Accuracy of pulsed laser atom probe tomography for compound semiconductor analysis

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Abstract. Atom probe tomography has recently experienced a renaissance, strongly promoted by the revival of pulsed laser atom probe. The technique is now widely employed to study semiconductor materials at the nanometre level. This paper summarises some aspects of the accuracy of pulsed laser atom probe relevant to semiconductor applications. It is shown that laser pulsing can reduce the lateral resolution due to thermally stimulated surface migration. Moreover, the commonly observed cluster ions can undergo field dissociation which results in an increased probability of ion loss due to pile-up effects at the detector. Field dissociation can also induce a new type of local magnification that increases spatial inaccuracy in the data reconstruction. These effects can be reduced by an appropriate choice of experimental parameters. Despite these difficulties, the atom probe technique can provide unparalleled insight into the nanoscale structure and chemistry of a wide range of semiconductor devices.

1. Introduction

Although first conceived and realized in the 1980’s [1], pulsed laser atom probe (PLAP) resurfaced just a few years ago, driven by the implementation of reliable, high repetition rate, ultra-short pulse width laser systems. It was established that the pulsing mechanism in PLAP is thermal, where a locally and temporally confined heating of the specimen apex triggers the field evaporation of surface atoms. Under normal operating conditions, the temperature rise should only moderately heat the apex from the cryogenic range to near room temperature [2,3] with decay times of only few tens of nanoseconds. The use of laser pulsing has unlocked atom probe tomography (APT) investigations of low electrical conductivity materials, and PLAP has since been applied successfully to a variety of materials that had previously been inaccessible. Many of those new applications are in the field of semiconductor analysis ranging from silicon-based materials and device structures, to semiconductor nanowires and compound semiconductor nanostructures [4,5]. The great success of PLAP applications in this field has somewhat outpaced fundamental studies addressing how the choice of experimental parameters affects the accuracy of the data obtained and how the performance of contemporary PLAP compares to conventional voltage-pulsed APT of metallic materials. This paper aims at providing a brief review of studies addressing those issues and assesses the relevance of PLAP for semiconductor analysis.
2. Spatial accuracy

As for all microscopy techniques, the spatial resolution is probably the most important benchmark, ultimately defining the instrument performance. However, it is not always trivial to quantify this measure. It is thus not surprising that there had been no procedure to define and measure the spatial resolution in APT data until very recently. Gault et al. [6] deployed a complex multi-step procedure to derive a measure for the spatial resolution and showed that contemporary voltage-pulsed APT can in fact yield data with sub-nanometer resolution in all three dimensions for pure metals like W and Al at low temperatures. In a subsequent study, the evaluation of the spatial resolution was extended to PLAP data [7]. The results show that in particular the lateral resolution is sensitive to the application of laser pulsing and monotonically deteriorates with increasing pulse energy. On the other hand, the in-depth resolution seems more tolerant towards laser pulsing. This observation can be explained by an increased likelihood of surface migration prior to field evaporation promoted by sample heating. The migration of surface atoms impedes the accurate reconstruction of the original crystal lattice. It is also important to mention that the evolution of the spatial resolution is material-dependent. In studies carried out on specimens held at equivalent fractions of their melting temperature, it degrades faster in FCC Al than in BCC W, likely due to more rapid surface atom migration on FCC surfaces [7].

All these studies were dealing with pure metals only. Similar studies for semiconductors are difficult, since the assessment procedure employed by Gault et al. [6] seems not easily applicable. However, Cadel et al. [8] and Geiser et al. [9], amongst others, were able to reveal lattice planes in APT datasets of silicon. With the help of further data analysis procedures, the depth resolution was estimated to be better than 200 pm under laser pulsing [8]. Very recently, Shimizu et al. [10] employed silicon isotope superlattices [11] to further evaluate the spatial resolution of PLAP. This method also allows for the assessment of the lateral resolution, if the growth direction of the stack is oriented perpendicular to the atom probe specimen axis. The authors estimated the depth resolution for a fixed laser pulse energy to be \( \approx 400 \) pm and the lateral resolution to be \( \approx 1000 \) pm [10]. More work still needs to be done, in particular to investigate how the spatial resolution depends on the pulse energy. Furthermore, no investigations seem yet to exist on the spatial resolution of PLAP for compound semiconductors, which have become an important area of application.

The studies published so far suggest that the lateral resolution for semiconductors may no longer be on an atomic level, which would explain why no real space crystallographic information can be generated to determine the lateral resolution with the procedure described in [6]. One possible explanation has already been presented, namely the application of laser pulses, which is expected to reduce the spatial resolution a priori. It is thus also conceivable that the spatial resolution in semiconductors deteriorates with increasing laser pulse energy as observed for pure metals [7]. Another aspect might be the different nature of the bonds in semiconductors. For pure metals with their delocalized bonds and electrons, detailed models for the field evaporation process exist [2]. However, less is known about the field evaporation of semiconductors with their highly directional, strong covalent bonds. This difference in the bonding character might impede single atom-by-atom field evaporation and thus reduce the spatial resolution.

Another interesting phenomenon potentially affecting the spatial accuracy of the data reconstruction is the change in the specimen apex shape during PLAP experiments [12,13]. Koelling et al. reported a unidirectional absorption regime for PLAP on silicon for laser wavelengths at which the optical skin depth is smaller than the specimen thickness [13]. Together with equally small thermalisation depths [14], this can result in inhomogeneous laser heating and the formation of pronounced apex asymmetries. Such asymmetries in the local radius of curvature cannot be easily accounted for in standard data reconstruction procedures [15] and are likely to cause artifacts and inaccuracies in the 3-dimensional datasets.
3. Cluster ion detection

A seemingly inevitable feature of PLAP studies of compound semiconductors is the detection of cluster ions \( \text{X}_n \), for compound semiconductors most abundantly detected as, for example, homonuclear group-V cluster ions. Recently observed cluster sizes \( n \) are up to 6 or beyond for arsenic [16], up to 4-5 for antimony [17,18], up to 5 for phosphorous [16,19], and 3 for nitrogen [20]. Furthermore, these clusters can exhibit different charge states commonly ranging from 1+ to 3+. Besides homonuclear group-V cluster ions, heteronuclear clusters of III-V [17] or V-V elements are also possible [21].

The formation mechanism of cluster ions during the field evaporation process of (compound) semiconductors is not very well understood. Cerezo et al. demonstrated that the concentration of larger arsenic clusters increased with increasing base temperature in voltage-pulsed atom probe of GaAs [3]. This indicates a temperature mediated process. Drachsel et al. also assumed high, temperature-mediated surface mobilities for the materials that showed cluster ions in their laser-assisted field evaporation experiments [22]. It is conceivable that enhanced surface migration at higher temperatures [7] promotes the agglomeration of, e.g., single, mobile group-V atoms and their field evaporation in form of a cluster ion. For PLAP, this would mean that with increasing effective pulse fraction, i.e., increased laser heating more and larger cluster ions should be detected. This has been observed for antimony clusters in PLAP studies of GaSb [17]. Tsong [23] argued that electric fields could penetrate much deeper into semiconductor materials than is the case for metals. Consequently, not only the outermost atoms, but also deeper atom layers might experience sufficient field strengths for field evaporation, potentially detaching larger agglomerates from the surface. The detachment of those larger building blocks might also be the origin for cluster ions in the mass spectrum. Finally, mass spectra from liquid metal ion sources also show an abundance of cluster ions [24,25] and their formation processes may also be relevant to the cluster ion formation under atom probe conditions. The presence of cluster ions in PLAP data has several consequences affecting the data accuracy.

3.1. Mass peak overlaps

A very obvious issue is the overlap of peaks in the mass spectrum. The position of each peak is given by the isotope mass \( m \) divided by the ion charge \( z \). Consequently, there can be more than one permutation of \( m \) and \( z \) giving the same mass-to-charge state-ratio \( m/z \). For example, the mass peaks for \( \text{As}_2^{1+} \) and \( \text{As}_4^{2+} \) have an identical \( m/z \) ratio of 150 Da and thus fully overlap. This issue is most pronounced for mono-isotopic group-V elements for which the overlap cannot be deconvoluted easily and compositional inaccuracies appear inevitable. However, for multi-isotopic elements like Sb the formation of cluster ions results in characteristic, additional mass peaks, for example \( ^{122}\text{Sb}_2^{2+} \), which can be employed to deconvoolute mass peak overlaps.

3.2. Field Dissociation

We recently investigated the cluster detection in PLAP studies of GaSb [17]. One of the main observations was that the size and concentration of cluster ions detected increased with increasing effective pulse fraction \( (\text{PF}_{\text{eff}}) \) and with decreasing field strength as shown in Figure 1 (a). At low \( \text{PF}_{\text{eff}} \) and thus high field strengths the majority of Sb ions detected were atomic Sb. In contrast, for higher \( \text{PF}_{\text{eff}} \) the \( \text{Sb}_3 \) cluster ions are predominant and overall more \( \text{Sb}_n \) clusters were detected. This pronounced change could be explained in two ways, firstly by thermally promoted cluster formation as described earlier or secondly, by reduced field dissociation. Careful investigations of the data suggest that field dissociation is the predominant process under the experimental conditions considered. An increase in laser pulse energy heats the sample more, but equally reduces the field strengths required for field evaporation. This drop in field strength is assumed to diminish field dissociation of antimony clusters, so they appear in higher concentrations and larger sizes \( n \) in the atom probe data. However, the assessment of cluster ion detection in atom probe is determined by two distinct processes, firstly the formation of the cluster ions, and secondly their field dissociation. Consequently, the high concentrations and larger sizes of cluster ions at high effective pulse fractions [17] would be
combined result of enhanced cluster ion formation and suppressed cluster ion dissociation. Unfortunately those two processes cannot easily be distinguished and studied separately.

3.2.1. Effects on chemical accuracy. Field dissociation of cluster ions may result in a multiplication of detector events [17]. Assuming, for example, a large Sb\textsubscript{5}\textsuperscript{1+} cluster undergoing complete field dissociation into five Sb\textsuperscript{1+} fragments, this would mean that five ions instead of only one are moving towards the atom probe detector. Figure 1 (b) demonstrates that PLAP studies of GaSb can exhibit a substantial fraction of multiple detector events. When operating at low effective pulse fraction, up to 45 % of all ions detected arrive within multiple events. The size of those events can be as big as 14 ions per pulse [17]. Given a detection efficiency of the instrument of 40 %, this implies that more than 30 ions were field evaporated during a single pulse. The proportion of multiple events reduces drastically with increasing pulse fractions indicating suppressed field dissociation [17]. Materials not normally forming cluster ions and thus not experiencing field dissociation like, for example, aluminium and tungsten have multiple fractions well below 5 %. If too many fragmentation products strike the detector in very close succession or proximity to each other then the detector signals they produce might no longer be resolved and some of those ions are simply lost. This is referred to as detector ion pile-up [2]. Since mainly group-V elements form cluster ions, their compositional accuracy will thus be affected more strongly i.e. their concentrations are likely to be underestimated. In addition, field dissociation may produce neutral fragmentation products. This has been indirectly proved for PLAP of GaN, where the field dissociation of GaN\textsubscript{3} led to Ga\textsuperscript{1+}, N\textsuperscript{1+} and neutral N\textsubscript{2} [20]. Any neutrals which are formed normally do not possess sufficient energy to trigger a detector signal or are lost in the instrument, thus they will also be lost from the chemical analysis.

![Figure 1](image1.png)

**Figure 1.** (a) Abundances of the various Sb cluster ions of size \(n\), expressed as percentages of the overall number of antimony ion counts, for three selected effective pulse fractions (PF\textsubscript{eff}). (b) Percentage of multiple events within the overall number of detector events for three different materials studied at various effective pulse fractions. Higher effective pulse fractions correspond to higher laser pulse energies and lower evaporation field strengths. Lines as guide for the eye.

3.2.2. Effects on spatial accuracy. Although hardly any knowledge exists on the trajectories of fragmentation products, one could assume that field dissociation leads to divergent ion trajectories. In particular so, since most fragments will possess positive charges either due to a split of multiple charges during dissociation [26] or post-ionisation, which result in electrostatic repulsion. An in-depth study of the distance distribution of detector events in GaSb atom probe data [17] revealed that antimony multiple detector hits have a particularly wide distance distribution. This is also shown in Figure 2 in direct comparison with a pure metal. The few multiple hits in aluminium are assumed to
originate exclusively from correlated field evaporation [27] and their distance distribution on the detector is indeed less wide compared to that of the Ga or Sb multiple hits [17]. The distance distribution of Sb-Sb multiple hits shows a shoulder at ≈ 0.5 mm, the peak position of the distance distribution of aluminium. This can be attributed to co-evaporation of adjacent Sb ions. However, the distance distribution also possesses a major peak at ≈ 1.1 mm which is believed to describe the more widespread impact of fragmentation products on the detector caused by trajectory aberrations. This means a large antimony cluster starting out as a point source on the sample surface is “blurred” into a finite disc on the detector. Applying basic data reconstruction algorithms to these widespread detector events results in a misallocation of antimony in the reconstruction. The reconstruction procedure translates the distance on the detector into a distance on the specimen surface, whereas in fact the ions originated at the very same point, i.e., where the cluster field evaporated. This results in a decrease in spatial accuracy. Interestingly, the distance distribution of Ga-Ga multiples does not exhibit such a pronounced peak, presumably due to the fact that Ga does not form stable cluster ions [22] which could experience strong field dissociation. Thus, the inaccuracies mentioned are expected to be most pronounced for the spatial allocation of antimony ions during the data reconstruction.

![Distance distribution of Al-Al, Ga-Ga, and Sb-Sb multiple hit pairs on the position-sensitive detector.](image)

**Figure 2.** Distance distribution of Al-Al in an Al6XXX reference material (-◊-), Ga-Ga in GaSb (-△-) and Sb-Sb in GaSb (-○-) multiple hit pairs on the position-sensitive detector. The numbers of hits were normalised to the position of the shoulder in the Sb-Sb distribution. Data acquired at low laser pulse energies. Lines as guide for the eye.

## 4. Optimisation strategies

A suitable choice of experimental settings can reduce the effects described here. As outlined in reference [7], the lower the laser pulse energy and the induced sample heating, the better the lateral resolution. Hence, it appears plausible that operating at lowest pulse energies and sample base temperatures can, to some extent, counteract the deterioration in spatial resolution. However, the colder the sample, the higher the field strength required for field evaporation, which in turn promotes field dissociation [17]. In order to reduce field dissociation and its deleterious effects, it is thus preferable to operate at higher laser pulse energies. Obviously, the two objectives are somewhat in conflict and a compromise needs to be established. This could mean applying intermediate laser pulse energies, reducing field dissociation significantly, but accepting that some degree of surface migration reduces the spatial resolution. We also showed that the compositional accuracy is highest when operating with intermediate laser pulse energies [17].

More work needs to be dedicated to optimising experimental settings, quantifying the spatial resolution and comprehending the formation and detection of cluster ions. However, it needs to be stressed that PLAP is indeed a very promising tool for quantitative tomography of compound semiconductors, with unrivalled chemical sensitivity and spatial resolution.
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