

# Rectifying and photovoltaic effects observed in mesoporous MCM-41 silica film on silicon

Q. Cai<sup>a,\*</sup>, W.Y. Zou<sup>a</sup>, Z.S. Luo<sup>a</sup>, Q.X. Wen<sup>b</sup>, W.Q. Pang<sup>c</sup>, F.Z. Cui<sup>a</sup>

<sup>a</sup>Department of Material Science and Engineering, Tsinghua University, Beijing 100084, China

<sup>b</sup>Changchun Institute of Physics, Academia Sinica, Changchun 130021, China

<sup>c</sup>Key Laboratory of Inorganic Synthesis and Preparative Chemistry and Department of Chemistry, Jilin University, Changchun 130023, China

Received 6 August 2002; received in revised form 6 May 2003; accepted 12 May 2003

## Abstract

Oriented mesoporous MCM-41 silica films have been synthesized on single-crystalline silicon (111) wafers by the self-assembly deposition in ammonia medium. For the first time, the  $I$ – $V$  curves and surface photovoltaic spectra of the films has been investigated. The  $I$ – $V$  curve of the as-synthesized film exhibits an excellent rectified ratio of  $\sigma^+/\sigma^- = 3 \times 10^3$  (where  $\sigma^+$ ,  $\sigma^-$  are the forward electrical conductivity and reverse electrical conductivity, respectively). The results of photovoltaic measurements indicate that the as-synthesized film possesses a significant surface photovoltaic increase.

© 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** MCM-41 silica film;  $I$ – $V$  curves; Surface photovoltaic spectra

## 1. Introduction

A self-assembly has been an important method for the fabrication of composite materials involving non-covalent interactions recently. The synthesis of mesoporous materials with structures and functions over different length scales has ramifications in diverse areas, such as catalysis [1], biomolecule separations, chromatographic supports, the development of medical implants, miniaturization of electronic devices, and the formation of semiconductor nanostructures [2]. The synthesis of MCM-41, a silicate compound that has a hexagonal array of uniform one-dimensional mesopores with diameters ranging from 20 to 100 Å, involves the assembly of silicate species around lyotropic surfactant molecules [3,4]. Such assembly processes are also used for the formation of multilayer membranes [5] and Langmuir–Blodgett films [6] with inorganic–organic hybrid structures. The self-assembly of surfactant molecules with silicates at the interfaces of solution/solid substrates [7–9], such as mica [7], graphite [8] and silicon [9], and air/solution [10,11] leads to the formation of MCM-41 films. The compound films possess mesoporous channels parallel to the surface of the substrates. Although a variety of

mesoporous films have been prepared, little is known about their physical properties, especially their electronic behaviors. In this paper, for the first time we presented measurements on the rectifying and photovoltaic effects of the MCM-41 film on single-crystalline silicon (111) wafer.

## 2. Experimental

The single-crystalline silicon substrate is n-type and the surface of the substrate is (111) crystallographic plane. It was pre-treated with a boiling aqueous solution of NaOH (20 wt.%) and H<sub>2</sub>O<sub>2</sub> (1 wt.%) for 5 min, and had been immersed in the cooling solution for 2 h, washed with and then kept in distilled water before use. For a typical preparation of MCM-41 film on the silicon substrate, 205 ml of the aqueous ammonia solution (25 wt.%) was mixed with 270 ml of distilled water followed by the addition of 2.0 g of cetyltrimethylammonium bromide (CTABr) under stirring. The pre-treated silicon plate was placed in the reaction system and 10 ml of tetraethylorthosilicate (TEOS) was added dropwise. The reaction system had been heated under stirring for about 2 h and the resulting film along with the substrate was washed with distilled water and dried at ambient temperature, followed by calcination in air at 823 K for 4 h.

\* Corresponding author.

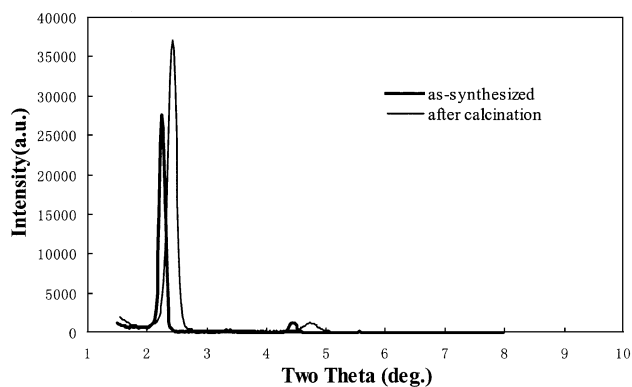


Fig. 1. X-ray diffraction patterns of as-synthesized and calcined MCM-41 silica films on single-crystalline silicon substrates.

The X-ray diffraction pattern was recorded on a D/max-rA Rigaku diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). The sample was scanned from  $0.8^\circ$  to  $10^\circ$  ( $2\theta$ ) with a step size of  $0.02^\circ$  and a count time of 1 s at each point. The transmission electron micrographs (TEM) were obtained on a Hitachi-8100 transmission electron microscope operated at 200 kV for a thin section prepared by ultra-microtomy: The TEM sample was prepared by scratching the films off the substrates using a tweezers. To prepare the cross-sectional sample, a thin film was polished till its thickness was 1  $\mu\text{m}$

in cross-section direction, then an ion-milling technique was used to thin the sample till it was electron transparent.

The  $I$ – $V$  measurements were carried out across the silicon substrate/mesoporous silica film interface with JT-1. The surface photovoltage, equivalent to a change of the surface potential barrier upon illumination, is related to a charge transfer normal to the surface of a semiconductor. The surface photovoltage spectra (SPS) were performed with a home-built apparatus described elsewhere [11,12]. In order to eliminate the casualness of the results, five measurements of reproduction had been done with each experiment.

### 3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the MCM-41 films on crystalline silicon substrate as-synthesized as well as calcined. The as-synthesized sample exhibits a strong peak at around  $2.30^\circ$  and a weak one around  $4.60^\circ$ . These two peaks correspond to the (100) and the (200) reflections of the mesoporous silica film [7]. The absence of the (110) reflection for the film indicates that the channel axis takes orientation parallel to the surface plane of the substrate. Upon calcination of the film, a contraction of the cell parameter of 2 Å is observed, due to the removal of

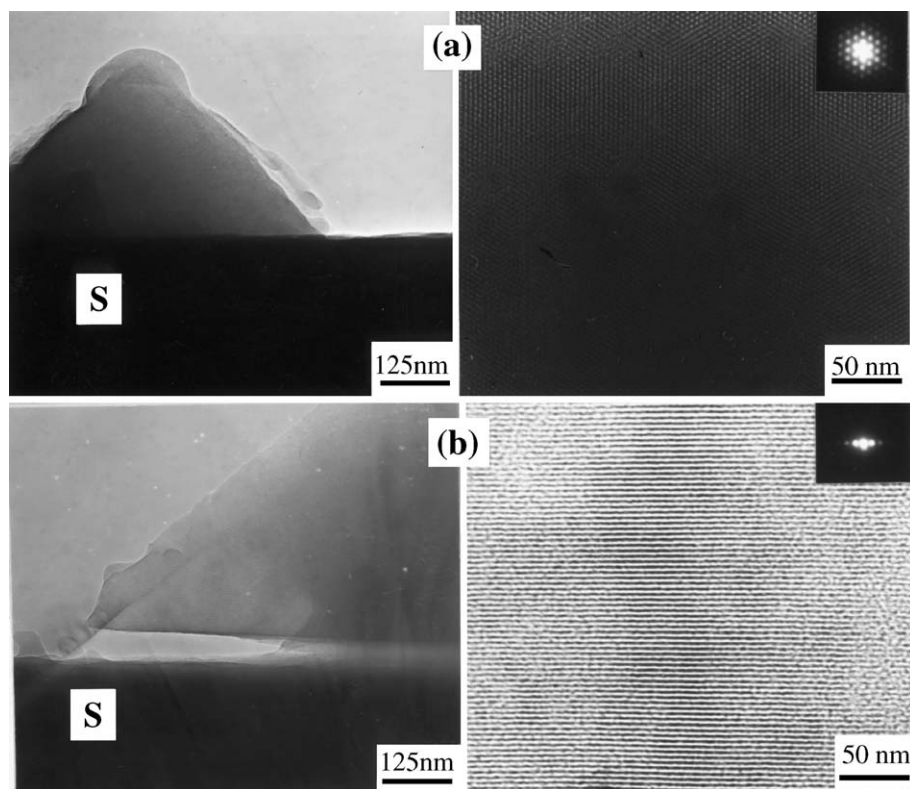


Fig. 2. High-resolution electron microscopic images of the cross-section of the MCM-41 silica film on the single-crystalline silicon substrate S. (a) A view along the channel axis showing the hexagonal arrays of the channels; the left: scale bar: 125 nm; the right: representative image of a thin film, scale bar: 50 nm; inset: selected area electron diffraction pattern of the structure. (b) The left: view normal to the channel axis (scale bar: 125 nm); the right: representative image of a thin film (scale bar: 50 nm); inset: selected area electron diffraction pattern of the structure.

the surfactant template from the channels, concomitant with the condensation of silanol (SiOH) groups in the walls. The cell parameter,  $a_0$ , between two pore centers in the as-synthesized MCM-41 film can be calculated from  $a_0 = (2/\sqrt{3})d_{100}$ , is about 44.35 Å.

High-resolution transmission electron microscopic (HRTEM) images (Fig. 2) clearly reveal the mesoporous feature of the MCM-41 film on a silicon substrate. The image viewed along the channel axis shows the hexagonal arrangement of the mesopores with a center-to-center distance of about 45 Å, which agrees well with the XRD result. When viewed perpendicularly to the channel axis, the image shows parallel stripes with a repeated distance of about 39 Å. It can be estimated from this image that the channels run parallel to the substrates surface.

$I$ – $V$  curves (Fig. 3) of the as-synthesized film on a silicon substrate were obtained using plating aluminum as the contact electrodes. The particularity of current–voltage indicates that the film on the silicon substrate has an excellent rectifying effect. When forward bias is applied (a positive voltage to the silica film), strong current can be detected whereas when reverse bias is applied (a positive voltage to the silicon substrate), no significant current can be observed. When the forward gate voltage is about +5 V, and the reverse gate voltage is about –5 V, the rectified ratio  $\sigma^+/\sigma^-$  is about  $3 \times 10^3$ , where  $\sigma^+$  and  $\sigma^-$  are conductivities under forward and reverse biases, respectively. This semiconducting behavior has been reproduced for five samples. As the n-type silicon substrate does not exhibit any rectifying effect, it can be only concluded that a  $p$ – $n$  heterojunction is formed at the interface between the silica film and the silicon substrate. It is well known that a dense silica film is an insulator that no such heterojunction is expected to form from a dense silica film on the surface of a single-crystalline silicon. However, when a silica film has periodically arranged mesopores in it, surface states may be

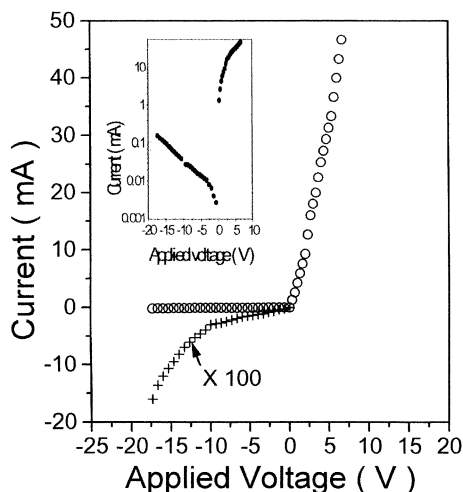


Fig. 3.  $I$ – $V$  curves for the as-synthesized MCM-41 silica film on single-crystalline silicon substrate; each “+” dot is represented that the current of “O” dot is multiplied by 100.

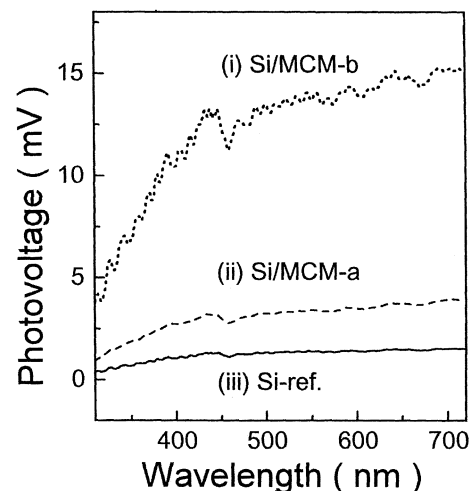


Fig. 4. Photovoltage spectra for (i) as-synthesized MCM-41 silica film on a silicon substrate; (ii) after calcination of the MCM-41 silica film on a silicon substrate; (iii) a silicon wafer.

present on the internal surfaces of the channels of the mesoporous silica. Due to the spatial periodicity of the channels, these surface states can overlap to form energy bands that are most likely located in between the intrinsic band gap of the insulating silica [13]. It is the band gap between the conduction and the valence surface state energy bands that makes the mesoporous MCM-41 film a semiconductor. The semiconducting property of the film combined with that of the silicon substrate is responsible for the formation of the  $p$ – $n$  heterojunction.

The SPS of the as-synthesized MCM-41 film on silicon is also an indication of the presence of  $p$ – $n$  heterojunction at the interface. It can be seen in Fig. 4 that a considerable photovoltage increase is present for the film on a silicon substrate, and the value of the photovoltage increases with the wavelength in general. The photovoltage spectrum for the silicon substrate and the calcined film are also shown in Fig. 4 for comparison. No significant photovoltage is observed for the substrate and the calcined film over the photo-wavelength ranging from 200 to 700 nm. The photovoltage of the as-synthesized MCM-41 film on a silicon substrate is about 10 times that of the silicon substrate on average, suggesting that a large amount of holes or electrons have been accumulated on either side of the heterojunction after photo-exposed the as-synthesized film on a silicon substrate.

#### 4. Conclusion

In summary, continuous mesoporous silica films have been synthesized by the self-assembly deposition on a single-crystalline silicon substrate. By means of the XRD measurement, and TEM observation, the films are determined to have a well-oriented MCM-41 structure. Its  $c$ -axis parallels to the surface plane of the substrate. This prepara-

tion strategy of the film is proved to be an effective route for the formation of  $p-n$  heterojunction that exhibits significant rectifying and photovoltaic effects which might find applications in electronics and optoelectronics.

### Acknowledgements

This work was in part supported by the National Natural Science Foundation of China, grant number 20273037.

### References

- [1] R. Hoppe, A. Ortlam, J. Rathousky, G. Schulz, E.A. Zukel, *Micro-porous Mater.* 8 (1997) 267.
- [2] D.O. Chomski, A. Kuperman, N. Coombs, G.A. Ozin, *Chem. Vap. Depos.* 2 (1) (1996) 8–13.
- [3] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710–712.
- [4] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Dchlenker, *J. Am. Chem. Soc.* 114 (1992) 10834.
- [5] D.Q. Li, M.A. Ratner, T.J. Marks, C.H. Zhang, J. Yang, G.K. Wong, *J. Am. Chem. Soc.* 112 (1990) 7389.
- [6] I. Moriguchi, I. Tanaka, Y. Teraoka, S. Kagawa, *J. Chem. Soc., Chem. Commun.*, (1991) 1401.
- [7] H. Yang, N. Coombs, I. Sokolov, G.A. Ozin, *Nature* 381 (1995) 589.
- [8] H. Yang, N. Coombs, I. Sokolov, G.A. Ozin, *J. Mater. Chem.* 7 (1997) 1285.
- [9] Y.F. Lu, R. Gangull, C.A. Drewien, M.T. Anderson, G. Jeffrey, I. Zink, *Nature* 389 (1997) 364.
- [10] M. Ogawa, *J. Am. Chem. Soc.* 116 (1994) 7941.
- [11] H. Yang, A. Kuperman, N. Coombs, S. Mamiche-Afara, G.A. Ozin, *Nature* 379 (1996) 703.
- [12] H. Du, Y.A. Cao, Y.B. Bai, P. Zhang, X.M. Qian, T.J. Li, X.Y. Tang, *J. Phys. Chem., B* 102 (1999) 2329.
- [13] S.R. Morrison, *The Chemical Physics of Surface*, Plenum, New York, 1977, p. 121.