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Determination of the lattice parameter and Poisson ratio for AlAs via high-resolution x-ray-diffraction studies of epitaxial films

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We have used high-resolution x-ray-diffraction studies of partially relaxed AlAs films grown on GaAs to determine the lattice parameter [5.661 20(6) Å at 300 K, assuming a GaAs lattice parameter of 5.653 25 Å] and the Poisson ratio [0.328(4)] of AlAs. Our results agree with (but are an order of magnitude more precise than) previous AlAs lattice-parameter measurements but contradict recent results obtained from measurements on $Al_xGa_{1-x}As$ films. Properly reinterpreted, the latter measurements, taken together with our results, imply that the $Al_xGa_{1-x}As$ lattice parameter deviates from Vegard's law.

Precise knowledge of the lattice parameter and Poisson ratio for AlAs and for $Al_xGa_{1-x}As$ is important for quantitative interpretation of x-ray-diffraction spectra of complex structures containing these materials.[1] Bulk AlAs is difficult to grow and is extremely hygroscopic; as a consequence, few studies of this material have been reported. Whitaker[2] and Ettenberg and Paff[3] reported powder-diffraction results for bulk AlAs, the latter as a function of temperature. In principle, high-resolution, double-crystal x-ray-diffraction measurements of epitaxial films are capable of much higher resolution than powder-diffraction measurements on bulk samples since the angular separation between peaks corresponding to diffraction from the epilayer and the substrate can be measured very accurately and since a GaAs capping layer can be used to inhibit reaction of the AlAs film with water vapor. However, interpretation of direct measurements on pseudomorphic AlAs films is complicated by the presence of strain in the epitaxial layer; thus one measures the strained perpendicular lattice parameter rather than the relaxed lattice parameter.

To avoid this difficulty, attempts have been made to determine the lattice parameter and Poisson ratio of AlAs by extrapolating measurements on pseudomorphic $Al_xGa_{1-x}As$ films. Xiong *et al.*[4] conducted high-resolution x-ray-diffraction measurements of pseudomorphic $Al_xGa_{1-x}As$ films and concluded that the perpendicular mismatch is a linear function of the Al mole fraction x. More recently, Goorsky *et al.*[5] and Tanner *et al.*[6] conducted similar measurements and found bowing in the relationship between the perpendicular mismatch and x. By assuming that the lattice parameter and the Poisson ratio are linear functions of x, the authors extracted values of both quantities for AlAs from their measurements. However, their results[5,6] conflict with the earlier results[2,3] for the lattice parameter and yield a value of the Poisson ratio that is low compared with theoretical estimates.[7] These discrepancies are sufficient to significantly affect the interpretation of x-ray-diffraction measurements of multilayer structures such as strained-layer superlattices containing alloys of AlAs.[8]

To reconcile these disparate results, and to firmly establish accurate values for the lattice parameter and Poisson ratio for AlAs, we have conducted a unique experiment in which the relaxation of strain in a series of AlAs films of different thicknesses grown on GaAs substrates by molecular-beam epitaxy is monitored via high-resolution x-ray diffraction. Thus, we can determine the lattice parameter and Poisson ratio to an order of magnitude higher accuracy than previous direct measurements on AlAs. Furthermore, as we show below, we can reconcile our results (and those of other direct measurements on AlAs) with those of Goorsky *et al.*[5] and Tanner *et al.*[6] by allowing for a deviation from Vegard's law (i.e., a bowing) in the $Al_xGa_{1-x}As$ lattice parameter. Vegard's law is generally assumed to hold for semiconductor alloys, yet deviations are well known to the metallurgical community[9] and were established in the (Si,Ge) semiconductor alloy system as early as 1939.[10]

For sufficiently small thicknesses, an AlAs film grown on GaAs is pseudomorphic: the mismatch is completely accommodated by elastic strain, the in-plane components of the lattice parameter match those of the GaAs substrate, and the perpendicular component of the lattice parameter is larger than that of unstrained AlAs by virtue of the Poisson effect. For layers thicker than a certain critical thickness, it is energetically favorable for dislocations to form and for the strain in the film to partially relax.[11] As a consequence, the average parallel lattice parameter increases and the perpendicular lattice parameter decreases so that the Poisson effect is maintained. By measuring both components of the lattice parameter for each of a series of samples with different film thicknesses, we extract precise values for the Poisson ratio and the lattice parameter for AlAs.

The most general distortion of the partially relaxed AlAs crystal lattice can be represented as a superposition of a tetragonal distortion, a monoclinic distortion, and a lattice tilt relative to the cubic[12] GaAs substrate. For an epitaxial AlAs film, the monoclinic distortion and lattice

tilt can occur either as a result of dislocation formation or because of a slight misorientation of the normal to the substrate from the (001) direction.[13] The Poisson effect in the substrate–epitaxial-film system results from the vanishing of the (33) component of stress, σ_{33}, in the growth-axis system. If the misorientation of the normal to the film relative to the (001) crystal direction is small, then one can show that σ_{33} vanishes (to second order in the misorientation angle) in the crystal-axis system also. In the latter system, we obtain from this condition the following:

$$m_\perp = (1+\gamma)m_0 - \gamma m_\parallel \,, \tag{1}$$

where $m_\perp = (a_\perp - a_s)/a_s$ and $m_\parallel = (a_\parallel - a_s)/a_s$ are the perpendicular and *average*[14] parallel mismatches of the film relative to the substrate, $m_0 = (a_0 - a_s)/a_s$ is the mismatch for the relaxed film, $a_\perp$ and $a_\parallel$ are the perpendicular and *average*[14] parallel lattice parameters of the film, a_0 and a_s are the relaxed lattice parameters for AlAs and for the GaAs substrate, respectively, $\gamma = 2\nu/(1-\nu) = 2C_{12}/C_{11}$, ν is the Poisson ratio, and C_{11} and C_{12} are components of the elastic stiffness tensor for AlAs.

To determine $m_\perp$ and $m_\parallel$, measurements were made for the symmetric (004) reflections and for both low- and high-incidence-angle geometries for the four (335)-like asymmetric reflections [i.e., for (335), ($\bar{3}35$), ($\bar{3}\bar{3}5$), and ($3\bar{3}5$) planes] using nearly monochromatic [approximately 12 arc sec full width at half maximum (FWHM)] Cu $K\alpha_1$ radiation obtained from a four-bounce Ge monochromator. For each geometry, the separation, $\Delta\omega$, between the angles of incidence for the AlAs peak and the GaAs substrate peak was determined by fitting each peak with a Gaussian function to determine its line center. For the symmetric (004) reflection, the measurement was repeated with the sample rotated 180°, and the results from both orientations were averaged to eliminate the effects of tilt of the AlAs planes relative to the GaAs planes to obtain $\Delta\theta_{004}$. For the asymmetric (335) reflections, results from the four (nearly) equivalent planes were averaged. It can be shown that this averaging eliminates the effects of nontetragonal deformations and tilt provided terms of second order and higher in these quantities are neglected. The average change in the (335) Bragg angle was calculated from the averaged low (L) and high (H) -incidence-angle measurements as $\Delta\theta_{335} = (\Delta\omega_H + \Delta\omega_L)/2$, and the average change in the angle between the (335) reciprocal lattice vector and the (001) substrate reciprocal lattice vector as $\Delta\phi_{335} = (\Delta\omega_H - \Delta\omega_L)/2$.

From these results, the parallel and perpendicular lattice mismatches can be determined as for a tetragonally distorted film in either of two ways. First, we can calculate the plane spacings for (001) and (335) planes using the appropriate Bragg conditions, suitably modified for refractive-index effects.[15] It is then a simple matter to determine the parallel and perpendicular mismatches from the plane spacings. Second, we can use Eqs. (9) and (10) of Macrander[16] (again, suitably modified for refractive-index effects) to calculate directly the parallel and perpendicular mismatches from the experimentally determined $\Delta\theta_{335}$ and $\Delta\phi_{335}$ data. For both methods of analysis, the error in each angular measurement was assumed to be proportional to the FWHM of the corresponding peak. (We chose the proportionality constant as 0.05; the errors in the derived values for the lattice parameter and the Poisson ratio are independent of this choice.) Errors were propagated in the usual fashion to obtain the errors in each extracted $m_\parallel$ and $m_\perp$, as well as the correlation coefficient between these two quantities (which is nonvanishing since the quantities are extracted from overlapping sets of measurements). This correlation must be accounted for in fitting the results to the straight line, Eq. (1). In performing the fit, the sum of squares of differences between calculated and measured $m_\perp$, with the kth term in the sum weighted by $[\langle \delta m_\perp^{(k)2}\rangle + \gamma^2\langle \delta m_\parallel^{(k)2}\rangle + 2\gamma\langle \delta m_\perp^{(k)}\delta m_\parallel^{(k)}\rangle]^{-1}$, is minimized to determine the unknown quantities m_0 and γ.[17]

Several samples were grown which consisted of a 0.25-μm GaAs buffer on a semi-insulating GaAs substrate, an AlAs layer whose thickness was varied between 0.2 and 8 μm, and a 500-Å GaAs cap. Representative results for the (004) reflection measurements are shown in Fig. 1. For sufficiently thin films, we observed broadening of the AlAs peak arising from the finite-thickness effect and slight shifting of the peak toward the substrate peak arising from interference.[18] (For films 1 μm or greater in thickness, these effects are negligible.) For films whose thickness is greater than the critical thickness, which we find to be about 1.5 μm, additional broadening of the AlAs peak occurs (indicating dislocation formation), accompanied by increasingly greater peak shifts toward the

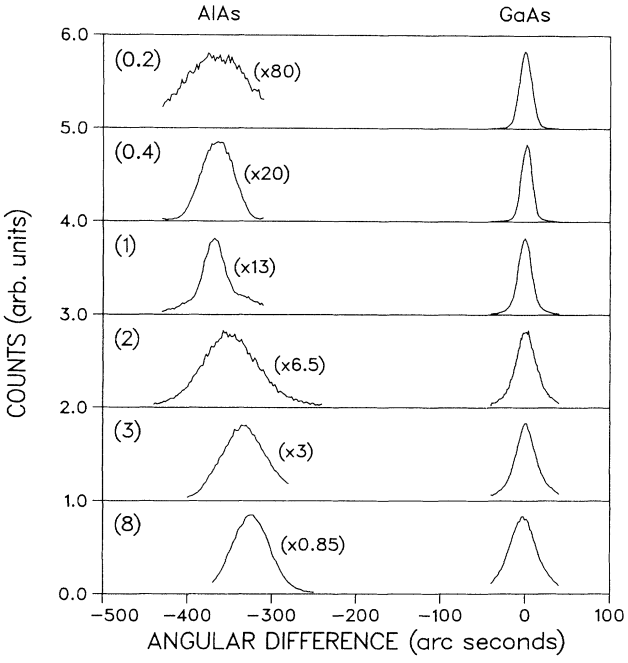

FIG. 1. Representative (004) x-ray-diffraction spectra for AlAs films grown on GaAs, with the corresponding film thicknesses, in μm, indicated in the upper left-hand corner of each spectrum.

substrate peak as the film thickness increases corresponding to increasing strain relaxation. Since the peaks remain well defined even for films much thicker than the critical thickness, these partially relaxed films are suitable for further analysis using Eq. (1).

Nine films were analyzed (one 1 μm thick, two 1.5 μm thick, two 2 μm thick, two 3 μm thick, and two 8 μm thick) using both of the above methods to extract the parallel and perpendicular mismatches. In Fig. 2 we show the results for the mismatches for these samples (from measurements at 296 K), determined using the Bragg angles for the (004) and (335) reflections, together with the best linear least-squares fit. Since for each point the curve of constant error is an ellipse, each point is represented by a cross whose constituent lines are the major and minor axes of the ellipse. (The lines are not parallel to the coordinate axes because of the correlation between the two variables.) Note that even for the 1-μm-thick sample there is a slight amount of strain relaxation ($m_{\parallel} = 0$ for a pseudomorphic film). The critical thickness (at which there is significant strain relaxation) is about 1.5 μm, although it depends to a degree on growth conditions: one 1.5-μm sample is nearly pseudomorphic whereas the other shows considerably more relaxation. Results obtained using Macrander's formalism[16] are nearly identical to those in Fig. 2, although the error ellipses are not as elongated since there is less correlation between $m_{\perp}$ and $m_{\parallel}$ in this method. The combined results of both fits, with errors obtained from the usual statistical methods, are $m_0 = 1.412(11) \times 10^{-3}$ and $\gamma = 0.977(18)$, from which we obtain $\nu = 0.328(4)$. Accounting for thermal expansion in both GaAs and AlAs, we obtain the value $m_0 = 1.407(11) \times 10^{-3}$ at 300 K. The corresponding value for the lattice parameter [assuming $a_s = 5.653\,25$ Å at 300 K (Ref. 19)] is $a_0 = 5.661\,20(6)$ Å.

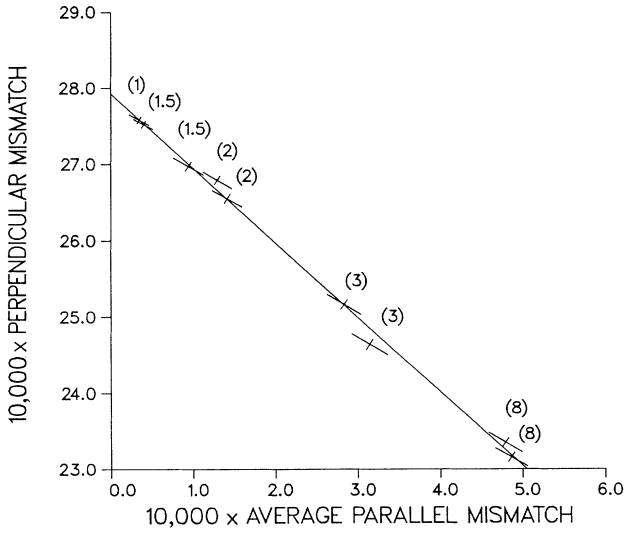

FIG. 2. Parallel and perpendicular mismatches for the measured films analyzed using the (004) and (335) Bragg angles, together with the best least-squares fit to the data. (For a description of the error bars, see text.) The thickness of each film, in μm, is indicated next to the corresponding data point.

The results described above agree with previous direct determinations of a_0; specifically, the result of Ettenberg and Paff,[3] extrapolated to 300 K, is $a_0 = 5.6613(5)$ Å, and that of Whitaker[2] is 5.6611(8) Å, the latter presumably measured at room temperature. Also, from Adachi's estimate[7] of the elastic constants of AlAs, one obtains $\nu = 0.322$. In contrast, the results of the investigations of pseudomorphic $Al_xGa_{1-x}As$ films described above are as follows: Goorsky *et al.*[5] obtain $m_0 = 1.583 \times 10^{-3}$ and $\nu = 0.275$ (no error bars quoted), and Tanner *et al.*[6] obtain $m_0 = 1.600(16) \times 10^{-3}$ and $\nu = 0.28(1)$. The clear conflict between the $Al_xGa_{1-x}As$ results and those obtained here arises, we believe, because of an erroneous assumption concerning the linearity of the lattice parameter for $Al_xGa_{1-x}As$ as a function of x. Since we do not make this assumption and since our results are based on direct measurements of AlAs films rather than extrapolations of results on $Al_xGa_{1-x}As$ films, we regard our results as definitive.[20]

Nevertheless, the results of Goorsky *et al.*[5] and Tanner *et al.*[6] can be reconciled with ours by allowing for a deviation from Vegard's law in the dependence of the $Al_xGa_{1-x}As$ lattice parameter on x.[21] For a pseudomorphic $Al_xGa_{1-x}As$ film, Eq. (1) yields $m_{\perp}(x) = [1+\gamma(x)]m_0(x)$. Taking the derivative of this relationship with respect to x and setting $x = 0$ gives $(dm_0/dx)_{x=0} = 1.584 \times 10^{-3}$, where we have used an average of the data from Refs. 5 and 6 to obtain $(dm_{\perp}/dx)_{x=0}$ and where we have applied the appropriate refractive-index correction. Since $(dm_0/dx)_{x=0}$ is different from $m_0(x = 1)$ as measured in this work, there is clearly bowing in $m_0(x)$ [and therefore in $a_0(x)$]. If we assume quadratic bowing we obtain, at 296 K, $m_0(x) = 1.412 \times 10^{-3}x + 1.72 \times 10^{-4}x(1-x)$. This dependence, together with a linear interpolation of the Poisson ratio (using the value obtained here for AlAs and $\nu = 0.311$ for GaAs), reproduces accurately the calibration curves presented in Refs. 5 and 6. Since the dependences of m_0 and ν on x may be more complex than assumed above, further studies will be needed to clarify these issues.

In conclusion, we have reported the results of a unique experiment that uses high-resolution x-ray-diffraction studies of strain relaxation in AlAs epitaxial films to determine the lattice parameter and Poisson ratio for AlAs. Our results for these quantities are sufficiently precise to significantly improve the interpretation of x-ray-diffraction spectra of complex structures containing AlAs and its alloys.[8] We have shown that previous experiments[5,6] on pseudomorphic $Al_xGa_{1-x}As$ films that claim to produce high-precision values of the AlAs lattice parameter and Poisson ratio were interpreted incorrectly and that our results, combined with the results of Refs. 5 and 6 (properly reinterpreted) show for the first time, to our knowledge, a deviation from Vegard's law in the physically and technologically important $GaAs/Al_xGa_{1-x}As$ alloy system.

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[20] Our results for *pseudomorphic* AlAs agree with those of Refs. 5 and 6; thus we can rule out differing concentrations of impurities in different samples as a cause of these discrepancies.

[21] An alternative reconciliation can be achieved by allowing for a value for the Poisson ratio (0.359) for GaAs that is considerably larger than published values. We do not, however, regard the larger value as reasonable.