Vol 17 No 8, August 2008
1674-1056/2008/17(08)/3021-05

Chinese Physics B

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# Influence of HF catalyst on the microstructure properties of ultra low-k thin films prepared by sol-gel method

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(Received 22 July 2007; revised manuscript received 9 December 2007)

This paper reports that by using the hydrofluoric acid (HF) as the acid catalyst, F doped nanoporous low-k $SiO_2$ thin films have been prepared by means of sol-gel method. The characterization of atomic force microscopy and Fourier transform infrared spectroscopy demonstrates that the HF catalyzed films are more hydrophobic. The $N_2$ adsorption/desorption experiments show that the suited introduction of HF increases the porosity and decreases the pore size distribution (about 10 nm) in the films. The above results indicate that the hydrofluoric acid is the more suitable acid catalyst than the hydrochloric one for preparing nanoporous ultra low-k $SiO_2$ thin films.

**Keywords:** microstructure, dielectric, catalyst, sol-gel
**PACC:** 6865, 7755, 8265J, 8270G

## 1. Introduction

As Si devices scale down to a deep sub-micron regime for fast switching speeds, the interconnect delay (RC delay) caused by the parasitic capacitance begins to govern the overall device delays.[1] In order to overcome the limitation, all kinds of low dielectric constant materials (low-k) are being studied.[2,3] Among them, fluorinated silica films made by plasma-enhanced chemical vapour deposition and nanoporous silica films made by sol-gel method have aroused many interests.[4,5]

In this study, we band the above two kinds of materials together, and firstly introduce the fluorine ion by sol-gel method. From the results of Fourier transform infrared (FTIR) spectroscopy, $N_2$ adsorption/desorption isotherm, and atomic force microscopy (AFM), we found that the incorporation of F ion effectively adjusts the microstructures and the chemical bonds, and thus significantly improves the dielectric properties of the films.

## 2. Experiments

The ultra low-k silica thin films were fabricated using Tetraethoxylane (TEOS) as precursors with acid as catalysts. In our experiments, two kinds of acid catalysts (HCl and HF) were used. Besides, the latter was used with two different doses (TEOS/acid = 1:0.6 and 1:10), and we named the corresponding samples as sample HCl, HFB and HFC, respectively. The prepared sol solutions were spin-coated on p-type silicon (100) wafers. It was followed a series of post treatment. The detailed procedures of preparing and electrical properties of the films had been reported previously.[6]

FTIR spectroscopy (Nicolet NEXUS 670) was employed to compare the changes of chemical bond structure of the samples as substituting the catalyst HCl with HF. The pore size distribution and the microstructure were characterized by the $N_2$ absorption/desorption isotherms and AFM with tapping mode operated at scan rate of 0.8248 Hz, respectively. The dielectric constant was determined from capacitance–voltage (HP 4140B) measurements.

## 3. Results and discussion

Figure 1 shows the AFM morphologies of the nanoporous silica films with catalyst HCl (Fig.1(a))

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and catalyst HF (Fig.1(b)). Comparing the two samples, we observe clearly a distinct effect of HF catalyst on the morphology of the film surface at the nanometre scale. The particle size in Fig.1(b) is much more uniform and smaller than that in HCl one. The distribution of the particle size shown in Fig.1(a) is 10–100 nm, and the average size is 50 nm, while it is only around 10 nm in Fig.1(b).

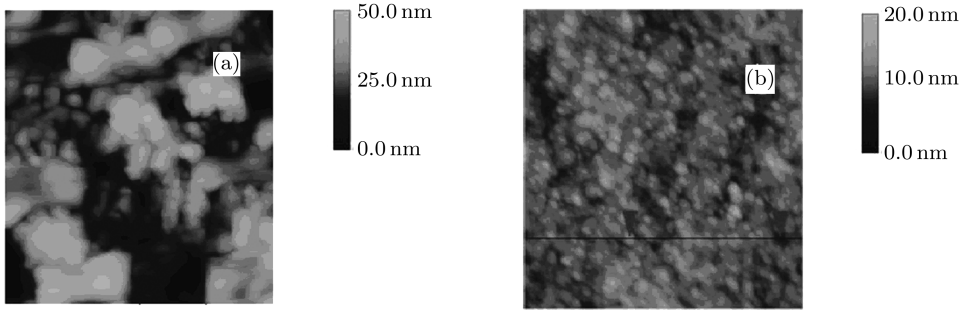



**Fig.1.** AFM morphologies of samples with different catalysts: (a) HCl, (b) HFB.

It is postulated that the uniformity of the microstructure of the films mainly involves in the chemical properties of the catalyst HF. There are two explanations for the role of HF in the processes of gel formation. Firstly, HF in the sol has the ability to adjust the balance of hydrolysis and condensation speed based on its weak acidity. The other is the partial causticity of HF on the silica materials. It is clear that the processes of hydrolysis and condensation of TEOS occurred in sol-gel method are so slow that the catalyst has to be introduced. In most groups, the catalyst is always the HCl, ammonia or the combination of them.[7−9] As we know, when the velocity of condensation process is quicker than that of hydrolysis, it becomes more difficult to form the nucleus in the sol. Therefore, some particles in the sol will grow bigger and bigger than the other, resulting in the relatively non-uniform microstructure. As a kind of weak acid, the HF has the alkalescence besides the properties of normal acid, and can automatically adjust the velocity of hydrolysis and condensation of TEOS, leading to the formation of much more nucleus than those in HCl catalyzed sol. Moreover, the acid of HF can react with silica material and restrain the growth of the nucleus at a certain degree. Therefore, when HF is used as catalyst, the balance of the two processes is obtained, resulting in the formation of highly cross-linked and uniform films.

The AFM observation indicates that the incorporation of HF leads to the marked uniformity of the film surface, and the root-mean-square of the surface roughness ($R_{\rm rms}$) drops from 2.4 to 1.8 nm.

Figures 2(a) and 2(b) are FTIR spectra of the samples HCl and HFB, respectively. In both spectra, the peak at 3650 $\rm cm^{-1}$ corresponds to the non-associated –OH bonds that exist in the surface of the pores in the $SiO_2$ films. Two absorption peaks at 1250 and 804 $\rm cm^{-1}$ are associated with the bending and stretching vibrations of the Si–$CH_3$ bonds, respectively.[10] The intensity of the absorption peaks of Si–$CH_3$ in Fig.2(b) increases significantly, while the intensity of the absorption peak at 3650 $\rm cm^{-1}$ decreases. This indicates that HF makes the surface modification becoming more sufficient than HCl, which is probably related to the uniform and preferable microstructure of gel. The increase in the intensity of Si–$CH_3$ bonds provides the evidence that the moisture resistance is improved. The methyl group (-$CH_3$) is a strong hydrophobic group, so the

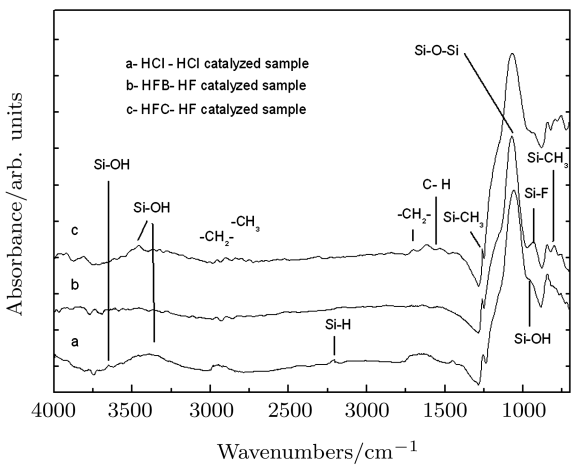



**Fig.2.** FTIR spectra of samples: a HCl, b HFB, and c HFC.

film with the more methyl is more hydrophobic. On the other hand, in comparison with that in Fig.2(a), there are additional Si–F bonds (930 $cm^{-1}$) and less Si–H bonds in Fig.2(b).[11] The decomposition temperature of Si–F bond is as high as 700°C, which ensures the heat resistance, leading to the improvement in the thermal stability of the films.[12] Moreover, Si–F bonds incorporated into the film can also reduce the dielectric constant of the film due to the highest electronegativity of fluorine atoms.

Besides that, the peak position of Si–O–Si stretching mode shifts to a higher wave number as changing catalyst HCl with HF, as summarized in Table 1. During the processes of hydrolysis and condensation of the solution, the introduction of HF attacks and deprives the network structure of the film, and terminates the Si–O–Si network instead of –OH or –H. As a result of the high electronegativity and the great affinity of fluorine for electrons, the positive charge density on Si atoms increases. So that the Si–O–Si bond angle becomes larger and the network becomes less polarizable, which also contributes to the decrease in k value of the film.[13]

**Table 1.** The wave number of Si–O–Si bonds in different samples HCl, HFB and HFC, respectively.

| Samples | HCl | HFB | HFC |
|---|---|---|---|
| Wave number/$cm^{-1}$ | 1056 | 1070 | 1068 |

Figure 2(c) is the FTIR spectrum of sample HFC, which was prepared with HF with mole ratio of 1:10. In comparison with that in Fig.2(b), the intensity of the absorption peaks of Si–$CH_3$ and Si–F in Fig.1(c) decreases, while the intensity of the peak at 3400 $cm^{-1}$ increases. Furthermore, using Gauss function, we can decompose the overlapped peaks, as shown in Fig.3.

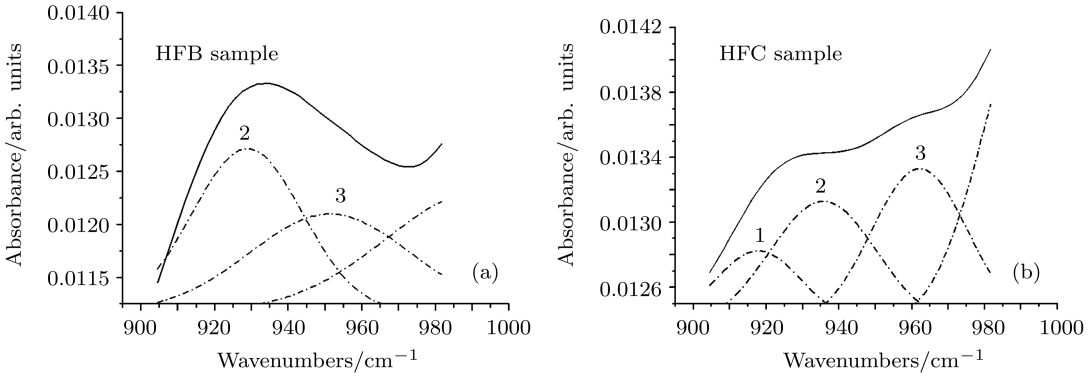



**Fig.3.** Gauss decomposition of FTIR spectra of samples: (a) HFB, (b) HFC.

The broken lines are the results of decomposition. The peaks of 915, 935 and 960 $cm^{-1}$ are corresponding to $SiF_2$ symmetrically stretching vibration, SiF stretching vibration and $SiF_2$ asymmetrically stretching vibration, respectively. In HFB sample, there are more SiF bonds than $SiF_2$ ones, leading to the better hydrophobic property. A $SiF_2$ bond contains two F atoms with strong electronegative properties, which are more lively to react with H–O–H, and enhance the polarity of the film. Therefore, the concentration of catalyst HF in our experiments is also important, which controls the speed of hydrolysis and condensation. The speed, either too quick or too slow, will both result in the uncompleted reaction. The higher intensity of C–H bonds around 1500–1700 $cm^{-1}$ further confirms the uncompleted hydrolysis or re-esterification of TEOS.

Figure 4 shows the $N_2$ adsorption/desorption isotherms of the samples HFB, HFC and HCl, respectively, as the function of the relative partial pressure. The isotherms in films catalyzed by HF almost show the similar behaviour. They both are typical behaviour for mesoporous films while they show hysteresis loops.[14,15] These indicate that there are only some mesopores exist inside the film. Comparing the two isotherms in detail, we find that for the sample HFB there is a triangular hysteresis loop between the adsorption and desorption curves, while a trapeziform hysteresis loop in the sample HFC. The hysteresis loop in isotherms suggests the importance of the pore connectivity.[16] As we know, if larger pores can only be accessed through neighbouring or interconnected narrow pores, the larger pores are not free to be desorbed at the relative pressure corresponding to their

critical capillary radius, which has been described as the ink-bottle effect in porosimetry literature.[15] Therefore, as indicated by the symmetric and relatively narrow hysteresis loop, the pore size distribution in the HFB is more uniform than that in the HFC.

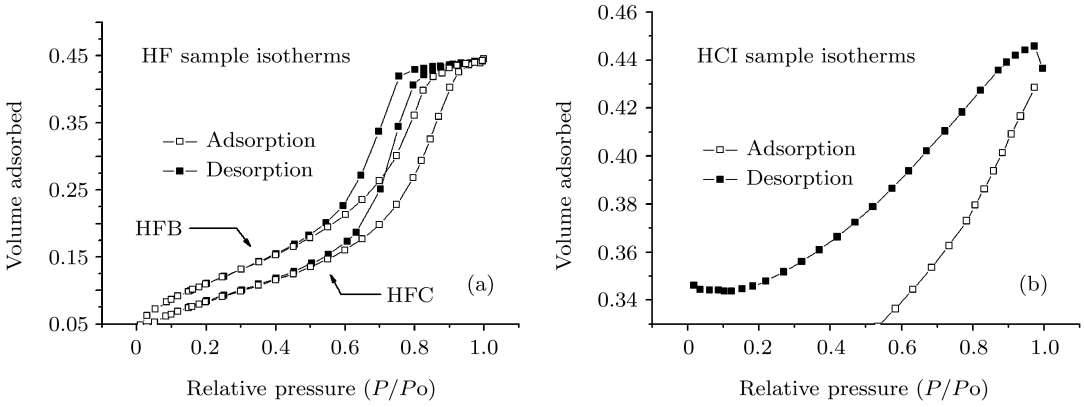



**Fig.4.** $N_2$ adsorption/desorption isotherms for (a) HFB and HFC, and (b) HCl.

On the other hand, the hysteresis loop may also result in the difference of average pore size between absorption and desorption isotherms. As shown in Fig.5, the average pore sizes obtained from the absorption isotherms are all larger than those from the desorption results. In this case, it is reasonable to apply the methodology, which is developed by Barret, Joyner and Halenda (BJH), to the desorption isotherm branch. The pore size distribution of HFB sample is centred around 2–10 nm, while for HFC sample it is in the range of 2–50 nm. There is no evidence of macropores in both samples. In microelectronic techniques, the smaller the pore size is, the more useful the low-k material is, because of the two disadvantages of porous materials. One is the water adsorption, the other is the penetration of Cu wire into the dielectric.[17] Therefore, the appropriate introduction of HF makes the microstructure of the samples more useful.

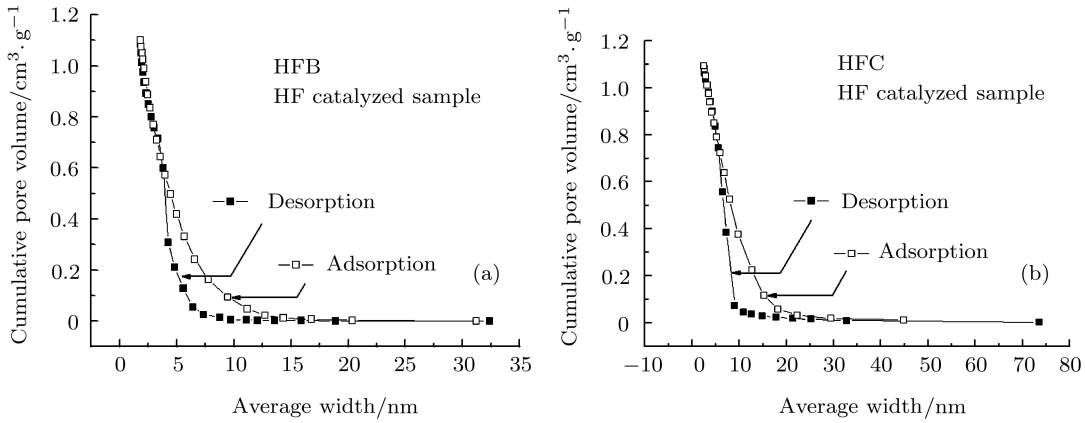



**Fig.5.** The date of pore size distribution of samples obtained from adsorption and desorption curves: (a) HFB and (b) HFC.

By comparison, in the film catalyzed by HCl (Fig.4(b)) there might be presence of much more macropores, due to the greater hysteresis phenomena, which can be confirmed by the AFM morphology shown in Fig.4(a).

# 4. Conclusion

F doped nanoporous silica films have been prepared by sol-gel method by using HF replacing HCl as catalyst. Through studying the results of AFM morphologies, FTIR spectra, and $N_2$ adsorption and

desorption isotherms, we find that the appropriate incorporation of HF effectively adjusts the microstructures and the chemical bonds, and thus significantly improves the dielectric properties of the films. This may be due to: (1) the weak acidity of HF which automatically adjust the speed of hydrolysis and condensation; (2) the etch ability of HF on silica materials; (3) the strong electronegativity of F atom.

## References


[1] Jin Y Y, Kim K and Lee G S 2001 *J. Vac. Sci. Technol.* B **19** 314

[2] Cheng S H, Ning Z Y, Wang T T and Ye C 2005 *Acta Phys. Sin.* **54** 892 (in Chinese)

[3] Gonda V, Jansen K M B, Ernst L J and Toonder J den 2006 *Microelectronics Reliability* **47** 248

[4] Wang Z B, Mitra A, Huang L and Yan Y S 2001 *Adv. Mater.* **13** 746

[5] Ma Y J and Yang H N 1998 *Appl. Phys. Lett.* **72** 3353

[6] He Z W, Zhen C M, Liu X Q, Lan W and Wang Y Y 2004 *Thin Solid Films* **462** 168

[7] Zhao D Y, Yang P D, Melosh N, Feng J L, Chmelka B F and Stucky G D 1998 *Adv. Mater.* **10** 1380

[8] Kawakami N, Fukumoto Y, Kinoshita T, Suzuki K and Inoue K 2000 *J. Appl. Phys.* **39** 182

[9] Chang C L and Huang T J 2003 *Materials Science and Engineering* B **98** 45

[10] Kim H J, Shao Q Y and Kim Y H 2003 *Surface and Coating Technology* **171** 39

[11] Xin Y, Ning Z Y, Ye C, Xu S H, Chen J and Lu X H 2005 *Thin Solid Films.* **472** 44

[12] Ding S J, Zhang D W, Wang J T and Lee W W 2001 *Chemical Vapor Deposition* **7** 142

[13] Chang T C, Tsai T M, Liu P T, Mor Y S, Chen C W, Mei Y J, Sheu J T and Tseng T Y 2002 *Thin Solid Films* **420–421** 403

[14] Simonutti R, Comotti A, Bracco S, Simonelli A and Sozzani P 2002 *Chem. Mater.* **14** 3377

[15] Lee H J, Soles C L, Liu S W, Bauer B J, Lin E K and Wu W L 2004 *J. Appl. Phys.* **95** 2355

[16] Kraemer E O *A Treatise on Physical Chemistry* 1931 edited by Taylor H S (New York: Macmillan) 1661

[17] Ding S J, Lee W W, Wang J T, Wang P F, Xia Z F, Zhang W and Zhang Y W 2000 *Chin. Phys.* **9** 778