrogen uptake with thickness becomes less pronounced. For the 200Å Nb thick film the parameter is approximately 4, for the 400 Å film it becomes a little less than 8. This parameter may correlate with the degree of clamping of the film to the glass and to the Pd layer.

The resistivity of the film was also measured at different hydrogen pressures, after giving the resistivity enough time to stabilize (not shown). We found that at low pressures (<~10 Torr) the resistivity was uniquely defined during charging and discharging. On the other hand at higher pressures hysteretic behavior was observed. This indicates that at the higher pressure the simple picture of constant chemical potential can not be quantitatively implied, since hydrogen in a metastable phase (probably a hydride phase in the Pd layers). Another interesting observation in these films is their mechanical properties. Thick films of a few thousand ångstroms thick tend to peal off the glass support after being charged and discharged with hydrogen a few times. We observed that films made of thicker Nb layers tend to peal off in bigger pieces. We also charged the films electrochemically, and found the same observation. We believe that when the thick films come off the substrate, they may hydride and turn to powder. In contrast, when the multilayer films come off the substrate they keep their integrity by coming off in large pieces. Thus for technical applications (mainly hydrogen storage batteries) maltilayered structures may be favorable.

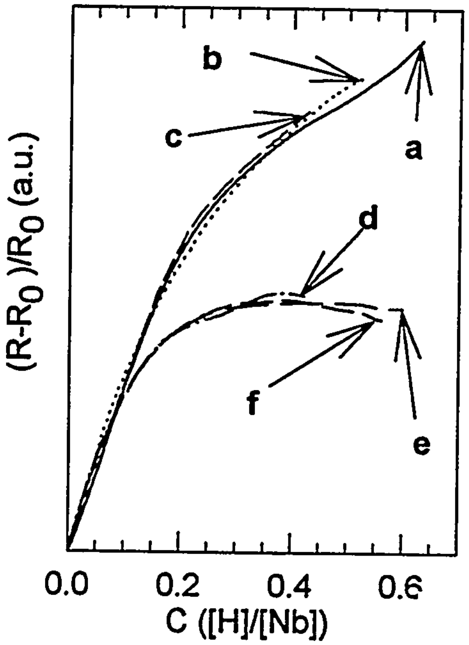

Figure 3: The relative change in resistivity vs. hydrogen uptake for various films : a: 100 Å Pd / 200 Å Nb, b: 3×(100 Å Pd / 200 Å Nb), c: 15×(100 Å Pd / 200 Å Nb), d: 3×(100 Å Pd / 800 Å Nb), e: 100 Å Pd / 400 Å Nb, f: 100 Å Pd / 2000 Å Nb . The different curves ($R-R_0$) were multiplied by a factor so that their initial slopes will be equal.

CONCLUSIONS

We found that multilayered and bilayer (Pd-capped Nb) films exhibit similar x-ray patterns and transport behavior. This implies rapid hydrogen motion between layers or grains. The hydrogen-metal phases depend on the thickness of the film and for the thinnest films there is no "bulk" hydride phase in the Nb. As hydrogen is discharged from a 70% concentration, there is co-existence between dilute and dense hydrogen-metal phases. X-ray data shows that the Nb layers are tightly clamped in the plane of the films (defined as the a-b directions) for both multilayers and bilayers. The Nb layers expand along the surface normal (c direction). The Pd layers expand isotropically with the uptake of hydrogen. We believe the differing behavior of Pd and Nb is dependent on the mechanical properties of the films and also note that the properties of bilayers and multilayers depend on the Nb film thickness.

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