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Nanoscale characterization of compound semiconductors using laser-pulsed atom probe tomography

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Abstract: Laser-pulsed atom probe tomography is introduced as a novel tomographic technique and its basic principles are explained. Atom probe provides 3-dimensional chemical maps with nanoscale resolution. For semiconductor research, needle-shaped atom probe samples are produced by focused ion beam lift-out and annular milling. An InAs buried quantum dot material was studied using laser-pulsed atom probe. The dot size, morphology and composition were evaluated as well as the wetting layers and interface composition. A laterally shifted In-rich core was visualised within the dots. Furthermore, a GeMn-based thin film was investigated to better-understand the mechanisms leading to the magnetic characteristics of this material system, which has potential applications as a magnetic semiconductor. We conclude that laser-pulsed atom probe has great potential for compound semiconductor research.

1. Principles of and recent developments in atom probe tomography

Three-dimensional nanoscale-analysis of semiconductor materials is an emerging and challenging area of research, and several advanced high-resolution methods like atom probe, electron and focused-ion beam tomography are now available. In terms of spatial resolution, atom probe tomography (APT) and electron tomography are the benchmark. In addition, atom probe tomography uniquely provides invaluable chemical information in 3D on the nanoscale.

1.1. Basic principles

APT relies on the successive removal of single surface atoms from a very sharp needle-shaped sample. Applying a high standing DC voltage in the range of 3-20 kV to this very sharp specimen ionizes surface atoms at sites of highest electrical field strength, which are then removed from the tip surface, by a process referred to as field evaporation [1]. In “conventional” APT, the standing DC voltage is held below the field evaporation threshold of the surface atoms, and nanosecond high-voltage pulses are applied to raise the field above the threshold and trigger field evaporation. The atoms removed subsequently pass through a time-of-flight (ToF) mass spectrometer equipped with a position-sensitive detector. The projection of atoms from the tip surface to this detector represents a point projection microscope and results in magnifications of up to $10^6 \times$. Based on the ion flight time and its position on the detector, the nature of the atom and its original position in the sample volume can be reconstructed [1].

Ultra short laser pulses can be used instead of voltage pulses to study materials with electrical conductivities lower than metals and alloys. For picosecond pulsing it is widely accepted that a short, spatially confined temperature rise at the specimen apex lowers the field evaporation threshold and leads to field evaporation at a given DC voltage [1,2]. This temperature rise just reaches from the tip...
base temperature (~ 50K) to about room temperature [1,3,4] and is therefore far below the threshold of thermal evaporation, sublimation or material breakdown.

With the implementation of laser pulsing “new” applications of APT have been progressing quickly. Various electronic materials have been successfully studied, addressing e.g. implantation profiling in silicon nanostructures, high-k dielectrics, compound semiconductors, photovoltaics and magnetic data storage materials [5-8].

For electronic materials, focused ion-beam lift-out and annular milling procedures [9,10] have become the predominant methods of sample preparation in order to achieve the very sharp needle-shaped specimen required. Generally, FIB-based preparation allows for flexible and reproducible tip preparation with limited ion-beam induced damage [11]. In particular, the combination of ion beam milling and high resolution SEM imaging (in dual-beam devices) has proven to provide maximal control throughout the entire preparation process.

Apart from laser pulsing and FIB sample preparation, further technological progress in recent years, e.g. the development of the local electrode technology [12], led to significantly increased data collection rates (reaching up to 5,000,000 ions/min), much larger field-of-views (FoV, up to 200 nm), improved mass resolution (better than 1/500 FWHM) and the use of “microtip arrays”. This enables the evaluation of sample volumes in the order of $10^7$ nm$^3$ in a fraction of the time needed by first-generation atom probes, resulting in more representative and comprehensive data sets [2]. For atom probe studies of semiconductor materials, laser assisted field evaporation (i.e. laser pulsing) has probably been the most significant progress in instrumentation pushing the frontiers of APT applications to this “new” class of materials.

2. Laser-pulsed APT applications in compound semiconductor research

2.1. Exploration of buried InAs quantum dots

Atom probe studies of buried quantum dots were conducted on a molecular beam epitaxy (MBE)-grown system of InAs quantum dots (material by courtesy of L. Chang, National Chiao Tung University, Hsinchu, Taiwan). The wetting layers with a thickness of about 2.6ML were grown at 485 °C with a growth rate of 0.28 Å/s. The capping with 30 nm of GaAs was realized at 600 °C and a growth rate of 3 Å/s. Microtip samples were prepared perpendicular to the (001) surface using the standard FIB preparation procedure introduced earlier, employing a Zeiss NVision40 dual-beam FIB. Atom probe experiments were carried using Imago’s LEAP™ 3000X HR equipped with a picosecond laser system under optimized experimental conditions.

In the 3D atom map the quantum dots are represented by regions of locally higher indium density. These regions can be represented by isosurfaces, i.e. surfaces of either equal concentration or count density. Based on these isosurfaces, it was found that the dots possess on average (~ 70 quantum dots evaluated) a lens-shaped morphology with a base length aspect ratio of around 1:1.5 with $X\sim(19.1\pm1.2)$ nm, $Y\sim(13.1\pm1.0)$ nm and an average dot height of $(4.1\pm0.2)$ nm.

Gallium was found to be substantially incorporated within the dots, the In-to-Ga ratio spatially averaged over the volume enclosed by the isosurfaces (~ 500 nm$^3$, typically confining 20,000-30,000 ion counts) was determined to be In$_{0.22\pm0.01}$Ga$_{0.78\pm0.01}$ (values derived from 70 quantum evaluated) in good agreement with kinetic modelling of intermixing during quantum dot growth [13] given the relatively high capping procedure (600 °C) for this material system. Two-dimensional indium concentration profiles derived from virtually projection-free cross-sections through the dots revealed the presence of a laterally shifted In-rich core within the dot with a maximum In-concentration of In$_{0.4}$Ga$_{0.6}$ [8]. Indium enrichment in the core was also observed by other authors [14-16], varying from e.g. $x=0.62$ [15] to $x=1$ [16] certainly at least partly depending on the different material systems studied and characterisation methods applied.

The comprehensive AP data also allows for wetting layer analysis. The as-reconstructed layer exhibit an asymmetrical In-concentration profile (Figure 1) steep at the InAs-on-GaAs interface but more gradual at the capping side, suggesting pronounced cation intermixing over around 3 nm. Given that this latter interface was grown at substantially higher temperatures, the stronger intermixing observed appears reasonable. Similarly, such asymmetry and its spatial extend were also indicated by various TEM studies [15,16]. The maximum indium concentration within the wetting layers reaches...
In$_{0.2}$Ga$_{0.8}$. This maximum In-content in the wetting layer agrees remarkably well with other studies stating $x$ to be between 0.15 [15] and 0.2 [16].

![Figure 1: In-to-Ga-ratio across the interfaces of the InAs wetting layer. The In-concentration profile (green, - - -) shows a clear asymmetry with a gradual InAs-on-GaAs interface, indicating stronger intermixing during the capping process.](image1.png)

For very well defined and consistent physical properties of QD-based devices, the quantum dots should possess highest uniformity in many aspects e.g. a narrow size distribution and similar compositions. The AP data derived, uniquely addresses the question of dot-by-dot variability providing firm statistics based on a large number of dots, but maintaining nanoscale accuracy. For example, variations in size and composition have been listed before [8]. In addition, Figure 2 illustrates the lateral positions of the In-rich cores in a stack of self-assembled dots. It is obvious that the core position varies from dot to dot as does the maximum indium concentration.

![Figure 2: Illustration of the maximal, local In-distribution within consecutive quantum dots of a stack. On the left hand side the dots (blue isosurfaces) are shown in an atom map displaying In-atoms (green) of the wetting layers only. On the right hand side the corresponding 2D-concentration profiles based on 1 nm thick cross-sections along the major dot axis are presented. The red regions within the dots represent the highest In-concentration normalized to the maximum In-concentration in c) (see white dashed circle) of In$_{0.4}$Ga$_{0.6}$.](image2.png)

2.2. Nanostructural analysis of a thin-film GeMn magnetic semiconductor

The GeMn system is a promising candidate as a versatile magnetic semiconductor material, with potential applications in spintronics [17]. Current interest surrounds the structure-property relationship determining the magnetic/conductive characteristics of Ge thin-films containing a few percent Mn in a highly super-saturated solution [18,19]. An understanding of these material systems requires chemically sensitive analysis of the nanostructure with the highest possible resolution in three dimensions.

Laser-pulsed atom probe tomography was used to characterize a GeMn thin-film (by courtesy of D. Bougard, Walter Schottky Institute, TU Munich, GER) containing 2-4% Mn, grown by MBE on a Ge(001) substrate to a thickness of approximately 100nm. String-like arrangements of Mn-rich clusters were found (Figure 3), oriented in the growth direction, with concentrations of 10-20% Mn at their centres. These observations are consistent with earlier characterization by TEM and X-ray diffraction [20], but provide new insights into the nanostructure that offer greater consistency with the magnetic and electrical characteristics.
Figure 3. Iso-concentration surfaces (yellow) showing the distribution of Mn-rich regions in a GeMn thin film grown by MBE. Characterisation of the morphology and chemical composition of these structures in 3D is necessary for understanding the magnetic properties of the film. Individual detected Mn atoms are shown as blue dots. The vertical, dashed lines (black) indicate column-like structures of Mn-rich regions.

3. Discussion

Although small in number, early applications certainly prove the applicability of laser-pulsed atom probe tomography in compound semiconductor research and cast a positive light on future studies. Since research is still in its infancy, issues like optimising experimental conditions, chemical accuracy and homogeneity as well as data reconstruction for (compound) semiconductor nanostructures (quantum dots, multilayer systems) need to be addressed in due course. In particular, besides just focusing on new applications, fundamental studies on basic reference materials are indispensable for a better understanding and assessment of the technique itself.

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