

# High Resolution XRD I – Epitaxial film composition

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## INTRODUCTION

This application note discusses how to determine the composition of epitaxial thin films by X-ray diffraction and will focus on the analysis of Al<sub>x</sub>Ga<sub>1-x</sub>As thin films. Since the discovery of X-ray Crystallography in the 1920s, it has been possible to indirectly measure the sizes of atoms. Researchers discovered that atomic radius varies from element to element. This means that when an atom of one element is substituted for a different element in an epitaxial (single-crystal) thin film, there will be a change in lattice parameter. Figure 1 shows this effect for a series of epitaxial Al<sub>x</sub>Ga<sub>1-x</sub>As thin films on GaAs substrates. As the aluminum content in the thin film decreases, the lattice parameter of the layer peak on the left due to the film moves toward the location of the GaAs substrate peak on the right. In principle, this change in lattice parameter can be used to determine the composition of an epitaxial thin film as long as the replacement atoms are substitutional. That is, the replacement atoms must replace other atoms in the actual crystal structure. Interstitial atoms do not significantly change a crystal's lattice parameters.

The expected changes in lattice parameters with atomic substitution are very small. For example, substituting 5% of the gallium atoms in a GaAs thin film with aluminum atoms changes the lattice parameter of the film by only 0.025%. This is too small a change to be detected with conventional X-ray diffraction tools having polychromatic and divergent X-ray sources. Instead, a high-resolution X-ray diffractometer with a monochromatic and parallel X-ray source is required. Figure 2 compares the intensity and resolution of a Si (004) diffraction peak from a silicon single crystal wafer using conventional XRD parafocusing optics with data obtained after adding a channel-cut 2xGe(220) incident-beam monochromator. The peak signal intensity drops 75%, but the resolution improves from 150 arc-seconds (0.0417 degrees) to 32 arc-seconds (0.0089 degrees). The use of a 4xGe(220) incident-beam monochromator or the addition of a 2nd 2xGe(220) diffracted-beam monochromator results in further intensity loss but can achieve peak resolution as low as 8 arc-seconds.

Instrument resolution is not the only relevant factor in measuring epitaxial film composition. Ideally, the elements present should also obey Vegard's Law [1][2]. That is, the change in lattice constant must be a linear function of composition. For example, Vegard's Law for the Al<sub>x</sub>Ga<sub>1-x</sub>As system may be written as:

$$(1) a^0_{AlxGa1-xAs} = a^0_{GaAs} + x(a^0_{AlAs} - a^0_{GaAs})$$

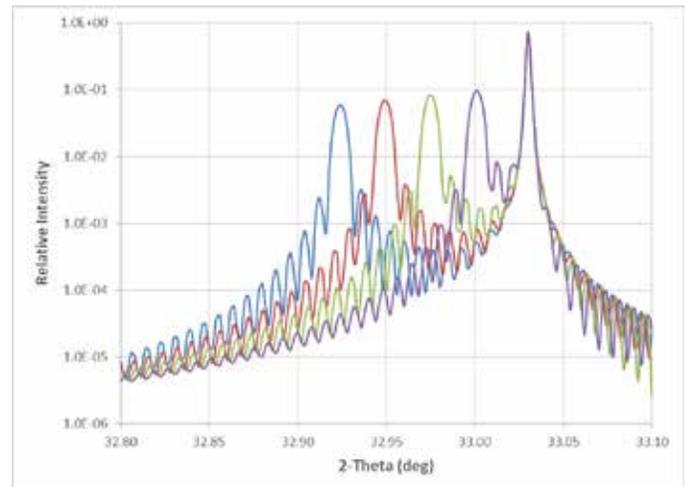


Figure 1 – Simulation showing change in position of (002) layer peak (left) with change in Al<sub>x</sub>Ga<sub>1-x</sub>As composition (Purple- 25% Al, Green - 50% Al, Red - 75% Al, Blue - 100% Al)

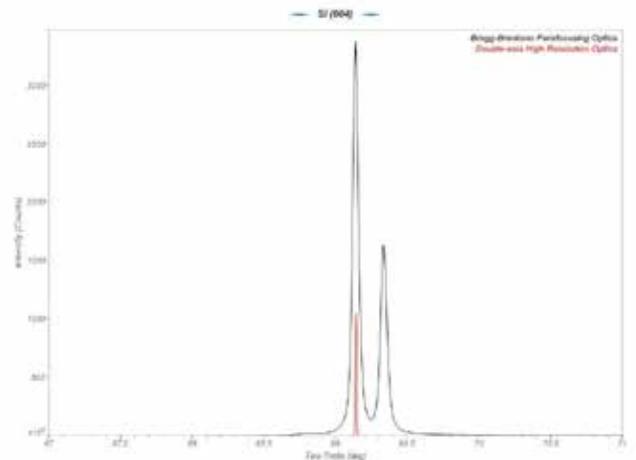


Figure 2: Comparison of Si (004) peak intensity and resolution from a single crystal silicon wafer

where  $a^0_{AlxGa1-xAs}$ ,  $a^0_{GaAs}$  and  $a^0_{AlAs}$  are the strain-free lattice constants for Al<sub>x</sub>Ga<sub>1-x</sub>As, pure GaAs and pure AlAs and x is the Ga concentration. Unfortunately, it was shown by Wasilewski et al [3] and confirmed by Zhou et al [4] that the Al<sub>x</sub>Ga<sub>1-x</sub>As system does not follow Vegard's Law exactly and requires a quadratic correction term. However, if the only variable in the corrected version of Vegard's Law is concentration, film composition may still be determined.

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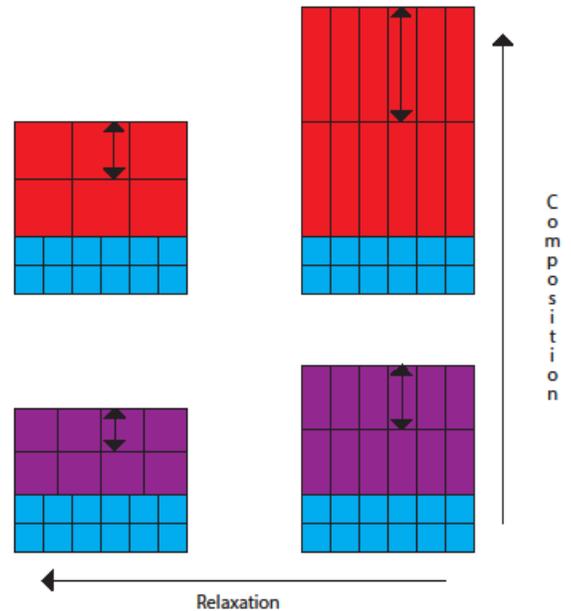
The last complicating factor in determining epitaxial film composition is related to strain and relaxation. Figure 3 shows changes in composition vertically and changes in degree of strain horizontally. Note that in all cases, the arrows, which indicate the d-spacing of a symmetric (crystal planes parallel to the sample surface) reflection change. This means that both composition and degree of strain affect the d-spacing of symmetric reflections. There are two ways of addressing this problem. (i) The first is to report the film composition assuming that the film is either a) fully relaxed or b) completely strained. The direction taken is usually based on the assumption that a film thinner than the critical thickness (the maximum film thickness before a film begins to create dislocations to relieve strain) is fully strained and films thicker than the critical thickness are fully relaxed. The critical thickness depends on both the material system and the film composition (more highly substituted films typically have smaller critical thicknesses). (ii) The second way of addressing the degree of strain is to measure it directly by a reciprocal space map (RSM) of an asymmetric reflection.

The d-spacing of a diffraction peak is the distance from the origin of the unit cell to a particular set of crystallographic planes. Reciprocal space simply plots the inverse of that d-spacing. Figure 4 shows reciprocal space for a (001) oriented GaAs substrate. Each point represents a diffraction peak. Notice that not all GaAs diffraction peaks can be accessed. The X-ray wavelength constrains the peaks that can be accessed near the curved top of the map while the two semicircles at the bottom represent areas where peaks cannot be accessed because either the incident beam or exit beam is below the surface of the sample. Measurement of lattice points close to, but not in the two lower semicircles are particularly surface sensitive because either the incident or exit beam is in grazing incidence.

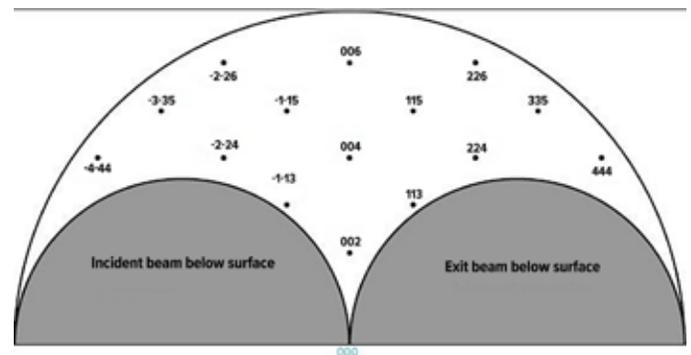
In practice, a reciprocal space map is constructed from a series of coupled Omega:2-Theta (or 2-Theta:Omega) scans acquired with different Omega offsets. Figure 5 shows the component scans making up an RSM near the GaAs (224) reflection. The direction of the Omega:2-Theta scans changes depending on the diffractometer optics but are generally in the direction of the origin while the Omega offsets are perpendicular to this direction. The upper dot is the GaAs (224) and the lower dot shows where the Al<sub>x</sub>Ga<sub>1-x</sub>As peak would be if this layer was fully relaxed. Note that relaxed layer peaks are found along a line between the substrate and the RSM origin while strained peaks will share the same x-axis value as the substrate. This is how the RSM of an asymmetric reflection makes it possible to separate composition and strain.

## EXPERIMENTAL

Four epitaxial thin film samples described in Table 1 were analyzed on a PANalytical X'Pert Pro MRD thin film diffractometer equipped with a copper X-ray tube, 6-axis sample stage, hybrid



**Figure 3 - Effect of change in epitaxial layer composition (red and purple layers) from top to bottom and change in strain from fully relaxed on the left to fully strained on the right, substrate in blue.**



**Figure 4 - Reciprocal space map for a GaAs (001) oriented sample**



**Figure 5 – Expanded view of RSM near GaAs (224) reflection**

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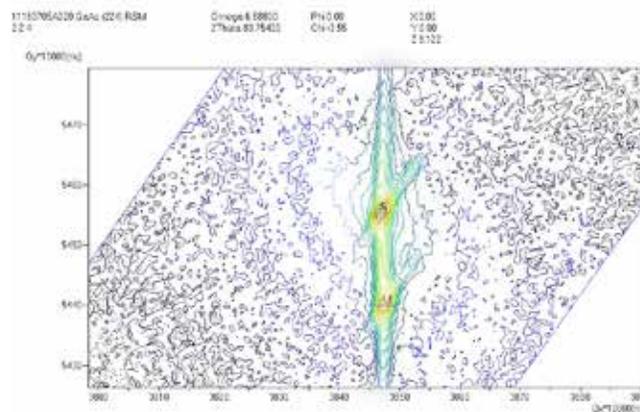
**Table 1 – Nominal sample composition**

Sample ID	Cap Layer	Bulk Layer	Substrate
A	40nm GaAs	680nm AlAs	GaAs
B	40nm GaAs	680nm Al <sub>0.9</sub> Ga <sub>0.1</sub> As	GaAs
C	---	780nm Al <sub>0.5</sub> Ga <sub>0.5</sub> As	GaAs
D	---	680nm Al <sub>0.05</sub> Ga <sub>0.95</sub> As	GaAs

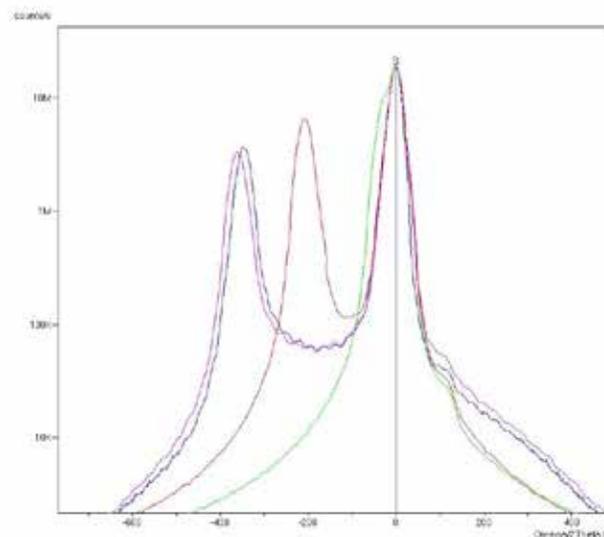
incident-beam monochromator (combination of a parabolic mirror and 2-bounce Ge (220) monochromator) and a gas-proportional detector. A 1mm fixed detector slit was used in symmetrical Omega:2-Theta scans near the GaAs (004) reflection while a 2-bounce Ge (220) diffracted-beam monochromator was used to measure asymmetric RSMs near the GaAs (224) reflection.

## RESULTS

Figure 6 shows the asymmetric RSM acquired near the GaAs (224) reflection for sample A. This sample was chosen because the pure AlAs thin film in this sample has the highest mismatch with respect to the GaAs substrate and should be most likely to show signs of relaxation. The bright area labelled S is the GaAs substrate while the spot below it labelled L1 is the AlAs layer. The diagonal lines through each of these points are beam conditioner streaks that are due to a small amount of Cu K $\alpha$ 2 radiation getting past the 2-bounce Ge (220) crystal in the hybrid incident-beam monochromator. Notice that the AlAs and GaAs spots have identical Qx values. This indicates that the AlAs, despite being much thicker than the critical thickness, is fully strained. This is not too surprising as the lattice mismatch between AlAs and GaAs is only about 0.1%. Similar measurements confirmed that the Al<sub>x</sub>Ga<sub>1-x</sub>As layers in the other three samples were also fully strained.



**Figure 6 - GaAs (224) RSM for 40nm GaAs/680nm AlAs/GaAs substrate sample**



**Figure 7 - Change in position of (002) layer peak (left) with change in Al<sub>x</sub>Ga<sub>1-x</sub>As composition (Green - ~5% Al, Red - ~50% Al, Blue - ~90% Al, Magenta - ~100% Al)**

**Table 2 – Al content of Al<sub>x</sub>Ga<sub>1-x</sub>As layer peak**

Sample	Nominal Al composition (%)	Measured Al composition (%)	Non-Linear Al composition (%)	RBS Al composition (%)
A	100.00	95.69	96.17	100.0
B	90.00	91.69	91.53	93.6
C	50.00	55.36	52.16	49.8
D	5.00	7.52	8.03	3.8

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Figure 7 shows Omega-2:Theta coupled scans acquired on the four samples near the GaAs (004) peak. Substrate offset has been corrected so that the substrate peaks (labelled S in the figure) for the four samples overlap. As expected, the layer peak moves to the left as the Al content of the film increases.

The peaks were profile fit using Gaussian profiles. The Al content was calculated from the peak positions using both Vegard's law and the non-linear correction. Table 2 shows the results. Notice that the non-linear correction makes very little difference at the ends of the composition range but makes a significant difference in the middle of the range. Included for comparison are results on the same samples from RBS (Rutherford Backscattering Spectrometry). Agreement between the two techniques are all within +/- 4% except for Sample D (5% Al). This is likely due to the high degree of peak overlap between the layer and substrate peaks in the HRXRD data.

## CONCLUSIONS

High resolution XRD can accurately determine substitutional elemental composition of epitaxial thin films if it is known whether the solid solution in question obeys Vegard's law and if the degree of relaxation has been measured. This technique is applicable a wide range of semiconductor thin films including group IV (such as SiGe), III-V (such as InGaAs or AlGaIn) and II-VI (such as CdZnTe) semiconductors.

## REFERENCES

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