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Quantitative Measurement of Volumes for Nanoparticles by High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy

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A quantitative method to determine sample thicknesses in Transmission Electron Microscopy (TEM) using the Scanning (STEM) mode is presented. A High-Angle Annular Dark-Field (HAADF) detector collects electrons scattered to high angles with its intensity proportional to the sample thickness and increasing with atomic number. Multilayered samples provided by TriQuint Semiconductors in Apopka (FL) are used for calibration yielding data on the interaction cross section per atom. Multislice simulations in C# .NET 3.5 are used for comparison with experimental results. The calibrations were used to determine concentration gradients in nanoscale Fe-Pt multilayers as well as thicknesses and volumes of individual Ag nanoparticles. Volumes of nanoparticles with known composition can be determined with an accuracy better than 15%.

The sizes, shapes and volumes of nanoparticles are very important for their macroscopic properties. Efforts to measure these parameters for individual particles and to obtain reliable statistics for a large number of nanoparticles require a fast and reliable method for 3-D characterization. In the approach presented here we use HAADF-STEM to determine the thickness of nanomaterials from individual calibrated micrographs [1-8]. Additionally, for a sample with constant thickness the composition of a binary alloy can be obtained. A Tecnai F30 from FEI operating at 300 kV and equipped with a field emission source was used. In the STEM mode a Fischione HAADF detector with a contrast/brightness setting of 12.5% and 46.875% and at a camera length of 80 mm was consistently used throughout this study. To obtain an absolute intensity calibration of the HAADF-STEM intensity, CBED was performed on Si single crystals.

The analysis of the sample shown in Figure 1 yields results on the Pt composition in the Fe-PT multilayers. The as-received samples are six [Pt(28nm)/Fe(22nm)] layers on a SiO_2/Si substrate [9]. After 10 minutes of heat treatment at 350°C, interdiffusion of Fe into the Pt layer and Pt diffusion into the Fe layer can be observed (Figure 1, left). The linescan in Figure 1 (right) shows that Pt diffuses into the Fe layer, while diffusion of Fe into the center of the Pt layer is limited.

A second focus of quantitative HAADF-STEM is the thickness and volume determination of nanoparticles [3-5]. In Figure 2 a plan view HAADF-STEM image of Ag particles on a SU8 polymer is shown. The average thickness of the Ag layer is 45 nm with a standard deviation of 18 nm. This high value for the standard deviation reflects the granular structure of the Ag layer, which is composed of individual nanoscale grains. Some Ag grains are on top of each other while other areas of the polymer between Ag nanoparticles are not covered by silver. The average particle volume was determined to be (65000±9000) nm^3, yielding an average particle diameter of 50 nm.

For binary alloys with known TEM sample thickness, the composition can be obtained from a single HAADF-STEM micrograph. A significant difference in atomic number of the two elements is required. For known compositions the thickness of nanoparticles can be determined by HAADF-STEM, and the volume of individual nanoparticles and growth rates can be directly measured.

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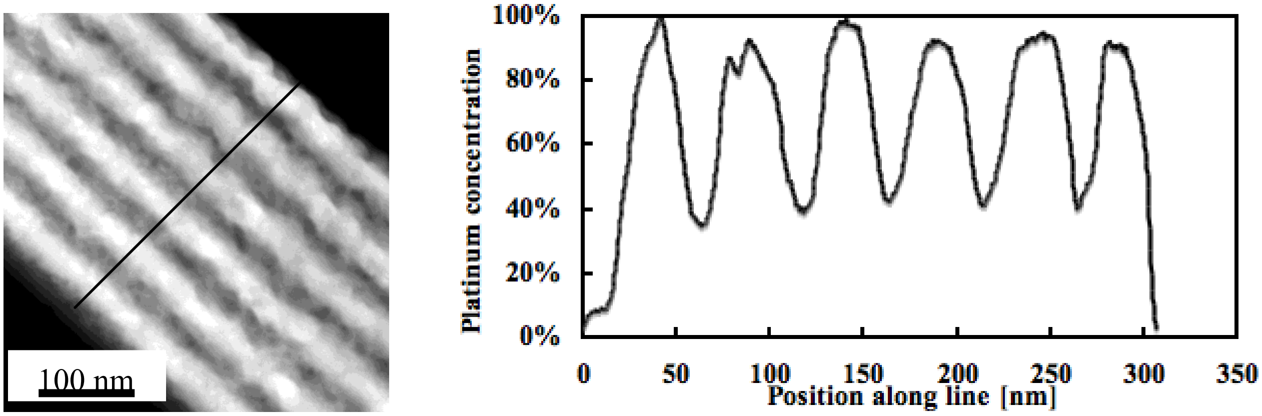

FIG. 1. Left: A HAADF-STEM micrograph of a multilayer system on Si and SiO_2 with six Pt (28 nm) and six Fe (22 nm) layers after 10 minute heat treatment at 350°C. Right: Linescan of the Pt composition as determined by HAADF-STEM across the Fe and Pt layers.

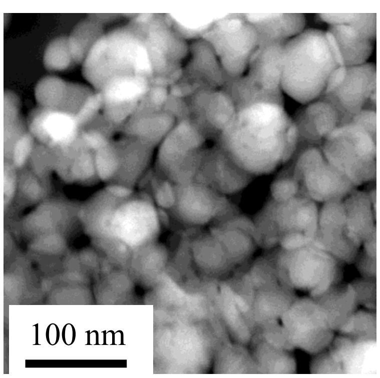

FIG. 2. Plan view HAADF-STEM of Ag nanoparticles on a SU8 polymer prepared by 6 hours of electroless deposition using $[Ag^+]$ = 5.6 mM in the presence of gum arabic.

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