Analysis of Optoelectronics with Atom Probe Tomography
3D Nanoscale Dopant Distribution in ALD-Grown ZnO

Application Note #APT-16

Atomic layer deposition (ALD) is a thin film growth technique that offers a high degree of control over thickness and composition. Growth is achieved through a cyclical process of repeated exposure and purging of chemical precursors that deposit a subnanometer layer with each cycle.

ZnO is an example of an optoelectronic material that can be easily grown by ALD with great precision. The precursors are diethyl zinc (DEZ) which provides the Zn, and deionized water, which causes an oxidation step. To make ZnO functional for optoelectronic applications, it must be made conductive. This is achieved by including an additional precursor, trimethyl aluminium (TMA), which provides Al atoms to the growth. By choosing the number of cycles between each TMA substitution the doping level can be tuned for the desired application, such as the channel in a thin-film transistor or a transparent conductor in next generation solar cells.

Although precise and repeatable thickness and doping levels are achievable, the electrical properties will be determined by the nanostructural details of the dopant distribution. In particular, not every Al dopant will be activated and contribute to the electrical performance; some may simply act as scattering centers, reducing carrier mobility. The mobility depends on whether the Al is incorporated into a ZnO grain or in a grain boundary.

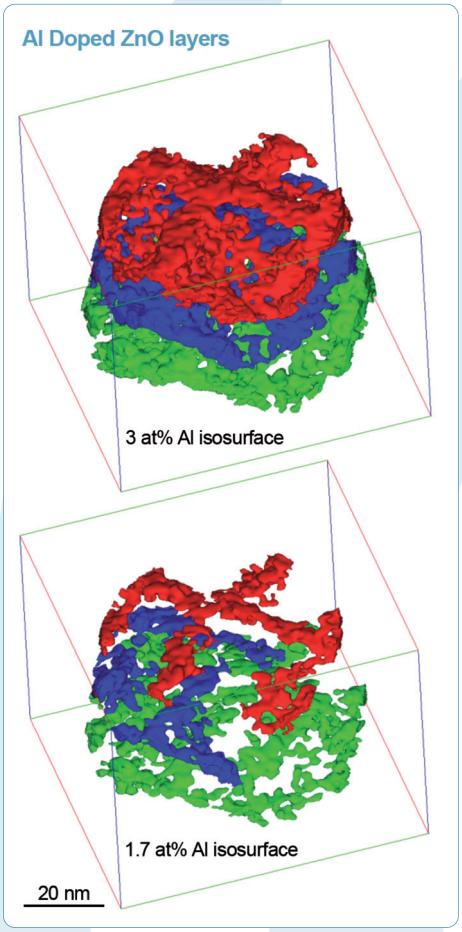
Measuring the location and concentration of the aluminum in the ZnO is extremely challenging for microscopies such as TEM. Until now, models based on the electrical characterization have had to be relied on. In this work we take advantage of the unique ability of the Local Electrode Atom Probe (LEAP®) to provide the high-sensitivity chemical information at atomic length-scales needed to explore the complex nanostructure of these materials. The data from the LEAP provide the insight needed to understand how to improve their performance.

LEAP measurements of ALD films with different levels of doping assist in understanding the proportion of aluminum atoms that contribute a carrier by identifying their locations within grains or at grain boundaries. As the dopant concentration increases from more frequent additions of TMA, different film morphologies and different phases may be formed and the LEAP system has been used very effectively to identify the morphologies and trends with respect to the doping levels.

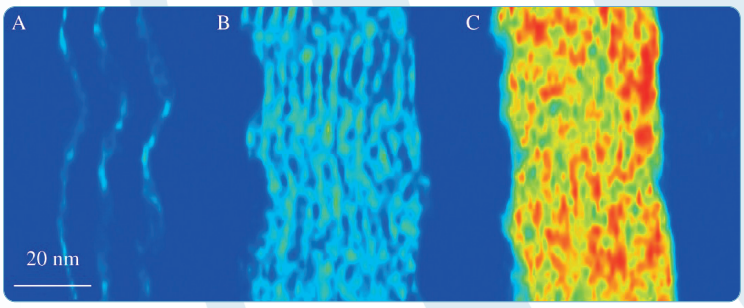
Three different Aluminum rich ZnO multilayer stacks were grown with pure layers of ZnO in-between to separate them. The top layer has 3 Al cycles, the middle one 11 cycles and the bottom one 19 cycles.

Isosurfaces showing 1.7% aluminum (top) and 3% aluminum (bottom) show that although there appears to be a very high coverage rate in each layer, regions of enhanced aluminium concentration exist, with the same periodicity of the grain boundaries identified in TEM.

The segregation of aluminum to grain boundaries, rather than being evenly distributed in the grains will have a significant detrimental affect to the conductivity of the film.



Two dimensional concentration plot (80 nm x 200 nm) showing the Al distribution in three different Al:ZnO multilayer structures. Color ranges from blue (0%) to red (16%) aluminum.



Adapted from A.D. Giddings et al., Compositional and Structural Analysis of Al-doped ZnO Multilayers by LEAP, Micros. Microanal. 20, 2014

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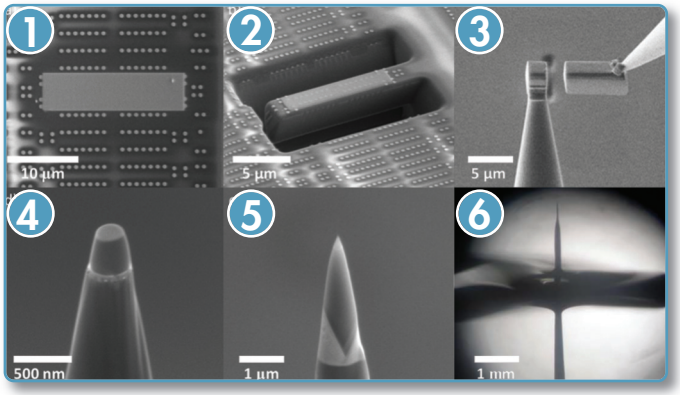
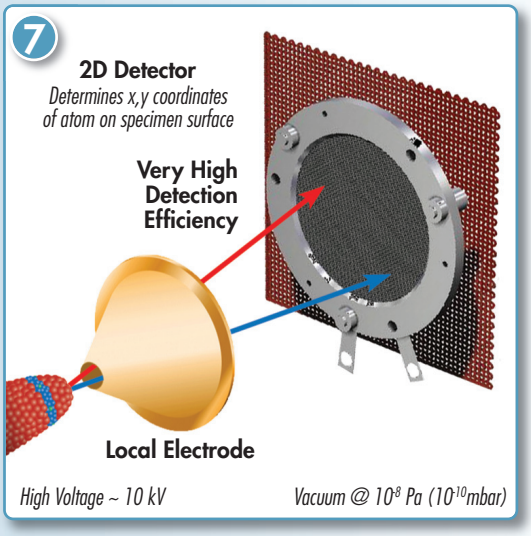
www.cameca.com • www.atomprobe.com
International Headquarters: 29 quai des Grésillons • 92622 Genevilliers • France • cameca.info@ametek.com
Atom Probe Technology Center: 5500 Nobel Drive • WI-53711 Madison • USA • cameca.leap@ametek.com
AMETEK® MATERIALS ANALYSIS DIVISION

Three Steps to 3D Nanoscale Analysis
An Introduction to Atom Probe Tomography

Step 1: Specimen Preparation

An atom probe specimen usually has a nanoscale region of interest (ROI) requiring both 3D compositional imaging and analysis. The sample is formed into a needle shape containing the ROI. Common APT specimen preparation methods using electropolishing or a Focused Ion Beam system (FIB) are very similar to TEM methods except instead of forming a thin sheet, a needle shaped sample is desired. At the right, standard FIB liftout and mounting of a specimen (figures 1 through 3) and then sharpening the sample with the ROI left at the very apex (4 and 5). In 6, a wire geometry sample is being electropolished.





Step 2: Data Collection

An atom probe produces images by field evaporating atoms from a needle-shaped specimen and projecting the resultant ions onto a detector 7.

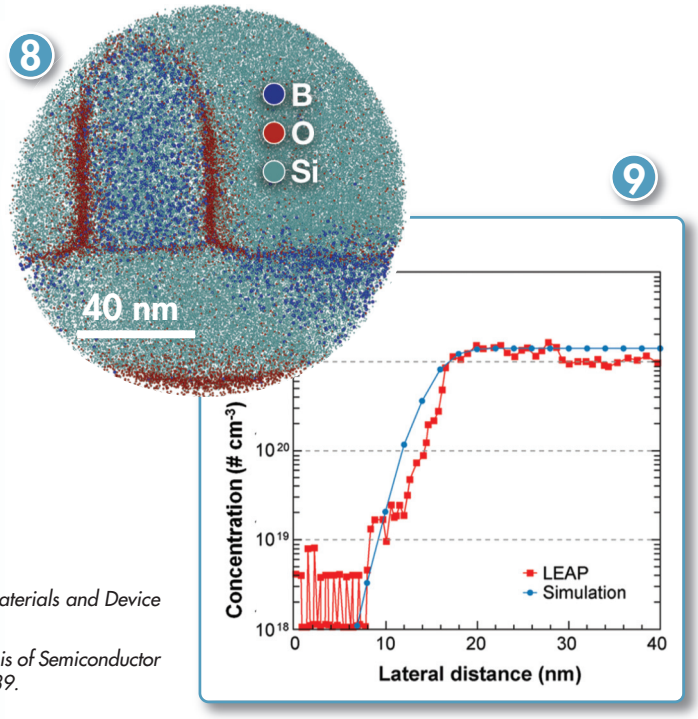
A high magnification results from the ~ 80nm tip being projected onto an 80mm detector resulting in a magnification of approximately 10^6.

An atom probe identifies atoms by their mass-to-charge-state ratio *(m/n)* using time-of-flight mass spectrometry. Charge state, *n*, is typically 1 to 3.

The specimen is held at approximately 50K to reduce surface diffusion during the experiment. The high electric field results in 100% ionization and the high speed detector is capable of measuring up to 80% of the collected ions, independent of ion mass.

Step 3: Data Visualization and Analysis

Examples of data output are illustrated by a slice of a 3D atom map of a transistor† 8, and a dopant composition profile‡ 9. The image shows the positions of individual atoms (oxygen is red and boron is blue) in the transistor with subnanometer resolution. From the reconstructed data set many types of useful analyses are possible. These include 3D visualization, 2D atom mapping 8, 1D depth profiling and line scanning 9, as well as mass spectra and compositional analysis from user-selected volumes.



† *Lauhon, L. J. et al, MRS Bulletin "Atom Probe Tomography of Semiconductor Materials and Device Structures" 34(10) (2009) 738.*

‡ *Moore, J. S.; Jones, K. S.; Kennel, H.; Corcoran, S., Ultramicroscopy "3-D Analysis of Semiconductor Dopant Distributions in a Patterned Structure using LEAP" (2008), 108, 536–539.*