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LETTER TO THE EDITOR

The structure of epitaxially grown thin films: a study of niobium on sapphire

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Abstract. The x-ray scattering from epitaxially grown films of niobium on sapphire has been measured as the thickness of niobium was varied. For thicknesses d larger than 80 Å, the mean square displacements perpendicular to the growth planes increase as d^x where $x = 0.68 \pm 0.08$, and the correlation length for these displacements increases as d^y with $y = 0.51 \pm 0.05$. A model is put forward to account for these results in terms of the strains when the film thickness is larger than the distance between the misfit dislocations.

The structure of epitaxially grown films is of importance for many areas of technology because of the need to grow material of high crystallographic quality to act as a substrate for devices while keeping the film thickness as small as possible. However, there have been few detailed studies of the way the structure of thin films change with the film thickness. Thin films are usually grown on single crystal substrates for which the lattice parameters are different from those of the material of the film when in its bulk form. This difference gives rise to elastic strains that are relaxed in several different ways. The simplest theory [1, 2] suggests that for films with a thickness less than a certain critical thickness, the structures are coherent and the film strained to the substrate lattice parameter. For thicker films misfit dislocations relax the strain so that both the substrate and the film have lattice parameters close to their respective bulk lattice parameters. Recently, more complex structures involving the formation of islands and of isolated rows have been found when the layer thickness is close to the critical thickness [3, 4]. These have attracted considerable attention because of the possibility of producing nano-structured materials. In this letter we report on measurements of the structure of films which are thicker than the critical thickness, but which still show appreciable strains associated with the lattice mismatch between the substrate and the film. Our results show that the deviations of the crystallographic structure from that of an ideal film change with the film thickness in a way that is not fully understood.

We have studied Nb films [5–7] grown on single crystal sapphire substrates because this system is frequently used as a substrate for metallic films and superlattices. Furthermore, the properties of these films are qualitatively and quantitatively similar to those of other epitaxial films, as we shall describe later. The films were grown by molecular beam epitaxy (MBE) using a Balzers UMS 630 facility in Oxford. Sapphire substrates of (1, 1, −2, 0) orientation ($\pm 0.5^\circ$) were obtained with 'epitaxial finish' on the growth surface. The substrates were

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solvent cleaned, loaded into the growth chamber and annealed under UHV at 800 °C. The substrate continued to be held at a temperature of 800 °C while the niobium was evaporated at a rate of 0.75 Å s^{-1}. The growth was monitored *in situ* by RHEED, and the growth direction of the niobium layer was found to be [110]. Fourteen samples were grown with varying thickness of the Nb layer. The thinner samples were capped with an Y layer so as to prevent oxidation of the Nb layer and to enable a study of how the thickness of the niobium influenced the structure of the Y layer, the results of which will be published elsewhere. The thicker layers were mostly not capped and so became oxidized when removed from the growth chamber. Examination of similar films with electron microscopy show that the films are homogeneous and do not have holes or islands.

We have chosen to use x-ray diffraction techniques because they are non-destructive, and because they can determine the structure on length scales between 1 and 50000 Å. Measurements were performed using high-resolution triple crystal x-ray diffractometers in Oxford and Linköping. Both diffractometers used laboratory sources of Cu K_α x-ray radiation, multiple bounce Ge(111) monochromators and Ge (111) analysers. Measurements, particularly of the thinnest films, were also performed on the X22A beam line at the National Synchrotron Light Source, Brookhaven. A Si(111) monochromator was used to produce an incident x-ray beam with $\lambda = 1.19571$ Å and slits were used to collimate both the incident and scattered beams. For all these experiments the experimental resolution in the scattering plane and transverse to the scattering vector was better than 0.0004 $Å^{-1}$. The resolution perpendicular to the scattering plane was larger and about 0.03 $Å^{-1}$.

Detailed studies were made of the scattering near the Nb (110) and (220) Bragg reflections for which the wavevector transfer, $\boldsymbol{Q}$, is almost parallel to the growth direction. The scattered intensity measures the displacements of the atoms parallel to $\boldsymbol{Q}$ and hence to the growth direction, and the wavevector transfer is given in units of $Å^{-1}$ and in a Cartesian co-ordinate system with the z-axis parallel to the growth direction, the x-axis parallel to the Nb [1, −1, 2] crystallographic direction, and the y-axis perpendicular to the scattering plane. The intensity observed when $\boldsymbol{Q}$ is scanned by varying q along the $[q, 0, \tau]$ trajectory in our coordinate system through the wavevector of the Nb (110) Bragg reflection, i.e. $(0, 0, \tau)$, is shown in figure 1 for three of the samples. The results clearly show that the scattering has two components: a narrow Bragg-like component whose width in wavevector is almost resolution limited and a broader diffuse component substantially wider than the experimental resolution. The existence of these two components has been reported previously [5, 6] for experiments on Nb films, and similar two component profiles have been observed for other systems: ErAs and $In_{0.7}Ga_{0.3}P$ on GaAs [8], AlAs on GaAs and $Si_{0.75}Ge_{0.25}$ on Si [9], $In_{0.1}Ga_{0.9}As$ on GaAs [10] and Co on sapphire [11]. We have also observed two components in the scattering from Y and Cu deposited on Nb on sapphire and these results will be reported in detail elsewhere. We therefore consider that a two component profile is characteristic of many epitaxial systems for which there is a lattice mismatch between the film and the substrate.

The width of the sharp component is only slightly larger than the width of the sapphire reflections. The Nb planes are therefore on average flat over distances of order 50000 Å. This is because the displacements of the niobium planes parallel to the growth direction, u_z, are constrained by the growth on the flat sapphire planes and so correlated over distances for which the sapphire is flat. The fraction of the scattered intensity in the sharp component, R, gives a measure of the square of the displacements of the planes perpendicular to the wavevector transfer. If the displacements are distributed as Gaussian random variables [12, 13], the displacements act in a fashion similar to that of a Debye–Waller factor in crystallography and the fraction of the intensity of the sharp component to that of the total

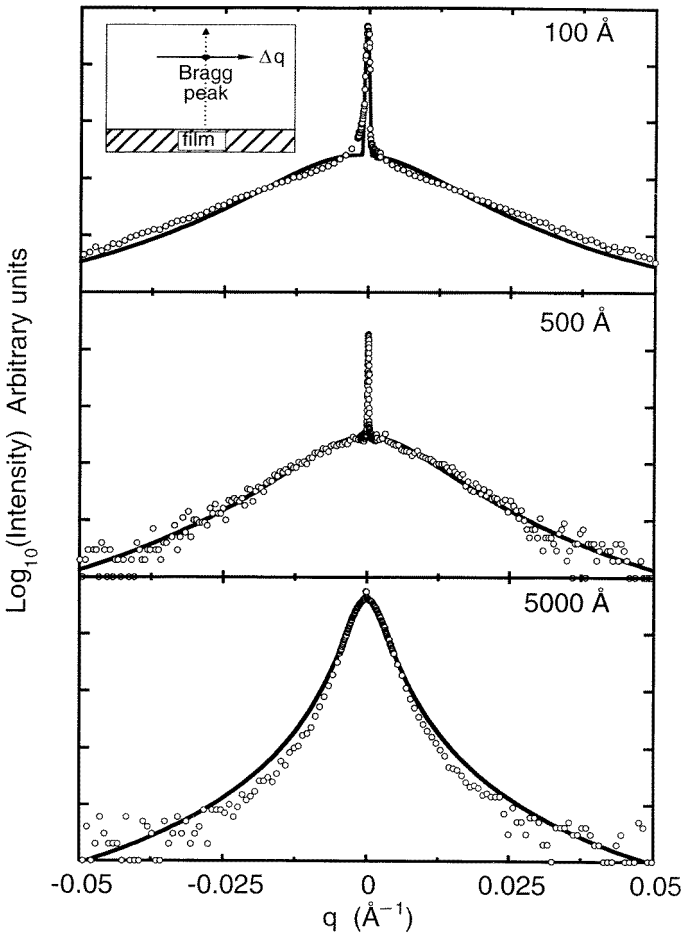

Figure 1. The x-ray scattering from Nb films. The wavevector transfer was varied perpendicular to and through the (110) Bragg reflection. The solid lines show fits to a Gaussian (narrow component) and Lorentzian squared (broad component). The inset indicates the direction of the wavevector scan in reciprocal space.

intensity is

$$R = \exp\left(-Q_z^2\langle u_z^2\rangle\right). \tag{1}$$

Figure 2 shows the values of $\langle u_z^2\rangle$ obtained from the scattering near the (110) and (220) reflections as a function of the thickness of the Nb layer. The mean square displacement increases with the thickness of the layer above about 75 Å. The value of R obtained for the thinnest film, 50 Å, is considerably smaller than the value obtained for the 75 Å and thicker films. We believe that this is because the growth mode of the Nb films changes between 50 Å and 75 Å and so we have not included the data from the 50 Å film in the subsequent analysis. The scatter of the experimental data for the different films is considerably larger than the experimental error in $\langle u_z^2\rangle$. This is possibly because the films have different off-cuts from the crystallographic planes, and because the top of the Nb films are either capped with Y or oxidized. We suspect that the spread of the points reflects the difference in the behaviour of films. A least squares fit of the function $\langle u_z^2\rangle = Ad^x$

was made to the results that were obtained from the scattering near the (110) reflection as shown in figure 2. The results, if d and u_z are expressed in Å, are $x = 0.68 \pm 0.08$ and $A = 0.002 \pm 0.001$ Å^{2-x}. For a 1000 Åfilm, these parameters correspond to mean displacement of $\langle u_z^2 \rangle^{1/2} = 0.47$ Å. The results, figure 2, also show that the $\langle u_z^2 \rangle$ deduced from scattering near the (220) reflection are systematically smaller than those obtained from the (110) reflection. This shows that the displacements are not Gaussian random variables and that the discrepancy is more pronounced for the thicker films as might be expected if the structure is becoming more similar to that of a mosaic crystal [8]

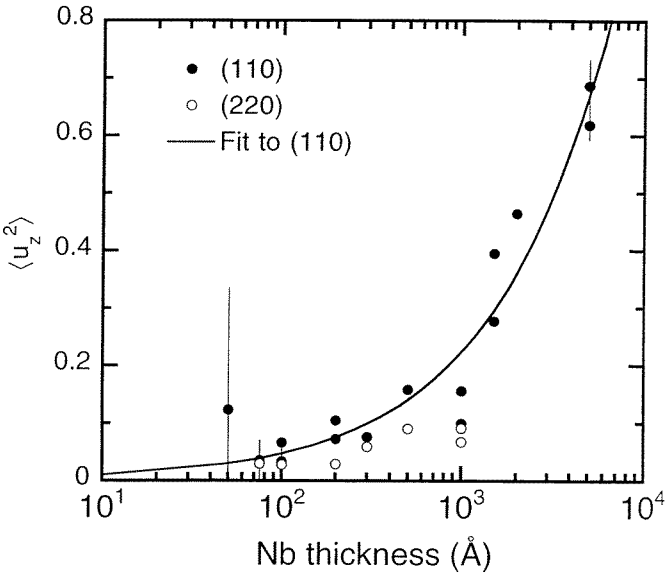

Figure 2. The mean squared displacements $\langle u^2 \rangle$ perpendicular to the growth direction as deduced from the scattering near the (110) Bragg reflection (solid points) and the (220) Bragg reflection (open points) The solid line is a fit to the former data as described in the text.

The broad component of the scattering has been analysed by fitting a variety of functional forms to the observed profiles. A reasonable description was not obtained with either the suggested [13] Gaussian or Lorentzian profiles but was obtained when a Lorentzian squared form was used to describe the results [5]. The values of the inverse correlation length κ, obtained from the fits to the intensity observed near the (110) and (220) Bragg reflections are shown in figure 3 and decrease with increasing film thickness. The results obtained from the film with a thickness of 50 Å differ in behaviour and were again neglected in the subsequent analysis. A least squares fit of the results obtained from the scattering near the (110) reflection, to a power law, $\kappa = ad^{-y}$, gives $a = 0.23 \pm 0.05$ Å^{y-1} and $y = 0.51 \pm 0.05$. The widths of the broad component obtained from the scattering near the (220) reflection are larger than those obtained from the (110) data (figure 3). The ratio varies from about 1.2 for films with a thickness of 100 Å to 1.7 for 2000 Å films. Since the small displacement model gives a ratio of one while a mosaic crystal model gives a ratio of two, the behaviour of the broad component of the scattering is intermediate between that expected for small displacements and a mosaic crystal.

The separation of the misfit dislocations for Nb on sapphire, L, is about 80 Å [2] so that the film thickness, d, is larger or comparable to L for most of the films measured.

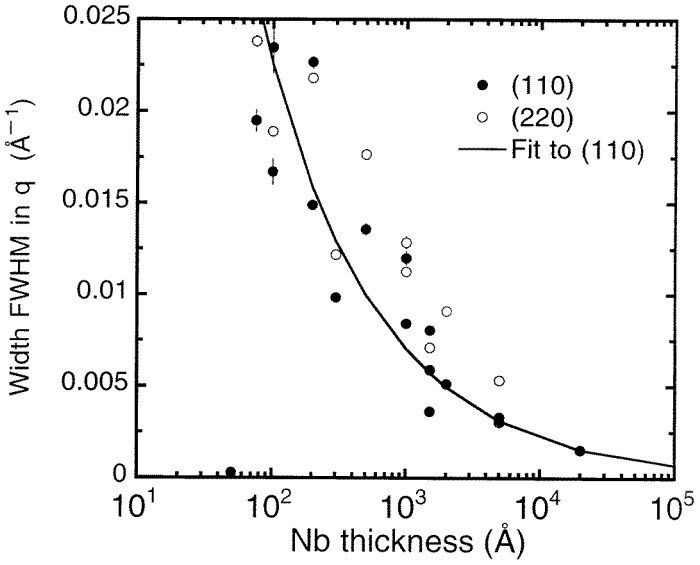

Figure 3. The inverse correlation length, κ, of the Lorentzian squared fit to the broad component for the (110) reflection (solid points) and the (220) reflection (open points). The solid line is a power law fit to the former data as described in the text.

Initially we expected that the width of the broad component of the scattering would be determined by the spacing between the misfit dislocations when the width of the scattering increases with increasing film thickness. The experiments give a decrease with increasing film thickness.

In order to characterize the scattering in more detail, the intensity was measured when the wavevector transfer was scanned along the line $\boldsymbol{Q} = (q_x, 0, \tau + q)$ by varying q with a fixed q_x. The peaks were fitted to Gaussian profiles and the widths are shown in figure 4. For q_x small and corresponding to a length scale larger than d, the widths are largely independent of q_x. The scattering then arises from the whole thickness of the film, as found previously [5, 6]. For larger q_x, the widths increase approximately linearly with q_x, showing that the displacements of u_z with these wavevectors do not propagate through the full thickness of the film.

These results suggest a model to describe the observed scattering. If the film thickness, d, exceeds the mean separation of the misfit dislocations, L, the strain is largely relieved by these dislocations. At the interface between the Nb and the sapphire, the displacements of the Nb atoms perpendicular to the interface, u_z, are small but there is considerable strain in the growth plane and corresponding displacements, u_x. These strains give displacements in the z direction through the equations of elasticity [14]. The displacements in the z direction are then the result of two conflicting effects. Firstly, they increase with the film thickness because they are the product of the strain and the thickness. Secondly, the strains at the interface can be decomposed into Fourier components that propagate into the film as surface waves. For an isotropic medium the surface waves with a wavevector q_x decay perpendicular to the surface as $\exp(-q_x z)$ [14]. Hence if $q_x d > 1$, the surface waves do not propagate through the whole film as shown in figure 4. The model is also qualitatively consistent with κ decreasing as d increases (figure 3), because only those wavevector components with $q_x < 1/d$ contribute to the displacements throughout the film. The increase in the average

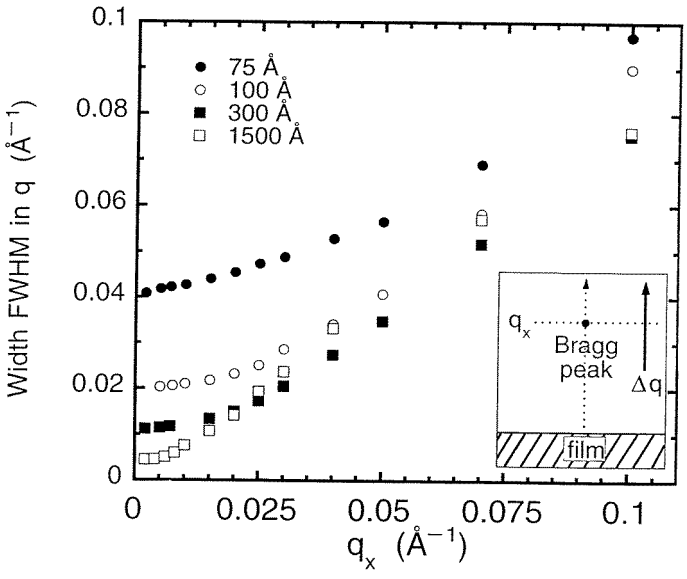

Figure 4. The width of the scattering in wavevector q when the wavevector transfer is scanned along $\{q_x, 0, q + \tau)$ for wavevectors q_x displaced from the (110) Bragg reflection of Nb. The insert indicates the scan direction in reciprocal space.

value of $\langle u_z^2 \rangle$ arises because the displacements with Fourier components smaller than $1/d$ increase with thickness as d^2, while those with larger wavevectors decay exponentially. This leads to an increase in $\langle u_z^2 \rangle$ that is slower than d^2 as shown in figure 2.

This model suggests that the growth planes are on average flat, but that there are displacements from the average position of each plane. As d increases, both the amplitude and the length scale of these displacements increases so that the intensity of the sharp component of the scattering decreases. For large d the film surface becomes flat for length scales less than d. The form of the fluctuations gives rise to a Lorentzian squared profile for which the real space correlation function has the form $(1 + \kappa r) \exp(-\kappa r)$ [5]. We do not have any explanation for this particular form of correlation function except to note that it decays exponentially at large distances and has zero derivative at $r = 0$.

The theory of the scattering from thin films has recently been discussed by Kaganer *et al* [9]. Firstly, they solve for the atomic displacements when the misfit dislocations are present. This involves the introduction of image dislocations so that the boundary conditions are satisfied [9, 15], and the results are dependent both on the details of these boundary conditions and of the structure of the dislocations. We consider, however, that neither of these plays a crucial role in the final results. The second step is to calculate the scattering from the calculated displacements. For the limit with $d \gg L$ they obtain a single Gaussian profile for the scattering with a half width for a scan, similar to those shown in figure 1, given by $0.33Qb(1/dL)^{1/2}$, where b is the Burgers vector of the dislocations. This result is in agreement with the d behaviour found in our experiments, and inserting the appropriate values for Nb gives the numerical factor for the half-width to be 0.31 Å^{-1}, which leads to a half-width approximately twice as large as that of the measured Lorentzian squared. The theory does not give a Lorentzian squared profile possibly because it neglects the correlations in the positions of the dislocations and gives a width that increases linearly with Q whereas experimentally the increase is less rapid. The theory for $d \gg L$ neglects

the sharp component and for $d < L$ it is predicted that $\langle u^2 \rangle$ is proportional to d, whereas experimentally we find a smaller increase. This comparison shows that the theory of Kaganer *et al* [9] does contain many of the essential ingredients of a theory of the structure of thin films but that further work is needed to calculate the scattering more precisely. The calculations need to explain the dependence of the scattering on the film thickness, the Lorentzian squared profile of the broad component of the scattering, and the failure of the Gaussian random variable approximation for $\langle u_z^2 \rangle$. Full details of our measurements of these Nb films and of the Y capping layer will be published elsewhere.

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