

**NIST Special Publication 260-163**  
*Standard Reference Materials 2840 to 2482*

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Standard Reference Materials (SRMs) 2840 to 2842 are semiconductor material artifacts that consist of an epitaxial layer of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  on a GaAs substrate. From the energy at the peak intensity in the photoluminescence (PL) spectrum, the composition of the film is determined to an expanded uncertainty of  $<0.002$ . The recommended storage conditions to minimize oxidation and hydrocarbon contamination are given. Suggestions for use as comparison standards are made for specific analysis methods, including PL, electron microprobe analysis (EMPA), x-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES). Because of variability in substrate lattice parameters, these films cannot be used as an absolute standard for composition determination solely from the angular separation of peaks in x-ray diffraction rocking curves. Further studies on other x-ray diffraction methodologies are underway.

Keywords: aluminum gallium arsenide, AlGaAs, composition, epitaxial films, photoluminescence

### 1. Introduction

There are many semiconductor alloys that can be grown as thin films on substrates, and most compound semiconductor devices are built from these thin films. For example, the materials used to manufacture semiconductor diode lasers, high-efficiency solar cells, high-speed photodetectors, heterojunction bipolar transistors, and light-emitting diodes contain multiple layers of thin films with several different alloy compositions, each layer varying from 10 to 6000 nm thick. The materials properties of these layers, such as the band gap or electron mobility, depend strongly on their chemical composition. The common methods of measuring epitaxial layer composition mostly invert this relationship by determining composition indirectly through measuring some other property of the material. A classic example is the measurement of composition of ternary alloy  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  from the energy of the peak of the photoluminescence (PL) from the layers. Here we use the conventional notation for Al mole fraction  $x$  that considers only the group III elements in the crystal. The PL method is indirect in the sense that it does not attempt to determine composition from Al, Ga, and As signals. X-ray rocking curves measurements of the difference between the lattice parameters in the film and in the substrate are also commonly used to determine Al mole fraction in epitaxial layers.

The correlation between PL peak energy and composition or between x-ray peak shift and composition had to be established by other methods. There were and still are disagreements within the scientific community as to what the correlation coefficients are and how other materials properties depend on composition. Interlaboratory comparisons of epitaxial layer specimens yield variations on the order of  $x = 0.24$  to  $0.34$  for  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  [1]. Another interlaboratory comparison [2] on InGaAsP found a 20 nm range of PL peak wavelength deviations, which is equivalent to a PL peak energy variation of approximately 1.107 eV to 1.127 eV. This variation in PL peak energy in turn corresponds to a possible range for In mole fraction from 0.37 to 0.27, assuming the alloys had constant lattice parameter. These variations are quite large compared with the quality controls needed for optoelectronic device manufacture. Although the underlying sources of the disagreements have not been definitively identified, the most likely causes are the sensitivity of the methods to environmental conditions such as specimen temperature, to non-compositional specimen properties such as doping concentration and strain, and to variability in instrument calibration.

This Standard Reference Material (SRM) is intended to enable alternative methods for high-accuracy composition measurements. A number of analytical chemistry methods, including electron microprobe analysis (EMPA), x-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES), have high precision in composition determination but have insufficient accuracy in the absence of comparison standards with properties similar to the materials to be tested. For example, the elemental sensitivity in most electron or x-ray spectroscopy methods can be influenced by scattering and re-absorption [3] that depend on the composition of the crystal, or by charging and variability in electron escape depth. An epitaxial AlGaAs reference specimen minimizes the corrections needed for these effects and thereby greatly increases the accuracy that can be achieved. Specific suggestions are given as to how to use the SRM as a comparison standard for a variety of analytical techniques. Because NIST cannot monitor individual laboratory practices or instrumentation, it remains the responsibility of the user to establish a comparison methodology and to assess the added uncertainty in those comparisons.

For many applications the SRM may be best used as a vehicle for making secondary reference specimens that are intermediate in properties between the SRM and the typical unknown specimen. For example, if test films must be moderately to heavily doped for manufacturing reasons and the preferred comparison method is PL, the recommended procedure is to grow a secondary reference film with the same doping concentration as the test films and to determine the composition of the secondary reference by comparison to the SRM using a method that is not sensitive to doping level, such as EMPA. The secondary standard can then be used as a PL comparison standard for films that match it closely in doping concentration. Secondary references could also be useful when the test films contain layers that are thinner than the depth sensitivity of the chosen measurement method. In this case, the secondary reference would be compared with the SRM using a method with high surface sensitivity and in situ cleaning capability, such as AES.

## 2. SRM 2840-2842 Description

The artifacts are epitaxial layers of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  grown on GaAs (100) substrates. The Al mole fraction  $x$  is approximately 0.1, 0.2, and 0.3 for SRM numbers 2840, 2841, and 2842, respectively. SRM number 2843 has been reserved for Al mole fraction 0.8; however, the certification methods and storage recommendations are sufficiently different from materials with lower Al mole fraction that a separate publication will be released when those artifacts become available. The mole fraction of the layer is determined from the PL peak energy, typically to an expanded uncertainty of 0.002 as detailed below, supplemented with reflection high-energy electron diffraction (RHEED) measurements of growth rate made at the time the epitaxial layer is grown. As detailed further below, the PL measurements are supported by extensive EMPA and absolute chemical composition measurements with inductively coupled plasma optical emission spectroscopy (ICP-OES). The AlGaAs layer is approximately 3  $\mu\text{m}$  thick. The films are grown with molecular beam epitaxy (MBE) at a growth temperature in the range 575 to 600  $^{\circ}\text{C}$  at a growth rate of approximately 1  $\mu\text{m}/\text{h}$  (0.3 nm/s). The epilayers and substrates are doped with Si to a concentration of 2 to 4  $\times 10^{16} \text{ cm}^{-3}$  and 0.5 to 5  $\times 10^{18} \text{ cm}^{-3}$ , respectively. Before growth of the AlGaAs layer, the substrates undergo a thermal oxide desorption step followed by the growth of a pure GaAs buffer layer between 400 and 500 nm thick.

The central region of each wafer is cleaved into four 1 cm  $\times$  1 cm pieces. These specimens are examined with PL. The PL measurements in early batches made use of thermal grease for mounting the specimens to the optical stage as well as graphite paint to attach a thermocouple to the edge of the specimens. In later batches, only graphite paint was used; tests showed that the laser heating effect was insensitive to mounting conditions. Following the PL measurements, the specimens were cleaned as follows: (1) Soak specimens in hexane. (2) Place specimens face down on clean-room grade, nonwoven cloth and swab back of specimens with methanol using five to six cotton swabs manufactured without glue. (3) Soak in fresh hexane, then acetone, then methanol, then isopropanol. (4) Rinse in deionized water. (5) Blow dry with a filtered nitrogen gun. (6) Place in precleaned polypropylene containers. The procedure for cleaning polypropylene containers is as follows: (1) Place containers in detergent and water mixture and agitate ultrasonically for 10 min. (2) Rinse in running deionized water. (3) Blow off most of the water, and allow to dry completely. (4) Place in acetone and agitate ultrasonically for 10 min. (5) Repeat with isopropanol. (6) Blow dry and store in a clean place.

After cleaning with solvents, the pieces are attached to a stainless steel disk, approximately 2.5 cm in diameter and engraved with the SRM series number and serial number. The pieces are attached with conductive carbon tape obtained from electron microscope suppliers and manufactured with a low-vapor-pressure adhesive. Experiments with silver epoxies designed for vacuum use indicated that the epoxies were unacceptable both due to metallic contamination (Ag, Fe, Cr, Mg, Si) on the specimen surface, detected with time-of-flight secondary-ion mass spectrometry (TOF-SIMS), and due to large, nonuniform strain placed on the specimen, as determined with x-ray diffraction. The mounted SRM is packaged in a clean polypropylene container face down with a spring to hold it steady during shipping. The container is sealed into a Mylar envelope under a nitrogen atmosphere for storage in the SRM office and delivery to the customer.

### 3. Composition Certification and Uncertainty

The primary method used to certify the composition of the AlGaAs epilayer is the correlation of the PL peak energy,  $E_{PL}$ , with Al mole fraction,  $x$ , as determined using the methods detailed in Robins, et al. [4]. This correlation enables more accurate composition measurements with PL than was previously possible because it uses multiple independent methods (EMPA and RHEED) on a large specimen set with rigorous uncertainty analysis. In addition, the correlation equation has been confirmed with a high-accuracy chemical analysis technique, ICP-OES [5]. Typical precision for PL measurements is significantly better than that for EMPA, RHEED and ICP-OES; the accuracy of the  $E_{PL}$  to  $x$  conversion is better than the typical uncertainty in a single EMPA, RHEED or ICP-OES measurement because the determination is improved by averaging over a large number of specimens of differing mole fraction. The best correlation between  $E_{PL}$  and  $x$  was obtained with the equation  $x = S \cdot (E_{PL} - R)$ , where the slope  $S$  is  $0.7134 \text{ eV}^{-1} \pm 0.0046 \text{ eV}^{-1}$  and the intercept  $R$  is  $1.423 \text{ 26 eV} \pm 0.000 \text{ 47 eV}$ . The values for the uncertainties in the previous equation are expanded uncertainties, that is, twice the standard uncertainty [6]. As shown in Table 1, the largest remaining source of uncertainty in the PL composition determination is the uncertainty in the slope value  $S$ . Because it is possible that future work with larger data sets might improve upon this uncertainty, we also provide the PL peak energy  $E_{PL}$  and its uncertainty as an uncertified reference value with the SRM.

A number of experimental factors must be controlled to obtain the highest accuracy with PL, as detailed in Ref. [4]. These include corrections for variations in ambient temperature, wavelength and spectral response calibration of the spectrometer used to measure the PL spectrum, and low laser power density (approximately  $40 \text{ W/cm}^2$ ) with correction for estimates of temperature changes due to laser heating. The specimens themselves must also be lightly doped ( $<5 \times 10^{16} \text{ cm}^{-3}$ ) and uniform in composition. The latter is confirmed by measuring the PL spectrum in 12 locations on each  $1 \text{ cm} \times 1 \text{ cm}$  square. Typical lateral variations correspond to less than 0.0001 standard uncertainty in  $x$ . Uniformity of the layer composition as a function of depth was confirmed with SIMS measurements. SIMS profiles on representative specimens set an upper limit of 1.2 % on the relative variation of the Al mole fraction with film depth. The doping concentration is measured for each growth run using electrochemical cell capacitance-voltage profiling on a region of the wafer adjacent to the SRM specimen pieces. The standard uncertainty in the measurement of the doping level concentration is large (approximately 30 % of the measured value) due to uncertainty in the area measured. We therefore do not report this value on the certificate and instead confirm that our measurements for each wafer fell within the range from  $1 \times 10^{16} \text{ cm}^{-3}$  to  $5 \times 10^{16} \text{ cm}^{-3}$ .

Correction for the true temperature of the excitation region is a major source of uncertainty in  $E_{PL}$  for a well-calibrated PL system. To minimize the uncertainty of this correction, we measure the specimen temperature coefficient of the peak luminescence energy for samples selected from each batch of growth runs and use the measured value of the temperature coefficient rather than a value determined from the empirical models in Ref. [4]. The slope and intercept values in Ref. [4] were calculated for an ambient temperature of  $24.0 \text{ }^\circ\text{C}$ , and the laser heating correction estimated for those experiments was  $1.2 \text{ }^\circ\text{C}$ . Thus the best estimate of the temperature of the specimen excitation volume during the acquisition of the data in Ref. [4] is  $25.2 \text{ }^\circ\text{C}$ . Any changes to the PL specimen mounting or optical excitation conditions require a

reassessment of the laser heating effect. Most of the production SRMs made to date were measured under conditions where laser heating was significantly less than 1.2 °C, and we therefore correct all  $E_{PL}$  data to 25.2 °C excitation volume temperature *including* laser heating effects.

As a secondary quality check on the manufacturing process, RHEED flux measurements [7] are used to estimate the Al mole fraction for the growth runs and monitor the stability of the growth system. The procedures for calculating the uncertainty associated with individual measurements are given in Ref. [7]. In order to enhance the stability of the growth process, the evaporation cells in the MBE machine are maintained at growth temperature during the entire batch production cycle, and growth runs are spaced close together in time. Growth runs occur in between RHEED flux measurements. The Al mole fraction reported for the growth run is the interpolated value for the time corresponding to the center of the run. The standard uncertainty in this mole fraction is calculated by treating any variation in time as a type B uncertainty, with both within-method  $u_w$  and between-method  $u_b$  uncertainty contributions added in quadrature. The equations from which these values are derived are  $u_w = \frac{1}{2} (u_1^2 + u_2^2)^{1/2}$  and  $u_b = |x_1 - x_2| / 2\sqrt{3}$ , where the subscripts 1 and 2 correspond to two sequential RHEED measurements, and the  $u$  variables are the standard uncertainties. The lower limit to uncertainty in RHEED measurements arises from spatial variations in the flux. The contribution of flux variation to composition inhomogeneity is mitigated significantly by substrate rotation at 30 to 60 deg/s during growth of the SRM films. RHEED intensity oscillation measurements cannot be made with substrate rotation, however, due to precession in the substrate rotation axis. We further find that variability in RHEED specimen mounting leads to variability in the noise in the signal from mechanical vibrations, and this contribution to the noise can double or triple the uncertainty relative to its optimal limit. This vibration noise is the primary source of the variability in RHEED uncertainty magnitudes for the different growth runs.

Because the Ga and Al fluxes can change over the course of the runs in a batch, small adjustments in the evaporation cell temperatures are sometimes needed to keep the growth rates and compositions within the desired range. In this case the RHEED data are acquired after the temperature changes, and corrections for the temperature change are applied to the fluxes to use as an endpoint for interpolation for the previous run. The change in the growth rate  $dG$  for small temperature changes  $dT$  is given by  $dG = (0.018 / ^\circ\text{C}) \cdot G \cdot dT$ , where the numerical coefficient is derived from measurements of growth rate when the cell temperature is increased or decreased repeatedly at one or two hour intervals. This interval is long enough to allow the cell flux to equilibrate, while being short enough to avoid drift due to material depletion within the cell.

The resulting mole fraction results are plotted in Fig. 1 along with PL data for the same run set. Data from run numbers B666 and B667 are also listed in Table 2. The results show that all of the SRMs met specifications, that is, the value for  $x_{PL}$  is within the expanded uncertainty range for  $x_{RHEED}$ . The flux correction procedure described above also tends to improve the agreement. The larger discrepancy between  $x_{PL}$  and  $x_{RHEED}$  for the final run is suggestive of a slight decline in Ga flux similar to that seen earlier in the batch set. Unfortunately, RHEED measurements could not be taken after the final run in this set due to equipment failure. The data in Table 2 also reiterate that the largest source of uncertainty in the SRM mole fraction derives from the uncertainty in the slope parameter  $S$  for the  $E_{PL}$  to  $x$  conversion.

#### 4. Storage and Handling Considerations

AlGaAs is a stable chemical compound but is subject to surface contamination and oxidation during storage. Whether or not the surface contamination is of concern depends on the intended use for the SRM, and this issue is discussed further in the next section. We have confirmed that a subset of four specimens with a range of Al mole fractions evidenced the same  $E_{PL}$  within the expanded uncertainty for  $E_{PL}$  over a three-year time span when stored in vacuum. We have studied [8] the effect of various storage conditions on AlGaAs and multilayer AlGaAs/GaAs specimens and concluded that long-term storage in a nitrogen atmosphere or under vacuum is required for stability beyond five years. Incidental exposure to air for transport to or use in an analysis system did not have a strong effect on contamination until such exposure exceeds thousands of hours. Exposure to air does increase the penetration of oxygen into the outer atomic layers of the specimen. Our procedures call for handling the SRM specimens with nonmetallic tweezers because we have seen test specimens acquire low levels of surface metal contamination after handling with steel tweezers. Additional storage studies have also shown that dust particles can collect on specimens handled in ordinary laboratory environments, and these particles typically lead to surface contamination with Na, K, and Ca. Because the dust particles are large, the contamination can persist far beyond the light sputtering recommended for removing surface oxides and hydrocarbon contamination. If the SRMs are being used with an analysis method that is sensitive to dust contamination, they should be stored and handled in moderate clean-room conditions. If recleaning is desired, a deionized water rinse and blow drying should be used. The carbon tape adhesive is soluble in most organic solvents including isopropanol and acetone, and therefore will decompose and contaminate the surface with adhesive and carbon flakes if exposed to organic solvents.

In our storage studies, hydrocarbon contamination appeared to be limited to the outer 3 nm of the surface, and was influenced by the storage container and handling. Silicone gels and oils are particularly to be avoided; hexane is the preferred solvent for removing these compounds and is therefore included in our cleaning procedure. The SRMs are delivered in polypropylene containers that have been cleaned to minimize hydrocarbon contamination. The initial storage studies described in Ref. [8] were performed with unmounted pieces of semiconductor material. In subsequent studies, SRM specimens mounted on a stainless steel disk with carbon adhesive tape were stored for approximately six months in nitrogen and examined with time-of-flight secondary ion mass spectrometry (TOF-SIMS), with conditions similar to those used in Ref. [8]. These experiments confirmed that the cleaning procedure described above reduces the level of hydrocarbon contamination to that found for specimens merely stored in nitrogen or vacuum. Specimens mounted on disks also showed slight contamination with metals such as Fe and Cr; this contamination may arise either from the disk or from the adhesive on the carbon tape. The metals were removed by the same sputtering that removes surface oxides and hydrocarbons, and the metal concentration was below the detection limits for most analytical methods such as XPS and AES.

The semiconductor can be removed from the mounting disk, although the user must have experience in handling GaAs due to the tendency of GaAs to cleave under lateral stress. The specimen should be soaked in acetone until the carbon tape softens, and then the semiconductor can be *gently* separated from the stainless disk. The semiconductor piece will require subsequent

cleaning in organic solvents to remove residual adhesive and carbon flakes. NIST cannot be responsible for specimens broken or contaminated during the removal process.

## 5. Suggestions for Use

The appropriate use of this SRM series depends on the analysis method being used for comparison of the SRM with test specimens. Table 1 in the example SRM certificate (Appendix A) gives an overview of suggestions for the more common analytical methods. Users are expected to be familiar with the limitations and uncertainties in their respective analytical methods.

PL is one of the most common methods of determining composition in AlGaAs films with Al mole fraction less than 0.35. A number of precautions for PL measurements are described in Ref. [4] in order to assure accuracy comparable to the certified value for this SRM. They include frequent wavelength calibration to 0.05 nm expanded uncertainty and accurate specimen temperature measurement (including laser heating effects). Direct comparison of PL data between an SRM and an epilayer specimen of unknown composition also requires that the unknown have a dopant concentration within the same range specified for the SRM. When unknown specimens are moderately to heavily doped, an intermediate reference specimen is needed. The composition of the intermediate reference can be determined through comparison with the SRM using a method that is insensitive to doping concentration, such as EMPA. If the unknown specimen is thinner than approximately 1  $\mu\text{m}$ , the peak PL energy for unknown specimens may also be shifted relative to an SRM of identical alloy composition by quantum confinement effects or self-absorption. Correction for these effects would require careful comparison of thickness and composition with a method that has depth resolution smaller than the layer thickness in the unknown specimen. AES is probably the best candidate for such comparisons, although the uncertainty in the unknown specimen determination is likely to be significantly larger than that for the SRM. The PL peak energy does *not* appear to be affected by the slight surface contamination that occurs under the recommended storage conditions.

X-ray diffraction rocking curves are frequently used as a nondestructive measure of Al mole fraction through quantifying separation between the diffraction peaks arising from the epilayer and substrate. These measurements are significantly less accurate than measurements of the PL peak energy. First, the total x-ray peak separation between AlAs and GaAs is only approximately 0.11 deg. Commercially available x-ray diffraction equipment is typically accurate to only about 0.0005 deg to 0.001 deg, giving a rather large uncertainty in  $x$  of 0.005 to 0.01. Second, the result can be further falsified by impurity concentration changes in the film or the substrate. Bassignana, et al. [9], found variations among GaAs substrates due to boron incorporation that shifted the substrate peak by 0.008 deg, for example. SRM artifacts are not useful in correcting x-ray diffraction data for these specimen differences unless the lattice parameters of the substrates for both the SRM and unknown specimen are measured to a high degree of accuracy. Even when a peak separation can be corrected for impurity shifts more precisely, accurate knowledge of the Poisson ratio and measurement of the degree of partial relaxation in the films is also necessary. Substrate strain and temperature effects may induce peak shifts on the order of 0.0003 deg, which again can be significant relative to the small change in lattice parameter with Al mole fraction.

More recently, Gehrsitz, et al., have published revised values for the Poisson ratio and measured the relaxed lattice parameters for AlGaAs epitaxial films as a function of composition [10], although the paper does not give an estimated uncertainty for Al mole fraction determination based on inverting the correlation. The lattice parameter correlation was based on measurement of several symmetric and asymmetric diffraction peaks from the epitaxial film itself, without reference to the substrate. This method may hold more promise than rocking curve analysis, especially as higher quality x-ray diffraction systems become more common. NIST has not confirmed any of the lattice parameter values or methodologies described in the open literature, however, and until additional tests are made, we cannot recommend this SRM as a high-accuracy reference for composition determinations based on x-ray diffraction. The method based on epilayer-substrate peak separation appears to be particularly problematic, with mole fraction errors of over 0.05 possible unless the lattice parameter variations in GaAs substrates and partial relaxation of epilayer films are accurately taken into account. We are planning follow-up studies to evaluate how the SRM may be employed in x-ray diffraction, especially for users who can derive value from mole fraction determination that is less accurate than the SRM uncertainty.

A number of commonly used analysis methods can be altered by surface contamination. As a general guide, we offer the following usage suggestions. For methods sensitive to oxides and hydrocarbons within the outer 10 nm of the film, a light sputtering to remove the outer layer is recommended for both the reference and test specimens. Auger spectroscopy, x-ray photoemission spectroscopy, and time-of-flight secondary ion mass spectrometry (TOF-SIMS) fall within this category. Sputtering should continue just until oxygen and carbon signals are no longer detectable. The ratio of Al, Ga, and As signals should be monitored during sputtering to confirm that the surface is not becoming selectively depleted of one of these elements. The SRM should be replaced if sputtering the film causes it to visibly roughen or to show signs of selective sputtering. Users are reminded that very few vacuum systems are of sufficient quality to avoid the reoxidation of AlGaAs to monolayer coverage levels within several minutes. Dynamic SIMS, Auger sputter profiling, glow-discharge mass spectrometry, and other methods that inherently include sputtering of the specimen should ignore data from the outer 10 nm of the specimens. An extensive discussion of methods that increase accuracy of Al mole fraction measurement using SIMS has been published by Bassignana et al. [1], who found that they could reproducibly measure Al mole fraction to 0.005. EMPA is generally not sensitive to the degree of contamination found in our SRM storage study because of the large sampling depth of the method for electron beam energies of 15 keV or greater.

Finally, analysis methods vary in their sampling depth sensitivity. The AlGaAs film in the SRM is approximately 3  $\mu\text{m}$  thick so that the signal from most analysis methods is unlikely to include contributions from the GaAs substrate in addition to the contributions from the AlGaAs epilayer. The *unknown* specimens, however, may contain AlGaAs layers that are substantially thinner. For example, in a direct comparison of a 100 nm AlGaAs film on GaAs with an AlGaAs SRM, the ratio of Al to Ga peak areas for XPS would not be the same even if the Al mole fractions were identical in the epilayers. Comparison with a more surface sensitive method would allow calculation of a thickness correction factor, although the reproducibility of the epilayer thickness must also be assessed in evaluating the accuracy of the comparison. It may be necessary to grow thicker layers for calibration of the crystal growth system and rely on the

reproducibility of the growth conditions to estimate the composition of thinner layers. While such a calibration trail will undoubtedly increase the uncertainty in the composition determination, the overall uncertainty is still likely to be less than that in an uncalibrated growth system.

## 6. Certificate

The certificate for SRM 2841 is presented in Appendix A. The certificate includes a certified value for the Al mole fraction for the epilayer and an uncertified reference value for the PL peak energy. Suggestions for storage, handling, and proper disposal are also included.

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Supporting data for the PL peak energy correlation with Al mole fraction were provided by John Armstrong, Ryna Marinenko, Marc Salit, Greg Turk, and Terry Butler of the Chemical Science and Technology Laboratory of NIST. Sally Asher of the National Renewable Energy Laboratory, Golden, CO, provided all the TOF-SIMS analysis and several useful insights on the storage and contamination analysis. Substantial financial support for the development of this SRM was provided by the Advanced Technology Program of the National Institute of Standards and Technology, U.S. Department of Commerce.

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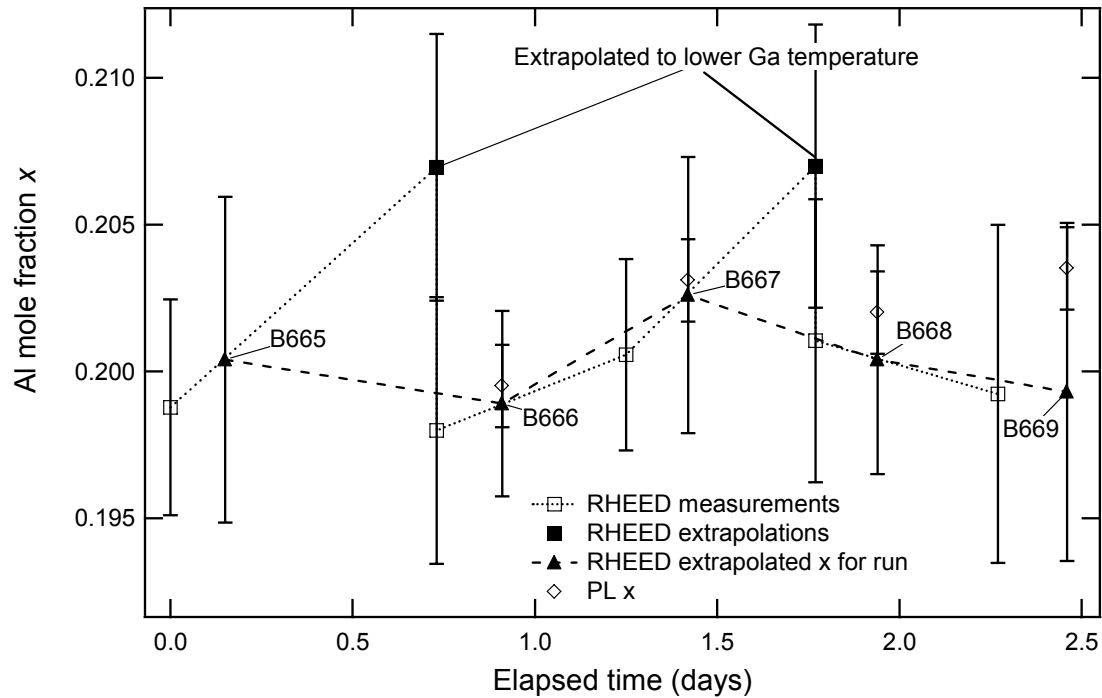


Figure 1. Al mole fraction  $x$  estimate for epilayers as function of time as determined by RHEED and PL for a batch of growth runs from B665 to B669. For two RHEED measurement sets (before B666 and B668), the Ga cell temperature was increased by 2 or 3 °C to increase the Ga flux. Details of the extrapolation procedure are given in the text. Run B665 was not used as an SRM because of low doping concentration. Error bars correspond to the expanded uncertainty.

Table 1. Uncertainty budget for PL determinations of Al mole fraction. With the exception of the final row, this table shows standard uncertainties. Uncertainty types A and B correspond to random and systematic error sources; see Ref. [6] for further information.

Contributing factor	Unc. type	Calculation details	Typical $\sigma$ values for $x = 0.20$	Contribution to $\sigma_x$	Typical contribution to $\sigma_x$
Sample inhomogeneity	A	from sampling 12 pts across specimen	0.000 05 – 0.000 2		< 0.000 15
Wavelength uncertainty of monochromator	A	$0.025 \text{ nm} \cdot E_{\text{PL}}^2 / 1239.5 \text{ nm} \cdot \text{eV}$	0.000 06		< 0.000 043
Temperature measurement uncertainty	A	$(E_{\text{PL}} - R)/dT \cdot \sigma_T$ ; $\sigma_T = 0.31 \text{ K}$	0.000 16		< 0.000 12
Subtotal: $\sigma_E$ , combined uncertainty in $E_{\text{PL}}$			0.000 26	$S \cdot \sigma_E$	< 0.000 20
$\sigma_S$ , uncertainty in slope $S = dE/dx$	B	$0.0023 \text{ eV}^{-1}$		$(E-R) \cdot \sigma_S$	0.000 65
$\sigma_R$ , uncertainty in intercept $R$ ( $E$ at $x = 0$ )	B	$0.000235 \text{ eV}$		$S \cdot \sigma_R$	0.000 17
Combined standard uncertainty, $\sigma_x$					0.000 7
Combined expanded uncertainty ( $k=2$ , 95 % confidence interval), $2 \cdot \sigma_x$					0.001 4

Table 2. Compositions and expanded uncertainties for representative samples from two growth runs. The RHEED mole fraction for growth run number B666 was  $0.1989 \pm 0.0032$ , and for B667 was  $0.2026 \pm 0.0047$ . Most of the uncertainty in  $x$  arises from the slope uncertainty  $2\sigma_S$ , as can be seen by comparing the slope contribution column  $2 \cdot (E-R) \cdot \sigma_S$  with the column for the total expanded uncertainty for  $x$ .

No.	$E$ (eV)	$x$	$2 \cdot (E-R) \cdot \sigma_S$	Exp. uncert. for $x$
B666A	1.70282	0.1994	0.00133	0.00136
B666B	1.70293	0.1995	0.00133	0.00136
B666C	1.70279	0.1994	0.00133	0.00137
B666D	1.70284	0.1995	0.00133	0.00137
B667A	1.70799	0.2031	0.00135	0.00138
B667B	1.70794	0.2031	0.00135	0.00138
B667C	1.70786	0.2030	0.00135	0.00138
B667D	1.70795	0.2031	0.00135	0.00139



# National Institute of Standards & Technology

## Certificate of Analysis

### Standard Reference Material<sup>®</sup> 2841

#### Semiconductor Thin Film: Al<sub>x</sub>Ga<sub>1-x</sub>As Epitaxial Layers

(Al mole fraction  $x$  near 0.20)

Serial Number:

This Standard Reference Material (SRM) is intended for use as a reference standard for analytical methods that measure the composition of thin films, such as electron microprobe analysis (EMPA), photoluminescence (PL), auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). SRM 2841 consists of an epitaxial layer of Al<sub>x</sub>Ga<sub>1-x</sub>As with certified Al mole fraction  $x$  grown on a GaAs substrate. Each unit of SRM 2841 is sealed in a Mylar envelop containing a nitrogen atmosphere. Proper use of the SRM as a comparison standard depends on the analytical method (see "Measurement Conditions and Procedures" and NIST Special Publication 260-163 [1]).

**Certified Value:** A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST [2]. The certified value for the Al, expressed as mole fraction, is provided in Table 1. The certified value is based on a confirmed correlation between Al mole fraction and the energy of the peak intensity in the PL spectrum of the film [3,4]. The uncertainty of the certified value is an expanded uncertainty ( $k=2$ ) intended to approximate a 95 % level of confidence [5]. Two additional quality checks were performed on each SRM unit. First, the molecular beam epitaxy growth system was monitored during the growth of the specimen. For acceptance as an SRM, the Al mole fraction determined from the intensity oscillations of reflection high energy electron diffraction for each unit had to agree with the certified value above within its expanded uncertainty. Second, the free carrier concentration of the film had to be between  $1 \cdot 10^{16} \text{ cm}^{-3}$  and  $5 \cdot 10^{16} \text{ cm}^{-3}$ .

Table 1. Certified Value (mole fraction) for Aluminum in SRM 2841

Aluminum: 0.1980    0.0014

**Reference Photoluminescence Peak Energy Value:** A NIST reference value is a noncertified value that is the best estimate of the true value based on a available data; however, the value does not meet the NIST criteria for certification [2] and is provided with associated uncertainties that may reflect only measurement reproducibility, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods. The reference value and expanded uncertainty ( $k=2$ ) for the energy of the peak intensity of the PL spectrum for this SRM composition value is provided in Table 2. The value has been corrected to a excitation volume temperature equivalent of 25.2 °C including a laser heating correction of 0.1 °C above ambient.

**Expiration of Certificate:** If stored as described in "Storage and Handling," the AlGaAs composition will remain stable for until at least June 30, 2011. Contact NIST for certificate renewal information. Surface oxidation and contamination will increase through use and storage of the specimen. For applications that are sensitive to surface contamination, the SRM and unknown specimens will require *in situ* cleaning, typically light sputtering. The SRM should be replaced if sputtering the film causes it to visibly roughen or to show signs of selective sputtering.

**Maintenance of SRM Value Assignment:** NIST will monitor this SRM over the period of its value assignment. If substantive technical changes occur that affect the value assignment before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Kent Rochford, Chief  
Optoelectronics Division

Gaithersburg, MD 20899  
Certificate Issue Date: 18 April 2006

Robert L. Watters, Jr., Chief  
Measurement Services Division

The overall direction and coordination of the technical work required for certification of this SRM lot were performed by K.A. Bertness of the NIST Optoelectronics Division.

Consultation on the statistical design of the experimental work and evaluation of the data were provided by C.-M. Wang of the NIST Statistical Engineering Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Table 2. Reference Value (energy value) for the Peak Intensity of the PL spectrum of SRM 2841

PL Spectrum: 1.70077 eV    0.00042 eV

## NOTICE AND WARNING TO USERS

**Note:** The GaAs substrate and the AlGaAs layer, along with arsenic and its oxides are hazardous. See MSDS 2841 for hazards information.

**Storage and Handling:** AlGaAs is a stable chemical compound but the film is subject to surface contamination and oxidation during storage and handling. The SRM should be stored in a dust-free, nitrogen atmosphere or under vacuum at temperatures below 50 °C. Incidental exposure to air for transport to or use in an analysis system was not seen to produce significant contamination until such exposure exceeds thousands of hours. The SRM should be handled by the metal mounting disk with clean, nonmetallic tweezers, without contacting the semiconductor region. Particulate contamination of the semiconductor surface may be removed with deionized water or dry nitrogen flow, and users must confirm that additional contamination has not been introduced. The adhesive tape used to mount the semiconductor to the stainless steel disk is soluble in isopropanol, acetone and other organic solvents, and use of those solvents could result in adhesive or tape particles migrating to the specimen surface. Extreme edges of the specimen surface should be excluded from analysis.

## INSTRUCTIONS FOR USE

**Measurement Conditions and Procedures:** Analytical methods vary in their sensitivity to materials properties unrelated to the film composition. A list of potential complications is provided in Table 3. More detailed discussion is contained in reference [1].

Table 3. Potential confounding factors in comparisons between SRM 2841 and AlGaAs test films of unknown composition. Glow discharge mass spectrometry (GDS) and secondary ion mass spectrometry (SIMS), both conventional and time-of-flight SIMS (TOF-SIMS) are included.

Method	Comments on comparison measurements
PL	Wavelength calibration, low doping concentration, and specimen temperature correction required. Thin layers may display quantum confinement energy shifts [3].
X-ray rocking curves	Not recommended for high accuracy comparisons.
AES, XPS, TOF-SIMS	Surface oxides and hydrocarbons alter results; remove surface contamination by sputtering both SRM film and test film. Monitor for selective sputtering. Sampling depth may be an issue for thin test films.
SIMS, GDS	Ignore data points from outer 10 nm of film. Monitor for selective sputtering, development of surface topography, and matrix effects.
EMPA	Compare films of similar thickness or of uniform composition over sampling depths.

## REFERENCES

- [1] K.A. Bertness; T.E. Harvey; C.-M. Wang; A.J. Paul; L.H. Robins; *Composition Standards for AlGaAs Epitaxial Layers*; SP 260-163; U.S. Government Printing Office: Gaithersburg, MD (2006)
- [2] May, W.; Parris, R.; Beck, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136; U.S. Government Printing Office: Gaithersburg, MD (2000); available at [http://www.cstl.nist.gov/nist839/NIST\\_special\\_publications.htm](http://www.cstl.nist.gov/nist839/NIST_special_publications.htm).
- [3] L.H.; Robins; J.T. Armstrong; R.B. Marinenko; A.J. Paul; J.G.; Pellegrino; K.A. Bertness; J. Appl. Phys., Vol 93, pp 3747–3759 (2003).
- [4] K.A. Bertness; C.M. Wang; M.L. Salit; G.C. Turk; T.A. Butler; A.J. Paul; L.H. Robins; *High-accuracy Epitaxial AlGaAs Composition Determination with Inductively Coupled Plasma Optical Emission Spectroscopy*; J. Vac. Sci. Technol.; B, 24 (2), pp 762-767 (2006).
- [5] ISO; *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, 1st ed.; International Organization for Standardization: Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at <http://physics.nist.gov/Pubs/>.

*Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail [srminfo@nist.gov](mailto:srminfo@nist.gov); or via the Internet at <http://www.nist.gov/srm>.*

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## *Periodical*

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