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Effect of surface physics of metal oxides on the ability to form metallic nanowires

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ABSTRACT

Through the control of surface physics of oxide films, nanowires of various metals can be readily grown on the surface of oxide films without templates and surfactants. To clarify how the characteristics of oxides affect the formation of metallic nanowires, this report investigated the influence of the surface physical characteristics, including morphological, electrical, optical and hydrophilic properties of the metal oxide substrates (TiO_2, CeO_2, and indium tin oxide), on the yield of Ag and Pt nanowires. In addition to the surface roughness, photo-induced defects were suggested to be the key factor dominating the number of nucleation sites and thus the population of nanowires.

1. Introduction

Among the common metal oxides, TiO_2 and CeO_2, which are regarded as wide band gap semiconductors, have attracted much interest due to their unique properties, such as high dielectric constant [1], high refractivity [2], and photocatalysis [3–6]. These two oxides are both regarded as photocatalysts and could serve as an excellent electron-transfer mediator for photo-excited electrons [7]. CeO_2 is also known to provide an effective reservoir of oxygen with a large capacity for storage and release of oxygen vacancies, and has been widely used in solid-oxide fuel cells and catalytic applications [8].

Recent research suggests that nanosized-metals supported by metal oxide thin films exhibit multi-functions and thus permit a wider range of applications. For example, Ag [9] and Cu [10] nanoparticles on TiO_2 can facilitate the water-gas shift reaction. As the anode for the oxidation of methanol or ethanol [11,12], the Pt-CeO_2 composite catalyst has a higher activity than the Pt catalyst because CeO_2 makes CO electro-oxidation easier. In terms of optoelectronic applications, Zhao et al. [13] reported that Ag nanoparticles on TiO_2 can absorb visible light in photoelectrochemical cells via surface plasmon resonance.

To date, one dimensional nanostructures have received considerable attention mainly due to the characteristic of high surface-to-volume ratios. In fact, most of the present-day techniques for the preparation of metal nanowires are based on the use of either templates [14,15] or surfactants [16]. A recent breakthrough developed by our group is capable of synthesizing ultra-long metallic nanowires of Ag, Cu, Au and Pt in large quantities [17–23] directly from molten salts or aqueous salt solutions on the surface of TiO_2 thin films using no templates or surfactants. It is interesting that when the anatase TiO_2 film is fully excited by ultraviolet (UV) light, only micro-sized particles appear on the TiO_2 substrate. In contrast, nanowires form abundantly on partially excited TiO_2 by blackbody radiation during annealing. In addition, the preferred orientation of TiO_2 films significantly affects the yield of metallic nanowires [23].

In order to further explore how the characteristics of oxides affect the formation of metallic nanowires and extend the utilization of this novel process, this report studies the influence of the physical, optical and hydrophilic properties of the metal oxides on the yield of Ag and Pt nanowires. In addition to the abovementioned two metal oxide photocatalysts, TiO_2 and CeO_2, a transparent conductive oxide film, ITO (indium tin oxide), was adopted for comparison.

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2. Experimental

2.1. Thin film preparation

TiO_2 and CeO_2 thin films were prepared via the sol gel method by dipping Si wafers into the gels and then were spun at 1000 rpm for 30 s. The TiO_2 and CeO_2 solutions used were prepared with isopropylalcohol (IPA)/titanium isopropoxide (TTIP)/hydrogen chloride (HCl) and $CeCl_3O{\cdot}7H_2O$/citric acid/ethanol with a volume ratio of 170:12:0.4 and 1:2.5:50 respectively, then stirred for 10 min before aging at room temperature (20 °C) for 2 days.

Deposition of ITO thin films on glass substrate was carried out using RF magnetron sputtering in an argon atmosphere. A 99.99% purity target of In_2O_3 (90 wt%)–SnO_2 (10 wt%) was sputtered. The substrates were clamped on a holder rotating at 4 rpm during the deposition. A base pressure below 8×10^{-3} torr was maintained prior to the deposition. The substrate temperature was set at 200 °C. RF power of 340 W was supplied for the sputtering of the ITO target.

All the oxide films were annealed at 500 °C in an oxygen atmosphere for achieving better crystallinity. The annealing time was controlled at 2 h, 4 h and 8 h respectively for obtaining various surface roughnesses.

2.2. Characteristics of thin films

A scanning electron microscope (SEM, JEOL JSM-6700) was used to observe the cross-sectional microstructures. The layer-thickness of the oxide films was measured using Scion Image 4.0.2 image analysis software. Each datum was the average of at least 15 measurements. The structure of the thin films was examined by X-ray diffraction (XRD, D8 Discover X-ray diffactometer) (incidence angle of 0.3°) with graphite monochromatic Cu Kα radiation ($\lambda = 0.15418$ nm) at a scanning rate of 2°/min from 20° to 50°. The surface roughness of the samples was measured using atomic force microscopy (AFM, D3100) with a scan rate of 1 Hz and measuring area of 9 μm^2. The surface roughness value we obtained is R_a (average roughness, the arithmetic average of the absolute values), of which the definition is given in literature [24].

In this study, the band gaps of the oxide thin films were determined by plotting $[F(R) \times E]^{1/2}$ versus E (eV) according to the Kubelka–Munk theory using the corresponding reflectance data [25], based on the UV–vis spectra recorded using a Jasco V-560 spectrophotometer. The modified work functions of the oxide thin films were obtained by an ultraviolet photoelectron spectrometer (AC-2, RIKEN KEIKI) operating at atmospheric pressure. The optical properties of the thin films were investigated using photoluminescence (PL) and time-resolved photoluminescence (TRPL). PL measurements were done using a helium-cadmium laser with a wavelength of 325 nm and power of 35 mW to excite electron states in the samples at 10k. The TRPL measurements were performed using a Hamamatsu streak camera with a time resolution of about 5 ps.

The hydrophilicity of the prepared thin films was evaluated by measuring the contact angle between 15 μl droplets of water and the film surface under ambient atmosphere (65% humidity) at room temperature (20 °C).

2.3. Synthesis and characteristics of nanowires

In order to compare the yield of NWs on various oxide thin films, 15 μl droplets of 0.05 M $AgNO_3$ and $Na_2Pt(OH)_6$ aqueous solution were dropped on the annealed substrates respectively. Afterward the samples were isothermally heated at 300 °C for 3 h in air by an infrared (IR) furnace and then furnace-cooled to the ambient temperature.

The morphology and number of NWs were investigated using a scanning electron microscope (SEM, JEOL JSM-6700) and Scion Image 4.0.2 image analysis software. Each datum was the average of 100 observations. For a better understanding, a transmission electron microscope (FEI-TEM, Technai G_2) was applied to reveal the structure of the nanowires, as well as the grown direction.

3. Results

3.1. Phase identification and surface roughness of oxide thin films

The cross-sectional structures of the annealed thin films subjected to annealing for 8 h are shown in Fig. 1, depicting that each oxide film exhibited a uniform thickness, which was about 873.3 ± 3.7 nm for TiO_2, 725.5 ± 2.1 nm for CeO_2, and 500.7 ± 2.5 nm for ITO. The crystallinity of the thin films was examined by X-ray diffraction (XRD) analysis. XRD patterns of TiO_2, CeO_2 and ITO are displayed in Fig. 2. Anatase TiO_2 can be identified by the position of the main reflections corresponding to the planes (1 0 1), (0 0 4),

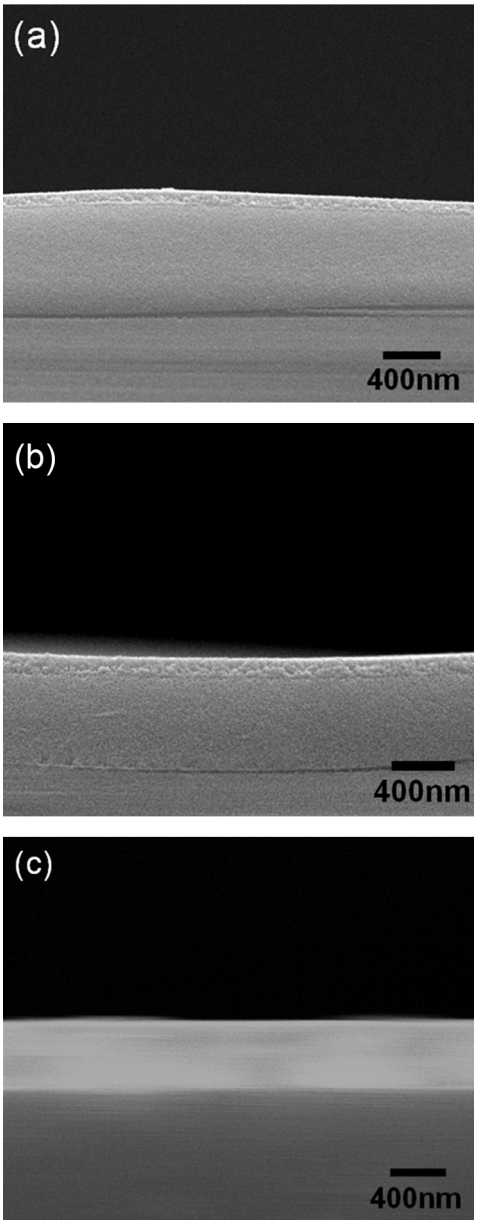

Fig. 1. Cross-sectional images of the oxide thin films: (a) TiO_2, (b) CeO_2 and (c) ITO.