



# Atomic Scale Characterization of Compound Semiconductors using Atom Probe Tomography

## Preprint

Brian P. Gorman  
*Colorado School of Mines*

Harvey Guthrey  
*Colorado School of Mines and National Renewable  
Energy Laboratory*

Andrew G. Norman and Mowafak Al-Jassim  
*National Renewable Energy Laboratory*

Dan Lawrence and Ty Prosa  
*Cameca Instruments, Inc.*

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# ATOMIC SCALE CHARACTERIZATION OF COMPOUND SEMICONDUCTORS USING ATOM PROBE TOMOGRAPHY

Brian P. Gorman<sup>1</sup>, Andrew G. Norman<sup>2</sup>, Dan Lawrence<sup>3</sup>, Ty Prosa<sup>3</sup>, Harvey Guthrey<sup>1,2</sup>, and Mowafak Al-Jassim<sup>2</sup>

<sup>1</sup>Colorado School of Mines, Golden, Colorado, U.S.A

<sup>2</sup>National Renewable Energy Laboratory, Golden, Colorado, U.S.A

<sup>3</sup>Cameca Instruments, Inc., Madison, Wisconsin, U.S.A

## ABSTRACT

Internal interfaces are critical in determining the performance of III-V multijunction solar cells. Studying these interfaces with atomic resolution using a combination of transmission electron microscopy (TEM), atom probe tomography (APT), and density functional calculations enables a more fundamental understanding of carrier dynamics in photovoltaic (PV) device structures. To achieve full atomic scale spatial and chemical resolution, data acquisition parameters in laser pulsed APT must be carefully studied to eliminate surface diffusion. Atom probe data with minimized group V ion clustering and expected stoichiometry can be achieved by adjusting laser pulse power, pulse repetition rate, and specimen preparation parameters such that heat flow away from the evaporating surface is maximized. Applying these improved analysis conditions to III-V based PV gives an atomic scale understanding of compositional and dopant profiles across interfaces and tunnel junctions and the initial stages of alloy clustering and dopant accumulation. Details on APT experimental methods and future in-situ instrumentation developments are illustrated.

## BACKGROUND

Interfacial abruptness, dopant location, and compositional uniformity in III-V semiconductor alloy multijunction solar cells are important factors to PV efficiency because they can control the built-in voltage and depletion width of the junctions. To fully understand the atomic scale chemistry and structure of junctions in compound semiconductor devices, new techniques with atomic scale spatial and chemical resolution need to be developed. Atom probe tomography (APT) is an imaging time-of-flight mass spectrometry technique with near atomic spatial resolution and approximately  $10^{17}$  /  $\text{cm}^3$  chemical resolution. Applying APT to PV materials and devices allows for interfacial abruptness, dopant concentrations, dopant clustering, and nanoscale phase separation to be determined with nearly atomic accuracy.

In this study, cross-correlative laser pulsed APT and analytical transmission electron microscopy (TEM) were used to determine the atomic scale chemistry of interfaces in III-V materials for PV devices. Though the use of laser pulsing in atom probe tomography has significantly increased the parameter space of materials that can be analyzed, its application in compound semiconductors has led to widely varying compositional data. To understand the effects of laser pulsing on III-V multijunction solar cells,

this study used state-of-the-art, ultra-low power laser pulsing, along with variations in Focused Ion Beam (FIB)-based, APT specimen preparation techniques.

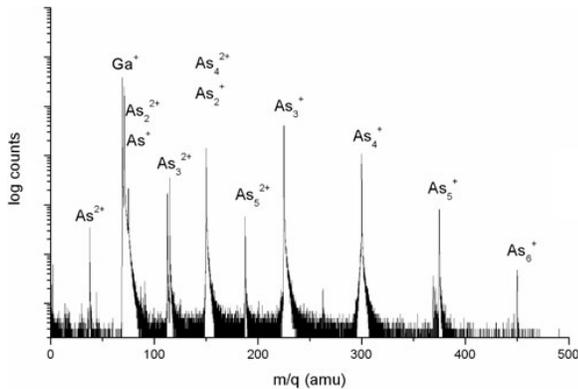
## EXPERIMENTAL

Specimens for TEM and APT were prepared using standard in-situ FIB liftout and thinning techniques [1]. Of particular future note to the PV community would be the combination of electron imaging techniques, such as electron backscatter diffraction (EBSD), electron beam induced current (EBIC), and cathodoluminescence (CL) for the identification of device defects, followed by site-specific FIB preparation of APT specimens. Such a combination would allow for atomic scale chemistry variations to be analyzed around dislocations, shunts, grain boundaries, and other internal junctions or defects. For this study, APT specimens of metal organic chemical vapor deposition (MOCVD) III-V devices were intentionally shaped to diameters between 70 and 500 nm, similar to previous studies [2,3]. APT data were collected on either a Local Electrode Atom Probe (LEAP) 3000 XHR or LEAP 4000 XSi, both manufactured by Cameca Instruments, Inc. Data was collected using a range of laser energies from 0.00005 to 0.5 nJ to evaluate the effects of specimen heating on APT reconstruction resolution.

## RESULTS

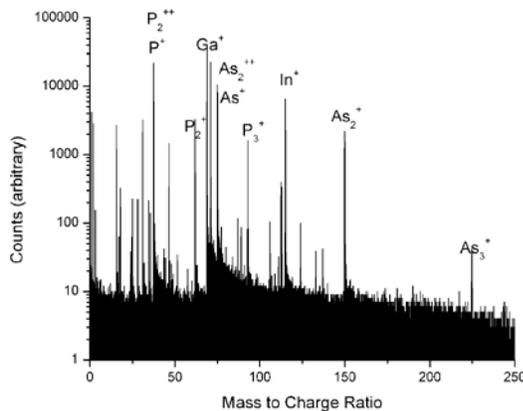
An APT mass spectrum acquired using 0.1 nJ laser pulse energy on a LEAP 3000XHR is illustrated in Fig. 1. Poor mass resolution is observed in this spectrum, presumably caused by "thermal tails", or the evaporation of ions during a time significantly past that of the pulse onset. This is indicative of specimen overheating caused by excessive laser pulse energy.

Also seen in Fig. 1 is atomic clustering, prevalent in the group V ion species. Clustering is observed out to masses that correspond to  $\text{As}_6$ , with no clustering observed in the group III species. It is worth noting that the largest intensity peak in the mass spectrum is attributed to  $\text{As}_3$ . If this peak were from a truly atomic resolution measurement, this ion would correspond to 75% of a single GaAs unit cell, in which there are not 3 As atoms bonded together.



**Figure 1 APT mass spectrum of GaAs using 0.5 nJ laser pulse energy.**

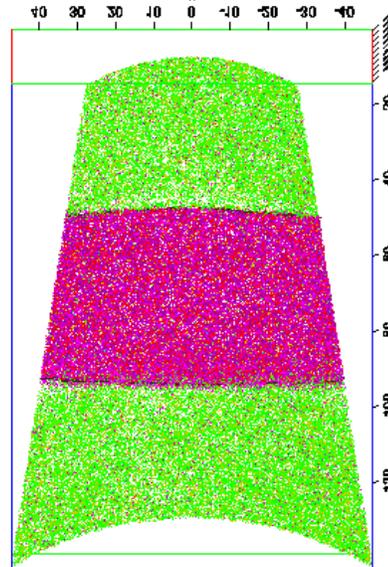
This large amount of group V clustering is therefore indicative of surface atom migration, and also a significant loss of spatial resolution. Although the specimen base temperature is near 20 K, surface migration indicates that specimen overheating caused by laser pulsing is occurring. Compared with previous studies of surface diffusion during molecular beam epitaxy (MBE) growth [4], the group V atoms are known to have several orders of magnitude higher diffusion coefficients and an 80% decrease in activation energy. This data agrees well with the current study and the supposition that group V clustering in laser pulsed atom probe tomography is, in fact, caused by surface diffusion and represents a subsequent loss of spatial resolution.



**Figure 2 APT mass spectrum of GaAs using 0.0005 nJ laser pulse energy.**

To study the heating effect further, APT studies at laser pulse energies of 0.0005 nJ were completed on a LEAP 4000XSi. A mass spectrum obtained under these conditions is illustrated in Fig. 2. Comparing the mass spectra in Figs. 1 and 2, a large decrease is observed in the group V clustering with a commensurate decrease in laser pulse energy; there is also a significant increase in mass resolution (reduction in thermal tails).

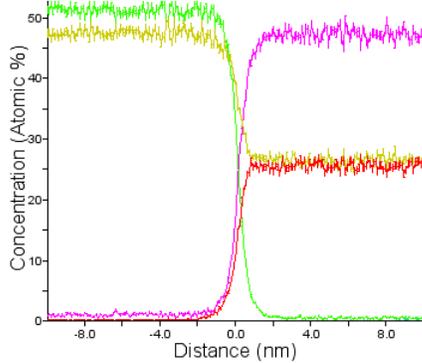
Clusters larger than  $As_2$  and P clusters larger than  $P_3$  are statistically non-significant, indicating a notable reduction in surface diffusion. It is estimated that the spatial resolution of the lower laser power data is at near atomic levels.



**Figure 3 APT reconstruction of a GaAs / GaInP / GaAs structure using 0.0005 nJ laser energy.**

Following interpretation of the mass spectrum in Fig. 2, an APT reconstruction was produced using an evaporation field of 25 V/nm, and is illustrated in Fig. 3. Using atomic positions produced from the APT reconstruction (IVAS 3.6.1 software, Cameca Instruments, Inc.), proximity histograms about the interfaces were obtained and illustrated in Fig. 4, for the top interface. Of particular note is the very good stoichiometry observed in the composition profile, where the III/V ratio is calculated to be 0.49. Close interpretation of the interface abruptness, using the distance between the 5 and 25 atomic % In levels (red curve) illustrates an interfacial abruptness of ~ 1 nm, whilst for As, an abruptness of ~ 1.5 nm is indicated using the distance between the 5 and 50 atomic % As levels (green curve).

Similar analyses of the bottom interface illustrates a significant broadening in the In, Ga, As, and P concentration profiles to a width ~1.5 nm for the In, and ~ 4nm for the As. Utilizing this information allows for a greater understanding of the device performance, and also provides feedback to the MOCVD community so it can develop the highest quality interfaces. The III-V growth community will likely have great interest in cross-correlative analyses between APT and RHEED oscillations or scanned probe microscopy.



**Figure 4 Compositional proxigram illustrating changes in composition around the top GaAs / GaInP interface. Interface abruptness is determined to be ~1 nm. Growth direction is from right to left. Color key: As profile = green; Ga profile = mustard; In profile = red; and P profile = purple.**

Surface diffusion caused by laser heating in APT experiments may be observed in many materials systems, especially those with high surface mobility. Indeed, clustering has been observed in II-VI semiconductors and also with group V dopants in Si and Ge. It is thus strongly suggested that all semiconductor systems be analyzed in APT using very low laser powers, and the mass spectra be interpreted carefully to ensure the highest possible spatial resolution.

### SUMMARY

This study illustrates atomic scale characterization of compound semiconductor PV device structures using atom probe tomography. Issues associated with laser pulsed APT of compound semiconductors include diffusion of atoms on the specimen surfaces, and a corresponding loss of spatial resolution. These issues can be avoided, given the correct instrumentation, specimen preparation techniques, and data analysis. Ultimately, atomic scale APT reconstructions of compound semiconductors can be achieved with careful experimentation and data analysis. Future experiments utilizing laser pulsed field ion microscopy (FIM) on semiconductor materials will quantify the surface diffusion of atoms on semiconductor surfaces.

### ACKNOWLEDGEMENTS

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