Electrochimica Acta 168 (2015) 365–369

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Development of pore interconnectivity/morphology in porous silica films investigated by cyclic voltammetry and slow positron annihilation spectroscopy

Xiuqin Tang, Bangyun Xiong, Qichao Li, Wenfeng Mao, Wei Xiao,
Pengfei Fang, Chunqing He*

Key Lab of Nuclear Solid State Physics Hubei Province, School of Physics and Technology, Wuhan University, Wuhan 430072, China

ARTICLE INFO

Article history:
Received 13 February 2015
Received in revised form 17 March 2015
Accepted 31 March 2015
Available online 3 April 2015

Keywords:
Cyclic voltammetry
Porous films
Positron annihilation
Pore interconnectivity/morphology

ABSTRACT

Cyclic voltammetry and positronium (Ps) 3γ-annihilation spectroscopy were applied to investigate pore interconnectivity/morphology of porous silica films fabricated with various loading of cetyltrimethyl ammonium bromide (CTAB). With increasing the ratio of CTAB up to 15 wt.%, the total charge Q, resulted from I^- diffusion across the silica films, increased remarkably, indicative of formation of highly interconnected pores in the films prepared with more porogen. However, it decreased dramatically with further loading CTAB of 25 wt.%. Interestingly, 3γ-annihilation fraction $I_{3\gamma}$ due to a triplet-state Ps (*ortho*-positronium, *o*-Ps) emission from the silica films showed a similar behavior as a function of CTAB loading. The abnormal decrement in Q and $I_{3\gamma}$ in the film fabricated with 25 wt.% CTAB was well explained by formation of long nanochannels aligning parallel to the film surface. The results indicated that the total charge Q and Ps 3γ-annihilation fraction were closely associated with I^- and Ps diffusion governed by the pore interconnectivity/morphology of the silica films, which made cyclic voltammetry possible to be a feasible tool to characterize pore interconnectivity/morphology of porous thin films.

1. Introduction

Recently, porous silica thin films have attracted considerable interests due to their potential applications, such as gas sensors [1], adsorbent, and separation [2], semiconductor devices with low dielectric constant [3], catalyst supports [4–6], biochemical analysis [7], optical and electrical materials [8], and so on. Porous materials usually possess high specific surface areas, uniform pore size distribution, tunable porosity and/or ordered pore arrangement. Particularly, porous materials with well-ordered pores and interconnected pores are very favorable for improving the stability of photovoltaic conversion efficiency. It is known that slow positron annihilation spectroscopy (SPAS) is a very useful tool to characterize interconnectivity of pores in porous thin films by detecting annihilation of positronium (Ps, a bound state of electron-positron) atoms out-diffusion from inside of the films [9–14]. When a positron is injected into thin films, it may annihilate with a surrounding electron directly or come into being a Ps atom which exists in either a spin anti-parallel singlet state (*para*-Ps, *p*-Ps) or a spin parallel triplet state (*ortho*-Ps, *o*-Ps). As for ground state Ps, the lifetime of *p*-Ps self-annihilation in vacuum via 2γ decay is 0.125 ns, while, that of *o*-Ps self-annihilation via 3γ decay is 142 ns. In mesoporous silica thin films, long-lived *o*-Ps can diffuse back to film surface along interconnected pores and then undergoes a 3γ-annihilation process in vacuum. Ps zeropoint energy is lower in a larger pore, therefore, it is easy for *o*-Ps atoms to diffuse from small pores to larger ones [15] through interconnected pores, but the reversible process is almost impossible. If the nanochannel contains relatively larger cage-like pores, Ps atom would be trapped in them and can hardly pass through the nanochannel. While an anion in a solution might diffuse along the nanochannel without such quantum confinement effect because of its heavy atom mass. Thus, electrochemical measurement seems to be a feasible method to characterize pore interconnectivity/morphology [16–20]. In this work, cyclic voltammetry as well as Ps 3γ-annihilation spectroscopy was used to explore evolution of pore interconnectivity/morphology in silica thin films with an anion, for instance, I^-/I_2 as a redox probe.

---

* Corresponding author. Tel./fax: +86 27 68752370.
E-mail address: hecq@whu.edu.cn (C. He).

http://dx.doi.org/10.1016/j.electacta.2015.03.225
0013-4686/© 2015 Elsevier Ltd. All rights reserved.

2. Experimental

2.1. Materials and sample preparation

Potassium hydrogen phthalate (KHP) and tetraethylorthosilicate (TEOS) were purchased from Tianjin Beilian Fine Chemicals Development Co., Ltd. Cetyltrimethyl ammonium bromide (CTAB) and potassium iodide (KI) were purchased from Tianjin Baishi Chemical Co., Ltd. All chemicals and solvents were analytical grade and used without further purification.

Silica films were deposited on silicon (110) wafers and indium tin oxide (ITO) slides by dip-coating. The coating solutions were prepared by addition of an ethanol solution of cationic surfactant template (CTAB:$CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$) to silica sols prepared by a two-step process [21,22] under stirring for 1 hour at room temperature. The silica sols were synthesized by stirring the mixture of tetraethoxysiliane (TEOS), ethanol, deionized water, and HCl at 60 °C for 1.5 hours. Subsequently, ammonia was added. The final reactant mole ratios were 1TEOS: $22C_2H_5OH$: $5H_2O$: 0.004HCl: $0.004NH_3$: 0.03-0.19CTAB. The surfactant template CTAB was introduced with various weight ratios assigned as 0 wt.%, 5 wt.%, 15 wt.%, and 25 wt.%, respectively, which were calculated as $W_{template}/(W_{template}+W_{TEOS})$. After being dried, the as-deposited films were calcined in a tube furnace at 400 °C in oxygen for 5 hours to remove the surfactant template CTAB.

2.2. Characterization

An ellipsometer was introduced to measure refractive indices of the calcined mesoporous silica films under flowing N_2 gas, thicknesses of the calcined silica films were determined as 200 nm, 516 nm, 242 nm, and 233 nm for those prepared with 0 wt.%, 5 wt.%, 15 wt.%, and 25 wt.% CTAB, respectively. Transmission electron microscopy (TEM, JEOL2010) was applied to investigate the morphology of mesopores in the silica films. For the purpose of comparison with porous films, nitrogen adsorption/desorption experiments were carried out for the corresponding porous silica powders using a JW-BK122W static nitrogen adsorption instrument. The samples were preheated at 150 °C for 5 hours. The Brunauer-Emmett-Teller (BET) specific surface areas were calculated from the adsorption data in a relative pressure (P/P_0) range from 0.05 to 0.29.

Slow positron annihilation gamma-ray energy spectra were collected using a high-purity Ge detector as a function of positron incident energy. The total count of each spectrum was 10^6. Positrons from a radioactive source ^{22}Na were moderated by a thin layer of solid Ne grown on a He cryostat, and subsequently were accelerated to 30 eV and guided to a positron penning trap [23]. Then the slow positrons were magnetically transported to the sample chamber, finally accelerated to the preset high voltages before reaching the surfaces of the target films. The vacuum in the positron beam chamber was maintained at approximately 10^{-8} torr. Ps 3γ-annihilation fractions were calculated from the gamma-ray energy spectra according to the previous report [10].

Cyclic voltammetry measurements were performed in a conventional three-electrode cell using an electrochemical workstation (CS310, Correst). The working electrodes were a bare ITO electrode and silica film/ITO electrodes, which were used after removal of template CTAB through calcination. The surfaces of the electrodes were confined in an area of about 1.0 cm^2 by fixing a Teflon reservoir on them for loading the electrolyte solution. Furthermore, a Pt wire electrode and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. The cyclic voltammetric curves were recorded within a range from -0.6 V to 1.6 V.

3. Results and discussion

3.1. Refractive index and apparent porosity

Apparent porosities (pore volume fraction V_p) of the mesoporous silica films were estimated from the refractive indices by Lorentz-Lorenz equation [24]. In this study, Lorentz-Lorenz equation can be described as

$$\frac{n_f^2-1}{n_f^2+2}=(1-V_p)\frac{n_s^2-1}{n_s^2+2} \tag{1}$$

where n_f and n_s stand for the refractive indices at the wavelength of 632.8 nm of the mesoporous silica films and silica skeleton, respectively. In Eq.1, the refractive index of amorphous silica (1.45) is adopted for n_s. As shown in Fig. 1, it can be found that the refractive index of the film decreases from1.434 to 1.373, indicative of formation of porous structure in the film, then it rises to 1.389; and the apparent porosity of the films raises from 3.1% to 15.2% with increasing porogen CTAB ratio from 0 to 15 wt.%. The apparent porosity calculated from the refractive index for the film prepared with 25 wt.% CTAB seems to decline comparing with that of the silica film synthesized by loading 15 wt.% CTAB. However, this is contrary to the fact that porosity of a silica film prepared via a template method becomes higher with increasing the amount of porogen [14,25,26]. Higher porosity in the silica films with loading more CTAB is also supported by our BET measurements, which showed that the specific surface areas were 683.3, 1097.7, and 1312.2 m^2/g for the silica powders prepared with loading CTAB of 5 wt.%, 15 wt.% to 25 wt.%, respectively. The overall refractive index of a silica porous film is determined by the intrinsic n_s of the silica skeleton and that of the pores in the porous film based on meanfield approximation. Hence, it is reasonable to state that the estimated apparent porosity of the porous silica film depends on not only the porosity but also the morphology of mesopores, which is out of the range of the present topics, and needs further extensive studies in the future. The *increment* in the refractive index of the silica film prepared with 25 wt.% CTAB might suggest a change in pore morphology rather than a decrement in porosity.

3.2. Cyclic voltammetry measurements for silica films/ITO

Fig. 2 displays the curves of cyclic voltammetry measurements carried out for an ITO and the silica films deposited on ITO slides. In Fig. 2(a), it is rational to see a couple of pronounced redox peaks around 0.92 V and -0.005 V for the redox of I^-/I_2 on the surface of a bare ITO electrode. Obviously, the current intensity for redox

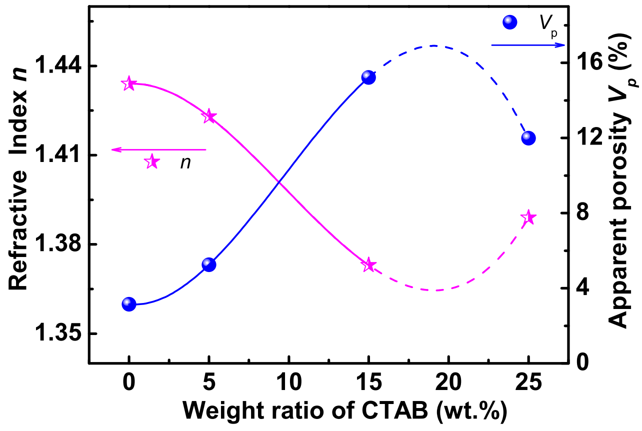

Fig. 1. Refractive index and porosity of the mesoporous silica films as a function of CTAB weight ratio. Lines are guides for the eye.