

## Extraordinary Adhesion of Niobium on Sapphire Substrates

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(Received 16 May 1997)

We have investigated the adhesion between a metal and a ceramic interface, in particular between Nb(110) films and Al<sub>2</sub>O<sub>3</sub>(11 $\bar{2}$ 0) substrates. We have tested the adhesion properties by hydrogen loading of the metal film. The resulting strains were measured by in- and out-of-plane lattice parameter measurements. In contrast to the bulk behavior, we find for hydrogen in thin Nb films a highly anisotropic in plane strain. Comparing the in-plane expansion with the free case, we observe a tensile stress exceeding the yield stress of bulk Nb by at least a factor of 10. This unusually large resistance against expansion is due to giant adhesive forces at the metal/ceramic interface. [S0031-9007(97)04843-6]

PACS numbers: 68.35.-p, 68.55.-a, 68.60.Bs, 61.10.-i

Understanding adhesion properties of metals on ceramic substrates is one of the most intriguing and important topics of current materials research [1]. High temperature composite materials, corrosion resistant coatings, and electronic packaging rely on the adhesive strength of metal/ceramic interfaces. Two different models have been brought forth to describe the interfacial bond energy. In one of them the electrostatic image charges between the oxide ions and the metallic surface are made responsible for the bonding [2,3]. Other models favor a hybridization effect between the oxygen *p*- and the metal *d*-orbitals, which may lead to a slightly covalent or ionic bond at the interface [4,5]. The latter model requires a well-defined epitaxial relationship at the metal/ceramic interface, whereas the former is independent of specific atomic coordinations. In practice, good adhesion has been observed at both, heteroepitaxial pseudomorphic, as well as amorphous metal/ceramic interfaces. Therefore, a decision in favor of one or the other model is difficult to make.

Niobium thin films on sapphire substrates can be considered as a model system for studying adhesion properties between metals and ceramics. The growth of Nb on sapphire has been studied in much detail recently and the epitaxial relation is well understood [6–11]. The Nb/Al<sub>2</sub>O<sub>3</sub> interface can be described by a unique three-dimensional epitaxy characterized the following orientational relationships [7–10]:

$$\begin{array}{l} \text{Al}_2\text{O}_3 \quad \text{Nb} \\ [11\bar{2}0] \parallel [1\bar{1}0] \\ [0001] \parallel [111] \\ [\bar{1}100] \parallel [11\bar{2}] \end{array}$$

Nb grows on the sapphire substrate almost strain free and forms a highly ordered crystal structure with large structural coherence lengths [12,13]. The residual epitaxial strain which depends on the film thickness is usually less than 0.05%. Small amounts of hydrogen may help to release residual stresses and the crystal structure

becomes even more perfect due to a “cold” annealing effect [14]. Furthermore, Nb and sapphire have nearly the same thermal expansion coefficients [15]. Therefore thermal strains are not confused with epitaxial or applied strains.

Measuring the adhesion of an epitaxial film is not an easy task. Usually the films are bent together with the substrate and the critical radius of curvature is determined before the film lifts off [16]. We have probed the adhesion properties of the metal/oxide interface in a different way. Loading thin epitaxial Nb(110) films with hydrogen up to saturation concentrations provides large tensile stresses in the in- and out-of-plane direction. We have determined these strains via lattice parameter measurements parallel and perpendicular to the film plane. From these experiments we find that the adhesion of Nb along specific directions on the sapphire substrates is very strong and highly anisotropic.

We have grown single crystalline Nb(110) oriented films by molecular beam epitaxy on Al<sub>2</sub>O<sub>3</sub>(11 $\bar{2}$ 0) substrates. The procedure for growing Nb films of high structural quality is well established and has been reported at several places [7,17,18]. Nb was evaporated with an electron beam gun at a substrate temperature of 900 °C. *In situ* reflection high energy electron diffraction (RHEED) confirmed a very smooth growth of the Nb films [17]. Subsequently, a Pd film with [111] orientation and about 2 nm thickness was deposited on the Nb surface. This enhances the catalytic dissociation of hydrogen molecules at the surfaces and at the same time protects the Nb surface from oxidation. The x-ray experiments were carried out using Mo-*K*<sub>α1</sub> and Cu-*K*<sub>α1</sub> radiation for measuring the in- and out-of-plane lattice parameter changes, respectively. For hydrogen loading we used an x-ray furnace with *in situ* loading capabilities via the gas phase by controlling the gas pressure. For further experimental details we refer to Ref. [18].

In the present study we compare in- and out-of-plane lattice expansions of the Nb film as a function of hydrogen

pressure and deduce in-plane tensile stresses from out-of-plane strains. For an infinite metal/oxide interaction the metal lattice would be allowed to expand only in the out-of-plane direction. Vice versa, for a very weakly interacting system a nearly isotropic expansion is expected and the expansion should be comparable to the bulk behavior. In the bulk, the lattice expansion is isotropic and is a linear function of the hydrogen concentration:  $(\Delta a/a)_H = \epsilon_H = 0.058c_H$ , and  $(\Delta V/V)_H = 3\epsilon_H$  [19]. Nb on sapphire is a highly anisotropic system. Therefore, we expect that the interaction is stronger along one in-plane direction than along others. This is indeed the case as we will see further below.

In Fig. 1 the hydrogen induced out-of-plane lattice expansion is plotted as a function of external hydrogen pressures for five Nb(110) films with different thicknesses on sapphire substrates. For all measurements the sample temperature was kept constant at 473 K. The lattice parameter measurements exhibit the typical S shape of solubility isotherms, which can be described by two parameters, the hydrogen-metal and the hydrogen-hydrogen interaction [18,20,21]. The solid line reproduces the expected lattice parameter changes for a free Nb sample. Most strikingly, the maximum lattice parameter change in saturation  $\epsilon_{H,max}$  depends strongly on the film thickness. In Fig. 2 we have plotted  $\epsilon_{H,max}$  as a function of the inverse sample thickness  $D$ . The solid line is a fit to the data points using a stress relaxation model discussed further below.

Next, we study the lattice parameter changes in the film plane under exactly the same conditions of hydrogen pressure and sample temperature as before. Figure 3 shows the results for the thinnest sample with  $D = 20$  nm and Fig. 4 for the thickest sample with  $D = 527$  nm. Both films exhibit in the film plane a highly anisotropic lattice expansion. In the 20 nm thick film

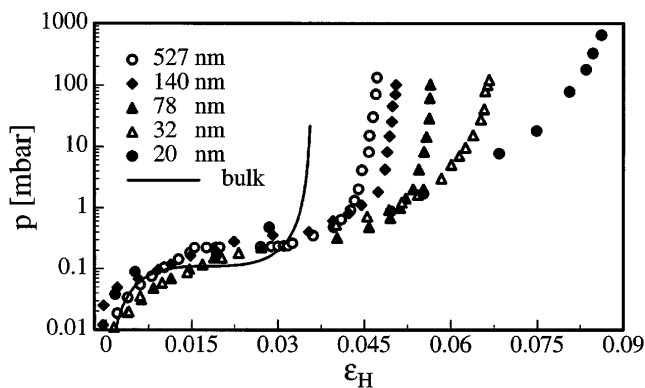


FIG. 1. X-ray measurements of the hydrogen solubility isotherms in Nb(110) thin films with different thicknesses at 473 K.  $p$  is the external hydrogen gas pressure and  $\epsilon_H$  is the relative lattice parameter change in the out-of-plane [110] direction. The solid line reproduces the isotherm for the unclamped bulk case. For the thin films the maximum lattice parameter change and the slope at the inflection point of the isotherms strongly depend on thickness.

the lattice parameters remain constant in all directions up to a hydrogen pressure of about 0.5 mbar, beyond which a separation occurs. At this point the out-of-plane expansion is already 3%. In comparison, the critical layer thickness in semiconductor heterostructures for this misfit strain is only about 5 nm [22,23], as compared to 20 nm in our case. After relaxation starts, the in-plane lattice expansions are highly anisotropic, being smaller along the [111] and  $[1\bar{1}0]$  directions than along the [001] direction. Nevertheless, the maximum lattice expansion observed in the plane is about 2.5%, much less than in the out-of-plane direction (9%). For the thicker Nb film again strong in-plane anisotropies are observed. Along the  $[1\bar{1}0]$  direction the lattice parameters undergo several jumps in a stick and slip type fashion. Sometimes the jumps occur even in the negative direction, which apparently locks the epitaxial Nb film to new adhesion sites. All expansions are reversible after annealing the films at about 400 °C in vacuum and are without any loss of adhesion to the substrate. In none of the cases have we observed a lift off of the Nb film.

We have evaluated the in-plane strain amplitude between the maximum expansion along the [001] direction and minimum expansion along the  $[1\bar{1}1]$  and  $[1\bar{1}0]$  directions, which is about 1.6% and fairly independent of the hydrogen pressure. The in-plane strain amplitude translates into an in-plane stress amplitude of 3.5 GPa between maximum and minimum, which is about 11 times higher than the yield point of Nb [24].

Obviously, there is an intimate relation between the huge and thickness dependent out-of-plane expansion and the high adhesion of Nb films to the sapphire substrate. This relation can be expressed in a quantitative way. For this evaluation, we will use the maximum lattice expansion in saturation which is independent of the shape of the isotherms and specific hydrogen pressure. A free Nb sample will exhibit in saturation a maximum expansion  $\epsilon_{free}^{max} = 0.04$ . The observed in-plane expansion

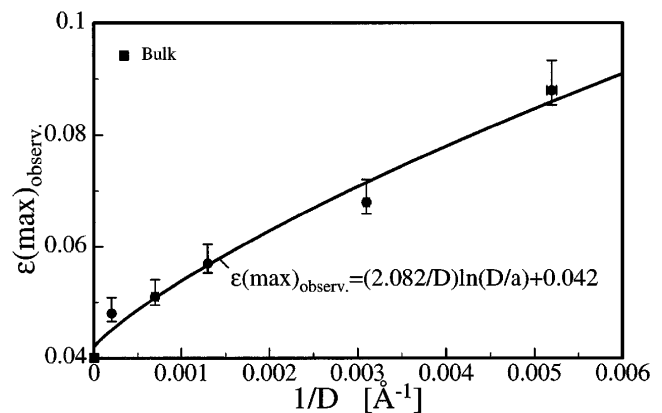


FIG. 2. The observed maximum relative lattice parameter change in saturation is plotted as a function of the inverse film thickness. At  $1/D = 0$  the bulk value known from literature is shown. The solid line is a fit to the data points with the expression in Eq. (2).

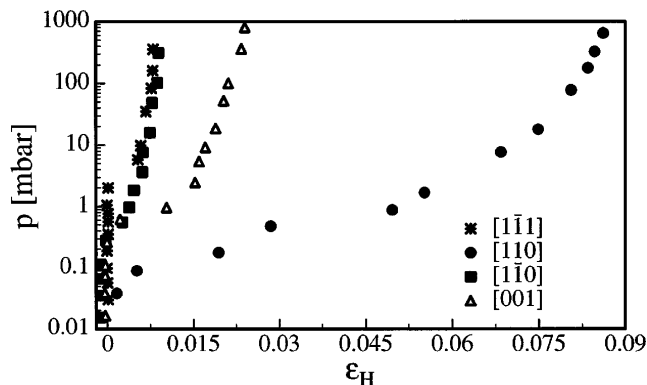


FIG. 3. The relative lattice parameter change of a 20 nm thick Nb(110) film on  $\text{Al}_2\text{O}_3(11\bar{2}0)$  substrate capped with 5 nm thick Pd overlayer at 473 K. The out-of-plane (filled circles) and in-plane lattice parameters for different directions are compared. The expansions along the  $[1\bar{1}1]$  and  $[1\bar{1}0]$  directions (ca. 0.8%) in saturation are much smaller than along the  $[001]$  direction (about 2.5%). The out-of-plane maximum expansion is about 9%.

falls short of this free expansion due to the adhesion of the metal film to the substrate. The difference is  $\Delta\epsilon_{\parallel}^{\max} = \epsilon_{\text{free}}^{\max} - \epsilon_{\parallel,\text{observed}}^{\max}$ . This difference is a measure of how easily the strain can be relaxed by the formation of dislocations. Setting the strain energy equal to the dislocation energy in equilibrium,  $\Delta\epsilon_{\parallel}^{\max}$  can be expressed in simple terms as [25]

$$\Delta\epsilon_{\parallel}^{\max} = \gamma \frac{a}{D} \ln\left(\frac{D}{a}\right), \quad (1)$$

where  $a$  is the Nb lattice parameter,  $D$  is the Nb film thickness. In classical relaxation theories [25],  $\gamma$  is a dimensionless parameter proportional to the product of the bulk shear moduli of the film and the substrate. In these models, the interfacial shear modulus is assumed to be on the same order as the film/substrate moduli. However, if the adhesion of the film to the substrate is very strong,  $\gamma$  is proportional to the interfacial shear modulus and is therefore an expression for the adhesion of the film to

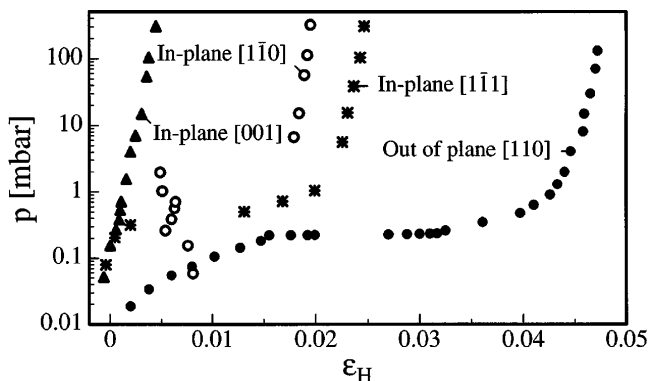


FIG. 4. The relative lattice parameter change of a 527 nm thick Nb(110) film on  $\text{Al}_2\text{O}_3(11\bar{2}0)$  substrate at 473 K is plotted as a function of hydrogen pressure. Along the  $[1\bar{1}0]$  direction the lattice expansion jumps several times with increasing hydrogen concentration.

the substrate. Otherwise, the use of the standard strain relaxation model is justified since the film thicknesses considered here are much larger than the radius of a dislocation core radius [26].

In the out-of-plane direction we observe the free expansion of the Nb lattice due to the hydrogen uptake, superimposed by the Poisson contribution from the in-plane contraction. Here we make a simplifying assumption, using an in-plane strain averaged over all in-plane directions for a hydrogen concentration in saturation. Then we expect a relative out-of-plane expansion given by

$$\begin{aligned} \epsilon_{\perp,\text{observed}}^{\max} &= p \times \Delta\bar{\epsilon}_{\parallel}^{\max} + \epsilon_{\text{free}}^{\max} \\ &= \frac{\lambda}{D} \ln\left(\frac{D}{a}\right) + \epsilon_{\text{free}}^{\max}, \end{aligned} \quad (2)$$

where  $\lambda = p\gamma a$  and  $\epsilon_{\text{free}}^{\max}$  are two fit parameters. The expected elastic or Poisson response can be calculated as follows. The in-plane lattice parameter  $a_{\parallel}$  of the strained layer is given by

$$a_{\parallel} = a_0(1 + \epsilon_{\parallel}), \quad (3)$$

where  $a_0$  is the bulk lattice parameter and  $\epsilon_{\parallel}$  is the in-plane strain. The out-of-plane strain  $\epsilon_{\perp}$  follows from minimizing the total elastic energy and is related to  $\epsilon_{\parallel}$  via [27,28]:

$$\epsilon_{\perp} = p \times \epsilon_{\parallel}, \quad (4)$$

with

$$p = \frac{2C_{44} - 3C_{12} - C_{11}}{2C_{44} + C_{12} + C_{11}}, \quad (5)$$

where  $C_{xy}$  are the bulk bcc elastic constants of Nb. Using for these constants the values  $C_{11} = 2.46 \times 10^{11}$ ,  $C_{12} = 1.34 \times 10^{11}$ , and  $C_{44} = 0.287 \times 10^{11}$  Pa at 300 K [29], we find for  $p = -1.35$ . The solid line in Fig. 2 is a fit of the data points to Eq. (2). The fit is surprisingly good in spite of the simplifying assumptions made. From the free fit parameter  $\lambda$  we have determined the adhesion parameter  $\gamma = 0.47$ , which is very large in comparison. For instance, for Cr(001) on MgO(001)  $\gamma = 0.032$  [30], for heteroepitaxial metal layers such as Cr(110) on Nb(110) the strain relaxation yields a  $\gamma$  factor of 0.056 [28], and for Fe(110) on Mo(110) a  $\gamma$  factor of 0.12 has been obtained [25]. Therefore, the Nb/sapphire interface shows an adhesion which is at least a factor of 10 bigger than for Cr on MgO, and a factor of 4 larger than for metal heterostructures. Furthermore, the average in-plane compressive strain  $\Delta\epsilon$  exceeds by at least a factor of 10 the elastic limit of the bulk metal.

All this shows that the adhesion of Nb(110) on  $\text{Al}_2\text{O}_3(11\bar{2}0)$  substrates is extraordinary. This may have a natural explanation. Gutkunst *et al.* [10] describe the unique Nb/ $\text{Al}_2\text{O}_3$  interface as a *three-dimensional coincidence-site lattice*, for which a strong Nb/sapphire bonding is expected. There is strong evidence that the  $\text{Al}_2\text{O}_3(11\bar{2}0)$  surface is oxygen terminated [31,32]. The orientation of Nb(110) on this surface is such that the Nb

atoms just fill the positions which otherwise would be taken by Al atoms. In these positions the energy gain from hybridization is large, contributing to a strong ionic bond and large strain amplitudes as observed here. The growth of Nb on sapphire as a continuation of the Al positions can then explain the three-dimensional epitaxial relation valid for this metal/ceramic interface [10].

At larger thicknesses of several 100 nm the semicoherent growth of Nb on sapphire breaks down and misfit dislocations are formed [11]. Hydrogen could, in principle, segregate at these dislocations, thus modifying the adhesion properties. However, we have no indication for such an effect to take place here.

In conclusion, we have studied the adhesion between Nb(110) films and  $\text{Al}_2\text{O}_3(11\bar{2}0)$  substrates by hydrogen loading of the Nb films. These experiments clearly show that the lattice expansions in epitaxial Nb films due to hydrogen uptake are strongly anisotropic. While the out-of-plane expansion is free, the in-plane expansion is substantially affected by the clamping or bonding to the substrate. The unusually large clamping effect is an expression of the giant adhesion of niobium on sapphire substrates, which is several times stronger than the metal to metal adhesion and is most likely due to a strong ionic Nb-sapphire bond. If the metal/ceramic bond were predominantly due to image charges, the in-plane expansion would be expected to be more isotropic and discrete relaxational jumps of the lattice parameter should not occur. Vice versa, the strong and anisotropic bonding of Nb(110) on  $\text{Al}_2\text{O}_3(11\bar{2}0)$  substrates hints to specific adsorption sites for the Nb atoms in the first monolayer. If the Nb atoms indeed fill the Al sites thus continuing the Al sublattice, a natural explanation for the unusual but intriguing three-dimensional epitaxy between the Nb and sapphire would be found. Most recent high resolution transmission electron microscopy determination of the Nb/sapphire interface confirms these conclusions [10].

This work was supported by the Bundesministerium für Bildung und Forschung under Contract No. ZA4BC1 and the Human Capital and Mobility program which is gratefully acknowledged.

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