# **Electrochemical and Electrochromic Properties of Nanoworm-shaped**

### Ta<sub>2</sub>O<sub>5</sub>-Pt Thin-Films

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#### ABSTRACT

A  $Ta_2O_5$ -Pt nanostructure electrode was fabricated by means of cosputtering. Wormlike Pt nanoparticles were produced in  $Ta_2O_5$  matrix as observed by transmission electron microscopy (TEM) and small angle x-ray scattering (SAXS). The electrochemical and electrochromic properties of nanoworm-shaped  $Ta_2O_5$ -Pt electrode are compared with those of  $Ta_2O_5$  thin-film electrode without Pt nanoparticles. Nanostructured materials are attractive due to the particular fundamental properties that are present in such low-dimensional systems, which have unique properties different from those found in bulk scale. Research on nanostructures provides the potential for a variety of chemical, electronic, catalytic, electrochemical, and photonic applications.<sup>1-4</sup> The electrical, optical and magnetic properties of nanostructures vary with factors such as size, shape and crystallinity. In particular, nanophase composite structures, which consist of nanoparticles in a matrix material, can have properties significantly different from those of the matrix. We have observed electrochemical, catalytic, and optical properties for nanostructure electrodes made of platinum nanoparticles in oxides.<sup>5,6</sup> The photoelectrochemical response of the nanophase composite, which serves as an electrochromic material, was different from that of tungsten oxide due to presence of the platinum nanoparticles near the oxide matrix.

The routes for preparation of metallic low-dimensional systems have mainly been by wet chemical synthesis, template synthesis, and vapor-liquid-solid condensation.<sup>7-14</sup> In general, conventional sputtering deposition with a single sputtering target cannot easily produce unique nanostructured electrodes, due to the thin-film type growth mode in sputter deposition. However, cosputtering is a promising technique in that it can provide two-phase electrodes consisting of metal and oxide, because cosputtering uses two independent sputter guns for the metal and oxide materials. It has been shown that electrodes cosputtered from metal and oxide sputtering targets produce a metallic nanostructure within an oxide matrix.<sup>15,16</sup> The formation of the nanostructure within the oxide may be due to the oxide material limiting growth of deposited metallic phase. Accordingly, the size and shape of nanophase formed in oxide matrix cany be controlled

by experimental parameters such as the power of each target and the working gas pressure.

In this paper, we describe a nanostructure  $Ta_2O_5$ -Pt electrode fabricated by means of cosputtering and characterization of its structural and electrochemical properties. The Pt particles in the electrode had a worm-like shape of several nano-meters in size as confirmed by both transmission electron microscopy (TEM) and small angle x-ray scattering (SAXS). The electrochromic properties of nanoworm-shaped  $Ta_2O_5$ -Pt electrode were observed and compared with thin-film  $Ta_2O_5$  electrodes.

The nanoworm-shaped ( $Ta_2O_5$ -Pt) and thin-film ( $Ta_2O_5$ ) electrodes were prepared using a sputtering system. Indium tin oxide (ITO) coated glass was used as transparent conducting substrate to observe electrochemical and electrochromic properties. The power of the Pt and  $Ta_2O_5$  sputtering guns was individually manipulated in order to fabricate a nanostructure electrode. The  $Ta_2O_5$  thin-film electrode was prepared using only the  $Ta_2O_5$  sputtering gun to compare with  $Ta_2O_5$ -Pt. Sputtering was carried out under an atmosphere of Ar gas at 40 SCCM at room temperature. Cu grids were also used as substrates for analysis by transmission electron microscopy (TEM). The TEM investigation was carried out using a Phillips CM20T/STEM Electron Microscope at an accelerating voltage of 200 kV.

SAXS experiments were performed at the IMM-CAT at the Advanced Photon Source at Argonne National Laboratory. The incident X-rays from an undulator were monochromatized with a double-bounce Si(111) crystal to an energy of 6.6 keV. Slits confined the incidence beam size to either 100 x 100  $\mu$ m (high resolution) or 250 x 250  $\mu$ m (low resolution). An area detector was used with a sample to detector distance of either 3330 mm (high resolution) or 420 mm (low resolution). The samples were positioned with the substrate normal coinciding with the incident beam. To reduce attenuation from the substrate, ~80  $\mu$ m Si substrates were used (which transmitted ~10% of the incident beam). Since scattering from such thin films is inherently weak, great care was used to reduce contributions from background scattering. First, double-sided polished wafers were used to eliminate scattering emanating from the surface roughness of the substrate. Parasitic slit scattering from the beam defining slits was minimized through the use of slits with hemispherical polished blades and the careful placement of guard slits. Finally, the sample was placed in vacuum and there were no windows between the beamstop and the beam defining slits (just after the monochromator). The SAXS data were background subtracted, circularly averaged, and normalized with respect to the transmitted beam intensity.

To characterize the electrochemical properties of electrodes, cyclic voltammetry was examined in 0.5 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 20 mV sec<sup>-1</sup>. The potential is reported with respect to normal hydrogen electrode (NHE). The electrochemical measurements for the direct observation of electrochromism in the electrodes was done in an electrochemical cell with optics consisting of a He-Ne laser as the light source and a power meter for detection of the optical signal modulation. During the electrochemical reaction with respect to the potential, the laser was transmitted through the thin-film electrode and the modulation of the signal intensity was continually detected. The electrochemical cell was comprised of Pt and Ag/AgCl as the counter and reference electrodes, respectively. The nanostructure and thin-film electrodes were used as the working electrodes in the electrochemical cell.

As can be seen in the TEM image of  $Ta_2O_5$ -Pt in Figure 1(a), the nanostructure electrode consists of worm-shaped Pt nanoparticles that are well dispersed in tantalum

oxide. The Pt nanoparticles show worm-like shape of about 2 nm in a diameter and of 5-6 nm in a length. In spite of the fact that the thin-film electrode was fabricated using sputtering deposition, discrete nanostructures are formed in the amorphous oxide. The possible origin of the formation of the Pt nanoparticles with an amorphous oxide matrix may be as follows: (1) thermodynamically stable phase separation between metal and oxide and (2) prevention of migration of deposited metal ad-atoms by oxide matrix. The size and shape of metallic nanophase in oxide matrix may be controlled by several experimental parameters such as oxide material, power of sputtering guns, and the working pressure and is presently being investigated. The diffraction pattern shown in the inset to Figure 1 indicates the formation of Pt metallic nanostructures with crystallinity. The rings correspond to indexing for face-centered-cubic (fcc) crystal planes such as (111), (200), (220), (311), (222). In addition, as shown in Figure 1(b), the high resolution TEM (HRTEM) image shows the formation of a worm-shaped Pt metallic structure in the amorphous tantalum oxide. The Fourier transform diffraction pattern at the inset in the Figure 1(b) indicates a polycrystalline structure of the sputtered Pt within Ta<sub>2</sub>O<sub>5</sub>.

To further characterize the nanophase electrodes, we have utilized SAXS, a wellestablished technique that probes structural correlations for length scales of 1-100 nm.<sup>17,18</sup> SAXS data are shown by the open squares in Figure 2 and are plotted as a function of the scattering vector,  $Q=(4\pi/\lambda)\sin(\theta)$ , where 2 $\theta$  is the angle between the scattered photon and transmitted beam. The strong peak at about 0.12 Å<sup>-1</sup> shows that the positions of the Pt nanoparticles are correlated, while the width of this peak indicates substantial disorder in this correlation, as expected for sputter deposition. Apparent in the inset is a weaker peak at about Q=0.2 Å<sup>-1</sup>; this is  $\sqrt{3}$  of the strong peak, as expected for two-dimensional (2D) hexagonal-close packing (hcp) of the wormlike Pt nanoparticles. The line in Fig. 2 shows a fit to the data assuming a 2D hcp arrangement of the Pt nanoparticles. This is a valid model for wormlike nanoparticles, since the length of the nanoparticles is significantly larger than their radius. As is apparent, the model fits the data well. From this model, we find that the average spacing between the particles is 6 nm and that the average diameter is 2.2 nm, in good agreement with the TEM data of Fig. 1. Hence, the structural picture that emerges for the Ta<sub>2</sub>O<sub>5</sub>-Pt electrodes is one where the Pt nanoparticles phase separate in the Ta<sub>2</sub>O<sub>5</sub> matrix. As results of the sputtering conditions, the nanoparticles have a wormlike shape with a diameter of about 2 nm and a length of 5-6 nm. The spacing between the Pt worms is about 6 nm, but there is considerable disorder in this spacing.

The electrochemical properties of Ta<sub>2</sub>O<sub>5</sub>-Pt and Ta<sub>2</sub>O<sub>5</sub> electrodes were analyzed in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution by means of cyclic voltammetry, as shown in Figure 3. The cyclic voltammogram (CV) of the Ta<sub>2</sub>O<sub>5</sub>-Pt electrode at room temperature was obtained with a scan rate of 50 mV s<sup>-1</sup>. The peaks for the reduction (Re(H)) and oxidation (Ox(H)) of hydrogen and oxidation (Ox(O)) and reduction (Re(O)) of oxygen on the Pt surface in H<sub>2</sub>SO<sub>4</sub> are clearly seen. Hence, the CV of the Ta<sub>2</sub>O<sub>5</sub>-Pt electrode demonstrates the presence of polycrystalline Pt. As also shown in Figure 3, the Ta<sub>2</sub>O<sub>5</sub> exhibits an extremely low current density, and there is no reaction of Ta<sub>2</sub>O<sub>5</sub> in the potential range for the Pt-related electrochemical reactions such as hydrogen oxidation/reduction.

Figure 4 shows a variation of optical transmittance in electrodes ( $Ta_2O_5$  and  $Ta_2O_5$ -Pt) with respect to an applied potential. According to an electrochromism of cathodic coloration materials, an optical signal intensity would be reduced (colored) at negative

potential versus normal hydrogen electrode (NHE) and increased (bleached) at positive potential versus NHE in parallel with the potential of the electrochemical cell. The sputtered  $Ta_2O_5$  electrode shows no change in intensity while the nanoworm-shaped  $Ta_2O_5$ -Pt electrode shows an optical signal modulation as a function of an applied potential. In general, during an electrochromic process, electrons are injected or extracted under an applied voltage and, at the same time, ions are moved uniformly into or out of the EC material for the balance of charge neutrality. However, it is likely that the  $Ta_2O_5$  electrode with a few nanometers in thickness has no sufficient electronic conductivity to produce an electrochemical motion and shows no electrochromic properties. On the other hand, the  $Ta_2O_5$ -Pt electrode with the same thickness as the  $Ta_2O_5$  electrode displays an electrochromism of cathodic coloration materials. This indicates that an injection or extraction of electrons in the  $Ta_2O_5$ -Pt is affected by welldefined Pt polycrystalline nanostructures, thus enhancing proton transfer phenomenon, i.e. cathodic electrochromic properties of  $Ta_2O_5$ .

In conclusion, the  $Ta_2O_5$ -Pt nanostructure electrode showed worm-like Pt polycrystalline nanoparticles in  $Ta_2O_5$  matrix as confirmed by transmission electron microscopy and small angle x-ray scattering. The  $Ta_2O_5$ -Pt nanostructure electrode displayed typical cathodic electrochromism compared to  $Ta_2O_5$  thin-film electrode with no electrochromism. Such an electrochromic phenomenon in the  $Ta_2O_5$ -Pt is likely due to the Pt polycrystalline nanostructure in a tantalum oxide material.

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#### **Figure captions**

**Figure 1**. (a) Transmission electron micrograph (TEM) images of nanoworm-shaped  $Ta_2O_5$ -Pt electrode (The inset in the Figure 1 (a) shows the ring pattern of the electrode by transmission electron diffraction (TED)). (b) High-resolution TEM (HRTEM) image of nanoworm-shaped  $Ta_2O_5$ -Pt electrode

**Figure 2.** SAXS data for  $Ta_2O_5$ -Pt electrode. The open symbols are the data, while the solid line is a best fit. The inset shows that data (dashed line) on a logarithmic scale, which makes the higher order peaks more apparent.

**Figure 3.** Cyclic voltammogram of Ta<sub>2</sub>O<sub>5</sub>-Pt ( $\bullet$ ) and Ta<sub>2</sub>O<sub>5</sub> ( $\odot$ ) electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

**Figure 4.** Optical intensity modulation of  $Ta_2O_5$ -Pt (**■**) and  $Ta_2O_5$  (**□**) electrodes as a function of electrochemical cell potential (-0.3 V to +0.5 V at interval of 0.5 sec).

Figure 1. K.-W. Park.





Figure 2. K.-W. Park.



Figure 3. K.-W. Park.



Figure 4. K.-W. Park.

