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Synthesis and characterization of mesoporous silica films by spin-coating on silicon: photoionization of methylphenothiazine and photoluminescence of erbium 8-hydroxyquinolinate in mesoporous silica films

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Transparent mesoporous silica films were successfully prepared by spin-coating on silicon wafers at room temperature. The x-ray diffraction patterns of the films indicate that both hexagonal and cubic mesoporous films can be formed by varying the surfactant to silicon mole ratio. These films have reasonable thermal stability and are calcinable up to 670 °C. Methylphenothiazine is incorporated into the silica films and after photoionization by ultraviolet light, the radical cation was characterized by electron spin resonance spectroscopy. Incorporation of erbium 8-hydroxyquinolinate into mesoporous silica films was characterized by photoluminescence.

1. INTRODUCTION

Scientists at Mobil Corporation synthesized silica-based mesoporous molecular sieves with hexagonal, cubic, and lamellar structure called M41S materials in 1992. Zhao et al. [1] and Kimura et al. [2] reported the successful formation of mesoporous hexagonal aluminophosphate and silicoaluminophosphate by a modified ion-pair process. Recently, hexagonal mesoporous silicoaluminophosphate possessing improved thermal stability (calcinable up to 670 °C) was synthesized by utilizing charge density matching with optimal composition and stirring conditions at room temperature [3,4].

For possible applications of mesoporous oxide materials as sensors and optical materials, it is important to develop thin film materials. Zhao, Yang, and Stucky [5] reported dispersion of a bulk silica phase into a liquid which was dip-coated onto silicon wafers and glass slides and resulted in a continuous, uniform coating of colloidal particles.

In the present study, optically transparent and crack-free mesoporous silica films have been synthesized by an evaporation-induced self-assembly process and spin-coated on silicon. Methylphenothiazine is incorporated into these films and photoionization yields stable radical cations. Incorporation of erbium 8-hydroxyquinolinate (ErQ) into mesoporous silica films is

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characterized by PL and isothermal nitrogen physisorption studies [6]. These materials are promising for applications such as sensor, optical devices, optical amplifiers, nanoreactors, and hosts for large organic molecules.

2. EXPERIMENTAL

Tetramethylorthosilicate (TMOS, Aldrich, 98%) was hydrolyzed under acidic conditions (HCl, J.T. Baker, 36.5–38%), and then methanol (CH_3OH, Merck, 99.8%) was added into the hydrolyzed TMOS at room temperature. Finally, cetyltrimethylammonium chloride (CTACl, Aldrich, 25%) was added so that the final reactant mole ratios were 1–3 TMOS : 8–16 H_2O : 0.09–0.11 HCl : 18–30 CH_3OH : 0.2–0.8 CTACl. The mesoporous thin films were calcined in flowing air at 550 °C for 12 h at rate of 1 °C/min.

Methylphenothiazine is incorporated into the silica films and after photoionization by ultraviolet light, the radical cations are characterized by electron spin resonance spectroscopy. Incorporation of erbium 8-hydroxyquinolinate (ErQ) into the silica films was characterized by photoluminescence and isothermal nitrogen sorption studies [6].

3. RESULTS AND DISCUSSION

XRD patterns of as-synthesized and calcined mesoporous silica films in Figure 1 indicate that a mesoporous structure is formed on the silica substrate. XRD patterns show a prominent peak at $2\theta = 2.0$–$4.0°$ and some broad peaks at $2\theta = 4.0°$–$7.0°$ characteristic of hexagonal structure, which is similar to the XRD of hexagonal MCM-41 materials. In addition to preparation of hexagonal mesoporous silica film, materials with cubic phase were also synthesized by varying the surfactant to silicon mole ratio. At a surfactant/Si ratio of less than 0.25, the predominant phase is hexagonal as shown in Figure 1. As the surfactant/Si ratio increases beyond 0.25, a cubic phase is produced as shown in Figure 1. These films have reasonable thermal stability and are calcinable up to 670 °C.

The ordered structure of the calcined mesoporous silica film was further confirmed by TEM as in Figure 2, which clearly shows a hexagonal periodicity. The calcined mesoporous silica film thickness is 433 ± 2 nm as measured by cross-sectional SEM. The surface roughness of the calcined film was studied by AFM, and the average roughness is estimated to be less than 2 nm over a length span of 1000 nm. Nitrogen sorption shows an IUPAC type IV nitrogen adsorption and desorption isotherm. Calcined films have a BET surface area of 920 m^2/g and an average pore diameter of 2.1 nm.

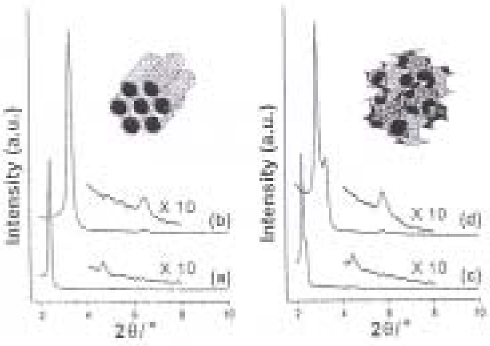

Fig. 1. XRD patterns of as-synthesized (a,c) and calcined (b,d) mesoporous silica films

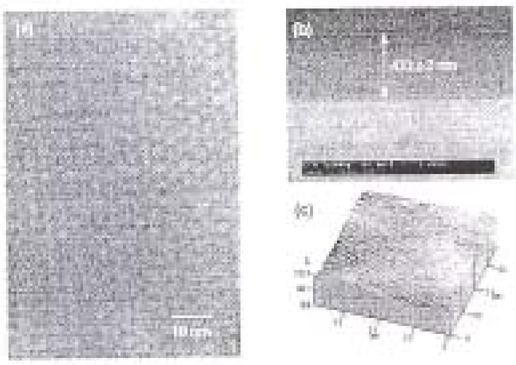

Fig. 2. TEM (a), SEM (b) and AFM (c) of calcined mesoporous silica films

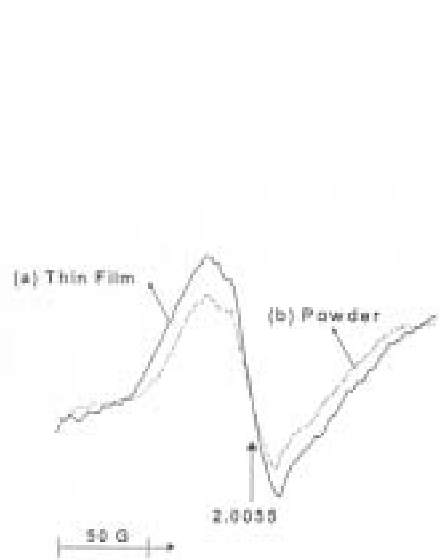

Fig. 3. ESR spectra of methylphenothiazine in mesoporous silica film (a) and powder (b).

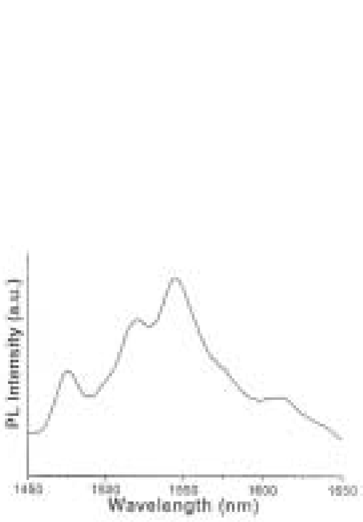

Fig. 4. PL spectrum of mesoporous silica film with incorporated ErQ at 300 K.

Mesoporous silica films with impregnated methylphenothiazine show a weak ESR signal before ultraviolet irradiation [3,7]. After being irradiated by 320 nm light at 100 K for 20 min, the samples showed a large ESR signal as shown in Figure 3. Figure 3 shows the ESR spectra of impregnated methylphenothiazine in mesoporous silica film (a) and powder (b) after being irradiated by 320 nm light at 100 K for 20 min. These ESR spectra are an asymmetric partially resolved sextet at $g = 2.0055$. The photoyield of methylphenothiazine cation radical is about 35 % higher in the film compared to the powder. The relative high efficiency of the formation and stabilization of methylphenothiazine cation radical in mesoporous silica films suggest that such films are promising materials for various applications.

Figure 4 shows the photoluminescence (PL) spectrum of mesoporous silica film with incorporated ErQ. It is expected that the peak at 1475nm is due to the gratings in monochromator. The main luminescence peak is at 1545nm. The bandwidth at half-maximum is 72nm. This is much wider than for any other Er-doped materials [8]. The wide bandwidth is obtained by emission from Er atoms in different local environments. Such a broad spectrum enables a wide gain bandwidth for optical amplification. Therefore it is considered that the mesoporous silica film is a good matrix to be doped by a rare-earth complex homogeneously.

4. CONCLUSIONS

Transparent mesoporous silica films with hexagonal and cubic phases are formed by control of the surfactant concentration. Transparent mesoporous silica films are fairly homogeneous and relatively easy to produce. The mesoporous silica films with hexagonal and cubic phases show possibilities of application as advanced materials. The incorporation of methylphenothiazine into mesoporous silica films shows successful photoionization by ESR and the incorporation of erbium 8-hydroxyquinolinate (ErQ) into mesoporous silica films is characterized by PL and isothermal nitrogen physisorption studies. Such mesoporous films with impregnated photo-functional materials may find application as sensor, optical devices, nanoreactors, and hosts for large organic molecules.

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