Vol 13 No 8, August 2004
1009-1963/2004/13(08)/1365-05

Chinese Physics

© 2004 Chin. Phys. Soc.
and IOP Publishing Ltd

Structural evolution of a-Si:H/SiO_2 multilayers upon step by step thermal annealing*

Mei Jia-Xin(梅嘉欣)[a], Xu Jun(徐 骏)[a,b], Ma Zhong-Yuan(马忠元)[a], Zhu-Da(朱 达)[a], Sui Yan-Ping(隋妍萍)[a], Li Wei(李 伟)[a], Li Xin(李 鑫)[a], Rui Yun-Jun(芮云军)[a], Huang Xin-Fan(黄信凡)[a], and Chen Kun-Ji(陈坤基)[a]

[a] *National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing* 210093, *China*
[b] *National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai* 200083, *China*

(Received 17 October 2003; revised manuscript received 12 February 2004)

a-Si:H/SiO_2 multilayers were prepared by alternatively changing plasma enhanced chemical vapour deposition of a-Si:H layers and *in situ* plasma oxidation process. Subsequently, as-grown samples were annealed at temperatures from 350°C to 1100°C in N_2 ambient with an increment of 100°C. The evolution of bonding configurations and structures with annealing treatments was systematically investigated by Fourier-transform infrared spectroscopy. The peak position of Si–O stretching vibration of SiO_2 layers shift to 1087cm^{-1} after annealing at 1100°C, which demonstrates that the SiO_2 films fabricated by plasma oxidation after high temperature annealing can have similar properties to the thermal grown ones. A Si–O vibration from interfacial SiO_x was identified: the value x was found to increase as increasing the annealing temperature, which is ascribed to the cooperation of hydrogen effusion and reordering of the oxygen bond in SiO_x networks. The H-related bonds were observed in the form of H–Si–O_3 and H–Si–$Si_{3-n}O_n$ (n=1–2) configurations, which are supposed to be present in SiO_2 and interfacial SiO_x layers, respectively. The H atoms bonded in different bonding configurations effuse at different temperatures due to their different desorption energies.

Keywords: a-Si:H/SiO_2 multilayers, annealing, bonding configurations
PACC: 7865T, 3320E

1. Introduction

The study of nanoporous Si and Si nanoparticles has become very active since the observation of efficient photoluminescence (PL) from porous Si.[1] Various techniques have been used to fabricate many kinds of Si nanostructures,[1–3] among which nanocrystalline Si (nc-Si) embedded in multilayered structures are of wide interest because the so-formed nc-Si can be well passivated and its size can be precisely controlled in these structures.[4–6]

A notable issue is that high temperature thermal treatments are involved in most of these fabrication methods: 1100°C annealing was used for the formation of Si nanocrystals prepared by ion implantation,[7] and 1000–1100°C annealing was used for nc-Si/SiO_2 and nc-Si/a-SiN_x:H multilayers in order to form nc-Si in the initial a-Si:H layers.[6,8] Since SiO_2 thin film is stable and compatible with the optoelectronic industry, more effort has been devoted to the Si/SiO_2 systems and their luminescence properties. However, it was demonstrated that the photoluminescence (PL) behaviour is quite different for samples after various treatment procedures. Lockwood *et al*[9] observed PL from their a-Si/SiO_2 superlattices, which was blue-shifted from 1.7eV to 2.3eV with decreasing the thickness of a-Si layers. In very recent studies, Hanaizumi *et al*[10] found a similar PL shift in the blue-violet region in a-Si/SiO_2 superlattices without thermal treatment. They attributed the visible PL to quantum confinement effect. On the other hand, Tsybeskov *et al*[11] only observed infrared PL (1.1 eV) in their nc-Si/SiO_2 multilayers obtained by thermal annealing. Some other groups also reported red-infrared PL in annealed samples.[12–14] They ascribed the PL to the defects or interface states asso-

*Project supported by the National Natural Science Foundation of China (Grant Nos 10374049, 10174035, 90301009), the State Key Programme for Basic Research of China (Grant No 2001CB610503) and the Natural Science Foundation of Jiangsu Province (Grant No BK2002407).

†Corresponding author. E-mail address: junxu@netra.nju.edu.cn

ciated with oxygen in the nc-Si/SiO_2 interfaces. The change of PL properties must be related to various film microstructures induced by the change of bonding configurations and compositions. Therefore, it is very interesting to trace change of the microstructure of Si/SiO_2 multilayers from the original a-Si/SiO_2 to the final formation of nc-Si/SiO_2 in the course of annealing treatment.

In this study, we try to follow the structural evolution of a-Si:H/SiO_2 multilayers step-by-step during thermal annealing, being motivated by the idea mentioned above. The bonds related to Si–O and Si–H were monitored by Fourier-transform infrared (FTIR) spectra and changes during the increasing of annealing temperature from 350°C to 1100°C were investigated systematically.

2. Experiment details

The samples of a-Si:H/SiO_2 multilayers were fabricated on the earthed electrode at the substrate temperature of 250°C in a computer-controlled rf plasma-enhanced chemical vapour deposition (PECVD) system. The a-Si:H layers were deposited from gas mixture of SiH_4 and Ar at the pressure of 260 mTorr. Subsequently an *in situ* plasma oxidation was carried out in pure oxygen at 280 mTorr. The rf power for both processes was kept at 50W. The processes were repeated alternately for 14 cycles. The thickness of a-Si:H and SiO_2 sublayers was designed at 6 nm and 12 nm, respectively.

A series of thermal after-treatment was performed using conventional furnace annealing (FA) in N_2 atmosphere. The annealing temperature increased step by step from 350 to 1100°C with the increment of 100°C. Every step lasts 30min and a subsequent FTIR measurement was performed to monitor the bond configuration and microstructure of the samples. The as-grown a-Si:H/a-SiO_2 multilayers were examined by transmission electron microscopy (TEM), which showed a clear, uniform periodic structures with every sublayer thickness consistent with the pre-designed values.

The FTIR spectra in the range of 400–4000cm^{-1} were obtained using the Nexus 870 FTIR spectrometer for sample deposited on double polished Si substrate. The signals of substrate were subtracted from the FTIR spectra. The microstructures of samples were also verified by cross-section TEM on a JEM200CX electron microscope working at 200kV.

3. Results and discussion

Figure 1 shows the FTIR spectrum of as-grown a-Si:H/a-SiO_2 multilayers. There are two fuzzy absorption bands in the range of 1400–1800cm^{-1} and 3500–4000cm^{-1} due to the water molecules in atmosphere. Vibrations of carbon dioxide are responsible for two weak but abrupt absorption peaks at 660 and 2350cm^{-1}. Some peaks located between 3000–3350cm^{-1} are believed to be organic contamination on sample surfaces, which seems to be easily removed by thermal treatment because the absorption band only appears for as-grown samples.

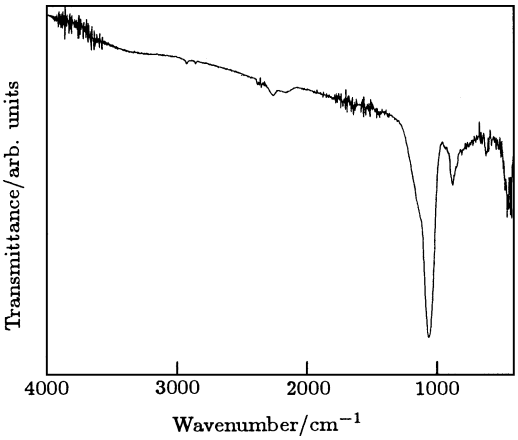


Fig.1. Fourier transform infrared (FTIR) spectra of as-grown a-Si:H/SiO_2 multilayers.

As shown in Fig.1, the very intense absorption band around 1058–1078cm^{-1} corresponds to Si–O–Si stretching vibration, which was also observed by Lucovsky[15] in amorphous Si:H:O alloys deposited by PECVD method. The shoulder on left-hand side of this vibration is due to the contribution of LO Si–O vibration.[16] Other absorption bands related to Si–O vibration modes can also be identified: an absorption band at 803–807cm^{-1} is ascribed to Si–O bending vibration.[16] An absorption band at 440–460cm^{-1} is due to Si–O out-of-plane rocking vibration which persists in our sample either before or after thermal treatment, and no obvious change about this peak has ever been observed. The absorption bands centred at 2260, 2160, 875 and 840cm^{-1} can be ascribed to stretching and bending vibrations of the Si–H monohydride[15] on various Si and O background. Lucovsky *et al*[17] and Tsu *et al*[16] demonstrated that the absorption peaks at 2260, 2195 and 2090cm^{-1} are relevant to stretching mode of monohydride Si–H bonds with one, two, and three oxygen atoms backboned to the silicon one. The absorption bands at 875, 850 and 700cm^{-1} are

due to the bending mode of these vibrations, respectively. The typical bonding configurations associated with Si–O and Si–H are summarized in Table 1.

Table 1. Vibration frequencies and proposed assignments of hydrogen and oxygen related infrared modes in a-Si:H/SiO_2 multilayers.

ν/cm^{-1}	Assignment of the infrared mode
460	Si–O out-of-plane rocking
700, 850, 875	Si–H bending in HSi–$Si_{3-n}O_n$ (n=1, 2 and 3, respectively)
810	Si–O bending
845–890	Doublet (wagging/bending) for $(SiH_2)_n$
880	Si–O–Si mode of a $(SiO)_n$ ring configuration
965	Si–O–Si asymmetric stretching in an a-Si:H network
1055	Si–O stretching in SiO_2 deposited by low-temperature PECVD system
1080	Si–O stretching in thermal grown SiO_2
2000	Single Si–H bond stretching in a-Si:H
2090, 2195, 2265	Si–H stretching in HSi–$Si_{3-n}O_n$ (n=1, 2 and 3, respectively)

The change of Si–O bond around 1058–1078cm^{-1} in FTIR spectra for samples before and after step-by-step thermal annealing is given in Fig.2. The slightly asymmetric characteristic of the Si–O–Si stretching vibration in the lower wavenumber side can be found. The spectra in this range can be well fitted by three Gaussian peaks as shown in Fig.2. The band centred at 1060cm^{-1} is related to Si–O–Si vibration and the band centred at 1130cm^{-1} is due to LO Si–O vibration. The third band added to the above two bands can be ascribed to the presence of Si–O bond stretching vibration in non-stoichiometric SiO_x layers,[16] which should be related to the Si/SiO_2 interface.[18] It is found that the peak position of the third band is shifted with the annealing temperature. Tsu *et al*[16] studied this Si–O vibration in SiO_x (x<2) film. They suggested the following formula for estimating the [O]/[Si] ratio x for the suboxides:

$$v = 965 + 50x(\mathrm{cm}^{-1}), \qquad (1)$$

where v is the peak frequency of Si–O stretching vibration. Figure 3 shows the evolution of the peak position of Si–O stretching vibration in SiO_x and the [O]/[Si] ratio with increasing annealing temperature. It is found that this SiO_x layer becomes more stoichiometric ($x \to 2$) as the annealing temperature increases. Simultaneously, the same trend is observed for the Si–O–Si stretching bond, which shifts from 1062 to 1085cm^{-1} as also shown in Fig.3. Another remarkable feature of Si–O vibration is presented in Fig.4, the absorption peak about 810cm^{-1} of the Si–O bending vibration mode increases with increasing annealing temperature. It was reported that this characteristic Si–O absorption band could occur only when the Si atoms are surrounded predominantly by four oxygen atoms.[16] This suggests that the SiO_2 domains and the stoichiometry of the films increases as the annealing temperature increases, which is consistent with the results mentioned above.

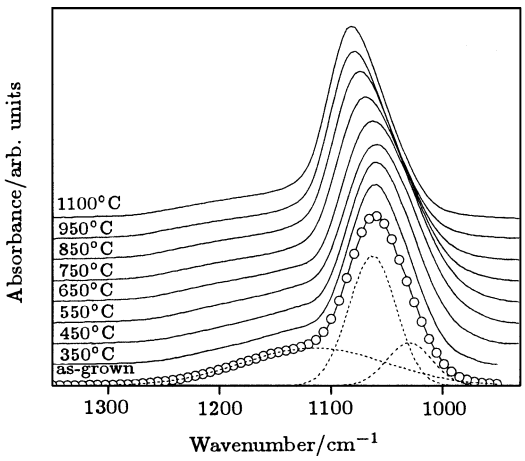


Fig.2. Deconvolution of FTIR characteristic absorption peak around 1075cm^{-1} for samples annealed at various temperature, the open circle is a result of Gaussian fitting (dashed line).

Several absorption bands due to Si–H vibration modes with various annealing temperature are presented in Fig.4. The peak at 875cm^{-1} is a little complicated because both the isolated SiH_2[19] and Si–O–Si mode in the form of a $(SiO)_n$ ring configuration have been found in this range.[20] The former one can be excluded since no SiH_2 signal is found in single a-Si:H thin films fabricated in our system under the same conditions, and no other SiH_2 signals are observed in Fig.4. We cannot completely exclude the ex-

istence of the latter one at the present stage. However, an almost linear relationship between this absorption band at 875cm^{-1} and Si–H vibration at 2260cm^{-1} was found as plotted in the inset of Fig.4. These results convince us to ascribe absorption bands at 2260 and 875cm^{-1} to Si–H stretching and bending vibration of monohydride Si–H bonds with three oxygen atoms backboned to the silicon one (H–Si–O_3). These bands become weak with increasing annealing temperature and disappear after annealing at 750°C. The absorption bands at 2160 and 840cm^{-1} are deviated from the positions of H–Si–SiO_2 at 2195 and 850 cm^{-1} or H–Si–Si_2O at 2090 and 700cm^{-1}, and they are eliminated after 550°C annealing. Tsu *et al*[16] revealed that the Si–H vibration frequency can be affected not only by changes in relative number of O and Si atoms occupying the three nearest-neighbour sites of the SiH group, but also by changes in [O]/[Si] ratio of the suboxide matrix itself. In comparison with their results, we ascribe these absorption bands to Si–H vibration in SiO_x matrix with [O]/[Si] ratio x of 1.2–1.5, which is in agreement with the value estimated from Si–O vibration as given in Fig.3.

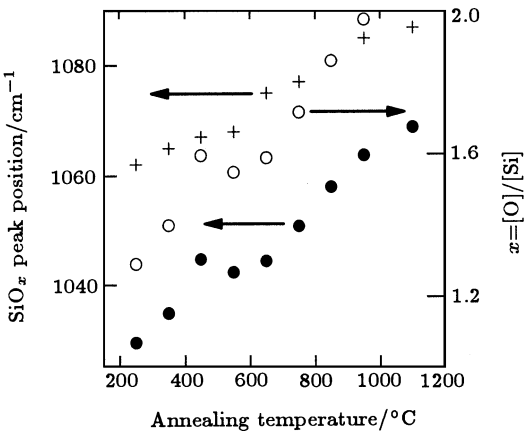


Fig.3. Dependence of the SiO_x peak and x= [O]/[Si] ratio with the annealing temperature. Crosses and closed circles correspond to peak positions of SiO_2 and SiO_x, respectively.

An approximately stoichiometric SiO_2 layer is confirmed by the IR absorption peak around 1062–1087cm^{-1} and the [O]/[Si] ratio in this layer is 1.94. However, it is found that this absorption band is shifted to the high-energy side steadily with increasing annealing temperature. This shift can be explained as a cooperation of hydrogen effusion and reordering of the oxygen bond in SiO_2 networks.[21] In the low temperature range, the insertion of interstitial oxygen into the bond vacancies created by the effusion of hydrogen leads to a shift of IR absorption peak.[21] Meanwhile, the SiO_2 matrix itself is also altered steadily with the thermal treatments, even when hydrogen had already completely effused from our sample. This atom migration and phase separation process drives the Si–O–Si absorption peak continuously to higher wavenumber side in the high annealing temperature range (say, 750°C annealing). After 1100°C annealing, the IR absorption peak finally reached 1087cm^{-1}. This peak position is similar to the observed Si–O vibration mode in high-temperature thermally grown SiO_2 film,[22] in which the bond angle at the O atom site is larger than that deposited by low-temperature PECVD technique.[19] The bonded hydrogen in this layer mainly exists in a configuration of H–Si–O_3, which shows absorption peaks at 2260 and 875cm^{-1} in FTIR spectra. It was reported that these features can only be observed in films with [O]/[Si] ratio greater than about 1.9,[16] which is consistent with our experimental results. The effusion of hydrogen from SiO_2 layer with increasing annealing temperature results in the decrease of these absorption peaks.

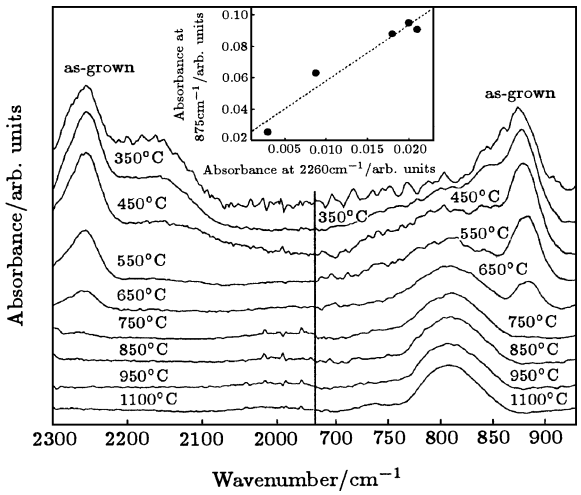


Fig.4. IR absorption bands in the range 2300–1950cm^{-1} and 680–930cm^{-1}. A comparison of the absorbance at 875cm^{-1} and 2260cm^{-1} is shown in the inset, dashed line is linear regression analysis of the data.

The existence of an interfacial SiO_x layer is also identified by FTIR measurements as shown in Fig.2. It is found that the [O]/[Si] ratio of this layer is altered from 1.3 to above 1.9 with increasing annealing temperature. The absorption bands within the range of 2100 and 2200cm^{-1} indicate that the bonded hydrogen in the SiO_x matrix is in the form of H–Si–$Si_{3-n}O_n$, where n is between 1 and 2. An average [O]/[Si] ratio of the suboxide matrix of unannealed

sample is estimated to be 1.2–1.5 as mentioned before. A slight fluctuation of the estimation of [O]/[Si] ratio indicates at the inhomogeneity of this interfacial SiO_x layer, which may be due to a gradient in distribution of ingredient. Hydrogen in this bonding configuration effuses at lower temperature than in H–Si–O_3 (in the SiO_2 layer), which can be explained by the fact that hydrogen is effusing from different H–Si–$Si_{3-n}O_n$ (n=1, 2, 3) with different desorption energies.[23]

FTIR absorption bands located around 2000 and 640cm^{-1}, which represent the stretching and bending vibrations of the Si–H monohydride, respectively, should be observed in a-Si:H sublayers as in the case of bulk a-Si:H films. However, these absorption bands are not present in our FTIR spectra, all of the Si–H vibrations being in environments of oxygen. To explain this, some hypotheses are suggested here. The first is the penetration of oxygen into a-Si:H layer during the process of plasma oxidation which during the deposition of a-SiH shifts the Si–H vibrations to the higher wavenumber side as shown in our results. Another possible explanation is that the hydrogen atoms are not uniformly distributed in the a-Si:H layer, they collect near the interface of Si/SiO_2, being affected by oxygen in this area. Further works will be performed to throw light on this question.

4. Conclusion

In summary, step-by-step thermal annealing treatments were performed on a-Si:H/SiO_2 multilayers fabricated by PECVD, and studied by FTIR measurements. It was found that a SiO_x layer exists in the interface of a-Si:H/SiO_2, which becomes more stoichiometric and thicker with increasing annealing temperature. The structure of PECVD fabricated SiO_2 layer evolves to one similar to thermally grown SiO_2 after annealing treatments. It was revealed that hydrogen exists as H–Si–O_3 group in the SiO_2 layer and H–Si–$Si_{3-n}O_n$ (n=1, 2) groups in the interfacial SiO_x layer, which effuses at different temperatures.

Acknowledgments

The authors acknowledge the support of the Centre of Materials Analysis of Nanjing University.

References

[1] Canham L T 1990 *Appl. Phys. Lett.* **57** 1046
[2] Ruckschloss M, Landkammer B and Veprek S 1993 *Appl. Phys. Lett.* **63** 1474
[3] Li J, Wang L, Huang X, Jiang M, Li W, Wang Z, Xu J, Liu Z and Chen K 2000 *Chin. Phys.* **9** 537
[4] Ma Z, Wang L, Chen K, Li W, Zhang L, Bao Y, Wang X, Xu J, Huang X and Feng D 2002 *J. Non-Cryst. Solids* **299–302** 648
[5] Sui Y, Ma Z, Chen K, Li W, Xu J and Huang X 2003 *Acta Phys. Sin.* **52** 989 (in Chinese)
[6] Chen K, Huang X, Xu J and Deng F 1992 *Appl. Phys. Lett.* **61** 2069
[7] Pavesi L, Negro L Dal, Mazzoleni C, Franzo G and Prioio F 2000 *Nature* **408** 440
[8] Wang L, Huang X, Ma Z, Li Z, Shi J, Zhang L, Bao Y, Wang X, Li W, Xu J and Chen K 2002 *Appl. Phys.* A **74** 783
[9] Lockwood D J, Lu Z H and Baribean J M 1996 *Phys. Rev. Lett.* **76** 539
[10] Hanaizumi O, Ono K and Ogawa Y 2003 *Appl. Phys. Lett.* **82** 538
[11] Tsybeskov L, Hirschman K D, Duttagupta S P, Zacharias M, Fauchet P M, Caffrey J P and Lockwood D J 1998 *Appl. Phys. Lett.* **72** 43
[12] Vinciguerra V, Franzo G, Priolo F, Iacona F and Spinella C 2000 *J. Appl. Phys.* **87** 8165
[13] Ternon C, Gourbilleau F, Dufour C, Doualan J L and Garrido B 2002 *J. Lumin.* **99** 361
[14] Portier X, Ternon C, Gourbilleau F, Dufour C and Rizk R 2003 *Physica* E **16** 439
[15] Lucovsky G, Yang J, Chao S S, Tyler J E and Czubatyj W 1983 *Phys. Rev.* B **28** 3225
[16] Tsu D V, Lucovsky G and Davidson B N 1989 *Phys. Rev.* B **40** 1795
[17] Lucovsky G, Santos-Filho P, Lu Z, Jing Z and Whitten J L 1995 *J. Non-Cryst. Solids* **190** 169
[18] Modreanu M, Gartner M, Aperathitis E, Tomozeiud N, Androulidaki M, Cristea D and Hurley P 2003 *Physica* E **16** 461
[19] Lucovsky G and Pollard W B 1983 *J. Vac. Sci. Technol.* A **1** 313
[20] Kriegsmann H and Anorg Z 1959 *Allg. Chem.* **298** 232
[21] Zacharias M, Dimova-Malinovska D and Stutzmann M 1996 *Philos. Mag.* B **73** 799
[22] Lucovsky G, Mantini M J, Srivastava J K and Irene E A 1987 *J. Vac. Sci. Technol.* B **5** 530
[23] Rinnert H, vergnat M, Marchal G and Burneau A 1998 *Appl. Phys. Lett.* **72** 3157