Extended abstract of a paper presented at CS-MAX, San Jose, CA, November 11–13, 2002
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Composition standards for III-V semiconductor epitaxial films*

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Abstract. NIST is establishing standard reference materials (SRMs) for the calibration of instruments used to measure the chemical composition of epitaxially grown III-V semiconductor thin films. These SRMs are designed for the calibration of measurement systems that measure composition directly, such as electron microprobe analysis (EMPA), x-ray photoemission spectroscopy, and secondary ion mass spectroscopy. The SRMs will also allow greater accuracy in the correlation of optical transitions (from photoluminescence) and film strain (from x-ray rocking curves) with film composition. We are certifying the composition with a rigorous correlation of EMPA, photoluminescence, analytical chemistry measurements on dissolved films, and *in situ* measurements during the film growth using molecular beam epitaxy. Our first release will be $Al_xGa_{1-x}As$ with Al mole fraction near $x = 0.20$ and uncertainty of approximately 0.003.

1. Introduction

The chemical composition of a compound semiconductor thin film is the most important materials parameter in determining how that film will perform in a processed device. Optical transitions, band structure offsets, lattice strain and carrier transport properties are all directly influenced by the film composition. Even in the mature AlGaAs alloy system, however, there is widespread disagreement on how to measure the composition of these films. Interlaboratory comparisons of measurements of Al mole fraction x in $Al_xGa_{1-x}As$ show a spread from 0.24 to 0.34 for nominally identical films[1]. This lack of standardization complicates exchanges of material between vendors and customers by forcing each customer to provide their own reference material. Literature data relating fundamental materials properties to composition are also of limited use for predictive modelling when the composition scale is poorly known. We are addressing this issue by developing standard reference materials (SRMs) that can be used to calibrate a variety of instruments. These SRMs will be certified by a combination of techniques including analytical chemistry methods that have not been previously applied to this problem.

2. Experimental Methods

AlGaAs thin-film specimens for this study were grown by molecular beam epitaxy (MBE). The films were grown at approximately 600 °C at a growth rate of approximately 0.28 nm/s to a total thickness of 3 μm. To avoid excessive oxidation in storage and handling, films with an Al mole fraction greater than 0.70 were capped with a 5 nm layer of GaAs.

There are four principal characterization techniques applied in this study. Prior to each MBE growth run, the growth rate at the substrate from the Al and Ga effusion cells was measured using RHEED intensity oscillations[2]. Tests of the flux stability over time have shown that the Al flux varied by less than 1 % even after twice the typical set-up and growth time for these runs, while the Ga flux typically registered a barely detectible decrease of 1.5 to 2 %. The Al mole fraction was calculated from the equation $a / (a+ g)$, where a is the AlAs growth rate and g is the GaAs growth rate. RHEED uncertainty has been reduced by increased control of the beam position, reduced RHEED substrate size, and direct measurement of flux transients. After growth, the specimens were measured with electron microprobe analysis (EMPA) and photoluminescence (PL). The EMPA measurements employed electron-beam energies of 15 and 20 keV to excite the Al K, the Ga L, and the As K and L x-ray emission lines, and the data were converted to absolute weight percent using the NIST CITZAF method[3, 4]. GaAs and Al_2O_3 were used as reference specimens. PL measurements were made with a calibrated spectrometer and corrected for variations in room temperature. The excitation source for the PL system was a CW Ar^+ laser operating at 2.54 eV (488.0 nm), 0.05 W incident power and peak power intensity on the specimens of 41 W/cm^2. The final method used is inductively coupled plasma optical-emission spectroscopy (ICP-OES), an analytical chemistry technique capable of very high

absolute accuracy[5]. ICP-OES specimens were prepared by dissolving 0.2 to 1 mg of AlGaAs film in a mixture of sulphuric acid, hydrogen peroxide, and water. In order to avoid contamination from the GaAs substrate, the films were transferred first to silicon substrates using the epitaxial lift-off method[6]. The ICP-OES instrument was calibrated for these runs using NIST Spectrometric Solution SRMs (3100 Series), making the ICP-OES results directly traceable to the mole.

3. Results

Comparison of the Al mole fraction determination by multiple techniques is plotted in Fig. 1 for a set of twenty-three specimens covering a broad range of Al mole fraction. It can be seen that the agreement is generally within the uncertainty ranges for the multiple techniques. Uncertainties were determined from the range of values obtained from multiple measurements on the same specimen after correction for known systematic effects; details descriptions will be given in forthcoming publications. Some of the disagreement at high Al mole fraction between the RHEED and the EMPA is attributable to limited experience with correcting the EMPA results for the presence of the GaAs cap. Large discrepancies between the RHEED measurements and the EMPA measurements may also be an indication that the cell flux was less stable than normal, resulting in drift in the composition between the RHEED measurements and film growth. The agreement between RHEED and EMPA can thus be used as a quality-control indicator on SRMs. PL has the highest precision of all three techniques, as indicated by a high degree of reproducibility over multiple measurements on multiple days. PL cannot be used above x = 0.4, however, because the luminescence intensity falls dramatically with the crossover to an indirect band gap at higher Al mole fraction. Changes in the electronic band structure due to doping or strain can also confound the determination of mole fraction from the PL peak energy. PL data on doped specimens are included in Fig. 1 to show how failure to correct for doping-related shifts in the band gap energy will cause false apparent shifts in Al mole fraction.

An expanded view of the region around $x = 0.20$ is given in Fig. 2, with additional data from specimens analyzed with ICP-OES. We see that agreement in this particular region of Al mole fraction is already quite good, and the ICP-OES results confirm that the absolute calibrations of the EMPA and PL are accurate. Analysis of these films against primary standards certified with ICP-OES would improve the accuracy of the EMPA even further. The next step in the development of the SRMs is thus the manufacture of primary standards to be used as reference specimens for EMPA. We have begun growing films on Ge substrates in order to avoid film fracturing during the lift-off process. Because the lift-off process relies on high etch selectivity between the films and pure AlAs, lift-off is also not suitable for films with Al mole fraction greater than 0.4. Primary standards will be certified by dividing the specimen into four 1 cm x 1 cm pieces taken from the center of the wafer and destructively analyzing one of the pieces with ICP-OES. Assessment of the lateral uniformity with PL and EMPA has shown that this center region of the specimens does not vary significantly in composition.

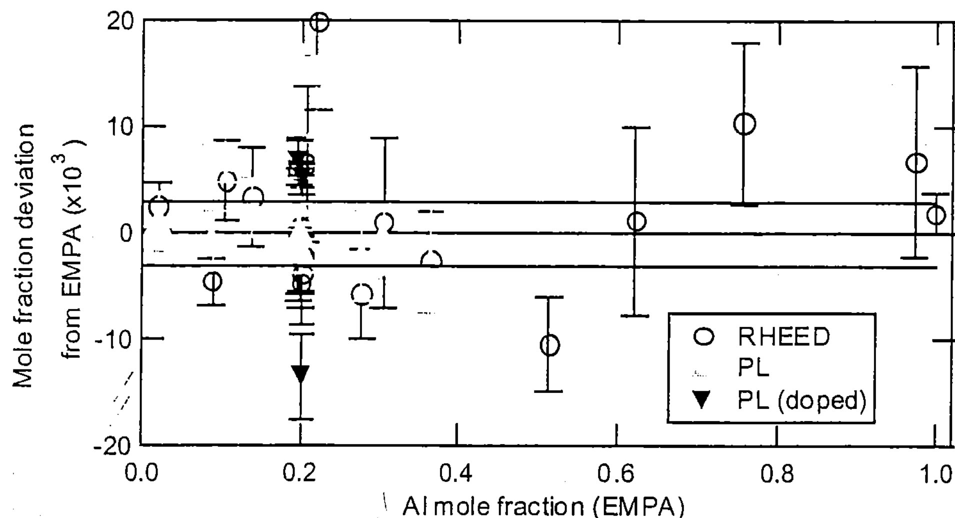

Fig. 1. Al mole fraction as determined by multiple techniques compared to the value obtained using EMPA. The area between the horizontal bars represents agreement to within 0.003 in mole fraction.

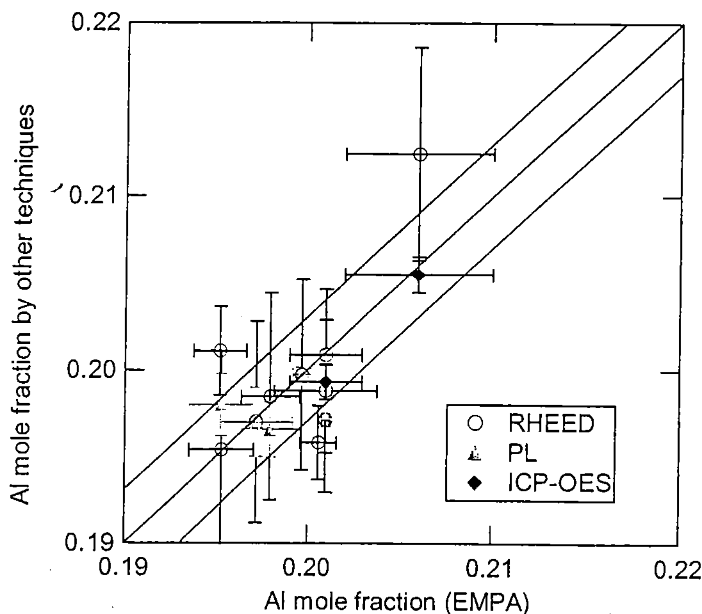

Fig. 2 Comparison of Al mole fraction determination by multiple techniques near x =0.20. The area between the diagonal bars represents agreement to within 0.003 in mole fraction.

Based on the results in Fig. 2, we are proceeding with the development of the first III-V semiconductor composition SRM[7] consisting of an AlGaAs film on a GaAs substrate with the Al mole fraction near $x = 0.20$ and the actual composition certified to an uncertainty of 0.003. Feedback from potential SRM customers is currently being sought concerning the specimen size and packaging.

4. Summary

Comparison of multiple techniques for the determination of Al mole fraction in AlGaAs films has identified RHEED growth rate, EMPA, and PL as reliable, nondestructive methods when properly applied. ICP-OES, a destructive analytical chemistry technique, has been demonstrated as a method for certifying primary reference standards for these films. The correlation of these measurements will be used to certify a family of SRMs consisting of AlGaAs films certified to Al mole fraction uncertainty of 0.003, beginning with mole fraction $x = 0.20$.

5. Acknowledgments

This work was sponsored in part by the Advanced Technology Program, administered by the National Institute of Standards and Technology for the U.S. Department of Commerce.

Footnote

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