Analytical Transmission Electron Microscopy Characterization of Nano-Structured Materials

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ABSTRACT

This paper reviews applications of analytical transmission electron microscopy (TEM) to characterize nano-structured materials and devices. Several practical examples are provided that show the diverse imaging and microanalysis mechanisms available in a modern TEM. By leveraging the right imaging and microanalysis technique, TEM can reveal the properties of materials at the nanometer scale.

Keywords: TEM, STEM, EELS, nanoparticles, microanalysis

1 INTRODUCTION

Contrast mechanisms in TEM are dependent on: a) the mass-thickness effect, b) diffraction effects (for crystalline materials) and c) phase contrast. Combined with the ability to form a sub-nanometer probe in the STEM mode and perform spectroscopy by either Energy Dispersive X-ray Spectroscopy (EDS) or Electron Energy loss Spectroscopy (EELS), TEM allows the characterization of materials at high resolution and in a spatially resolved manner [1]. We present several practical examples where the TEM based techniques have characterized the structure and/or composition of material at nanometer scale. This analysis would have been difficult, if not possible by other characterization techniques.

2 EXPERIMENTAL

For this study, the TEM samples were prepared by standard preparation methods involving Focused Ion Beam (FIB) milling, mechanical polishing followed by Ar+ milling or by dispersing nano-particles on carbon-support films. An FEI Altura 835 FIB mill equipped with Omniprobe lift out tool was used for FIB preparation. GATAN PIPS system was employed to polish and clean the mechanically prepared samples at low energies and low angles (2-3keV & 4-6 degrees respectively). TEM characterization was performed on a FEI Tecnai TF-20XT FEGTEM equipped with a 30mm^2 Oxford INCA EDS detector, Fischione HAADF-STEM detector and a GATAN ENFINA PEELS system.

3 RESULTS AND DISCUSSION

Fig. 1 shows two bright field (BF) TEM images of a) cross-section of a microelectronic device with poly-silicon gates connected to copper metal lines and b) a MOSFET gate in cross-section. In addition to measuring critical dimensions with high precision, information about the phase and structure of different materials is possible. The crystalline nature of the poly-Si and Cu and their grain shape and size is easily seen. Crystallographic defects at the edge of the transistor are revealed in the second image. Also, note the presence of nitrided gate oxide as indicated by the dark contrast in the thin (~2nm) gate dielectric film. Nitridation is frequently employed to increase the effective dielectric constant of the gate oxide so that the transistor gate can maintain better control of the conduction channel in the Si substrate [2].

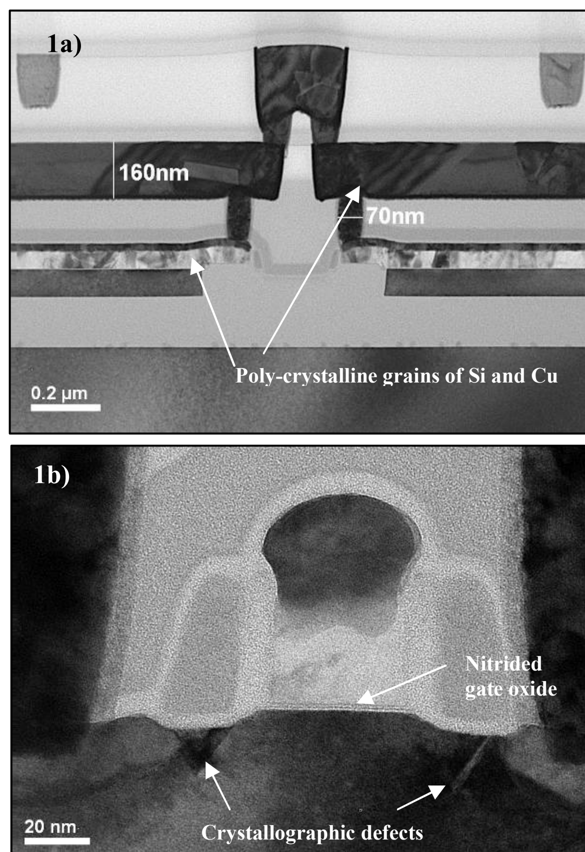

Figure 1 BFTEM images of a microelectronic device a) along the poly-Si gate and b) across the poly-Si gate.

High Resolution (HR) TEM imaging allows observation of the atomic arrangements in a crystalline lattice. These images are formed by utilizing the phase contrast that arises when an electron beam encounters the periodic atomic potential from a crystalline material. On exiting the sample the many diffracted beams interfere to form a 'lattice fringe' image. The fringe spacing corresponds to the inter-planar spacing of the atomic planes along that particular zone axis. Below, we present two examples where HRTEM imaging was employed to study the crystalline structure of nanostructures. This information would not have been available by other analytical techniques due to sample preparation and/or resolution limitations.

Fig. 2 shows a) schematic layout of a transistor device constructed by utilizing directionally grown Si nano-wires as gate elements between metallic source and drain regions; b) a tilted, top-down SEM image showing the location of the site-specific FIB lift out TEM sample; c) a low magnification BFTEM image showing three nano-wires in cross-section embedded in a dielectric shell and surrounded by a poly-Si casing; and d) a HRTEM image confirming the crystalline nature of the nano-wire and also confirming its orientation to be [110] in the plane of the cross-section.

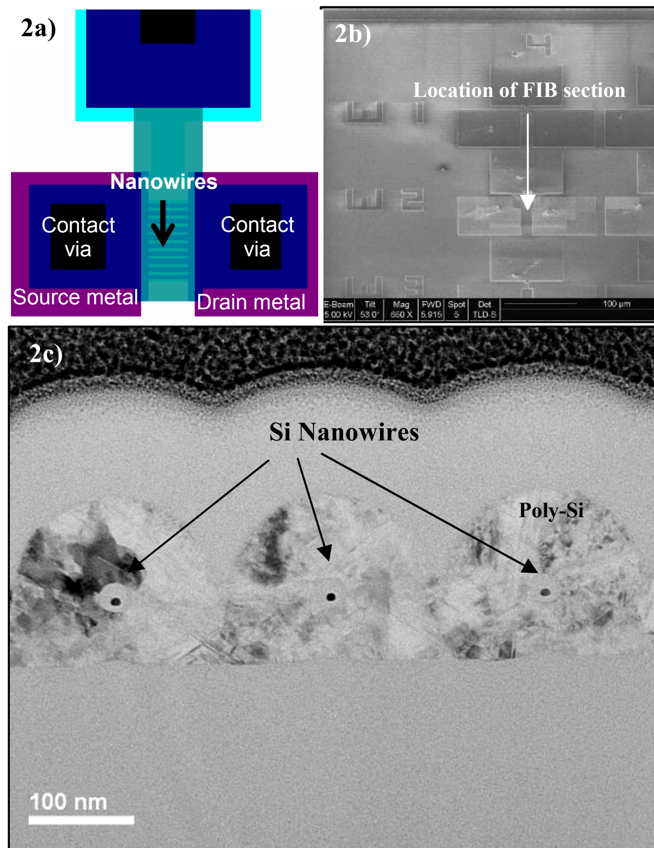

Figure 2 a) Schematic of transistor device with Si nanowire gates, b) Location of FIB lift out sample and c) BFTEM of nanowires in cross-section.

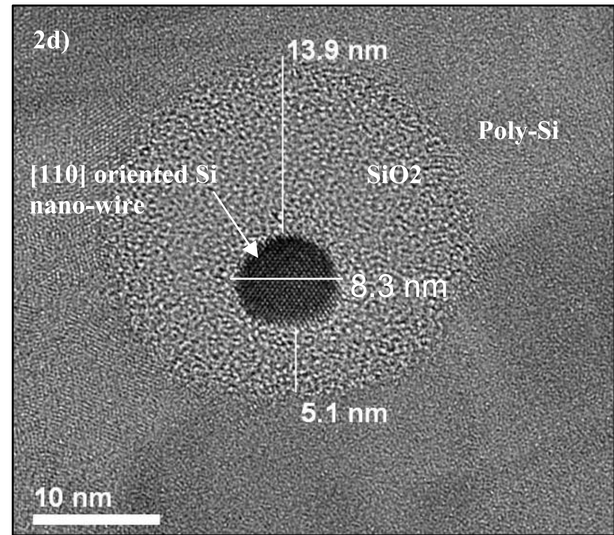

Figure 2 d) (contd.) HRTEM image of the silicon nano-wire in cross section confirming it to be crystalline and oriented in the [110] direction.

Fig. 3 shows several nanoparticles of CdTe suspended on a carbon thin film. From the lower magnification BFTEM image in fig. 3a, it is possible to discern the shape and size of the nanoparticles. These are observed to be ovoid in shape with ~6-8nm in width and ~17-21nm in length. HRTEM imaging of these nanoparticles allows direct measurement of lattice spacings as shown in fig 3b. One such interplanar spacing is measured to be 3.74Å which corresponds to the (111) set of planes of CdTe. Also, the dark bands in several of the particles, as seen in the lower magnification image in fig. 3a are observed to be crystal growth twins. While the comparative analytical technique of x-ray diffractometry (XRD) would have been able to measure the d-spacings and size distribution of these nanoparticles as a group, TEM is able to provide the size as well as crystallographic information from within individual nano-particles.

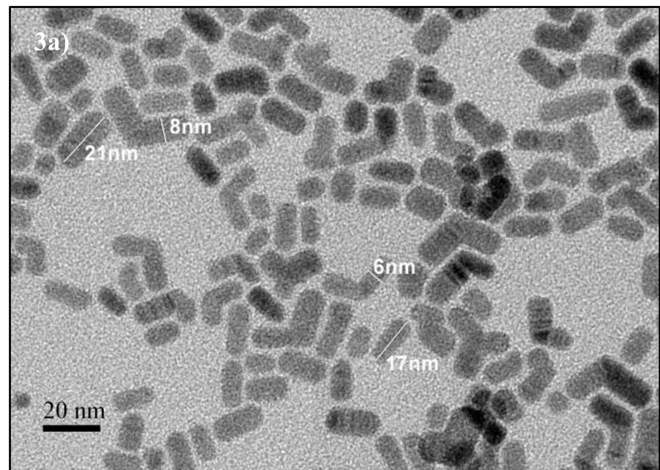

Figure 3 a) low magnification BFTEM image of CdTe nanoparticles on a carbon support film.

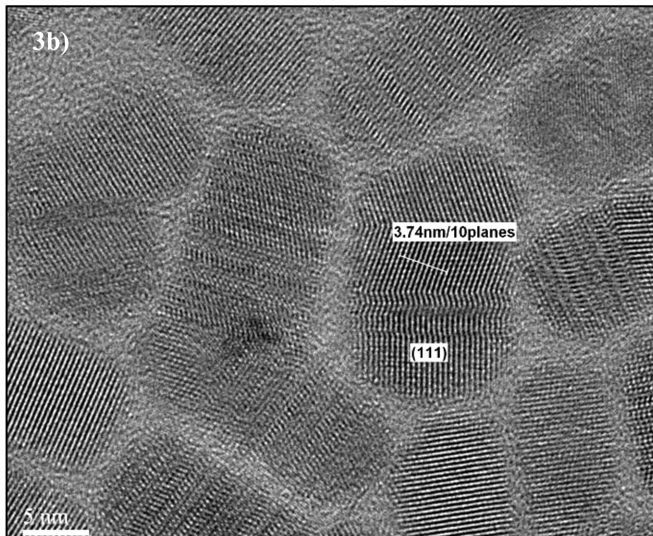

Figure 3 b) (contd.) HRTEM image of CdTe nanoparticles showing crystal growth twins. One set of (111) planes is measured and annotated.

An important advantage for TEM is its ability to obtain local electron diffraction information. It can be from a region as small as a few hundred nanometers, obtained with a parallel beam of electrons and by using an appropriately small selected area aperture, giving rise to a Selected Area Diffraction Pattern (SADP). Alternatively, a convergent beam electron diffraction (CBED) pattern can be formed by focusing the electron beam to a few nm size on the sample. Below we present two examples where the diffraction information from localized regions, or the use of one of the diffracted beams to image the sample in certain illumination conditions, was useful in studying the structure of the material at the nanometer scale.

Fig. 4 a) and c) show BFTEM images of a two phase mixture of aluminum hydroxide particles supported on a holey-C film. Large flat grains are mixed with smaller needle shaped grains. Indexing of the SADPs from the two different types of particles identify the larger, flat particles to be Gibbsite phase (Fig 4b) while the smaller, needle shaped particles to be Boehmite phase (Fig. 4d).

Instead of using the central, transmitted electron beam, a diffracted beam can be used to form a Dark Field (DF) TEM image to enhance certain grain orientations or compositions. This technique finds widespread application in the imaging of III-V optoelectronic devices. The alloys of InP or GaAs are closely matched intentionally in composition and crystal orientation for minimizing strain during epitaxial growth. Thus usual contrast mechanisms of mass thickness or diffraction contrast are not very useful in normal BFTEM imaging. [200] DFTEM imaging enhances composition contrast while suppressing strain contrast. Fig. 5 a) is a BFTEM image of InGaP/GaAsP thin layers on a GaAs substrate. Imaging with the composition sensitive [200] diffraction spot enables characterization of thickness and interfaces of these layers as shown in fig. 5b.

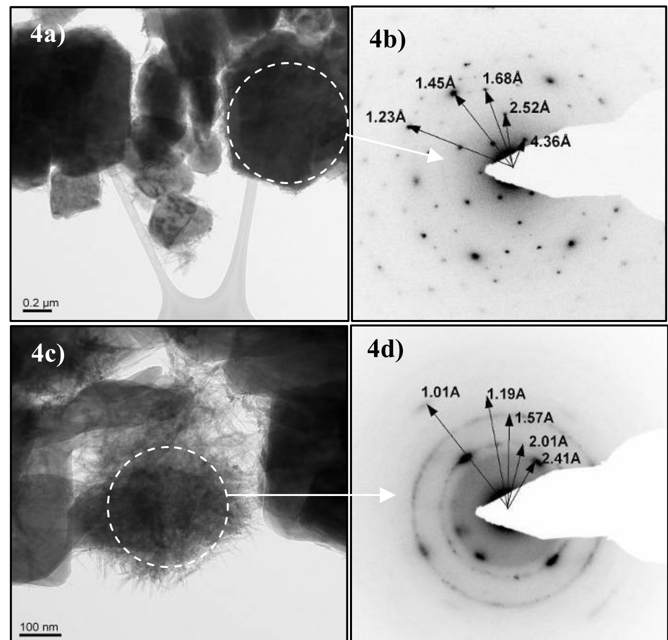

Figure 4 a) BFTEM image of large flat particles of aluminum hydroxide, b) indexed SADP from one large particle identifies it to be Gibbsite, c) BFTEM image of small, needle shaped particles and d) indexed SADP from these particles identifies them to be Boehmite.

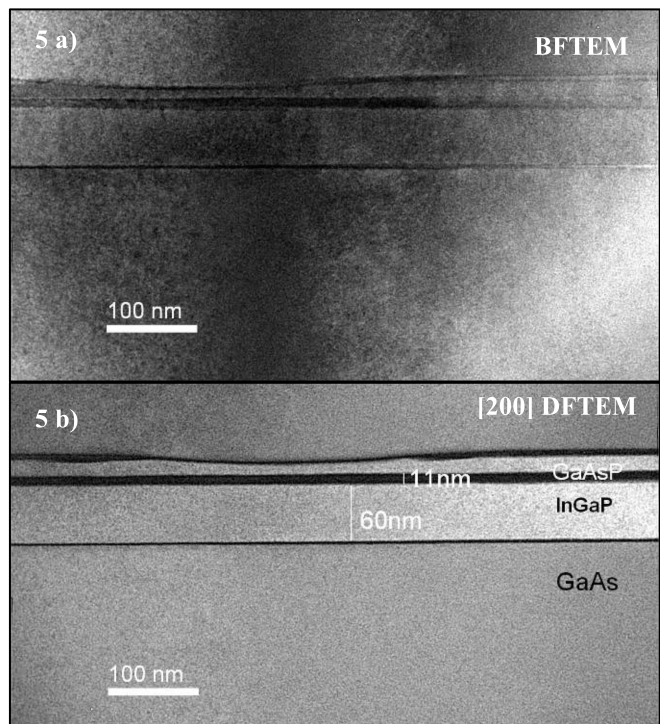

Figure 5 a) BFTEM and b) [200] DFTEM image of a GaAs based III-V multilayer stack. Note the compositional contrast in the DFTEM image.

Spatially resolved microanalysis is enabled by forming a sub-nanometer sized probe in the Scanning Transmission Electron Microscopy (STEM) mode and controlling its location on the sample while simultaneously collecting spectroscopic data by EDS or EELS. This approach, combined with the capability to extract site specific samples by FIB milling, allows characterization of materials and devices in a way not possible by other micro-analytical techniques.

As an illustration, Fig 6 a) shows a HRTEM image of a MOSFET gate in cross-section. The gate dielectric layer is ~2nm thick, and the gate length is <50nm. While several surface analysis techniques like SIMS and XPS have excellent depth resolution, they do not possess sufficient lateral resolution to analyze patterned devices. Spatially resolved STEM EELS is found to be useful in this case. Fig. 6b presents a High Angle Annular Dark Field (HAADF)-STEM image of the same region. HAADF enhances the composition contrast while minimizing diffraction contrast. Location of an EELS linescan starting from the silicon substrate, through the gate dielectric and into the poly-Si gate is shown on fig. 6b. N was detected in addition to Si and O in the gate dielectric confirming it to be a nitrided gate oxide. The profiles for N and O are presented in fig. 6c.

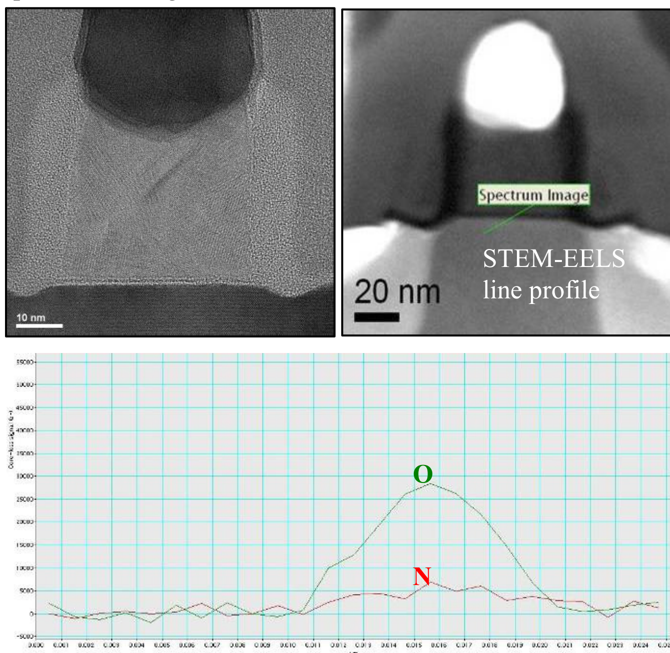

Fig. 6 a) HRTEM image of MOS-FET gate in cross section, b) HAADF-STEM image showing location of EELS linescan from substrate to poly-Si gate and c) EELS intensity profiles of N and O.

An another example where site-specific FIB sample preparation and spatially resolved EELS were uniquely employed to characterize the nano-structure is presented in Fig. 7. A thin TiN adhesion/barrier layer exists around the W contact in a typical microelectronic device. This layer is so thin that it is not fully resolvable by Scanning Electron Microscopy (SEM). Even cross-sectional TEM (Fig. 7a) suffers from artifacts caused by rounding effects as the width of the contact is of similar size as the thickness of a TEM sample (~50nm-150nm). In this case the TEM sample was prepared in the plan view and is able to resolve the substructure in the liner. Fig. 7b shows a low mag. image in plan orientation. A higher magnification image in Fig. 7c shows two sub layers in this liner that were obscured in the cross-sectional view. An EELS linescan across the liner that monitors Ti signals (Fig. 7d) shows changes in Ti levels in the regions corresponding to brighter sublayers.

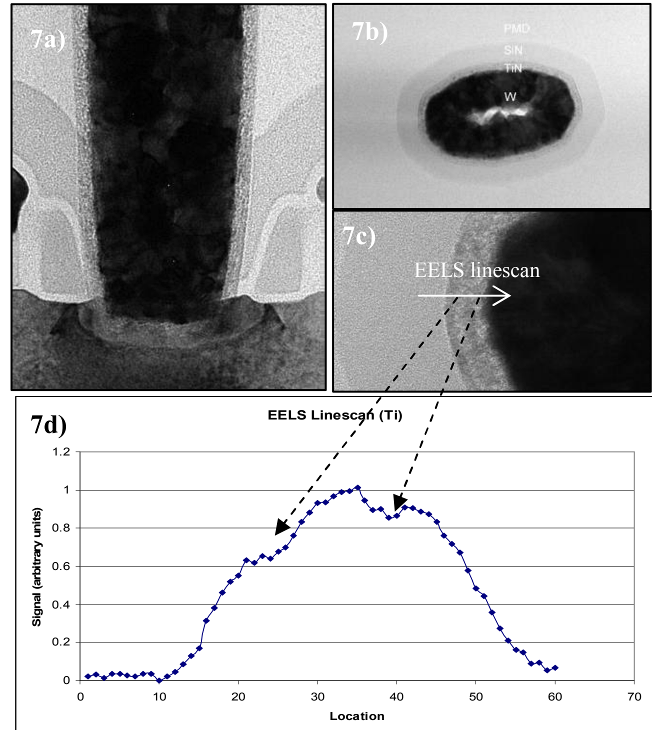

Fig. 7 a) cross section TEM image of W contact with TiN liner, b) plan-view TEM image of contact, c) sublayers in TiN liner and location of STEM-EELS linescan and d) profile of Ti showing dips in lighter regions of the liner.

4 SUMMARY

We have presented several practical examples that illustrate the breadth of capabilities inherent in a modern analytical TEM and their application in uniquely characterizing the structure and composition of nano-structured materials and devices.

REFERENCES

[1] Williams and Carter, “Transmission Electron Microscopy”, Plenum, 1996.
[2] Stegmann and Zschech, “Quantitative EELS of nitrided gate oxides”, Microsc. Microanal., vol.9 (suppl.3), 096, 2003.