Benchtop Electrochemical Growth and Controlled Alloying of Polycrystalline In$_x$Ga$_{1-x}$As Thin Films

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**ABSTRACT:** Compared to Si, GaAs offers unique material advantages such as high carrier mobility and energy conversion efficiency, making GaAs a leading competitor to replace Si on several technological fronts related to optoelectronics and solar energy conversion. Alloying the GaAs lattice with elemental In allows the direct bandgap of the resulting ternary alloy to be tuned across the near-infrared (NIR) region of the electromagnetic spectrum from ~0.9 to 3.5 μm. However, methods of fabricating high-quality crystalline GaAs are currently limited by their high cost and low throughput relative to Si growth methods, suggesting the need for alternative low-cost routes to GaAs growth and alloying. This research documents the first instance in the literature of the electrodeposition and controlled alloying of polycrystalline In$_x$Ga$_{1-x}$As films at ambient pressure and near-room temperature using the electrochemical liquid–liquid–solid (ec-LLS) process. X-ray diffraction and Raman spectroscopy support the polycrystalline growth of (111)-oriented In$_x$Ga$_{1-x}$As films. Consistent redshifts of the GaAs-like TO peaks were observed in the Raman data as the In composition of the liquid metal electrode was increased. Optical bandgaps, determined via diffuse reflectance measurements, displayed a consistent decrease with the increase in the In composition of In$_x$Ga$_{1-x}$As films. While Raman, diffuse reflectance, and energy-dispersive X-ray spectroscopy data support controlled alloying efforts, all techniques suggest an overall decrease of the In/Ga ratios present in deposited films relative to those of the liquid metal electrodes. These results lend support for the continued development of ec-LLS as a viable method of achieving crystalline growth and alloying of binary and ternary semiconductor material systems using a benchtop setup under ambient pressure and near-room temperature.

**1. INTRODUCTION**

While silicon (Si) remains the most widely used semiconductor across the microelectronics industry, III–V semiconductor materials are fundamental to many optical, electronic, and energy conversion applications. Among these materials, gallium arsenide (GaAs) has become a leading competitor of Si on several scientific fronts due to its advantageous material properties such as high carrier mobility, small dielectric constant, large absorption coefficient, and record-setting solar energy conversion efficiencies. These characteristics support the extensive utilization of GaAs across a wide range of applications, including photovoltaics, high-frequency and high-speed electronics, and infrared emission and detection. With a direct bandgap of 1.42 eV at room temperature, the GaAs lattice can be alloyed with indium (In) atoms to form In$_x$Ga$_{1-x}$As, which offers a broader range of wavelength-detection capabilities. Increasing the In composition of the ternary alloy provides tunability across the near-infrared (NIR) region of the electromagnetic spectrum to a minimum value of 0.354 eV at 300 K. This optical tunability allows extended applications related to infrared optics and laser materials. However, methods of achieving the growth of high-quality crystalline GaAs are currently not cost-competitive...
due to their higher production costs and lower throughput relative to Si growth methods. Thus, the development of alternative low-cost routes to GaAs growth is required to meet the growing needs of the optoelectronics industry.15

Currently, established deposition processes for growing high-quality crystalline GaAs and InGaAs include molecular beam epitaxy (MBE), organometallic vapor-phase epitaxy (OMVPE), liquid-phase epitaxy (LPE), and other methods that require high-cost and high-energy growth setups and the use of toxic precursors, ultrahigh vacuum, and extreme temperatures during growth.16−19 Conventional electrodeposition is an alternative growth method that eliminates the necessity of high-cost experimental setups, hazardous precursors, or extreme pressures but faces other obstacles that lead to impurity contamination from the electrolyte solution and amorphous growth without subsequent annealing at temperatures above 250 °C.21−23 The growth method implemented in this research is known as the electrochemical liquid−liquid−solid (ec-LLS) process, which overcomes obstacles to crystalline growth typically faced by electrochemical methods by utilizing a liquid metal electrode of a select composition to perform the electroreduction of compounds in solution and serve as a platform for semiconductor growth.24 Several recent studies have shown evidence of the ec-LLS growth of crystalline semiconductor thin films achieved at ambient pressure and near-room temperature via benchtop growth setups.24−28

Fahrenkrug et al. first demonstrated the ec-LLS growth of crystalline GaAs at temperatures ≥90 °C,25 and recent work from our group displayed the first instance of the ec-LLS growth and alloying of a ternary semiconductor system via the selective modification of the elemental composition of the liquid metal electrode.29 Further investigation of this method’s alloying and doping capabilities is crucial to provide extended support for ec-LLS as a viable means of fabricating optical-quality semiconductor films. This research posits that ec-LLS methodologies can be implemented to controlably alloyed crystalline InGaAs thin films through the selective modification of the elemental composition of the liquid metal working electrode (WE). By varying the In/Ga mass ratio of the WE, InGaAs thin films of desired In compositions were deposited and analyzed to determine their crystal quality and degree of In alloying using various characterization techniques. X-ray diffraction (XRD) and Raman spectroscopy were performed to probe the chemical identity, crystal quality, and vibrational modes of as-grown samples. In addition, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and absorption spectroscopy were used to characterize deposited thin films in terms of surface morphology, elemental composition, and optical bandgap, respectively.

2. EXPERIMENTAL DETAILS

2.1. Materials. Gallium bulk metal (99.99%) and indium pellets (99.9999%) used in the composition of the liquid metal working electrode were obtained from Gallant Metals and Alfa Aesar, respectively. Platinum wire (99.95%), which was used to provide connectivity to the working and counter electrodes in solution, was obtained from Surepure Chemetals, and the platinum mesh counter electrode (≥99.99%; ~2 cm²) was obtained from VWR. For precursor and electrolyte formation, arsenic trioxide (As₂O₃; 99.995%), anhydrous sodium hydroxide (NaOH; ≥98%), and anhydrous sodium sulfate (Na₂SO₄; ≥ 99%) were obtained from Sigma-Aldrich. Water used in all depositions (with resistivity >18.2 MΩ·cm) was sourced from a Labconco Water Pro Plus purification system.

2.2. Growth Cell Design. The electrochemical growth cell used to deposit all samples produced in this research was based on a similar design used in the work of Demuth et al.27 with several implemented modifications intended to simplify preparations for the growth and removal of as-grown samples from the cell. A 3D model of the basic growth setup is shown in Figure 1, including an electrochemical cell with a three-electrode configuration comprised of a platinum (Pt) mesh counter electrode (CE) and liquid metal working electrode (WE) housed within a 150 mL Pyrex beaker. A machined polytetrafluoroethylene (PTFE) crucible was modified from previous designs to accommodate the entry of the Pt wire into the liquid metal electrode from the side of the crucible rather than the top (which inhibited continuous film growth across the top surface of the liquid metal) or the bottom (which applied excessive stress on the platinum wire). All Pt wires used to apply potentials within the cell were isolated from the surrounding solution using PTFE heat-shrink tubing. The Ag/AgCl reference electrode (RE) was connected to the growth cell through a salt bridge to discourage the contamination of deposited films by the RE fill solution. The cell was capped by a machined PTFE lid and placed inside a sand bath before heat was applied via a digital hot plate. The temperature of solution was measured using a glass thermometer before and during depositions.

2.3. Experimental Methods. The general growth chemistry and deposition parameters were based off those documented in a previous study performed by Fahrenkrug et al.25 For each deposition, a Gamry 1010E potentiostat was used to apply and maintain a constant bias voltage of −1.58 V (versus the Ag/AgCl RE) to the liquid metal WE for 180 min in chronoamperometric mode. The electrolyte/precursor solution was prepared to achieve the desired concentrations (0.1 M NaOH, 0.1 M NaSO₄, and 0.0001 M As₂O₃) and heated to the target temperature (95 ± 5 °C) before growth was initiated. The bias voltage was consistently applied a few seconds prior to submerging the liquid metal electrode into the heated electrolyte/precursor solution to discourage oxide formation on the liquid metal surface. The temperature of solution during all depositions was maintained at 95 ± 5 °C over the entire 180 min period, and the PTFE lid covered the top of the beaker to minimize evaporation of the solution throughout each deposition. In contrast to the previous study of the ec-LLS growth of GaAs,25 all samples grown in this research were deposited using a simple benchtop growth setup under ambient pressure without a pressurized reaction vessel. After each deposition was complete, the PTFE crucible was removed from the cell and
cooled until the liquid metal electrode solidified. The solid metal pellet and semiconductor film were then removed from the crucible and placed on a glass slide. A heat gun was used to slowly melt the solid metal pellet, while a glass pipet was used to remove the liquid and placed on a glass slide. A heat gun was used to slowly melt the crystalline thin film. In addition to simplifying the overall growth setup, this work investigates the ability to selectively alloy the GaAs lattice with elemental In to produce crystalline thin films of InGaAs.

To encourage thorough mixing of the liquid metal electrode prior to its incorporation into the growth cell, appropriate masses of liquid Ga and solid In pellets were placed in a glass beaker and mixed with a glass stir rod over an open flame until the In pellets visibly melted into the liquid gallium pool. This process was performed for each of the desired InGaAs compositions (x = 0.1, 0.2, 0.3, 0.4, and 0.5). The liquid metal mixture was then immediately transferred into the PTFE crucible before the remaining steps of the deposition process were initiated.

X-ray diffraction was performed using a Panalytical Empyrean multipurpose diffractometer. Raman spectroscopy was performed using a BWTek iRaman spectrometer (785 nm excitation wavelength) and a video microscope sampling system equipped with a 20x objective. Optical bandgap characterization was performed using diffuse reflectance measurements obtained using a Jasco V670 UV–Vis-NIR spectrophotometer with a 150 mm integrating sphere attachment. Scanning electron microscopy images were produced using a Hitachi S-3000N scanning electron microscope, and energy-dispersive X-ray spectroscopy was performed using a Hitachi SU-8230 cold-field emission scanning electron microscope equipped with an Oxford Instruments X-Max 80 detector. Semiquantitative elemental analysis was performed using Oxford Instruments AZTek software (version 3.0).

3. RESULTS AND DISCUSSION

Raman spectroscopy data were obtained at room temperature for all thin film samples using a 785 nm excitation wavelength. For pure GaAs (x = 0), measured values for the transverse optical (TO) and longitudinal optical (LO) peak locations of 267.2 and 287.2 cm⁻¹, respectively, were consistent with theoretical values obtained via selection rules for the TO (268 cm⁻¹) and LO (292 cm⁻¹) modes of cubic GaAs. However, a nontrivial redshift (5 cm⁻¹) was observed in the LO peak position of GaAs, indicating the presence of tensile strain in the film. As the In/Ga ratio of the liquid metal electrode was increased, Raman shift measurements of the resulting InGaAs films displayed expected shifts of the TO peak positions toward the InAs-TO peak location (216 cm⁻¹). As shown in Figure 2, the consistent redshift observed in the GaAs-like TO peak positions as the In composition was increased supports controlled alloying of the GaAs lattice. In contrast, the GaAs-like LO peaks displayed less consistency in the degree of the redshift observed as the In composition was increased (likely due to nonuniform local lattice strain introduced by the film-harvesting process).

The major obstacle to achieving high-quality crystalline growth via ec-LLS is the film harvesting process that follows deposition, where the structure of the semiconductor film atop the liquid metal electrode experiences significant distortion and deformation as the liquid metal is removed from underneath the film (via a syringe). This process degrades sample crystallinity, induces defects, and increases the number of grain boundaries, which is evident from the broad linewidths of the Raman spectra. Measured Raman spectra displayed more significant peak broadening relative to highly crystalline samples, likely due to quantum confinement effects related to the reduced physical sizes of the crystallites within the deposited film structures and increased surface areas of the film morphologies. Table 1 shows the measured peak locations and the corresponding full-width at half-maximum (FWHM) values of the TO and LO modes of deposited InGaAs films. Optical bandgap values were determined via diffuse reflectance measurements and the Tauc method. Diffuse reflectance measurements were converted to corre-
Table I. Measured Values Obtained from Harvested InGa_{1-x}As Thin Films^a

| x  | peak position (TO) (cm\(^{-1}\)) | FWHM (TO) (cm\(^{-1}\)) | peak position (LO) (cm\(^{-1}\)) | FWHM (LO) (cm\(^{-1}\)) | \(E_g\) (eV) | \(\Delta E_g\) (eV) |
|----|----------------------------------|--------------------------|----------------------------------|--------------------------|-----------|------------------|
| 0.0| 267.8                           | 15.31                    | 287.2                            | 12.95                    | 1.564     | 0.002 |
| 0.1| 267.0                           | 15.54                    | 284.5                            | 12.25                    | 1.471     | 0.003 |
| 0.2| 266.0                           | 24.73                    | 282.5                            | 23.55                    | 1.429     | 0.003 |
| 0.3| 265.8                           | 16.48                    | 285.5                            | 13.66                    | 1.393     | 0.009 |
| 0.4| 263.5                           | 9.419                    | 288.5                            | 11.42                    | 1.330     | 0.002 |
| 0.5| 263.3                           | 19.43                    | 281.8                            | 22.37                    | 1.280     | 0.007 |

\(^a\)Measured values include peak positions with FWHM measurements of GaAs TO and LO modes determined from Raman spectra and measured optical bandgaps \((E_g)\) with corresponding uncertainties \((\Delta E_g)\) determined from diffuse reflectance data. The \(x\) values represent the composition of the liquid metal electrode used in each deposition.

where \(h\) is Planck’s constant, \(\nu\) is the photon frequency, \(E_g\) is the bandgap, \(C\) is a proportionality constant, and \(n\) is determined by the nature of the electronic transition. For allowed transitions, direct and indirect bandgap transitions correspond to values of \(n = 1/2\) and \(n = 2\), respectively. Since GaAs and InAs are both direct bandgap semiconductor systems, \(n = 1/2\) was used throughout this analysis. By inserting \(n = 1/2\) and substituting the Kubelka–Munk function for the absorption coefficient in eq 2, the specific form utilized in this work can be expressed as

\[
[F(R_\infty)]^2 = C(h\nu - E_g)
\]

After \([F(R_\infty)]^2\) was plotted versus the photon energy \((h\nu)\), linear fits were applied to the data at the absorption edge. The \(x\)-intercepts were determined from extrapolations of the linear fits and subsequently used to obtain measured values of the optical bandgap for each film. Table I shows the measured bandgap values and corresponding uncertainties determined from each linear fit, and Figure 3a shows a series of stacked Tauc plots obtained from diffuse reflectance measurements for each InGa\(_{1-x}\)As film. As shown in Figure 3b, a consistent decrease in the optical bandgap was observed as the nominal In composition of deposited films increased. While this trend supports In alloying of the GaAs lattice, bandgap measurements indicate a consistent lack of the stoichiometric preservation of the In/Ga ratio from the liquid metal electrode to deposited films. A similar shortage of In incorporation from the WE to the deposited films was observed in previous work performed by our research group on the ec-LLS growth of InGa\(_{1-x}\)Sb films. Additionally, the measured bandgap of the pure GaAs film (1.56 eV) is mildly blueshifted relative to accepted literature findings for highly crystalline GaAs but compares well with results from a recent study of polycrystalline GaAs films grown via CVD under ambient pressure, which displayed a measured bandgap of 1.52 eV.38

![Figure 3](image-url)

Figure 3. (a) Tauc plot series obtained via diffuse reflectance measurements. Linear fits applied to the absorption edge display the corresponding bandgaps determined for InGa\(_{1-x}\)As films (plots are offset for ease of comparison). (b) Plot showing the measured optical bandgap as a function of the nominal In composition of InGa\(_{1-x}\)As films.
To further investigate the elemental composition of the deposited films, EDS spectra were recorded and analyzed. To ensure that the electron beam penetrated any surface oxide layers formed from extended sample storage in atmosphere, a beam voltage of 15 kV was used in efforts to effectively probe the elemental composition of the In$_x$Ga$_{1-x}$As films. The plots in Figure 4a and b provide a comparison of the EDS spectra obtained from GaAs and InGaAs films grown in this research and highlight the similarity of the spectra, with the exception of the peaks attributed to electronic transitions within elemental indium that were obtained from the InGaAs films. EDS spectra were obtained for films with each nominal In composition ($x = 0.0 - 0.5$), and the raw data were overlaid across the interval containing the In-L$_{\alpha}$ (3.28 keV), In-L$_{\beta_1}$ (3.49 keV), and In-L$_{\beta_2,\gamma}$ (3.71 keV) X-ray emission energies, as shown in Figure 4c. Several spots were analyzed across each film surface, and a general trend of the intensities of the In-L$_{\alpha}$, In-L$_{\beta_1}$, and In-L$_{\beta_2,\gamma}$ emission peaks increasing with the nominal In composition was observed in EDS data.

To determine semiquantitative elemental compositions of the alloyed films from the EDS data, elemental weight percentage measurements were obtained from multiple spots (10 $\mu$m $\times$ 10 $\mu$m) across each sample surface. For each sample, weight percentages were converted to atomic percentages for each detected element, and the resulting In compositions are shown in Figure 5. The error bars in Figure 5 represent the variability of In composition measurements performed at multiple spots across each film surface.

Figure 4. EDS data obtained for select (a) GaAs and (b) InGaAs films grown in this research, which were used to determine the elemental composition and probe the In content of the deposited films. (c) Stacked EDS spectra obtained for deposited In$_x$Ga$_{1-x}$As films showing the increase in the intensities of the In-L$_{\alpha}$, In-L$_{\beta_1}$, and In-L$_{\beta_2,\gamma}$ X-ray emission peaks with the increase in the nominal In composition ($x$) of the In$_x$Ga$_{1-x}$As films.

Figure 5. Semiquantitative measurements of the In composition within In$_x$Ga$_{1-x}$As films (determined via EDS data) versus the In composition of the liquid metal electrode used during growth. Vertical error bars represent the variability of In composition measurements performed at multiple spots across each film surface.

preservation from the electrodes to the deposited films. EDS data collected in this research suggest the sample environment was Ga-rich, which can likely be attributed to the presence of underlying residual Ga in all harvested films. Due to the Ga-rich nature of the samples, it is likely that the actual In compositions of In$_x$Ga$_{1-x}$As films deposited in this study are systematically higher than the measured values determined using the EDS data. The authors would like to emphasize that the elemental composition measurements presented in this research are meant to serve as semiquantitative means of
demonstrating controlled alloying efforts and to provide estimations of the In compositions within deposited In$_x$Ga$_{1-x}$As films.

The lack of pristine surfaces in harvested films added substantial uncertainty to the XRD analysis process of quantifying changes in the lattice constant by measuring Bragg angle shifts. Figure 6a shows an XRD glancing angle scan obtained from a harvested GaAs ($x = 0$) thin film, which demonstrates polycrystalline growth of cubic GaAs with a preferred orientation in the (111) growth direction. However, XRD scans of harvested In$_x$Ga$_{1-x}$As films yielded inconsistent (111) peak locations that varied as the X-ray beam illuminated different spots across the surface of a given sample. The rough morphology of the film surface caused by the harvesting process is further demonstrated by the SEM image of the side profile of a harvested GaAs film shown in Figure 6b. Similar rugged morphologies were observed in all films grown and harvested in this study, and the large inconsistencies in the observed XRD scattering angle positions made it difficult to extract any conclusive evidence of In alloying from the XRD data of the harvested films. However, the XRD data shown in Figure 6a were used in conjunction with the Scherrer equation to determine the average crystallite size for a harvested GaAs film ($x = 0$). The Scherrer equation is given as:

$$D_{hkl} = \frac{K\lambda}{B_{hkl}\cos \theta}$$

where $D_{hkl}$ is the average crystallite size in the direction perpendicular to the $hkl$ lattice plane, $\lambda$ is the Cu Ka$_1$ X-ray wavelength ($1.540598$ Å), $K$ is the crystallite shape factor ($K = 0.89$ was used in this case due to cubic crystal symmetry), $B_{hkl}$ is the FWHM of the $hkl$ diffraction peak, and $\theta$ is the Bragg angle (of the $hkl$ reflection). For the pure GaAs film, the (111) diffraction peak was used to determine an estimated average crystallite size of 24.5 nm. Relative to micrometer-scale crystallites typically found in highly crystalline GaAs, the nanocrystalline structures of samples grown in this work are in good agreement with the slight blueshift observed in bandgap measurements, considering that optical bandgaps have been shown to increase as the sizes of nanorods, nanowires, nanoparticles, and nanofilms decrease.$^{43-48}$

### 4. CONCLUSIONS

This work demonstrates the first instance in the literature of ec-LLS growth and alloying of polycrystalline In$_x$Ga$_{1-x}$As thin films. To the authors’ knowledge, this also represents the first evidence of the controlled alloying and growth of polycrystalline In$_x$Ga$_{1-x}$As films using any liquid-phase electrochemical method without the use of an additional annealing step. Indium compositions of the deposited films were controlled by varying the In/Ga ratio of the liquid metal WE before each deposition, while all other parameters were maintained at constant values. Controlled alloying efforts were supported by Raman spectroscopy data via consistent redshifts of GaAs-like TO modes as the In/Ga ratio of the WE was increased. Further support of In alloying was observed in room-temperature diffuse reflectance data, which displayed a decreasing trend in the optical bandgap measurements as the nominal In composition of the deposited films increased. The measured bandgap of 1.56 eV for GaAs ($x = 0$) displayed a slight blueshift relative to the accepted value of 1.42 eV, likely due to increased quantum confinement effects attributed to excessive grain boundaries and nanometer-scale crystallites in deposited films. Additional semiquantitative support for In alloying was observed through elemental composition analysis performed using EDS data. Consistent increases in the emission intensities of the X-ray wavelengths associated with elemental indium were observed in deposited films as the In composition of liquid metal electrodes was increased. Similar to previous results obtained by our research group for the ec-LLS growth and alloying of In$_x$Ga$_{1-x}$Sb films, significant decreases of the In/Ga ratio from the liquid metal electrode to the deposited In$_x$Ga$_{1-x}$As films were observed in all data.

The results of this research lend additional support for ec-LLS as a growth methodology capable of achieving crystalline semiconductor growth under ambient pressure and near-room temperature without the need for postgrowth annealing. By employing the benefits of a liquid metal to serve as an electrode, a growth reactant, and an alloying platform, this
method has the potential to overcome conventional obstacles associated with electrochemical growth methods for crystalline semiconductors. The primary challenge to achieving highly crystalline growth via ec-LLS is the curvature of the liquid metal electrode. However, adverse effects on the crystallinity of deposited films could be minimized by confining the surface of the liquid metal during growth to achieve a flatter surface more suitable for crystalline growth. Future work includes adapting the ec-LLS process to achieve the confinement of the liquid metal electrode and improving film harvesting methods to increase the overall crystal quality of the deposited films. In addition, this confinement would decrease the volume of the liquid metal electrode, which could facilitate the increased preservation of the In/Ga ratio from liquid metal electrodes to deposited films. Furthermore, ec-LLS continues to show promise as an alternative low-cost technique for crystalline growth and alloying of binary and ternary semiconductor material systems.

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**Notes**

The authors declare no competing financial interest. The data that support the findings of this study are available within the article. However, additional supporting data are available from the corresponding author upon reasonable request.

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