Extraordinary alignment of Nb films with sapphire and the effects of added hydrogen

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We present the results of high-resolution x-ray scattering studies of the structural coherence of niobium [110] films grown by molecular-beam epitaxy on sapphire [11$\bar{2}$0] substrates. In transverse scans of the out-of-plane (110) Bragg peak we find two components, the sharper of which implies mosaicities an order of magnitude better than bulk single-crystal Nb, and transverse structural coherence lengths exceeding 10^4 Å. In addition, we observe that the planes associated with the sharp component are exactly aligned with the sapphire (11$\bar{2}$0) planes. Upon hydrogen loading of the Nb film, we find evidence for a dramatic increase of the lateral coherence length.

It has been shown that Nb thin films with exceptionally high crystal quality can be grown by molecular-beam epitaxy (MBE) methods on sapphire substrates.[1−3] Such metal films approximate the best mosaicity values known for bulk metal single crystals. Moreover, Nb films on sapphire are extensively used as buffer layers for epitaxial growth of other metal films or superlattices.[4] In the technology of high-quality metal thin films the use of buffer layers is as important as in semiconductor epitaxy, and Nb has become a favorite choice. In spite of a number of experimental investigations of the Nb/Al_2O_3 system there are still many open questions concerning the growth mode of Nb on sapphire, the bonding sites of the Nb atoms on the terminating sapphire lattice, the relaxation at the interface as the film grows, etc. Durbin and co-workers[1,2] showed that the Nb film grows with a unique relationship to the sapphire substrate without forming large-angle domain boundaries. In fact, for each of the main sapphire orientations, the A plane or [11$\bar{2}$0] orientation, the R plane or [1$\bar{1}$02] orientation, and the C plane or [0001] orientation, there exists a well-defined epitaxial relation. These relations can be combined into one unique three-dimensional epitaxial relationship between the Nb film and sapphire substrate expressed by[3]

$$[0001]Al_2O_3 \| [111]Nb \text{ and } [10\bar{1}0]Al_2O_3 \| [1\bar{2}1]Nb .$$

It should be noted that the epitaxy of the Nb film to the sapphire substrate is mainly of the orientational type since the lattice-parameter misfits for all three orientations are rather large. Nevertheless, Lamelas, He, and Clarke[5] reported for Nb[110] films on sapphire [11$\bar{2}$0] substrates of a Nb (1×4) in-plane supercell, which would possibly explain the high degree of structural coherence. While *in situ* reflection high-energy electron-diffraction studies during Nb growth appear to indicate that the surface structural coherence increases with film thickness and is rather poor for the first few monolayers,[6,7] high-resolution electron microscopy studies of the final Nb/Al_2O_3 interfacial structure by Mayer and co-workers[3] show a high degree of atomic order already very close to the interface.

All experiments reported in this paper were performed on Nb films with [110] orientation grown by MBE methods on sapphire A planes. The growth conditions

have been reported elsewhere.[1,2,6] For the substrate, polished epitaxial grade sapphire from Union Carbide, with a miscut angle of less than 0.5°, was used. Each sapphire substrate was precleaned and then outgassed at high temperatures before initiating metal growth.

For the x-ray measurements we used two different high-resolution triple-axis diffractometers equipped with flat [111] Si single crystals for both the monochromator and analyzer. Both diffractometers, one with a fixed anode and one with a rotating anode, were operated with $MoK\alpha_1$ radiation. Due to a slightly different geometrical arrangement, the fixed anode diffractometer had a resolution of $\delta Q/Q = 9 \times 10^{-4}$ for longitudinal (radial) scans and an angular resolution of 0.003°, while the rotating anode machine provided a resolution of $\delta Q/Q = 6 \times 10^{-4}$ and 0.002°, respectively. (110) scans were performed in reflection (Bragg) geometry, while in-plane scans were carried out in transmission (Laue) geometry such that the scattering vector lay in the plane of the film.

We present results on two different samples with the following characteristics: Sample I was 3000 Å thick and loaded with hydrogen. Sample II was 950 Å thick. One-half of the latter, II(a), was loaded with hydrogen, and the other half, II(b), was not. We will show that the niobium films may exhibit a very large structural coherence length parallel to the film plane and that this coherence length even increases upon loading with hydrogen. We discuss first features of the x-ray line shapes common to both hydrogen-loaded and pristine films of Nb[110] on sapphire [11$\bar{2}$0]. The second part of the paper deals with the effect of hydrogen on these line shapes.

Figure 1 shows a typical transverse scan of the Nb(110) reflection of sample I. This peak is normal to the surface of the substrate and the transverse scan runs parallel to the surface. (In this paper we use the convention that the z component of the scattering vector, Q_z, is the projection along the film normal. The x direction is perpendicular to z and lies in the film and diffraction plane.) The peak exhibits a two-component line shape with a very narrow component superimposed on a broader contribution, with widths of 0.0050° and 0.085°, respectively.

Very good single crystals of bulk Nb have typical rocking widths of 0.070°,[8] slightly less than the width of
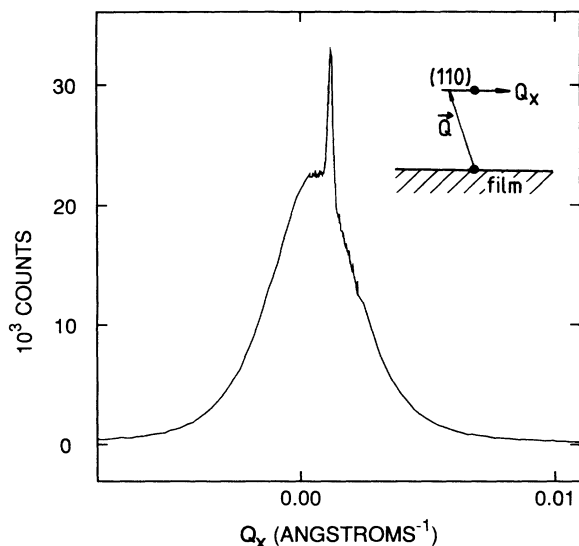
FIG. 1. A transverse scan (rocking curve) of the out-of-plane (110) peak from a 3000-Å-thick, MBE-grown Nb film (sample I) shows two components. Q is the scattering vector. Q_x is the component of the scattering vector parallel to the film. The width of the narrower peak implies an in-plane correlation length of about 29 000 Å.

0.085° of the broader component of sample I. Wolf *et al.*[9] also grew Nb[110] on sapphire [11$\bar{2}$0] and found film-rocking widths of the order of $\frac{1}{10}$ of a degree. However, the sharper peak has a noticeably smaller width than any bulk Nb crystal. We conjecture that the broad peak is due to a "bulklike" portion of the Nb film, while the narrow peak is coupled to the substrate planes. This conjecture is further supported by observations of the nearby sapphire (11$\bar{2}$0) reflection (see Fig. 2). We find that the Nb lattice planes causing the narrow component are

"exactly" lined up with the sapphire planes (to within $< 0.0005°$, small compared to the transverse resolution), while the lattice planes of the broad component are misaligned by 0.015°. In fact, upon rotating the sample about the surface normal the sharp component tracks the (11$\bar{2}$0) substrate peak, while the broad component shows an angle-dependent misalignment.

The transverse scan shown in Fig. 1 is a measure of two film properties: the lateral domain size of the epitaxial film as well as the mosaic distribution among the domains. Usually these two properties are intermixed. Only in the case of very high film quality may the transverse width be taken as a measure of the lateral domain size. This is most likely to be the case for the narrow component in Fig. 1. Interpreting the narrow width of $\delta Q = 2.0 \times 10^{-4}$ Å^{-1} as due to domain size effects (even with mosaic spread we may safely interpret this as a lower bound on the domain size), we obtain a lateral domain size of roughly 29 000 Å.

We took a series of transverse scans (see Fig. 2) at different radial distances in reciprocal space for the sample I. The very sharp and resolution-limited peak at $Q_z = 2.64$ Å^{-1} is due to the sapphire substrate (11$\bar{2}$0) reflection. We fitted each transverse scan of the Nb(110) reflection with two Gaussian line shapes yielding intensity maxima I_b and I_n for the broad and narrow components, respectively. In Fig. 3, the intensities are plotted as a function of Q_z. This is akin to making individual radial scans for each of the two components. In the radial direction the two components exhibit similar line shapes with identical (to within the instrumental resolution) peak widths: The radial width for the narrow and broad components is 0.0035 Å^{-1}, for an out-of-plane correlation length of about 1700 Å. The simplest explanation of this similarity is that both components of the transverse scan
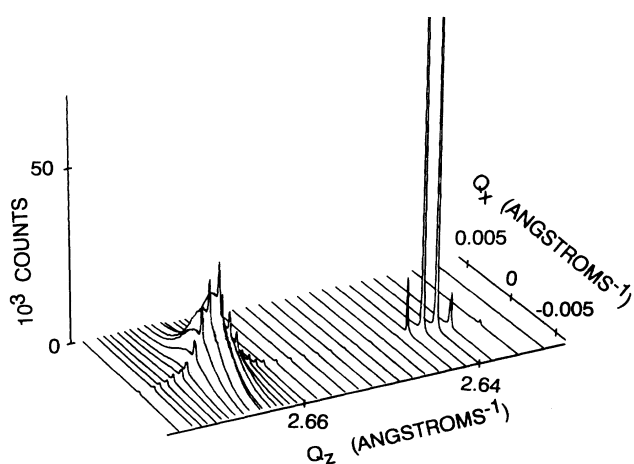

FIG. 2. A series of transverse scans near the Nb(110) peak of Fig. 1 at different radial distances in reciprocal space (Q_z) also shows the sharper sapphire (11$\bar{2}$0) substrate reflection at slightly lower Q_z. We find that the narrow component of the Nb(110) peak is accurately aligned with the substrate reflection (i.e., both peak at the same value of Q_x), while the broader component is misaligned by 0.015°.
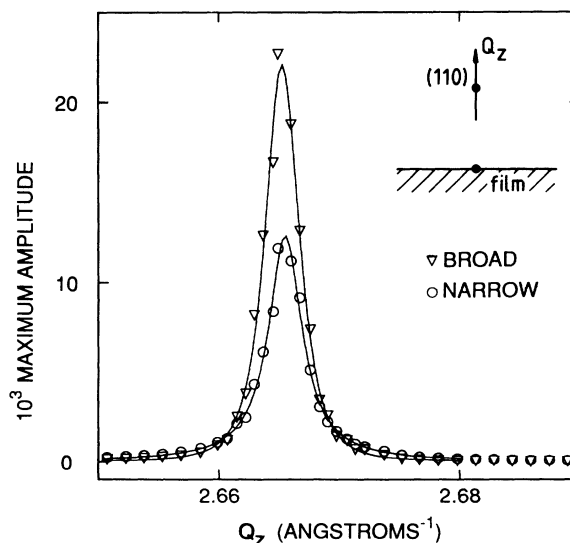

FIG. 3. Amplitudes of the narrow and broad components of the Nb(110) reflection in Fig. 2 shown as a function of Q_z. The identical peak shapes and half-widths lead us to conclude that the two components originate in the same layer of the metal film.

originate from the same layer with the same vertical coherence length. Two-component line shapes have recently been observed for epitaxially grown thin films, for instance, for Co on sapphire,[10] and for ErAs on GaAs.[11] Note in addition that the broad and the narrow components are centered at very nearly the same radial position, implying that they exhibit the same interplanar spacing.

An in-plane correlation length can also be determined directly from the radial width of in-plane Nb reflections. We investigated the two orthogonal ($1\bar{1}0$) and (002) Nb Bragg peaks of sample II(a) in transmission geometry. Both peaks had only a single-component line shape and their widths corresponded to in-plane atomic correlation lengths of 596 and 660 Å, respectively. This is in stark contrast to the implied correlation length from the transverse scan of the (110) out-of-plane peak shown in Fig. 4, which yielded a domain size more than an order of magnitude larger. However, it should be remembered that the two scans compared here do not, in fact, measure the same structural property. By way of example, perfectly aligned and stacked atomic planes of amorphouslike in-plane correlation would yield an out-of-plane Bragg peak due to the regular array of these planes with a transverse peak width inversely proportional to their lateral size. In contrast, an in-plane scan of the same layers would yield an amorphous structure factor but no Bragg peak. In the present less extreme case, we are led to the conclusion that the narrow component of the out-of-plane (110) peak is due to the parallel alignment of the (110) *planes* over a much larger length scale than the positional correlation of the Nb atoms *within* the (110) planes.

We turn now to a discussion of the effect of hydrogen loading on these films. It has recently been shown[12] that

small amounts of hydrogen in epitaxial Nb films lead to a one-dimensional expansion of the Nb lattice: The in-plane lattice parameter remains constant while the lattice expands normal to the film plane in proportion to the concentration of dissolved hydrogen. The limit of stability of the one-dimensional expansion is about $\delta d/d \approx 0.016$, beyond which the Nb film breaks up into incoherent domains.

We have studied the coherence of the Nb lattice planes with hydrogen concentrations well below the stability limit. A 950-Å Nb film, sample II, was cut into two pieces. One of the resulting samples, II(a), was loaded with hydrogen as follows: The sample was mounted in an x-ray transparent vacuum furnace, then gradually heated to a maximum temperature of 260 °C under a hydrogen atmosphere at pressures below 2.5×10^{-4} Torr. The Nb(110) peak was monitored until a shift in lattice parameter of $\delta d/d \approx 0.010$ has taken place. Subsequently, the sample was cooled to room temperature and exposed to the atmosphere.

We scanned the out-of-plane Nb(110) peak in the transverse direction for both the hydrogen-loaded sample II(a) and the reference sample II(b). The results, shown in Fig. 4, indicate a significant narrowing of the sharp component on loading with hydrogen, while the broad component remained unchanged. The width of the narrow component dropped from 7.7×10^{-4} Å^{-1} to a resolution-limited 1.2×10^{-4} Å^{-1}, implying an increase of the lateral coherence length from 8000 to over 40 000 Å.

On integrating the intensities from the broad and narrow components over Q_x and Q_z (collimation is already relaxed in the Q_y direction with our scattering geometry) we found that the narrow component accounted for 7% of the total intensity before loading with hydrogen. After loading, the figure increased slightly to 9%. From this we conclude that the main effect of hydrogen loading is to improve the alignment of the lattice planes of that portion of the Nb film which was already well oriented.

There is striking evidence from electron microscopy studies, in which hydrogen is introduced into stressed bcc metals during direct observation, that the added H causes a very substantial increase in dislocation mobility.[13] Dislocations in static equilibrium under the existing stresses, and inactive dislocation sources, are seen to respond by rapid time evolution as hydrogen is introduced. Recent numerical modeling[14] involving rather general, linear elasticity assumptions indicates that hydrogen shields defects from elastic stress barriers. H acts as a sort of mechanical screen to reduce dislocation interactions in much the same way a dielectric screens the interaction between charges, thereby helping to unblock dislocation tangles and facilitate slip. In the present case the added dislocation mobility presumably helps dislocations to move to interfacial positions that eliminate inhomogeneous strains, thus minimizing the energy, and producing improved alignment between the Nb and sapphire lattice planes. Hydrogen can therefore improve the epitaxial metal film quality by acting as a very effective "cold" annealing agent.

From these experiments we conclude that in epitaxial Nb films, regions exhibiting a very high degree of lattice
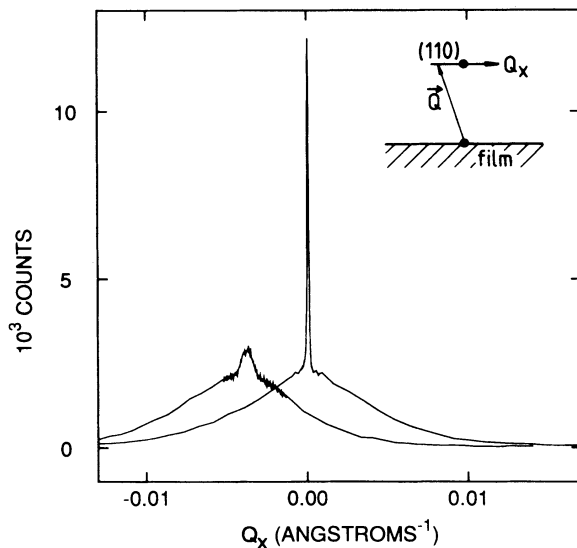

FIG. 4. Transverse scans of the Nb(110) peak of a 950-Å film before [left, sample II(b)] and after [right, sample II(a)] loading with hydrogen show significant narrowing of the already narrow component. One data set is offset along the Q_x axis for clarity. The peak on the right is sharper by at least a factor of 5 and resolution limited.

plane parallelism alternate with regions showing moderate mosaicities ($\sim 0.1°$). In a film 3000 Å thick the well-ordered regions with lateral correlation lengths of 29 000 Å made up a volume fraction of about $\frac{1}{10}$. This narrow line shape is not reproduced in radial scans of in-plane Bragg peaks. We therefore argue that the alignment (flatness) of the lattice planes extends over a larger length scale than the positional correlation of the Nb atoms within the planes. In addition, the high-quality regions of the Nb(110) planes are exactly aligned with the sapphire (11$\bar{2}$0) planes. Hydrogen in the Nb film has the effect of further increasing the lateral domains of the perfectly aligned lattice planes to an extraordinary size above 3×10^4 Å, while the positional correlation of the atoms in the planes remains below 1000 Å.

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