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Determination of the x-ray scattering lineshape from a Nb thin film using synchrotron radiation

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Abstract. Detailed measurements of the x-ray scattering from a 400 Å thin film of Nb grown on sapphire have been performed using synchrotron radiation from a bending magnet. Bragg reflections from Nb planes perpendicular to the surface normal have a two-component lineshape: a sharp, essentially resolution-limited peak, superimposed on a diffuse Lorentzian-squared component. In contrast, Bragg peaks with a finite wavevector transfer in the plane of the film display the broad component only. These measurements indicate that the lattice mismatch between the metallic overlayer and substrate is relieved by the formation of domains randomly rotated in the plane of the film.

1. Introduction

Molecular beam epitaxy (MBE) is being used to produce ever more diverse systems, which now include thin films and superlattices of transition and rare-earth metals. To date, probably the most significant breakthrough that has allowed such systems to be produced was the discovery by Kwo *et al* [1] that Nb can be grown on single-crystal sapphire. Apart from the need to understand the detailed structure of the Nb, so that the growth techniques can be further refined, there are also fundamental questions to be addressed about the nature of the metal–insulator interface, and the mechanisms by which the lattice parameter mismatch is relieved. The structure of niobium thin films grown by MBE on sapphire substrates has been the subject of numerous studies in recent years, including our own recent scattering experiments using x-rays from a rotating anode. In this paper we report further enhancements to our understanding of the structure that have followed from using the higher x-ray flux available from a synchrotron.

The work of Kwo *et al* [1] established that Nb films have a well defined epitaxial relationship to the sapphire substrate which can be summarized as $[0001]_{Al_2O_3} \parallel [111]_{Nb}$ and $[1\bar{1}00]_{Al_2O_3} \parallel [\bar{1}\bar{1}2]_{Nb}$ (figure 1). As emphasized by Reimer *et al* [2], it should be expected that the epitaxy of the Nb films on sapphire is of the orientational type because of a large mismatch between the in-plane lattice parameters. To achieve a better understanding of the Nb structure, high-resolution x-ray scattering studies of Nb thin films using a rotating-anode generator have been performed [2–5]. For films grown on a $[11\bar{2}0]$ sapphire substrate, for which the Nb direction normal to the surface is $[1\bar{1}0]$, our earlier work [3–5] showed that there were several unusual features observed in the scattering for transverse scans through the Nb $1\bar{1}0$ reflection. The most striking of these is that the Nb $1\bar{1}0$ Bragg reflection has a two-component lineshape composed of an extremely narrow component on top of a broad peak.

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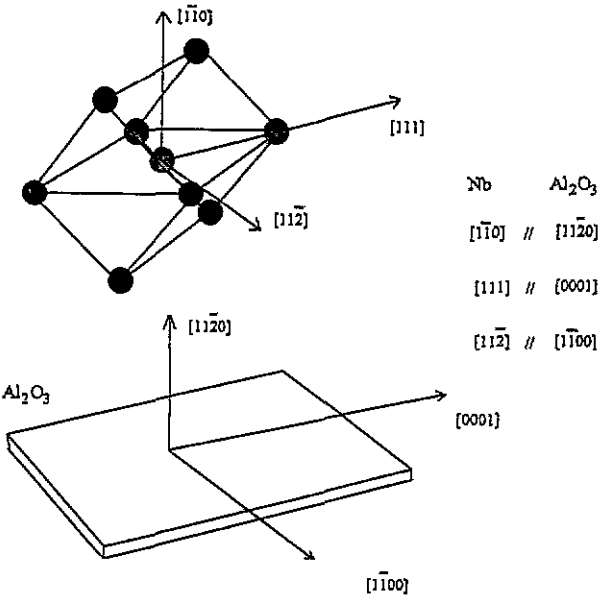

Figure 1. A schematic diagram of the epitaxial relationship between Nb and sapphire for a $11\bar{2}0$ substrate.

An analysis of the lineshape revealed that the broad component has a Lorentzian-squared profile with a correlation length of approximately 75 Å, whereas the narrow component is almost resolution limited, implying a structural coherence in excess of 10 000 Å. The existence of the narrow peak is undoubtedly related to the extreme flatness of the substrate, and hence to the highly parallel Nb planes [2–4]. On the other hand the origin of the broad peak is more problematic, mainly because a detailed study was made of the $1\bar{1}0$ reflection only. Our tentative suggestion based on these measurements was that the broad component arose from the in-plane lattice mismatch between the Nb and sapphire substrate. For films thicker than the critical thickness, this will necessarily produce domain walls defined by misfit dislocations separated by a distance that we estimated to be approximately 100 Å, close to the observed correlation length of 75 Å. We also demonstrated how such domains may produce a Lorentzian-squared component in the scattering.

A third, more subtle feature of the scattering was the observation of a single sharp satellite peak on either side of the Nb $1\bar{1}0$ Bragg peak [3–5]. The presence of a single satellite, with no higher-order harmonics, indicates that there is a sinusoidal modulation of the Nb atoms in the direction normal to the film. The existence of this feature was traced to the presence of terraces on the vicinal surface of the substrate. As there is a mismatch between the lattice spacing of the Nb and the substrate in the growth direction, such terraces will produce a periodic distortion of the Nb, and indeed it was shown that a frozen-phonon model provided an excellent description of the position and intensity of the satellite reflection.

In order to investigate the distortions of Nb on sapphire in more detail, we have performed a synchrotron radiation experiment of the same film used in our previous experiments. We were particularly interested in exploiting the higher flux available from a synchrotron to make more accurate measurements of the lineshape, to study the scattering at higher wavevector transfers, and to look in detail at reflections with a finite wavevector

transfer in the plane of the film.

2. Experimental details

The Nb thin film has a nominal thickness of 400 Å and was grown by MBE using the Balzer UMS630 facility of the Clarendon Laboratory (Oxford, UK). The sapphire substrate of $[11\bar{2}0]$ orientation has a miscut angle of 0.067° in the [0001] zone-axis reflection geometry. The sample preparation was previously described in [3].

The experiments were performed in reflection geometry at the X22B beam line of the National Synchrotron Light Source, Brookhaven National Laboratory. The wavelength was selected from the white beam using a Ge [111] monochromator and was fixed at 1.546 Å. The scattered beam was analysed by reflection on the [111] scattering planes of a flat Ge crystal. The possible Nb reflections that could be accessed in this scattering plane are shown in figure 2.

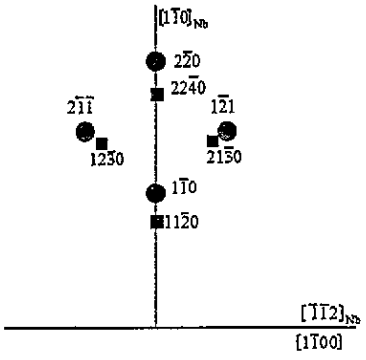

Figure 2. The accessible reflections in the scattering plane corresponding to a Nb 111 zone axis and an x-ray wavelength of 1.54 Å: ●, Nb; ■, sapphire.

3. Results

3.1. Reflectivity measurements

The first part of the experiment was devoted to the basic characterization of the thin film using reflectivity. The sample was not capped, and it had been found that a natural niobium oxide layer is growing slowly as a function of time on the surface. The measurement of the reflectivity curve is an ideal way to characterize the macroscopic properties of the film in the direction normal to its surface, and this was carried out by scanning the wavevector transfer Q along the reflectivity ridge. This was made possible because transverse scans through the ridge showed that the specular component dominated the diffuse scattering. The results are reported in figure 3 and show the presence both of the Nb film (quick oscillations) and of the niobium oxide (slow oscillations) up to $Q \simeq 1$ Å^{-1}. In contrast with our previous report, it was not possible to fit the data with a two-layer model (oxide and Nb) and we have had to introduce four layers to obtain good agreement between the observed and calculated intensities. The additional two layers were located in contact with the sapphire substrate. Thus with time a slow kinetic reaction is probably occurring between the sapphire and Nb. Similar extra layers were also reported by Lee *et al* [6]. The parameters of the fit are reported in table 1.

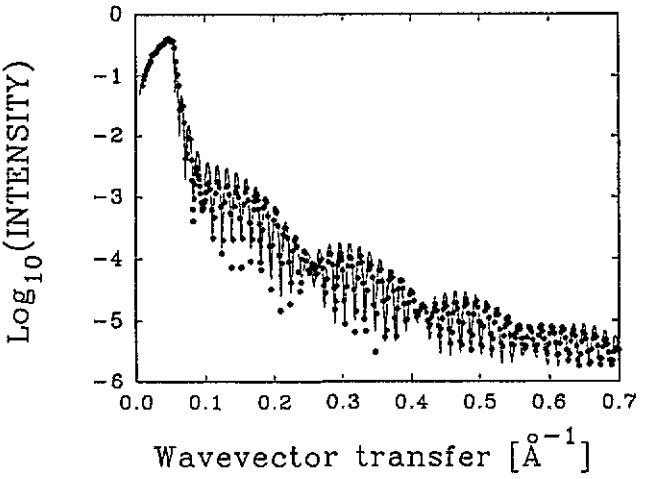

Figure 3. The x-ray reflectivity observed from the 400 Å thin film of Nb on sapphire: ——, the result of a least-squares fit of a scattering model to the data, the parameters of which are given in table 1.

Table 1. Parameters used in the calculation of the reflectivity curve.

	Critical wavevector q_0 (Å^{-1})	Layer roughness σ (Å)	Layer thickness t (Å)
Al_2O_3	0.041(1)	2(1)	
Layer 1	0.036(1)	2(1)	7(2)
Layer 2	0.025(1)	2(1)	3(2)
Nb	0.054(1)	2(1)	403(2)
Nb oxide	0.033(1)		38(2)

3.2. Scattering around the Nb reflections

As mentioned above, the normal to the face of the sample is parallel to the Nb[1$\bar{1}$0] axis. The Nb[$\bar{1}\bar{1}$2] axis was brought into the horizontal plane of the diffractometer to define the scattering plane. Thus the diffraction was performed in the Nb[111] zone axis. The BCC structure of the niobium does not allow many reflections to be accessed in this scattering plane and, working with an x-ray wavelength $\lambda = 1.546$ Å, it was possible to measure the scattering from Nb around the 1$\bar{1}$0, 2$\bar{2}$0, 1$\bar{2}$1 and 2$\bar{1}\bar{1}$ Bragg reflections only. The first two reflections lie along the normal to the face, and the latter two are off-axis reflections with a finite wavevector transfer in the plane of the film. As we were mainly interested in investigating the origin of the two length scales, we have focused our attention on transverse scans through the former group of reflections which are displayed in figure 4.

A comparison of the data taken at 1$\bar{1}$0 (shown in figure 4(a)) with our previous measurements obtained with the rotating anode set-up shows that the higher flux available from a synchrotron enables the lineshape to be measured over at least another two decades of intensity. The qualitative features of the scattering are, however, the same, with the broad and sharp components evident, in addition to the satellite peaks. To check the functional form of the lineshape a least-squares fit of the sum of a Gaussian, to represent the narrow component, and a Lorentzian squared, to represent the diffuse component was performed. The Lorentzian-squared lineshape is written as

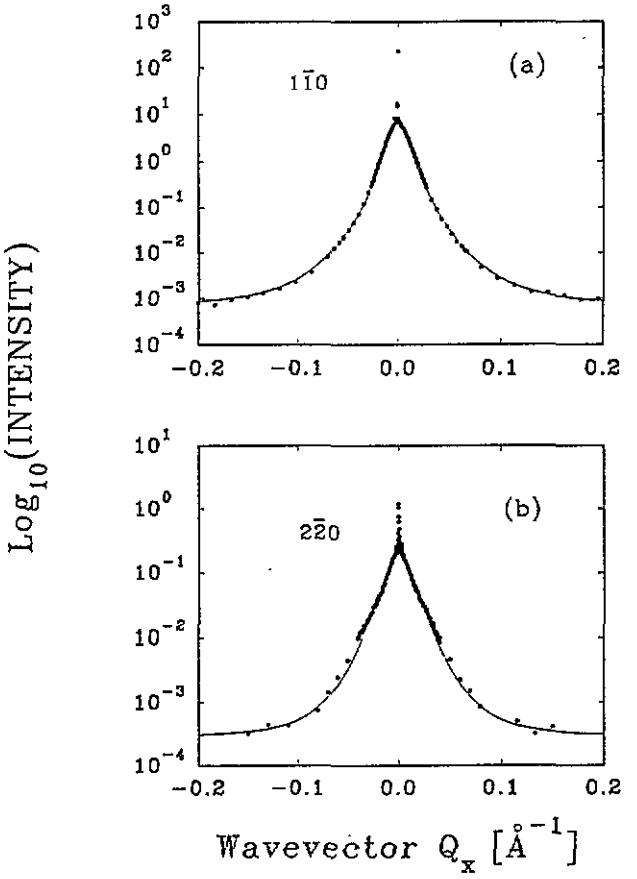

Figure 4. The x-ray scattering observed from the 400 Å thin film of Nb in transverse scans of through the (a) $1\bar{1}0$ and (b) $2\bar{2}0$ on-axis Bragg reflections. For clarity we have shown, as a solid curve, only the least-squares fit of a Lorentzian squared to the diffuse component.

$$I(Q_x) = \frac{A}{(1 + Q_x^2/\kappa^2)^2} \tag{1}$$

and we found that this provided an excellent description of the diffuse component over four decades of intensity, as shown by the solid curve in figure 4(a). In the above expression, Q_x is the wavevector transfer along the Nb[$\bar{1}\bar{1}2$] direction and $\kappa = 1/\xi$ to the inverse correlation length of the Nb atomic displacements. We find a correlation length $\xi = 78(5)$ Å, in agreement with our earlier measurements, and we estimate that the ratio of the integrated intensity of the broad component to that of the narrow component as 3.5. This value shows that the entire Nb film is contributing to the broad diffuse scattering and that only part of the film is responsible for the narrow component. It is also interesting to note, in comparison with the scattering at the $2\bar{2}0$ Nb reflection, that the FWHM of the narrow and broad peaks are 0.000 16 Å^{-1} and 0.017 Å^{-1}, respectively.

With the high flux from the synchrotron, it was possible to measure in detail the transverse scattering at the second-order Nb $2\bar{2}0$ Bragg reflection, as shown in figure 4(b). In this case, we observe broad and narrow components, with accompanying satellites. The narrow peak has broadened in accordance with what is expected for a mosaic spread effect, since doubling the Q position in reciprocal space has produced exactly a doubling of the FWHM of this peak to a value of 0.000 32 Å^{-1}.

The displacement of the satellites from the $2\bar{2}0$ Bragg peak is the same as at the Nb $1\bar{1}0$ reflection, as shown in figure 5. However, the relative intensity of the satellites with respect

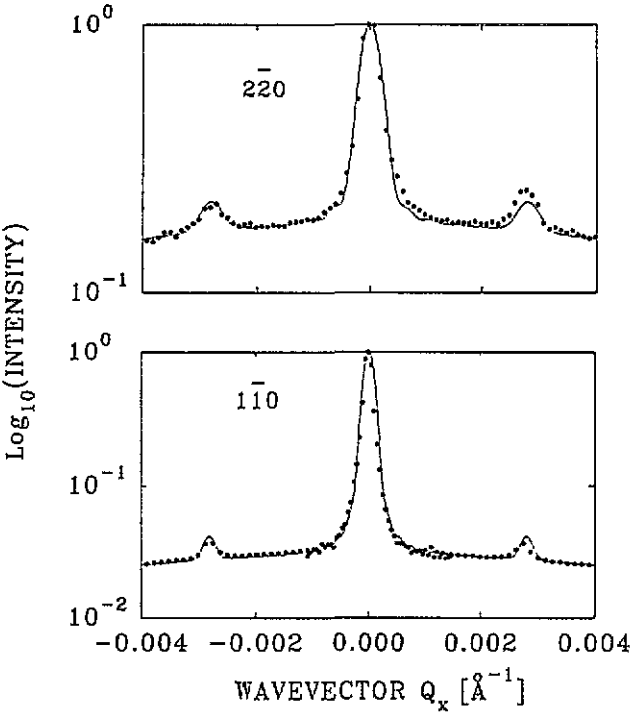

Figure 5. Evidence for the increase in the intensity of the satellites at higher-Q wavevector transfer. Note also the narrow component width has doubled when going from Nb $1\bar{1}0$ to Nb $2\bar{2}0$.

to that of the Bragg peak is much higher than at the Nb $1\bar{1}0$ reflection. This is a good illustration of the validity of the frozen-phonon model for which we expect the intensity of the satellites to increase as $(Q_z u)^2$. The calculation of the peak and satellites intensity can be made via a simple model at the two Bragg positions and allows the determination of the atomic Nb displacement u of the sinusoidal modulation in a direction normal to the face. The on-axis scattering cross section along a transverse direction is given at a Bragg position along Q_z by [5]

$$S(Q_x, Q_z) = \frac{\sin^2(N_1 Q_x a_1/2)}{\sin^2(Q_x a_1/2)} + \frac{Q_z^2 u^2}{4} \frac{\sin^2[N_1(Q_x \pm q_\Lambda)a_1/2]}{\sin^2[(Q_x \pm q_\Lambda)a_1/2]}. \tag{2}$$

The measured intensity is the convolution of the scattering cross-section with the resolution function of the instrument. The results of this calculation in which we have added a diffuse background are shown in figure 5 and led to the following values: $u = 0.09$ Å, $N_1 = 12\,000$ with a terrace length $\Lambda = 1830$ Å. It is important to note that only three parameters are used in this calculation to describe the intensity at two locations of reciprocal space, and that the good agreement between the calculated and observed values supports the picture of the frozen-phonon model.

The lineshape of the broad component of the $2\bar{2}0$ reflection is also Lorentzian squared, but the correlation length determined from a least-squares fit is not $\xi = 53$ Å. This result shows that the width of the broad peak varies as a function of the wavevector transfer Q. However, in contrast with what was found for the Q-dependence of the narrow component,

the increase in the transverse width of the broad component as a function of Q is not consistent with a mosaic spread effect. If that were the case, we should expect a constant angular width, i.e. a doubling of the transverse width in going from $1\bar{1}0$ to the $2\bar{2}0$ reflection. We believe that the correlation length is in fact constant as a function of Q, and that the observed discrepancy might be related to the poor vertical resolution of the instrument, which introduces an effective broadening as Q is increased. Indeed, we have assumed that the vertical resolution was completely relaxed, which is a crude approximation.

It is also worthwhile to compare the relative intensities of the narrow and broad components at this position. In this case we end up with an intensity ratio of 13.4. We thus observe that this ratio is roughly the square of that observed at the $1\bar{1}0$ Bragg position, so that we can infer that the broad component intensity is also related to frozen atomic displacements of the Nb atoms in a direction perpendicular to the face of the sample. We consider that these facts rule out the idea that the broad component is a simple consequence of the mosaic spread and support the picture of atomic displacements induced by a lattice mismatch between Nb and sapphire.

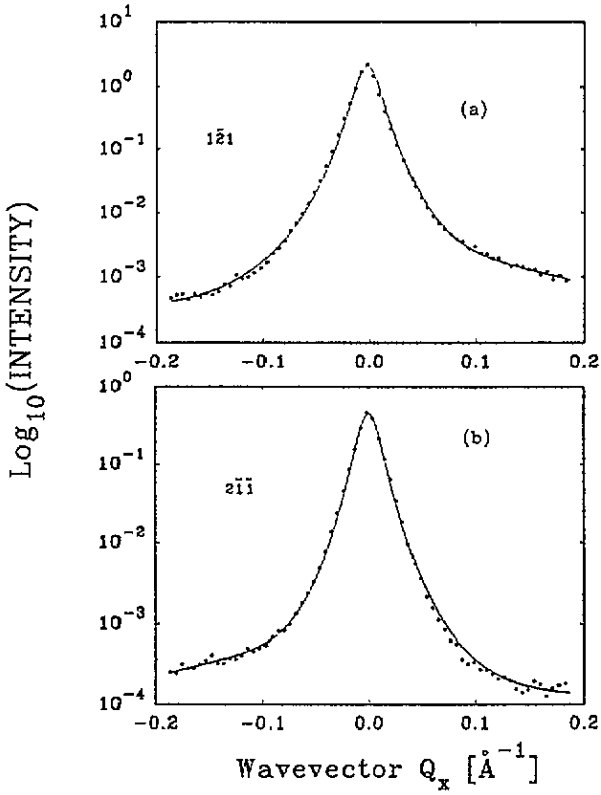

Figure 6. The x-ray scattering observed from the 400 Å thin film of Nb in transverse scans of through the (a) $1\bar{2}1$ and (b) $2\bar{1}\bar{1}$ off-axis Bragg reflections: ——, the results of a least-squares fit of a Lorentzian-squared lineshape to the data.

The results of transverse scans through the symmetry related off-axis Bragg peaks $1\bar{2}1$ and $2\bar{1}\bar{1}$ are shown in figure 6 and exhibit a single component lineshape which can be

associated with the broad component observed at reflections along the growth direction. The lineshape is again well described by a Lorentzian squared, with a correlation length $\xi = 63$ Å. This value is intermediate between the correlation lengths measured at the $1\bar{1}0$ and $2\bar{2}0$ Bragg reflections. A sloping background was introduced into the fits to account for the difference between the intensities on the left- and right-hand sides of the peak (this is probably due to an absorption effect in the sample). The fact that we do not observe the narrow peak in off-axis reflections is similar to what has been observed in a previous transmission experiment [2] and will be considered in the next section.

4. Discussion

For Bragg reflections with a non-zero wavevector transfer in the plane of the film we have shown that the narrow component in the scattering is lost, and only the broad component retained. The observation of a narrow peak in an x-ray scattering experiment is only valid under one of two possible conditions. The first is realized whenever a crystalline solid presents a periodicity in a direction which reproduces itself over a distance so large that the resolution of the instrument prevents its real determination. This is well understood in terms of the Laue function which is given for a one-dimensional problem by

$$I = I_0 \frac{\sin^2(N_1 Q_x a/2)}{\sin^2(Q_x a/2)}. \tag{3}$$

The Laue function approaches a delta function in Q when N_1 tends towards infinity, and a sharp peak in the Q_x direction is observed. The other alternative arises when the electron density of scattering particles can be considered as effectively uniform relatively to the wavevector transfer used in the experiment. In that case, the measured intensity, which is the square of the Fourier transform of the electron density, is a delta function. However, there is a major difference between these two possibilities. In the first case the scattering is periodic with periodicity $2\pi/a$ in all three dimensions (in the cubic assumption), whereas in the second case the scattering is visible only at a zero-wavevector transfer in the direction of the uniform density, as illustrated in figure 7.

Of course the immediate question which arises is the following: when is it possible to consider that the electron density is uniform? The answer is that a uniform electron density never exists at the atomic level. However, the electron density can be considered as uniform whenever a measurement in a certain direction is performed at a wavevector transfer which is close to zero in this direction. This is the typical example of reflectivity measurements which are made at nearly grazing angles of incidence and for which the wavevector transfer is generally from 0.001 to 0.1 Å^{-1}. In this range, the atomic structure of usual crystalline materials ($d < 10$ Å) is not relevant and only on average does a uniform electron density contribute to the scattering. The other alternative for performing scans at small wavevectors, which was used in this study, is to carry out transverse scans at wide angles of diffraction. In that case, if the scattering particles are confined on average in extremely flat atomic planes, the scattering will consist of a narrow Bragg reflection at zero-wavevector transfer in any direction parallel to the surface of the atomic planes. If the particles are randomly distributed in these planes or if they are arranged in small clusters of finite extension, the on-axis reflections will be sharp parallel to the surface and the off-axis reflections will be either absent (in the random case) or enlarged in the case of the clusters.

In thin films of Nb on sapphire, we observe both sharp and broad peaks at zero-wavevector transfer in the direction parallel to the surface and only broad peaks when the

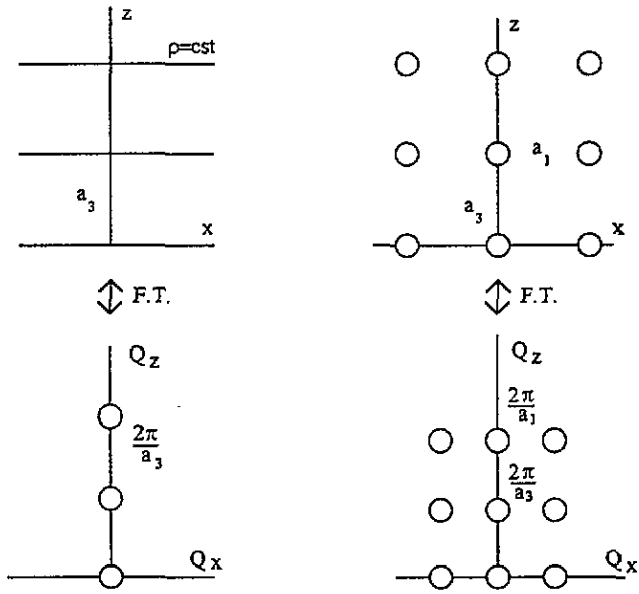

Figure 7. A schematic presentation of two lattices: one with a constant electron density along the x direction and periodic along the z direction, and the other with a double periodicity along x and z, together with their respective Fourier transforms (FT)s.

wavevector in this direction is non-zero. This is a situation intermediate between the two extremes outlined above to explain the presence of a sharp peak. Thus there are domains of Nb, approximately 100 Å across, that maintain a definite epitaxial relationship to each other on this length scale in the plane of the film. Although the atomic planes are flat on average from one domain to the next, out to a distance of order 10 000 Å, there are small random rotations of the domains that result in the loss of the sharp component for off-axis reflections.

The higher flux from the synchrotron has also enabled us to measure the lineshape of the broad component over four decades of intensity at the $1\bar{1}0$ reflection and three decades of intensity at the $2\bar{2}0$ reflection, and to confirm that it is well described by a Lorentzian squared. In our earlier work [3], we showed that the Lorentzian-squared lineshape can be produced by the scattering from a random two-dimensional network of domains, by making a suitable choice of the pair correlation function. In the light of this work, it may now be interesting to investigate whether such a lineshape occurs ubiquitously, or even universally, in the growth of thin films. A partial answer to this question has been given recently by Miceli and Palstrom [7] and by Miceli [8]. In their study of an ErAs thin film deposited on GaAs, they observe very similar scattering features and draw the conclusion that the two-lineshape scattering is due to rotational disorder. They attribute the non-observation of the narrow component in off-axis reflections to the weak adhesion of the film to the substrate and even show that, if the adhesion is enhanced, a narrow peak can be observed in off-axis reflections. However, their data are slightly different from ours since, on the contrary to what we have observed, they show that the *angular width* of the broad component is constant. In addition the diffuse scattering seems to fall off linearly in a semilogarithmic plot, ruling out a Lorentzian-squared lineshape. Another interesting difference is observed; the narrow component is visible only on the first 002 Bragg reflection and is absent at higher orders (004 and 006). Such differences clearly show that it is necessary to study

in detail the relationship between the scattering features and the physical properties of the film deposited on a certain kind of substrate. As shown recently by Sürgers *et al* [9] in their study of Nb on sapphire, it seems that the substrate temperature plays a key role in the observation of the narrow component. More specifically at low temperatures of deposition, the narrow component can even disappear with the simultaneous increase in the width of the diffuse scattering.

5. Summary

In summary, we have performed measurements of the x-ray scattering lineshape from a thin film of Nb on sapphire using synchrotron radiation. From these experiments we have been able to derive a detailed picture of the complex atomic correlations, as viewed on different length scales. On length scales in excess of 10 000 Å the Nb planes parallel to the substrate are on average essentially flat. Periodic sinusoidal distortions of the Nb atoms perpendicular to the planes occur at the edge of the terraces on the sapphire surface. Within one terrace length, the Nb forms domains on a length scale of approximately 100 Å. The size of these domains is primarily determined by the mismatch of lattice parameters between the Nb and substrate in the plane of the film, and this also produces a slight random rotation of domains with respect to their neighbours.

Acknowledgments

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