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Mesoporous titania films investigated by positron annihilation based on a slow positron beam

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ABSTRACT

Tunable mesoporous titania (TiO_2) thin films were synthesized via a sol-gel method using an amphiphilic triblock copolymer F38 as the structural template. The dependence of crystalization, pore morphology and interconnectivity of TiO_2 films on the weight ratio of F38 was studied by wide-angle X-ray diffraction, field emission scanning electron microscopy and Doppler broadening of positron annihilation radiation spectroscopy based on a slow positron beam. By loading more F38, the crystallization of TiO_2 films is enhanced, accompanied by a decrement in oxygen vacancies/grain boundaries. Smaller and isolated mesopores are formed in the films prepared with F38 less than 15 wt%. The pore percolation occurs when the weight ratio of F38 is up to 20 wt% and larger and interconnected worm-like pores are formed.

1. Introduction

Mesoporous transition metal oxides have attracted much attention because they exhibit both intrinsic optical and electronic properties of transition metal oxides and the advantages of mesopores [1,2]. Among mesoporous transition metal oxides, mesoporous titanium dioxide (TiO_2) is one of the most vigorously studied materials owing to its versatile applications such as photocatalysts [3], photovoltaic solar cells [4–7], and chemical sensors [8,9]. The defects and pore structure in mesoporous TiO_2 significantly affect the performance of TiO_2-based functional devices [2]. Therefore, understanding of the microstructure and mesostructure is important for improving or expanding porous TiO_2-based systems for specific applications. Unfortunately, there are relatively few techniques capable of investigating defects and nanovoids in submicron films on thick solid substrates. Although scanning tunnel microscopy has been widely employed since it can provide direct images of surface or subsurface defects, it is difficult to use it to provide information about atomic level defects with a low density such as monovacancy or bivacancy defects, which also play a significant role in physicochemical properties of materials.

In recent years, positron annihilation spectroscopy (PAS) has been used to probe defects in a range inaccessible to classic defect probes [10,11]. PAS can give information on the pore size, concentration and defect type of the films. Various techniques based on a variable energy slow positron beam, such as positron annihilation lifetime spectroscopy [12–15], Doppler broadening of positron annihilation radiation (DBAR) spectroscopy [16–21], positronium time-of-flight [22,23], have been used as a powerful probe for characterizing film materials. For instance, it has been revealed recently by positron annihilation spectroscopies based on slow

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positron beams that gas permeability and separation properties of carbon molecular sieve membranes are strongly correlated to the pore volume [15,21]. Positrons can easily penetrate the structure and probe vacancy type defects, voids and pores, while the conventional sorption methods only measure the fraction which is open to outside and accessible to adsorbate molecules (nitrogen, argon, etc.). In an effort to understand the porous structures of synthesized TiO_2 films, we have applied DBAR spectroscopy to samples. The DBAR measurements were conducted using a variable-energy positron beam to implant positrons with energies of 0–24 keV to different depths in the film.

The positrons then diffuse until they annihilate with an electron from either a free positron state or an electron-positron bound state (positronium, Ps) in the bulk lattice, trapped at vacancy defects and voids/pores. The annihilation process results in the emission of two 511 keV γ photons or three γ photons (with less then 511 keV energy), which are detected using a high-purity Ge detector. The local environment of positron annihilation is reflected in the energy spectrum of the emitted photons, which is Doppler broadened due to the momentum of the annihilating electrons. The measured momentum distribution is described using two lineshape parameters, S and W. The S parameter reflects the number of photons with a low momentum shift, while the W parameter represents the photons with a high momentum shift. Generally, the reduced electron density at open-volume defects narrows the momentum distribution, which leads to an increase in S and a decrease in W parameters. On the other hand, the S, W parameters also depends on the chemical environments of positron annihilation sites. For instance, in hydrocarbons, decoration of the vacancies by oxygen may induce an increase in W but a decrease in S, because the valence electrons of O are strongly localized and have higher momentum then that of carbon atoms. Positron annihilation spectroscopy thus gives information both on the size/number of the vacancies and on the chemical surroundings [17]. In the presence of silica thin films with interconnected pores, long-lived o-Ps is able to diffuse back to film surface along the interconnected pores and emits into the vacuum, and then undergoes 3γ annihilation [23,24]. Thus, the relative intensity of the positronium 3γ annihilation fraction ($I_{3\gamma}$) can serve as a measure of pore connectivity of porous thin films [25–28].

In this study, mesoporous TiO_2 thin films were synthesized by the addition of a triblock copolymer F38 (BASF surfactant) as a structure-directing agent. Fourier transformation infrared spectroscopy (FTIR), wide-angle X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and DBAR spectroscopy based on a slow positron beam were used to characterize the synthesized TiO_2 films. The crystallization and mesostructure of the TiO_2 films are found to be successfully tuned by changing the copolymer loading.

2. Experimental

2.1. Sample preparation

Titanium tetrachloride ($TiCl_4$) was chosen as the titanium source and a nonionic amphiphilic triblock copolymer ($EO_{43}PO_{14}EO_{43}$, Pluronic F38, M_w = 4700 g/mol) was used as the structure-directing agent, respectively. Ethanol was chosen as solvent owing to its surface wetting properties and good solubility of all organic and inorganic precursors [30]. The polymeric template was introduced with various weight ratios, i.e. $W_{template}/(W_{template} + W_{TiCl_4})$, which were assigned as 5, 10, 15, 20 and 25 wt%, respectively. According to the above ratio, a certain amount of F38 was firstly dissolved in 60 ml of anhydrous ethanol (EtOH). A typical solution was prepared by dropping 4.5 ml of $TiCl_4$ stepwise into ethanol/surfactant solutions under vigorous stirring at room temperature. Upon mixing $TiCl_4$ and ethanol, a marked yellow color was developed. Subsequently a small amount of diluted hydrochloric acid and distilled water was added. Then the clear yellow sols were stirred continuously at room temperature. The molar compositions of the final solutions were 1 $TiCl_4$: 25 EtOH: x F38: 4 H_2O: 0.002 HCl, where x ranged from 0 to 0.013 determined by F38 weight ratio. The resultant sols were spin-coated on polished silicon (100) wafers. After aging at room temperature, the as-deposited films were dried at 100 °C for 2 h and then cooled in vacuum. The as-dried films were subsequently elevated at a heating rate of 1 °C/min to 500 °C and kept at this temperature for 4 h under nitrogen atmosphere to remove the organic species.

2.2. Characterization of titania films

FTIR was used to characterize the chemical behavior of TiO_2. FTIR spectra in the range of 400–4000 cm^{-1} were recorded with a Thermo SCIENTIFTC NICOLET is 10 FTIR spectrometer. The crystal phase of the TiO_2 films were measured by wide-angle XRD. The XRD patterns of the TiO_2 films were obtained by a D8 X-ray diffractometer (Bruker AXS D8-Focus, Germany) using monochromatic Cu Kα radiation (λ = 0.15406 nm) with an accelerating voltage of 40 kV, current of 40 mA, and the scanning angle ranged from 20° to 60° with an interval of 0.01°. FE-SEM images were obtained on a FEG SEM sirion microscope operated at 12 kV accelerating voltage. Positron annihilation γ-ray energy spectra were measured with a high-purity Ge detector as a function of the incident positron energy E using a monoenergetic positron beam at Wuhan University. A spectrum with about 10^6 counts was collected for each incident positron energy. The positron annihilation line shape parameter S for the 511 keV γ-annihilation peak is defined as the ratio of the annihilation events in the central region (511 keV $\pm$ $|\Delta E_\gamma|$, where $|\Delta E_\gamma| \sim$ 0.76 keV) to the total area of the peak. The positron annihilation line shape parameter W is defined as the ratio of the annihilation events in the wings region (511 $\pm$ 1.44 keV $\leq E_\gamma \leq$ 511 $\pm$ 4.81 keV) to the total area of the peak. Positronium 3γ-annihilation fractions were calculated from the measured gamma-ray energy spectra in the same way as a previous report [26]. Prior to the measurements, the porous silica films were baked at 200 °C for 30 min to eliminate some adsorbed water.