Three-Dimensional Nanoscale Composition Mapping of Semiconductor Nanowires

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ABSTRACT

We demonstrate the three-dimensional composition mapping of a semiconductor nanowire with single-atom sensitivity and subnanometer spatial resolution using atom probe tomography. A new class of atom probe, the local electrode atom probe (LEAP) microscope, was used to map the position of single Au atoms in an InAs nanowire and to image the interface between a Au catalyst and InAs in three dimensions with 0.3-nm resolution. These results establish atom probe tomography as a uniquely powerful tool for analyzing the chemical composition of semiconductor nanostructures.

Semiconducting nanowires of controlled composition and doping1−4 show great promise as multifunctional components in a number of emerging device technologies.5−7 The continued advancement of these nanometer-scale devices will depend critically on knowledge of their atomic-scale structure8 because compositional fluctuations as small as a single dopant atom can affect device performance. It is therefore highly desirable to determine the composition of individual nanowires with the utmost precision. The spatial resolution of secondary ion mass spectroscopy (SIMS) has been pushed below 100 nm,9 but the nanowire length-scales of interest are much smaller. Transmission electron microscopy (TEM) is capable of imaging single dopant atoms under specific conditions10 but TEM cannot yet be considered a general tool for the volumetric mapping of low-concentration elements in nanostructures. The important challenge of doping atoms into the “bulk” of nanowires and nanocrystals while avoiding surface segregation further emphasizes the need for three-dimensional composition characterization in these nanostructures.

Here we demonstrate the three-dimensional composition mapping of a semiconductor nanowire with single-atom sensitivity and subnanometer spatial resolution using atom-probe tomography.11 A new class of atom probe, the local electrode atom probe (LEAP) microscope,12,13 was used to map the position of single Au atoms in an InAs nanowire and to image the interface between a Au catalyst and InAs in three dimensions with 0.3-nm resolution. These results establish atom probe tomography as a uniquely powerful tool for analyzing the chemical composition of semiconductor nanostructures.

Functional one-dimensional semiconductor nanostructures have been synthesized by a number of methods.14 In the present study, electron beam lithography followed by metal evaporation and lift-off was used to pattern an array of Au catalyst disks on a GaAs(111)B wafer. The Au seeds catalyzed the growth of InAs nanowires in a quartz metal-organic vapor-phase epitaxy (MOVPE) reactor with trimethylindium and arsine as reactant chemical precursors and hydrogen as the carrier gas under conditions described previously.15 In this manner, arrays of epitaxial vertically oriented InAs nanowires 100−140 μm long and spaced 500 μm apart were generated, which facilitated analysis with the LEAP microscope (Figure 1a).

The capability of mapping nanowire composition at the atomic scale originates from the sequential field evaporation of individual atoms from a nanowire tip (Figure 1a inset, Figure 1b). When a positive voltage is applied to a nanowire through the growth substrate, a very large electric field develops at the nanowire tip because of the high local radius of curvature. This local electric field reduces the potential energy barrier that bonds an atom to the surface, resulting in field evaporation of a positive ion (Figure 1c). In the LEAP microscope, subnanosecond voltage pulses are applied at 200 kHz to a conical electrode positioned above the nanowire,
leading to sequential field evaporation of single ions at the pulsing frequency (Figure 1d). The mass-to-charge state ratio, \( m/n \), of an evaporated ion is determined by measuring the time delay between the local electrode voltage pulse and the signal generated when the ion strikes a two-dimensional position-sensitive detector; the calibrated time-of-flight between the nanowire tip and the detector is proportional to the square root of \( m/n \). The initial position of an atom on the nanowire tip is determined by reconstructing the flight path between the detector and the tip. In this manner, a three-dimensional reconstruction of the nanowire composition may be generated atom-by-atom with subnanometer resolution.

Figure 2 presents a three-dimensional reconstruction of an InAs nanowire generated from a data set of \( 1.3 \times 10^6 \) atoms evaporated sequentially in the LEAP microscope. Single atoms are represented by dots, and the dot color indicates its chemical identity as determined by the time-of-flight measurement. The side view of Figure 2a shows that analytical volumes comparable to an entire nanowire-based device, such as the channel of a nanowire transistor, are well within the capabilities of this technique. When looking along the nanowire axis (Figure 2b), hexagonal facets are clearly observed, and comparison with a scanning electron microscopy image (Figure 2c) verifies that we have reconstructed the nanowire cross-section accurately. More significantly, a magnified view perpendicular to the nanowire axis reveals distinct planes of atoms extending across the nanowire (Figure 2d). These planes lie perpendicular to the wurtzite [0001] growth direction at a spacing of 0.35 nm, as determined by transmission electron microscopy (TEM), and the observation of atomic planes in the LEAP reconstruction demonstrate the achievement of subnanometer resolution.

It is important to note that while Figure 2 presents useful two-dimensional projections, the three-dimensional position and chemical identity of every atom is retained in the original data set, which is not generally the case for projections generated in transmission electron microscopy (TEM) measurements. To emphasize this point, Figure 2e presents an enlarged section of the nanowire of Figure 2a using spheres to represent each individual Au atom found within the analyzed volume. From the figure, it is obvious that dopant concentrations and fluctuations on any length scale and along any axis can be extracted by averaging over a chosen volume. The implications of our observation of catalyst atoms within the nanowire are not discussed here, but we can immediately draw two important conclusions regarding the potential for LEAP tomographic analysis of nanostructures. First, one can now determine whether the catalyst used in nanowire growth schemes becomes incorporated in the bulk of the nanowire for nanowires of arbitrary composition. This question is of critical importance to the performance of nanowire devices because metal atoms such as gold can strongly influence electronic properties. Second, and more generally, LEAP microscopy can be used to reveal the concentration and distribution of dopants in a range of chemically synthesized nanostructures, and may therefore play a critical role in addressing the major challenge of dopant incorporation and segregation in nanomaterials.

Another important capability of the LEAP microscope is the imaging of interfaces within a nanostructure because functional heterointerfaces form the basis of most semiconductor devices. In particular, one would like to be able to analyze the compositional abruptness of junctions within nanowires without averaging over the nanowire diameter. Analysis of a reconstructed nanowire section including a Au catalyst/InAs nanowire heterophase interface is displayed in Figure 3. As expected, the gold catalyst lies atop the nanowire during and after growth. The four “slices” of Figure 3a, two on either side of the interface, demonstrate that...
tomographic analyses can reveal both radial and axial composition variations within a nanowire. Although the catalyst-nanowire interface appears qualitatively abrupt in Figure 3b, the interface width is more readily ascertained by plotting a one-dimensional composition profile derived from a cylindrical section perpendicular to the interface (Figure 3c); the interface between the catalyst (Au$_{0.9}$In$_{0.1}$) and nanowire (In$_{0.5}$As$_{0.5}$) is extremely abrupt with a width of less than 0.5 nm. Because nanowire growth occurs at this interface, its structure may influence the widths of intrawire semiconductor heterojunctions formed by similar nanowire growth processes, particularly the metal-catalyzed vapor—liquid—solid growth process.

Nanowire heterointerfaces have also been analyzed in some detail by TEM, but the one-dimensional composition profiles determined by energy-dispersive X-ray spectroscopy or electron energy loss spectroscopy may show artificially large interface widths because the signal is averaged over the entire volume through which the electron beam passes. This represents a serious limitation when

Figure 2. Three-dimensional reconstruction of an InAs nanowire. (a) Side view (perpendicular to growth axis) of a $25 \times 25 \times 300$ nm$^3$ reconstruction of nanowire. In, As, and Au atoms are rendered as green, purple, and yellow dots, respectively. Only 5% of the atoms are shown to provide a sense of depth. (b) A $21 \times 21$ nm$^2$ end-on view of nanowire reconstruction showing hexagonal faceting. (c) Scanning electron micrograph of an InAs nanowire showing hexagonal cross section ($1.7$ $\mu$m$^2$). (d) Magnified side view of the nanowire showing (0001) atomic planes. The dimensions are $23 \times 14$ nm$^2$. The slight curvature of the planes is an artifact; the software used for the reconstruction assumes a hemispherical end-shape for the evaporating nanowire. (e) A $27 \times 27 \times 29$ nm$^3$ reconstruction of the nanowire with Au atoms enlarged and 2% of In and As atoms shown for clarity; the growth axis runs left to right. The 18 Au atoms within the volume correspond to a concentration of 100 atomic parts per million.
analyzing nanostructures of varying radial composition, such as core–shell nanowires. Furthermore, TEM elemental analysis has a sensitivity of approximately 1% for general chemical identification. In contrast, the LEAP microscope provides single-atom sensitivity that could be used to image small concentrations of dopant atoms on either side of an intrawire p–n junction. Cross-sectional scanning tunneling microscopy (XSTM) is also a powerful tool for analyzing interfaces in nanowires with atomic resolution, but we do not believe that the XSTM will be as generally useful as atom-probe tomography because it cannot provide general chemical identification and is restricted to two dimensions. Historically, atom-probe tomography has been applied more extensively to metals than semiconductors, but atom-probe analysis of semiconductors and semiconductor devices is likely to increase greatly because advances in instrumentation now enable the analysis of sample volumes comparable to the active region of semiconductor devices.

The present demonstration of three-dimensional composition mapping of a semiconductor nanowire with subnanometer resolution establishes that LEAP microscopy can play an important role in the development of semiconductor nanostructure device technology by providing critical insight into the connection between synthesis schemes and nanoscale composition. LEAP microscopy has the potential to be applied to other semiconductor nanostructures, including zero-dimensional nanocrystals, by depositing samples on arrays of posts elevated from the substrate. Furthermore, considering the concurrent development of nanoscale property measurements via scanned probes, LEAP microscopy promises to advance materials science by extending our understanding of structure–property relationships to the nanoscale limit.

Figure 3. Catalyst nanowire interface in three dimensions. (a) 1-nm-thick slices through the nanowire over the region defined by the white bar in b. The diameter of the slices is 10 nm. The color coding is identical to that of Figure 2. (b) A 14 × 14 × 23 nm3 reconstruction of an InAs nanowire tip showing Au catalyst particle at the top. (c) One-dimensional composition profile plotted along the growth axis and through the catalyst/nanowire interface. The plotted composition is a radially averaged value within a 4-nm-diameter cylinder centered in the middle of the nanowire.

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References

(9) For example, NanoSIMS50, manufactured by Cameca, France.
(12) Imago Scientific Instruments, Madison, Wisconsin.
(16) The static bias used for nanowire analysis was 500–2500 V. The pulse voltage was fixed at 20% of the static bias. The very high evaporation fields generated by these voltages are not expected to lead to electromigration because the low temperatures used (50–100 K) preclude significant vacancy-mediated atomic motion.
(17) The position-sensitive detector consists of a multichannel plate (MCP) behind which is a delay line detector. The MCP is used to measure the ion time-of-flight and the delay line detector the ion position with respect to the nanowire tip.
(18) Reconstructions of the position-resolved time-of-flight data were performed with the software program IVAS, provided by Imago Scientific Instruments.
(19) The sample temperature ranged from 50 to 100 K and the ambient pressure was 10^{-10} Torr during pulsed field-evaporation.
(21) Although a thin (1–2 nm) amorphous oxide layer is seen on InAs nanowires in TEM measurements, we do not observe oxygen-related peaks in the time-of-flight mass spectra. We believe that the oxygen species are evaporating between voltage pulses, that is, that the static field near the nanowire tip is sufficient to evaporate the oxide.
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