doi:10.1017/S1431927613009483
Microsc. Microanal. 19 (Suppl 2), 2013
© Microscopy Society of America 2013

An Analytical Electron Microscopy Study of Au/TiO_2 Thin Films Deposited on the Glass Substrate

Masahiro Kawasaki[1], Miin-Jang Chen[2], Jer-Ren Yang[2], Wen-An Chiou[3], Makoto Shiojiri[4]

1. JEOL USA Inc., 11 Dearborn Road, Peabody, MA 01960, USA
2. Dept. of Materials Science and Engineering, National Taiwan University, Taipei 10617, ROC
3. NISP Lab, NanoCenter, University of Maryland, College Park, MD 20742-2831, USA
4. Professor Emeritus of Kyoto Institute of Technology, 1-297 Wakiyama, Kyoto 618-0091, Japan

Gold/TiO_2 films have attracted much attention due to the high catalytic activity, and have recently been characterized using surface enhanced Raman scattering (SERS) technique [1]. Red-shift in the extinction spectrum was observed with the increase of TiO_2 film thickness and has ascribed to the increase in effective refractive index of the substrate slab and coupled plasmon resonance. A similar Au/TiO_2 structure was hence investigated in confirming the propriety of the SERS analysis and disclosing the point at issue using analytical electron microscopy.

A TiO_2 thin film was deposited on an optical microscope glass slide (FEA, ground edges, plain) at 200°C, by 417 cycles of atomic layer deposition (ALD) using alternating pulses of tetrakisdimethylamido titanium and H_2O with an Ar carrier gas flow. The deposition rate for TiO_2 was 0.045 nm per ALD cycle [1], and the estimated film thickness was 20 nm using a spectroscopic ellipsometer. An Au layer was then deposited on the surface of TiO_2 film by thermal evaporation. The thickness of the Au layer was ~ 3 nm as indicated by a quartz crystal thickness monitor. The specimen was reinforced with carbon and Pt layers, and then thinned by focused ion beam (FIB). Analytical TEM was performed using a JEM-2100F UHR STEM, equipped with an Oxford Instruments 30 mm^2 EDS spectrometer, a Gatan Orius model US1000FT CCD camera, and a GIF Tridiem (model) energy filter.

HR-TEM revealed that the 3 nm thick Au film was composed of round particles with diameters of ~15 nm or less [2]. Based on TEM images, the thickness of TiO_2 layer was measured to be 11 nm though the expected thickness was 20 nm (as mentioned above). STEM HAADF image, as shown in Figure 1a, depicts each Au^{79} particle clearly. The $Ti^{22}O^8{}_2$ layer (arrow in Fig. 1a) is shown with light (contrast) gray band that is laid in between dark areas of the glass ($Si^{14}O^8{}_2$) and bright Au^{79} layers. EFTEM thickness map (Fig. 1b) illustrates t/λ, where λ is the average mean free path of inelastic scattering of electrons and t is the local specimen thickness, which can be evaluated from $t = \lambda \log (I_T / I_0)$ [3]. I_0 is zero-loss intensity, obtained from zero-loss image (0±5 eV) (Fig. 1c), and I_T is the total intensity in EELS, obtained from conventional EFTEM image (Fig. 1d). This thin specimen, with $t < 0.31\lambda$, warrants the accuracy of the EELS analysis. The EFTEM Ti-L map (Fig. 1e) and EFTEM C-K map (Fig. 1f) indicate the TiO_2 layer and the reinforcement of C, respectively. Figure 2 shows EDS analysis of the Au/TiO_2 microstructure. HAADF image (Fig. 2a) and Au-L map (Fig. 2b) reveal an Au particle. The Ti-L map (Fig. 2c) indicates the TiO_2 layer whereas Si-K map (Fig. 2d) indicates the glass substrate. However, these images exhibit artifact contrasts due to the higher background of X-rays stimulated by strong emissions from Au particle. The Ca-K map (Fig. 2e) illustrates Ca atoms on the common soda lime glass substrate. EELS maps (Fig. 3) do not exhibit any artifact in the gold region. The O-K map (Fig. 3a), O-K map with energy-loss near-edge structure for Ti-O (Fig. 3b) and together with Ti-L map (Fig. 3c) confirmed the existence of TiO_2 layer. It is known that the density of amorphous oxide films is ~30 % less than that of the bulk oxide and the amorphous films may contain many voids [4]. As the soda lime glass substrate was heated to 200 ^oC during ALD, Ca atoms in glass surface have become mobile and readily diffused a

https://doi.org/10.1017/S1431927613009483 Published online by Cambridge University Press

few nanometers into the thin amorphous TiO_2 film (Fig. 3d). Those voids in the thin amorphous TiO_2 layer might have been immediately occupied by diffused Ca atoms while heating the substrate (i.e., before the deposition of Au). Therefore, Au atoms that lately evaporated/deposited on the surface of amorphous $Ti(Ca)O_2$ could easily migrate around and formed larger Au nuclei. In contrast, the surface of the thicker amorphous TiO_2 layer was consisted of pure TiO_2 with more voids and thus Au particles are confined and formed smaller nuclei compared to a thin amorphous $Ti(Ca)O_2$ layer. The difference in the number of Au nuclei on different TiO_2 layers may explain the geometrical differences of Au particles that have reported in ref (1).

The diffusion of Ca atoms into TiO_2 film during ALD might have resulted in the followings: 1. the different chemical composition in different thickness of TiO_2 layers especially at the surface of substrate, 2. the different growth behavior of Au particles, and 3. variation of electric and optical properties of the deposited films. Ultra-high resolution analytical microscopy study is, thus, indispensable in the characterization of nanoscale novel materials and devices.

References

[1] M. C. Lin et al., *Appl. Phys. Lett.,* in print.
[2] M. Kawasaki et al., *Appl. Phys. Lett.,* Accepted.
[3] T. Malis et al., *J. Electron Microsc. Tech*. **8**, (1988) 193-200.
[4] M. Shiojiri et al., *Jpn. J. Appl. Phys*. **18**, (1979) 1931-1936
[5] TEM work performed at the NISP Lab was partially supported by NSF-MRSEC (DMR 05-20471, Shared Experimental Facility) and UMD.

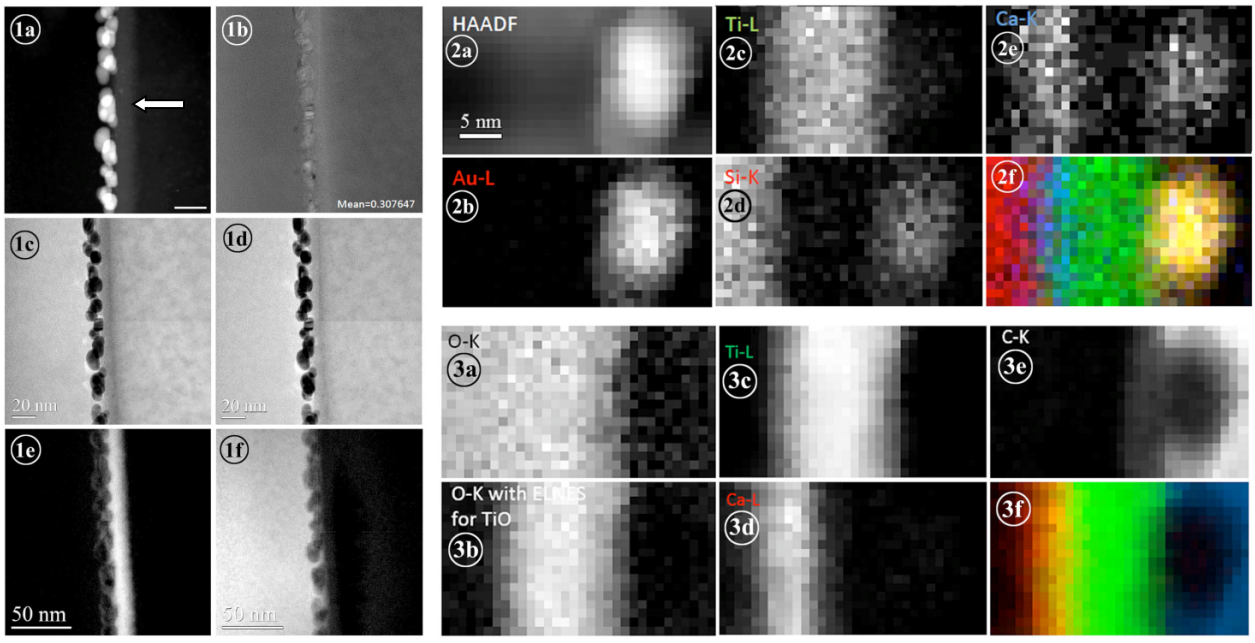

Fig. 1. EFTEM of Au/TiO_2 microstructure. (a) STEM HAADF image. (b) EFTEM thickness map. (c) Zero-loss image (0 ± 5 eV). (d) Conventional EFTEM image (e) EFTEM Ti-L map. (f) EFTEM C-K map.
Fig. 2. EDS mapping of Au/TiO_2 structure. (a) HAADF image. (b) Au-L map. (c) Ti-L map. (d) Si- K map. (e) Ca-K map. (f) Composite EDS map (Si: red, Ca: blue, Ti: green and Au: yellow).
Fig. 3. EELS maps of Au/TiO_2 structure. (a) O-K map. (b) O-K map with energy-loss near-edge structure for Ti-O. (c) Ti-L map. (d) Ca-L map. (e) C-K map. (f) Composite EELS map (Ca: red, Ti: green and C: blue).

https://doi.org/10.1017/S1431927613009483 Published online by Cambridge University Press