HRTEM and Nano-Beam Diffraction Analysis of Metal-Molecule Interface


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We report results on high resolution (HR) imaging and nano-beam diffraction (NBD) analysis of molecular devices,

namely the morphology and structure of interface between the molecular layer and the contact electrode. High
resolution TEM (HRTEM) imaging is a direct way to review the morphology of an interface and to measure
projected interface roughness. Electron diffraction analysis provides data that allow identifying structure and
orientation of crystalline materials. Nano-beam diffraction (NBD) allows local structure and orientation to be
determined with a probe size a few nanometers in diameter [1]. Molecular device are composed of a molecular layer
attached to metallic electrodes (Figure 1). The characteristic of such molecular device can be dominated by the
details of the metal-molecule interface [2]. Therefore characterization of crystal orientation of metal particles,
interface roughness and thickness of the molecular layer will help to understand the interaction and diffusion of
metal atoms and molecules during processing and its effect on device properties. Combining HRTEM and NBD
analysis provides a complete morphological and crystal structure analysis of metal-molecule interfaces. Multilayer
(Au-molecule-Si) devices were prepared by grafting Nitroazobenzene (NAB) molecules onto p-doped silicon
followed by deposition of a Au film in an electron beam evaporator [3]. Sidewall (Au-molecule) junctions were
fabricated through surface diffusion-mediated deposition (SDMD) [4], in which metal atoms were deposited
remotely and then allowed diffuse onto the molecular layer. NAB molecules were grafted onto side wall of patterned
Pyrolyzed photoresist films (PPF). Au film was then deposited at Au vapor incidence angle between 0° - 5° from the
sample surface normal, and the overhang of the Cr/SiO$_2$ etch mask shadowed the molecular layer from direct
impingement of both incident gold atoms and radiation from the evaporation source. Electronic contact to the
molecular layer occurs through surface diffusion of the deposited Au atoms towards and eventually on top of the
molecular layer. Figure 1 shows schematic diagrams of cross section views of Au-NAB-Si and side wall junction
samples. TEM samples of both devices were prepared in a Zeiss Nvision SEM/FIB dual beam system. A 30 keV Ga
ion beam was used to cut and mill a TEM lamella with a thickness below 100 nm suitable for TEM examination.
Final polishing was done using 5 keV Ga ion beam to minimize ion beam damage. HRTEM images and NBD (with
about 2 nm beam diameter) were taken on a JEOL 2200 FS TEM equipped with a Schottky gun and in-column
omega filter. Figure 2 shows a HRTEM image of Au/NAB/Silicon interfaces. The Au/NAB interface is not flat and
the average NAB film thickness is 3.1±0.6 nm after Au deposition (compared with as-deposit film thickness of
4.8±0.2 nm measured by AFM “scratching” technique), suggesting that there is certain degree of Au penetration into
the NAB molecular layer. Alternatively the disagreement between TEM and AFM can be explained by the
projection nature of TEM, a surface roughness will result in overlap that is integrated along the beam resulting in
apparent reduction of NAB thickness. BFTEM images in Figure 3 show surface diffusion mediated Au on the
PPF/NAB sidewall, which has different morphology from Au film deposited on horizontal SiO$_2$ surface. NAB
molecular layer is not resolved here due to very weak contrast between PPF and the NAB molecular layer. Crystal
orientation of each individual Au particle was characterized by NBD analysis as shown in Figure 4. Preferential
orientation of Au was not found for the SDMD-deposited Au.
References:


Figure 1. Schematic Diagrams of
a: Au-NAB-Si multilayer device
b: side wall Au-NAB-PPF junction

Figure 2. HRTEM images of Au/NAB/Si interfaces.

Figure 3. BF TEM images of side wall junctions, showing non-continuous Au films on side walls – insert is a low mag. Image of the whole side wall cross section.

Figure 4. HR TEM images of Au particles on side wall junctions. Inserts are NBD patterns from individual particles (No.4 and No.5 in the image).