



Effect of catalyst HF concentration on the electrical characteristics of ultra low- k materials

Zhi-Wei He^{1,2,*}, Shi-Qiu Zhu¹, Sheng-Li Wang¹, Zheng Qi¹, Yu-Yuan Guan¹

¹Department of Applied Physics, China Agricultural University, Beijing 100083, P.R. China

²Key Laboratory of Semiconductor Materials Science Institute of Semiconductors, Chinese Academy of Sciences P.O.Box 912, Beijing 100083, P.R. China

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Abstract

The effects of catalyst HF concentration on the dielectric and electrical properties of SiOF films are discussed. From the current density-voltage and capacitance-voltage curves, we observed that the film catalyzed with the special concentration of HF (the ratio of HF/H₂O = 1/5) shows good moisture resistance, low leakage current (10^{-11} A/cm² at 1 MV/cm) and high breakdown field (6 MV/cm), which can be explained by the results of Fourier transform infrared spectra. The dielectric constant value is also very low and reaches about 1.75 after annealing at the temperature of 450 °C. Therefore, the concentration of HF catalyst is an important factor in the sol-gel process.

Keywords: SiOF films, FTIR, SAXS, electrical properties, low dielectric constant

I. Introduction

In ultra large scale integrated circuits, interlayer dielectrics with a dielectric constant (k) of 2.1 or less are required for 32 nm technology nodes [1]. The ultra-low k films should meet strict requirements in terms of their dielectric constant loss, moisture resistance, thermal stability and mechanical properties [2,3]. One such candidate is fluorine doped silica oxide, which consists of Si-F groups as well as Si-O groups [4,5]. However, the deposition of the film and the injection of fluorine ions are usually performed by plasma-enhanced chemical vapour deposition method, which is complicated. On the other hand, due to the ease of processing and the controllable k value, the sol-gel derived nanoporous silica oxide films have attracted considerable attention [6]. However, the decrease of k in this kind of films comes at the price of lower mechanical properties and moisture resistance.

In our work, we successfully combined the two kinds of materials mentioned above, and, for the first time introduced the fluorine ion into the sol-gel method by using hydrofluoric acid (HF) as a catalyst. This method

was used to prepare the ultra-low k films and in this paper, we discuss the effects of the HF catalyst concentration on the electrical properties of the film in detail.

II. Experimental

The spin-coating solutions were prepared by mixing tetraethyl orthosilicate (TEOS), deionized water (DI), ethanol (EtOH) and hydrofluoric acid (HF). Among them, the molar ratio of TEOS/ DI/ EtOH is 1/ 15/ 3. The ratios of HF/H₂O are 1/3, 1/5, 1/10, and we name the corresponding films as samples HFA, HFB and HFC, respectively. After spin-coating for 30 s at 4000 rpm, the Si (100) wafers were subjected to a series of soft baking steps on a hot plate, including 1 min at 150 °C and 2 minutes at 250 °C, and then dipped in trimethylchlorosilane (TMCS) for surface modification. The nanoporous thin films were produced by annealing the wafers in a tube furnace at 450 °C for 2 hours under N₂ atmosphere.

The electrical properties of the films were characterized by capacitance-voltage (C - V) and current density-voltage (J - V) measurements using the HP4248A capacitance meter and the HP4145B semiconductor parameter analyzer with the voltage ramping from 0–100 V. The composition and the bonding configuration of the films were studied by Fourier transform infrared

* Corresponding author: tel: +86 10 62 73 6711
fax: +86 10 62 73 6777, e-mail: hezw@cau.edu.cn

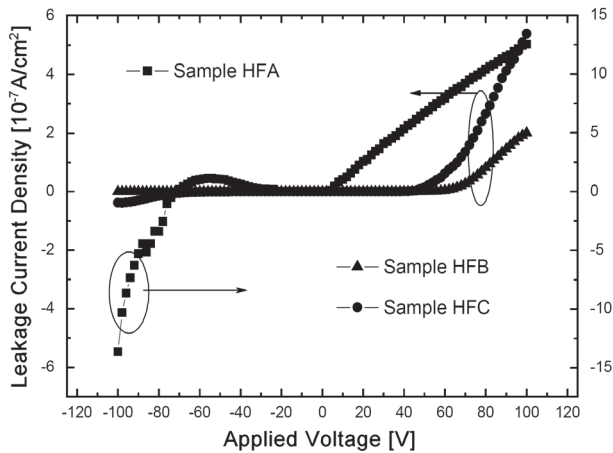


Figure 1. J-V characteristics of the samples HFA, HFB, and HFC

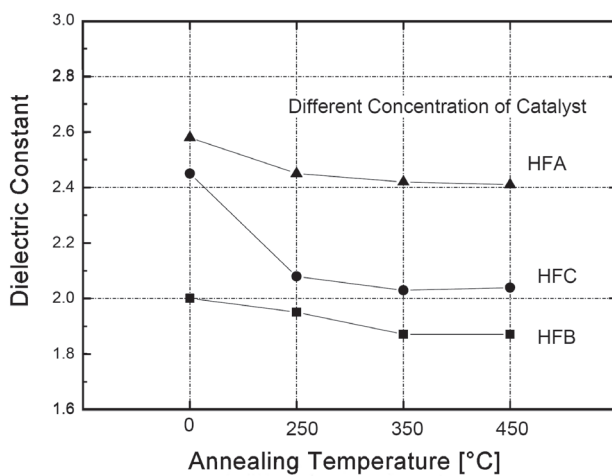


Figure 2. The dielectric constants of different samples as a function of annealing temperature

(FTIR) spectroscopy (Nicolet NEXUS 670) and Small Angle X-Ray Scattering (SAXS, Rigaku D/max 2550 V) with CuK α radiation (40 kV, 100mA).

III. Results and discussion

The thickness of the films is 150 nm. Figure 1 shows the J - V characteristics of the films with various HF concentrations. At the electric field strength of 1 MV/cm, the leakage current density of sample HFA, HFB and HFC are 1.9×10^{-7} A/cm 2 , 1.62×10^{-11} A/cm 2 and

3.22×10^{-11} A/cm 2 , respectively. The leakage current density of HFB is the lowest among the three synthesised samples. In the sample HFB, fluorine ions adequately substituted the weak bonds such as Si-H and Si-OH. Furthermore, the elimination of the interface dangling bonds and the inner unsaturated bonds also contributed to the improvement of the leakage current [7].

In semiconductor devices, the dielectric layer on the silicon substrate will be subjected to very large electric fields. Therefore, the dielectric strength plays an important role on the reliability of the devices [8,9]. The dielectric strength is defined as the ratio of the breakdown voltage and the dielectric thickness. As can be seen in Fig. 1, when the HF concentration in the solution was changed, the break-down voltage of samples changed as well and reached about 6 MV/cm 2 for the sample HFB. The break-down voltage is related to the film properties which are determined by the deposition conditions and the chemical environment. It is believed that the reduction of the dangling and unsaturated bonds contribute to the improvement of break-down voltage improvement, which also results in the decrease of the k value of thin films [10].

Figure 2 presents the k value of the thin film as a function of post the annealing temperature. The dielectric constant of the film is dependent on the number of electric dipoles (polarizable unit) per unit volume and the ability of the polarizable unit to orient itself fast enough to keep up with the oscillations of the applied electric field [11]. Compared to the conventional sol-gel deposited film, all of the samples exhibited lower k values in the same condition, especially for the sample HFB. This indicates that the HF catalyzed SiOF film has greater porosity. As the annealing temperature increased, the k value of all samples demonstrated a decreasing trend. This reveals that our samples consist of some adsorbed water and un-reactive organic compounds regardless of catalyst type and catalyst concentration. However, the sample HFB showed the smallest decrease. Therefore, we conclude that the optimal concentration of the HF catalyst can adjust the reaction course of hydrolysis and condensation of TEOS and result in the preferable fine network structure and less defects in the films.

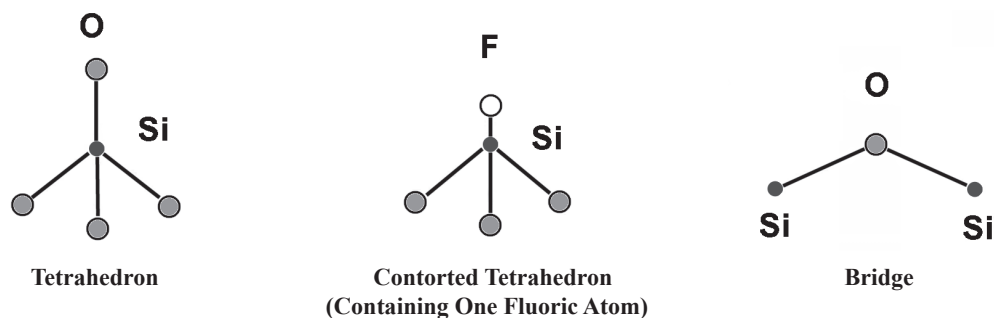


Figure 3. Three different structures of the bonds in the SiOF thin film

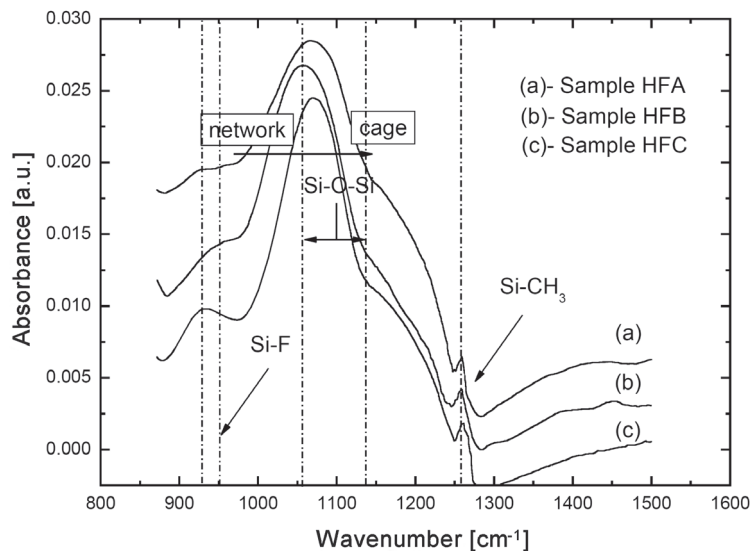


Figure 4. FTIR spectra in the range of 900–1500 cm^{-1} of the samples: a) HFA, b) HFB, c) HFC

The decrease of the k value is also ascribed to the relaxation of the microstructure. From the results of Lee's research [5], the relaxation of the microstructure leads directly the decrease of the film density, because of the increase of the Si-O-Si angle. As we know, the pure SiO_2 has a normal tetrahedron structure. When introducing

F^- ions into the film, the former structure of the SiO_2 is destroyed. As shown in Fig. 3, there are three new structures in the SiOF thin film: the natural Si-O tetrahedron, the destroyed F-O tetrahedron, and the bridge oxide, which lead to the relaxation of the network structure leaving more space and more pores in the films.

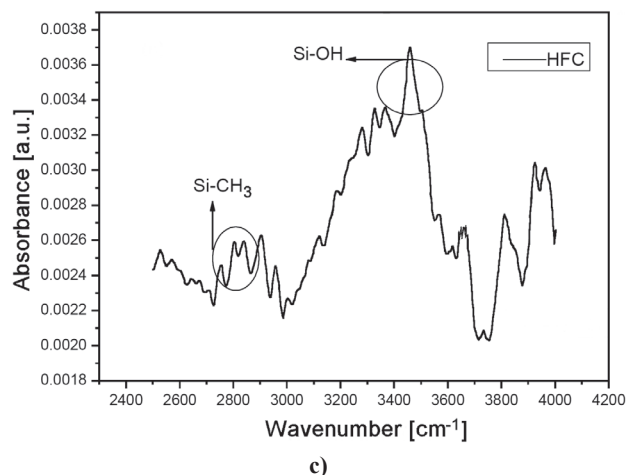
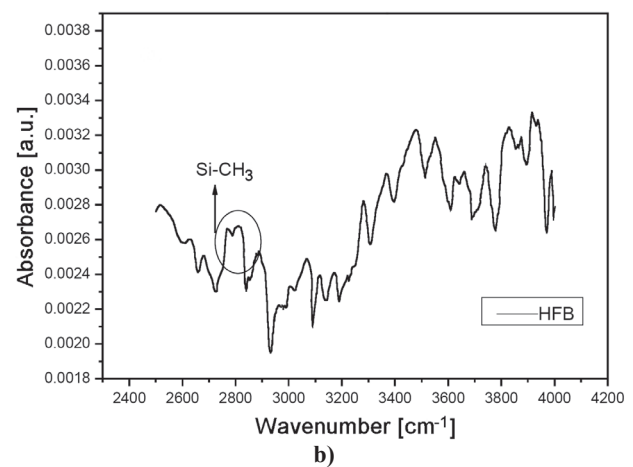
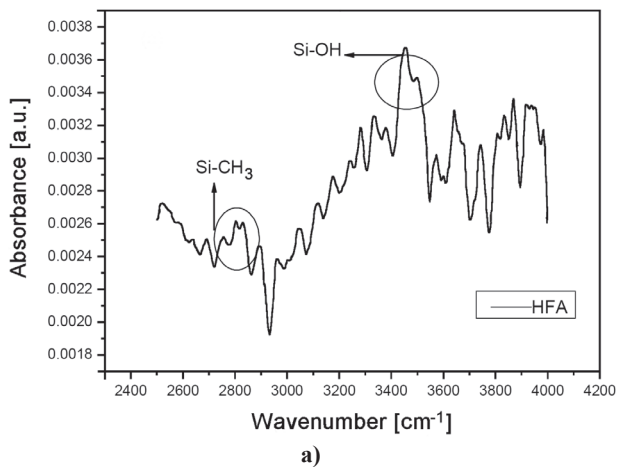


Figure 5. FTIR spectra in the range of 2500–4000 cm^{-1} of the samples: a) HFA, b) HFB, c) HFC

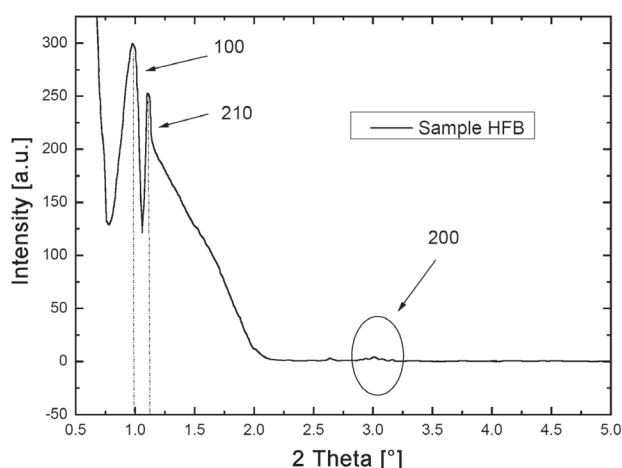


Figure 6. SAXS pattern of the sample HFB

In order to clarify the reaction course, we investigated the chemical bond states of all the samples through FTIR, as shown in Figs. 4 and 5, which show two different regions of the FTIR absorption spectra for samples HFA, HFB and HFC.

As shown in Fig. 4, the peak ranging from 900 cm^{-1} to 980 cm^{-1} corresponds to the Si-F bonds. When compared to the normal HCl catalysed films, the presence of the Si-F bond in the film ensures the improvement of the thermal stability. This is because the decomposition temperature of Si-F bond can be as high as 700°C [12]. Using different concentrations of the HF catalyst shifts the peaks in the samples HFA and HFC. Such behaviour might be explained by the presence of the Si-F₂ bonds. A SiF₂ bond contains two F atoms, which, due to their high electronegativity, react easily with the Si-OH bond. The presence of the SiF₂ bond

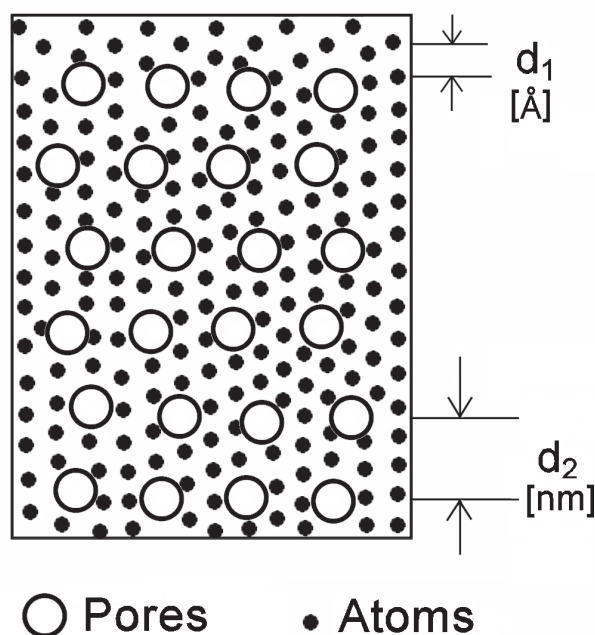


Figure 7. Schematic representation of ordered porous structure

enhances the polarity of the film, and induces the increase of the k value of the thin films. So the concentration of the HF catalyst in our experiment is very important, as it controls the speed of hydrolysis and condensation. In the HFB sample, there are more SiF bonds than SiF₂ ones, which leads to the better hydrophobic properties.

There is also some variation related to the SiOF backbone structure. The vibration of the Si-O-Si skeleton of the SiOF film is observed as a dominant single peak located between 1054 cm^{-1} and 1070 cm^{-1} , which is ascribed to the network structure. In samples HFA and HFC, this peak moves to a higher wavenumber. Since there is a shoulder peak near the SiOF peak in these two samples, such movement may be influenced by the other peak belonging to the Si-O-Si skeleton, which is localized at 1135 cm^{-1} and ascribed to the cage structure. The ratio of network and cage structure is related to the shrinkage, which is the major factor influencing the porosity. We observed that the higher porosity is caused by a higher network/cage ratio. This is also the reason why the k values of the samples HFA and HFC decrease obviously with the increase of the annealing temperature.

The higher SiF₂/SiF ratio directly leads to the higher intensity of the Si-OH peak around $3100\text{--}3600\text{ cm}^{-1}$ [13], as shown in Fig. 5, which depicts the FTIR absorption spectra in the range of $2400\text{--}4000\text{ cm}^{-1}$. There is a broad absorption band related to H-O-H stretching bonds between 3000 and 3800 cm^{-1} , indicating the quantity of the absorbed water in the pores of thin films. In the sample HFA, the concentration of HF catalyst is so large that it accelerates the reaction obviously. The gelation time is so short that the TEOS has no time to hydrolyse and condense to form large network structure, but instead forms lot of SiO₂ grains in this film. Random pores and hanging bonds appear in the film, leading to the decreased water resistance and the higher k value. On the other hand, in the sample HFC, the TEOS has enough time to hydrolyze to form the network structure. However, there are also two disadvantages. One is too long reaction time (in the usual conditions, it needs about fifteen days to finish the gelation) and the other is the residual water, which stays in the network structure of the film. Water can increase the k value of film because of its polar molecules. Furthermore, when annealing the film, the residual water will evaporate, leaving many connected pores, which worsen the mechanical properties and increase the hydrophilic property of the film.

Only the sample HFB, which was catalyzed with the optimal concentration, provides the improved electrical and hydrophobic properties, such as the lower leakage current density, reduced dielectric constant, inconspicuous trend of k value variation with annealing temperature and lower amounts of adsorbed water.

The improvements in the above stated properties result from the chemical bond states and the microscopic network structure of the sample HFB, which can be detected by the SAXS spectra.

Figure 6 shows the SAXS spectrum of the sample HFB. There are two high intensity peaks between $2\theta = 1\text{--}2^\circ$, which is the characteristic peak of the microporous SiO_2 , confirming the well-ordered structure and good uniformity of the thin film. A strong and narrow peak (100) and a weak peak (200) corresponding to the hexagonal microstructure [14] were clearly observed in Fig. 6. From the basic theory of the SAXS technology, we know that $l = 2d \cdot \sin q$, where l is the wavelength of the incident ray, q is the incidence angle, d is the space of the lattice. In the normal conditions, the incidence angle is larger, so the d value is the distance between the atoms, just like d_1 , as shown in Fig. 7. However, when the incidence angle is decreased to a very low value, the obtained d_2 is the space between the nanometer-sized pores [15]. Therefore, the SAXS technology can be used to determine the pore structure of the film with uniform nanopores.

IV. Conclusions

The nanoporous SiOF films were prepared by sol-gel method. The dielectric and electrical properties of the film were investigated. A higher HF/ H_2O solution ratio led to an increased Si-F₂ bond concentration in the deposited films, and the absorption peak corresponding to Si-OH stretching vibration also increased. In addition, lower HF/ H_2O solution ratio also led to the similar results. Only the sample HFB with catalyst ratio of 1/5 shows better water resistance and has a low leakage current (10^{-11} A/cm²) at 1 MV/cm and a breakdown field of 6 MV/cm. Its dielectric constant is also very low and reaches about 1.75 after annealing at the temperature of 450 °C. So the concentration of the HF catalyst is an important factor in the sol-gel process.

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References

- X. Xiao, X.M. Shan, Y. Kayaba, K. Kohmura, H. Tanaka, T. Kikkawa, "Young's modulus evaluation by SAWs for porous silica low-k film with cesium doping", *Microelectron. Eng.*, **88** (2011) 666–670.
- H.L. Chang, C.T. Kuo, M.S. Liang, "Mechanical properties and fracture mechanism of porous SiOCH low-k dielectrics", *Microelectron. Eng.*, **88** (2011) 1623–1627.
- C. Zhang, H.Y. Xu, X. Zhao, "Structure and properties of low-dielectric-constant poly (acetoxystyrene-co-octavinyl-polyhedral oligomeric silsesquioxane) hybrid nanocomposite", *Chinese Chem. Lett.*, **21** (2010) 488–491.
- L. Wang, S. Yu, J. Cho, "Properties of liquid-phase deposited silica films for low-k dielectric applications", *J. Am. Ceram. Soc.*, **92** [10] (2009) 2388–2391.
- T. Lee, S.S. Park, Y. Jung, S. Han, D. Han, I. Kim, C-S. Ha, "Preparation and characterization of polyimide/mesoporous silica hybrid nanocomposites based on water-soluble poly(amic acid) ammonium salt", *Eur. Polymer J.*, **45** (2009) 19–29.
- K. Hamioud, V. Arnal, A. Farcy, V. Jousseau, A. Zenasni, B. Icard, J. Pradelles, S. Manaklia, Ph. Brunb, G. Imberta, C. Jayetb, M. Assousb, S. Maitre-jeanb, D. Galpina, C. Mongeta, J. Guillana, S. Chhuna, E. Richarda, D. Barbierc, M. Haonda, *et al.*, "32 nm node BEOL integration with an extreme low-k porous SiOCH dielectric $k = 2.3$ ", *Microelectron. Eng.*, **87** (2010) 316–320.
- N. Biswas, X. Wang, S. Gangopadhyay, "Electrical properties of amorphous silicon carbide films", *Appl. Phys. Lett.*, **80** (2002) 3439–3441.
- S. Lee, J. Woo, D. Jung, J. Yang, J-H. Boo, H. Kim, H. Chae, "Effect of etching on dielectric constant and surface composition of SiCOH low-k films in inductively coupled fluorocarbon plasmas", *Thin Solid Films*, **517** (2009) 3942–3946.
- M. Ueki, M. Zanin, "Influence of additives on the dielectric strength of high-density polyethylene", *IEEE Trans. Dielect. Elect. Insulation*, **6** [6] (1999) 876–881.
- N. Fainer, Y. Rumyantsev, M. Kosinova, E. Maximovskii, V. Kesler, V. Kirienko, F. Kuznetsov, "Low-k dielectrics on base of silicon carbon nitride films", *Surf. Coat. Tech.*, **201** (2007) 9269–9274.
- K. Maes, M.R. Baklanov, D. Shamiryan, F. Lacopi, S.H. Brongersma, Z.S. Yanovitskaya, "Low dielectric constant materials for microelectronic", *J. Appl. Phys.*, **93** (2003) 8793–8841.
- S-J. Ding, D.W. Zhang, J.T. Wang, W.W. Lee, "Low dielectric constant $\text{SiO}_2\text{:C,F}$ films prepared from $\text{Si}(\text{OC}_2\text{H}_5)_4/\text{C}_4\text{F}_8/\text{Ar}$ by plasma-enhanced CVD", *Chem. Vapor Depos.*, **7** [4] (2001) 142–146.
- H-W. Su, W-C. Chen, "Preparation of nanoporous poly(methyl silsesquioxane) films using core-shell silsesquioxane as porogen", *Mater. Chem. Phys.*, **114** (2009) 736–741.
- H. Sugimura, A. Hozumi, T. Kameyama, O. Takai, "Controlled growth of mesostructured organic-inorganic composite films on oxide substrates defined with micrometer-scale dimensions", *Adv. Mater.*, **13** (2001) 667–670.
- J. Shen, A. Luo, L.F. Yao, X.J. Lin, B. Zhou, G.M. Wu, X.Y. Ni, "Low dielectric constant silica films with ordered nanoporous structure", *Mater. Sci. Eng. C*, **27** (2007) 1145–1148.

