Application Note

Aduro™

Correlative Analysis in the TEM and SEM Kirkendall Effect Zinc Oxide/Alumina Spinel Formation Observed *In Situ*

Introduction

The electron microscope provides a means to image nanoscale features and analyze chemical components in materials. Materials properties such as crystalline phase can be studied with electron diffraction and constituent elements identified with x-ray analysis (EDS).

In the scanning electron microscope (SEM) nanoscale features are usually resolved via two types of imaging techniques. Surface topology can be analyzed with secondary electron imaging and element specific contrast is possible with backscatter electron imaging. EDS can also be used in the SEM to identify elements. Together the SEM and TEM offer innumerable ways to analyze samples and correlate data to form a complete picture of material properties.

The Aduro heating and electrical biasing platform is compatible with both the TEM and SEM, transforming new and existing microscopes into *in situ* nanoscale laboratories. Aduro utilizes E-chip™ semiconductor devices, which act as the sample support and active area. Depending on the type of experiment, users can choose between Electrical E-chips for electrical biasing experiments, or Thermal E-chips for heating experiments. The electrical or thermal stimulus is controlled via Protochips designed software, which communicates to an electronics control unit or ECU.

The ECU supplies stimulus to the E-chip through the TEM or SEM holder. With this configuration, the E-chips, software, and ECU can be used with either the SEM or TEM, only the holders are different for each instrument.

In this experiment, the Kirkendall effect was observed in zinc oxide/alumina concentric layers. This effect occurs when metal atoms diffuse at elevated temperatures and displace an interface. In this experiment Zn diffuses into alumina making a spinel structure at >700 °C. This diffusion process also creates voids, called Kirkendall voids. This effect is well known, and used to fabricate nanomaterials such as hollow spherical shells, nanotubes and dendrites. Using Aduro in both the TEM and SEM, formation of the spinel structures and the subsequent voids were captured *in situ* in real time.

Experiment

Hollow tube composed of three coaxial layers of 35 nm Al_2O_3, 30 nm ZnO, and 38 nm Al_2O_3 were formed using atomic layer deposition (ALD). For the experiment in the SEM, a polymer fiber was electrospun onto a Thermal E-chip membrane. The fibers were coated with the three layers using ALD. The polymer fibers were dissolved leaving Al_2O_3/ZnO/Al_2O_3 microtubes. The tubes were imaged in secondary electron mode in a Hitachi SU-6600 SEM. For TEM imaging, microtubes were prepared and thin sections were created using a FIB. The sections were transferred to a Thermal E-chip membrane. Images were taken in bright field mode using a JEOL 2010F operating at 200 kV.

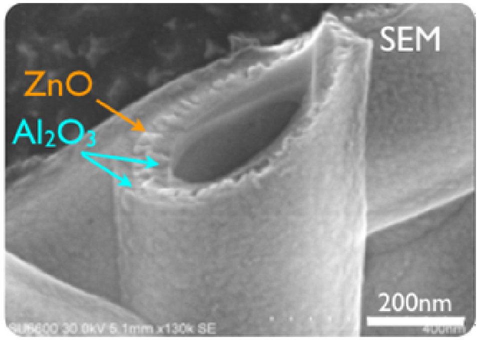

Figure 1A

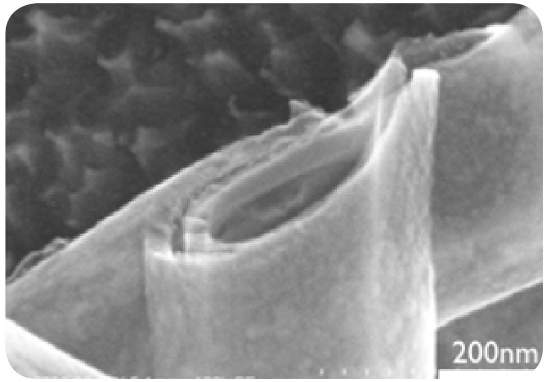

Figure 1B

Discussion

An SEM image of a tube before heating is shown in Figure 1A. The arrows indicate the coaxial layers of ZnO and Al_2O_3 After heating to 750 °C, the ZnO diffused into the Al_2O_3 layers creating the $ZnAl_2O_4$ spinel. Void formation was readily apparent and visualized in real time over the course of 10 minutes in the center layer where the ZNO layer originally formed. The formation of these voids were imaged and visualized in real time. Figure 2A shows a TEM image of the thin section created with FIB, and the 3 layers are indicated in this image. After heating to 750 °C for 10 minutes, the Kirkendall effect was visualized in high resolution. The image formation in the TEM is different from the SEM, so different features can be seen in this image. As the Zn diffuses into the Al_2O_3, larger crystal grains result. Differences in contrast were also noted. However, voids were not observed to form in this case, but grain growth in the microtubes, was dynamically observed.

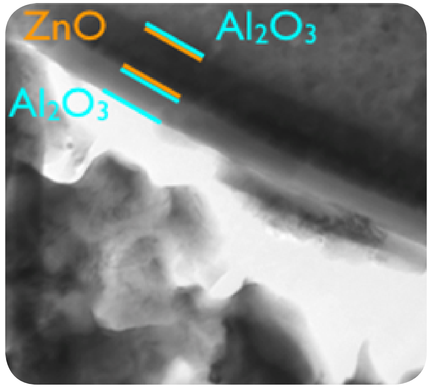

Figure 2A

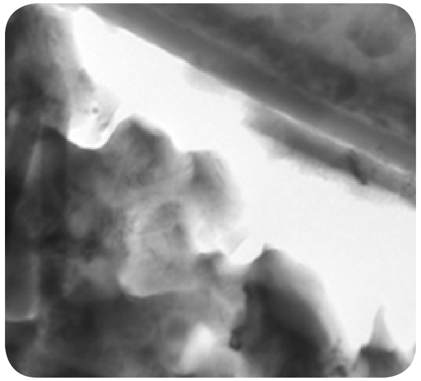

Figure 2B

Applications

These correlative imaging experiments showing the Kirkendall effect in real time are applicable to research and development in batteries, drug delivery, and semiconductors. Correlative imaging is not limited to the processes described above as many different types of material processes can benefit from using this technique. The flexibility and versatility of Aduro makes doing correlative experiments fast and easy without compromising data quality.

Contact us to discuss the full range of capabilities of Aduro with the Thermal E-chip sample supports.