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PREPARATION OF Pd/TiO_2 NANOCOMPOSITE BY MAGNETRON SPUTTERING

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Abstract—Pd/TiO_2 nanocomposite films have been prepared by co-sputtering method at room temperature. Film thickness and the Pd/TiO_2 ratio are function of the length of the Pd wire placed on the rutile target. XPS study reveals that Pd exists both in metal and oxide states in as-deposited films. As-deposited films were amorphous and nucleation of PdO phase started at around 500 °C. Anastase-rutile phase transition tendency of TiO_2 increased as the concentration of Pd increased in the films. PdO started to decompose to metallic Pd at 800 °C but complete conversion was not achieved even annealed at 1200 °C in air. The controlled annealing of as-deposited films in hydrogen environment was the most suitable way to precipitate metallic Pd nanoparticles with controlled size at rather lower temperature.

Keywords: Co-sputtering; XRD; XPS; Pd/TiO_2 Nanocomposite

Introduction

Composites dispersed with nanosized metallic clusters or crystals in an insulating matrix become a popular area of intense research because of their promising optical, electrical, magnetic and mechanical properties (1). Researches on optical properties of metal, more precisely of noble metal nanoclusters in solid matrices have been focused on their surface plasmon resonance phenomenon (2,3). The absorption peak of these metals can be shifted towards higher wavelength side when embedded in a high dielectric material like TiO_2 (4).

Especially the attention on Pd/TiO_2 composites for the possibilities to use as photocatalyst, sensor material and anti-reflecting coating for solar cell is growing rapidly (5,6). Particle size of Pd plays an important role in these composites to tune the properties for the exact technical need (7). In this report we will present elaborately the crystallization of TiO_2 matrix and precipitation of Pd nanoparticles in the matrix by post annealing the as-deposited films at various temperatures under different atmosphere.

Experimental

Pd/TiO_2 nanocomposite films were deposited at room temperature on quartz glass substrates by co-sputtering using a Shimadzu (HSR-521) r.f. sputtering apparatus. Palladium wires of 0.5 mm in diameter were placed symmetrically on a hot-pressed rutile TiO_2 target of 100 mm in diameter. All the depositions were carried out in argon atmosphere with a constant pressure of 0.53 Pa for 120 minutes. Thickness of the as-deposited films was measured from the edge profile using a surface roughness meter (Tencor, Alpha-Step 3000). Chemical state and concentration of all the species in the as-deposited films

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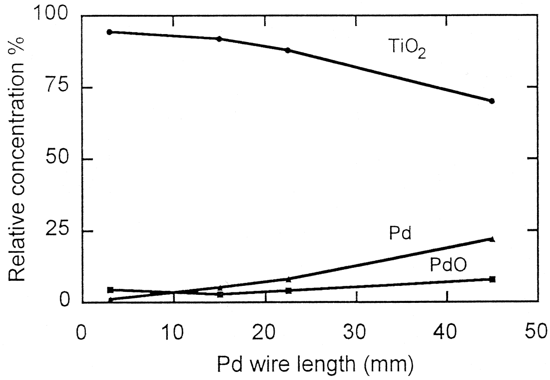

Figure 1. Relative % of metal and oxides in as-deposited Pd/TiO_2 films prepared with different Pd wire length (sputtering power 100 W, deposition time 120 min, Ar pressure 0.53 Pa).

were estimated by X-ray photoelectron spectroscopy (XPS) using PHI, 5600ci. Investigation on nucleation and growth of crystalline phases and the particle size calculation of annealed films were done by X-ray diffraction (XRD) analysis using Rigaku, RAD-C with CuKα radiation.

Results and Discussion

As-deposited films were almost uniform in thickness and also amorphous within the experimental sensitivity of XRD. Thickness increased from 175 nm to 270 nm when the length of the Pd wire varied from 3 mm to 45 mm. Figure 1 shows the composition of the metallic components of as-deposited Pd/TiO_2 films estimated from XPS spectra. Both the metal and oxide states were observed in Pd3d photoelectron peaks. The concentration of metallic Pd increased with the length of Pd wire while concentration of TiO_2 decreased. The concentration of Pd oxide component, however, was almost constant. The peak position for $Ti2p_{3/2}$ levels is around 458.2 eV and almost same for all the films. Slight decrease in the binding energy of $Ti2p_{3/2}$ peak position from TiO_2 standard (458.7 eV) can be attributed to the reducing tendency in presence of argon atmosphere during deposition.

XRD study of the films annealed in air reveals that all the films first transformed from amorphous into anatase at around 300 °C. XRD patterns of the films deposited with different length of Pd wire annealed at 600 °C are presented in Fig. 2. Anatase to rutile transformation tendency increased as the palladium content increased in the films. Similar trend was observed in Pt/TiO_2 and Au/TiO_2 system (8). Possibly, during annealing the radiant energy absorbed by dispersed Pd is transferred to the host matrix very fast, which starts phase transformation locally (9). It was observed that precipitation of PdO phase started from 500 °C for all the films.

Decomposition of PdO into Pd metal was detected when films were annealed at 800 °C. Figure 3 presents the XRD patterns of Pd/TiO_2 film ($Pd/Ti = 0.49$) annealed at different temperatures, which is typical for others. The reaction process of nucleation of PdO and its decomposition to Pd metal are the same as the earlier report (10). However in our case the temperature for the growth of PdO and its reduction to Pd metal takes place at lower temperature. On the other hand, the problem of this process for preparation of Pd/TiO_2 composite is that PdO was not completely reduced to Pd metal even annealing at 1200 °C, clearly shown in Fig. 3. We also did not achieve the total decomposition of PdO by changing the annealing atmosphere to nitrogen or vacuum. In case of chemical process like sol-gel method, carbon component from organic groups in precursors may act as a reducing agent and help to decompose PdO, which is not possible in case of sputtering process due to less amount of carbon

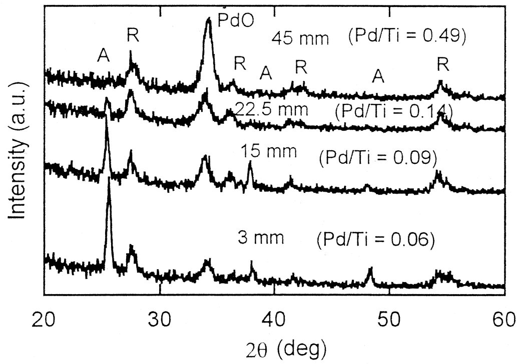

Figure 2. X-ray diffraction patterns of the Pd/TiO_2 composite films deposited with different Pd wire length (sputtering power 100 W, deposition time 120 min, Ar pressure 0.53 Pa) and annealed at 600 °C.

contaminant. Anyway in all the physical and chemical process it needs at least 800 °C to precipitate Pd metals by annealing in air. This is rather high temperature to control the size of nanoparticles.

To overcome those problems we used hydrogen atmosphere (2.5% H_2 + 97.5% N_2) for the precipitation of Pd metals in nanocrystalline form. As-deposited as well as annealed (in air) films have been treated in hydrogen atmosphere at 500 °C. XRD patterns for the samples annealed in hydrogen are shown in Fig. 4. Most prominent features in Fig. 4 are the complete reduction of PdO phase and TiO_2 only in rutile phase. Disappearance of anatase phase by hydrogen annealing is attributed to the creation of oxygen vacancy that facilitate the phase transition to rutile (11). The average particle size of Pd metal was estimated from XRD (111) peak using the Scherrer‘s equation. Average particle size changes from 10.5 to 20.5 nm when annealing time in hydrogen atmosphere varies from 1 h to 2 h. Thus varying the time of annealing in hydrogen can change the size of Pd metals. Pre-heat treatment in air at the temperature below the decomposition of PdO does not affect the size of Pd metal particles nucleated by subsequent annealing in hydrogen environment.

Conclusions

Pd/TiO_2 nanocomposite films deposited by co-sputtering method were amorphous and anatase phase started to grow from 300 °C. Tendency of anatase to rutile transition of TiO_2 increased as the

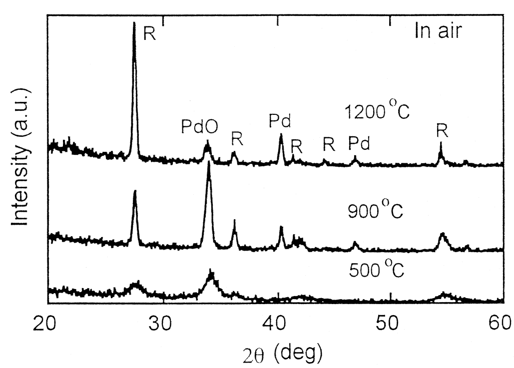

Figure 3. X-ray diffraction patterns of the Pd/TiO_2 composite film deposited with 45 mm Pd wire (sputtering power 100 W, deposition time 120 min, Ar pressure 0.53 Pa, Pd/Ti = 0.49) and annealed in air at different temperature.

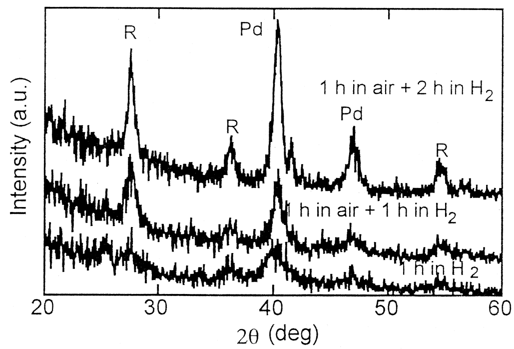

Figure 4. X-ray diffraction patterns of the Pd/TiO_2 composite film deposited with 22.5 mm Pd wire (sputtering power 100 W, deposition time 120 min, Ar pressure 0.53 Pa, Pd/Ti = 0.14) and annealed in hydrogen atmosphere at 500 °C.

concentration of Pd increased in the films. Nucleation of PdO started from 500 °C and its conversion to Pd metal started from 800 °C in air. Complete reduction to Pd, however, could not be achieved even by annealing at 1200 °C in air. Annealing of the as-prepared films in hydrogen atmosphere is the easiest way to precipitate nanocrystalline Pd metal particles in the TiO_2 matrix at lower temperature.

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