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MICROSTRUCTURE OF SiO_x:H FILMS PREPARED BY PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

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The micro-Raman spectroscopy and infrared (IR) spectroscopy have been performed for the study of the microstructure of amorphous hydrogenated oxidized silicon (a-SiO_x:H) films prepared by Plasma Enhanced Chemical Vapor Deposition technique. It is found that a-SiO_x:H consists of two phases: an amorphous silicon-rich phase and an oxygen-rich phase mainly comprised of HSi-SiO_2 and HSi-O_3. The Raman scattering results exhibit that the frequency of TO-like mode of amorphous silicon red-shifts with decreasing size of silicon-rich region. This is related to the quantum confinement effects, similar to the nanocrystalline silicon.

PACC: 7830; 6146

I. INTRODUCTION

The photoluminescence (PL) and the microstructure of nanocystalline silicon films have been extensively studied since the discovery of strong PL from porous silicon.[1] In recent years, renewed interest has been stimulated to study the silicon-rich SiO_2 (SiO_x) fabricated by using ion implantation method[2] and Plasma Enhanced Chemical Vapor Deposition (PECVD) technique[3] because of the interesting optical properties that could be applied in the field of optoelectronics. Despite a large number of studies on PL, the structural property is still a basic aspect to be clarified. There have been three different models proposed to elucidate the microstructures of suboxide silicon films: (a) the random-bonding model[4] in which Si-Si and Si-O bondings are statistically distributed throughout SiO_x; (b) the shell model[5] in which crystalline or amorphous silicon grains encompassed by an inner shell consisting of SiO_x and an outer shell of SiO_2; and (c) the phase-separated model[6] in which the alloy is composed of silicon-rich and oxygen-rich phases. Each of the models, to a great extent, correctly describes the structures of these films fabricated under different preparation conditions, but it is important to fully understand the local microstructures of these kinds of films.

We have fabricated a series of a-SiO_x:H films by PECVD and observed strong photoluminescence, as reported elsewhere[7]. In this paper, we investigate the microstructure of these films by means of infrared and microscopic Raman spectroscopies, as functions of thermal annealing. It is found that the SiO_x:H, even for the film with high oxygen content, consists of two phases: silicon-rich and oxygion-rich regions. The silicon-rich region is encompassed by the oxygen-rich region which is mainly composed of HSi-SiO_2 and HSi-O_3. Heat treatment leads to a great change of microstructure and nanocrystalline silicon embedded in SiO_2 is formed at high annealing temperature (T_a). The Raman results show that the frequency of TO-like mode of amorphous silicon redshifts with the decrease of both T_a and silicon content. This is lated to the quantum confinement effects.

II. EXPERIMENTAL

A set of a-SiO_x:H specimens was deposited onto crystalline (100) Si and fused quartz substrates by rf (13.56 MHz) PECVD, using a gas mixture of VLSI grade pure SiH_4,N_2O and H_2. The flow ratio R=[SiH_4]/([SiH_4]+[N_2O]) was varied from 0.31 to 0.35. The chamber pressure, rf power, total flow rate, and substrate temperature were kept at 1.06×10^2 Pa, 0.1 W/cm^2, 35 sccm and 300 ℃, respectively. On the quartz substrates, these specimens changes from clear to dark brown with increasing R under the natural light, indicating an increase in absorption. All specimens were cut into several pieces for different measurements. Each piece was annealed in N_2 at different temperatures from 800 to 1170 ℃ for 30 min.

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In this work, the Raman spectroscopy of the films deposited on quartz substrates was recorded at room temperature with a Renishaw System 1000 Raman Imaging Microscope (Renishaw PLC) and a 5 mW (632.8 nm) He-Ne laser (model 127-25RP) and a peltier-cooled CCD detector. A 50X objective mounted on an Olympus BH-2 microscope was used to focus the laser onto a spot of $\sim 1\,\mu$m in diameter, and to collect the back-scattered light from the specimens. The IR spectra of the films deposited on crystalline Si substrates were measured with a Perkin-Elmer system 2000 FTIR equipped with a liquid nitrogen cooled MCT detector. The thickness of all the films used is about $1\,\mu$m.

Ⅲ. RESULTS AND DISCUSSION

To investigate the microstructure of a-SiO_x:H, we have measured the micro-Raman spectra of the films as-deposited on quartz substrates. Figure 1 shows some typical Raman spectra of the measured specimens. The TO and TA phonon modes[8] of amorphous silicon, located at around 480 and 170 cm^{-1}, respectively, can be clearly seen. This means that there is amorphous silicon phase existing even in high-oxygen-content a-SiO_x:H films. It is quite evident that as R decreases from 0.53 to 0.31 the linewidth of TO mode becomes large, and the frequency of TO mode shifts from 484 to 474 cm^{-1}. Meanwhile, the intensity of TA mode[8] gradually increases but it becomes weak when R=0.31 due to much less silicon contained in the film.

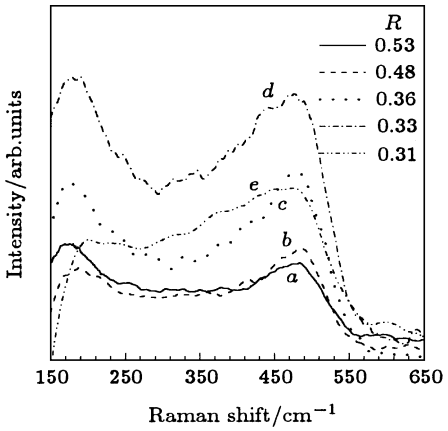


Fig.1. Some typical micro-Raman spectra of a-SiO_x:H films.

The samples were annealed at different temperatures in flowing nitrogen environment for 30 min in order to trace the changes in microstructure of SiO_x:H and further to investigate the microstructure of a-SiO_x:H. The evolution of the Raman spectra as a consequence of the heat treatment for the sample with R=0.36 is illustrated in Fig.2. The peaks at about 480, 170 and 320 cm^{-1} are assigned to TO, TA and LA phonon modes of amorphous silicon[9], respectively. It is found that with increasing T_a from 300 to 1000 ℃ the peak position of the TO mode shifts from 479 to 490 cm^{-1}, similar to the variation of R, and the TO and TA modes are much enhanced due to the precipitation of silicon from SiO_x network, or connection of the neighboring silicon clusters. In addition, the peak width of TO mode is narrowed with increasing T_a; this indicates the modification in short-range order. An analysis on Raman scattering indicates that the TO peak width is sensitive to the short-range structure order and is proportional to the bond angle dispersiion[8], while the low-frequency Raman scattering (170 cm^{-1}) is determined by structural order on a medium-range scale.[10] The gradually narrowed width of TO mode presents the more ordered structure of silicon grains. The more ordered structure also can be indicated by the growing TA mode known as the existence of the medium-range order. When T_a = 1170 ℃, however, an asymmetric peak sharply arises at 519 cm^{-1} with a FWHM of 17.5 cm^{-1}. The spectrum exhibits a shift of the bulk Si optical mode frequency of 522 cm^{-1} towards lower energy that is accompanied by a broadening. This is indicative of confinement effects in nanocrystalline silicon[11], that is, the Raman shift of optical phonon mode depends on the diameter of Si nanocrystallites. According to the calculations[11], the Raman shift of 519 cm^{-1} corresponds to the nanocrystals with 6 nm in diameter.

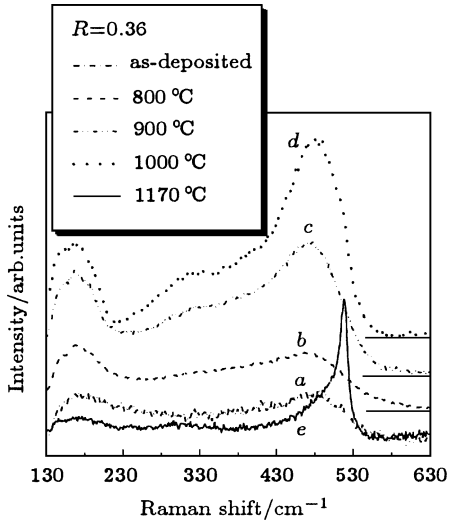


Fig.2. The evolution of the Raman spectra as a consequence of the heat treatment for the sample with R=0.36.

The Raman spectra of the as-deposited and annealed films demonstrate that a-SiO_x:H contains amorphous silicon grains. As the annealing temperature

increases, the Raman spectra demonstrate the solid phase crystallization of amorphous silicon grains occurs in the films, that is, the silicon grains precipitate from SiO_x network or neighboring silicon grains connect together, eventually, the crystalline silicon grains in nanometer scale are formed in SiO_2 matrix as the T_a is up to 1170 ℃. This means that the diameter of amorphous silicon grains in the sample with R=0.36 should be less than 6 nm. Many results[5,6] demonstrate that the a-SiO_x:H consists of two phases, a silicon-rich phase and an oxygen-rich phase. In our case, not only the existence of amorphous silicon is verified, but also the Raman scattering presents a small size effect. As shown in Fig.3, the frequency of TO mode of the amorphous silicon grains shows a blueshift as R and T_a increase, because when R and T_a increase, the size of amorphous silicon grains would be enlarged. This is probably due to the phonon confinement effect of amorphous silicon grains, similar to the case of nanocrystalline silicon as mentioned above.

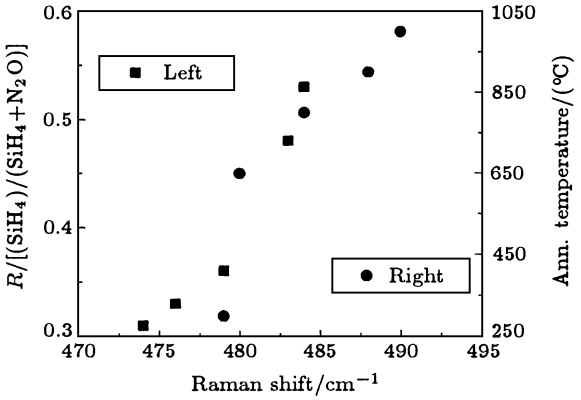


Fig.3. The dependence of the frequency of TO mode in Raman spectra on both R and T_a.

The changes of local oxygen environment, however, can be traced by the infrared spectra. The evolution of transmission spectra with different R is shown in Fig.4. It is seen that several absorption features appear around 1040, 870 and 2100 cm^{-1}, which are assigned[12] to SiO bond-stretching vibration, Si-H bond-bending and stretching mode in the HSi-$Si_{3-n}O_n$ configurations, respectively. With decreasing flow ratio R from 0.53 to 0.29 the double peaks ranging from 2000 to 2300 cm^{-1} become weaker, indicating that the hydrogen content in the films decreases with increasing oxygen content. At the same time, the main peak changes from 2140 to 2248 cm^{-1}, the former of which is attributed to Si-H stretching mode of HSi-SiO_2 and the latter to the HSi-O_3 configuration.[12] The Si-H bending mode at about 870 cm^{-1} also takes on a redshift from 877 to 865 cm^{-1} with silicon content. An analysis of chemical-bonding effects on the frequencies of SiH stretching vibrations predicts that the presence of a strong electronegative atom, such as oxygen, backbonded to one of the three positions available on the silicon atom of an SiH group would shift the SiH stretching frequency to higher frequency. The then establishes the reasons of the shift of stretching and bending modes of SiH bonds.

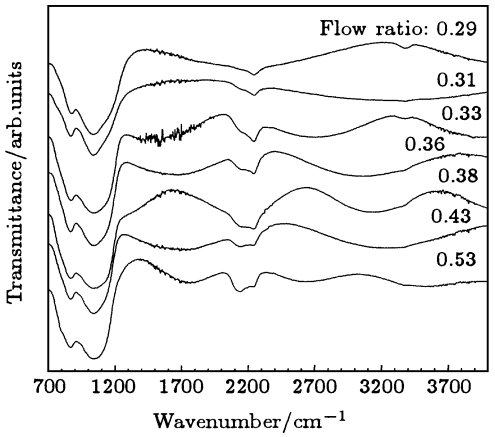


Fig.4. The IR spectra of a-SiO_x:H with different silicon content.

Based on the above analysis, the presence of amorphous silicon grains in a-SiO_x:H is confirmed by the prominent first-order TO-phonon mode, while oxygen is mainly combined in the form of HSi-SiO_2 and HSi-O_3 configurations. Therefore, our results support the phase-separation model[6], namely, the alloy is composed of silicon-rich and oxygen-rich phases. According to this model, the carriers in silicon-rich region are confined by the oxygen-rich regions which have a larger bandgap due to stronger Si-O bonds. This offers a possibility of fabrication of deep-well silicon cluster or silicon quantum dot systems.

IV. CONCLUSION

In conclusion, we have investigated the microstructure of photoluminescent SiO_x:H films by means of infrared and micro-Raman spectra, and found that the SiO_x:H consists of two phases. The silicon-rich phase is encompassed with oxygen-rich phase which mainly composed of HSi-SiO_2 and HSi-O_3 configurations. The Raman results exhibit that the TO-like mode of amorphous silicon shifts to lower frequency as decreasing both silicon content and annealing temperature, that is, with decreasing size of silicon-rich phase grain, the TO mode of amorphous silicon redshifts as much as 10 cm^{-1}. This is probably related to the quantum confinement effects, similar to the nanocrystalline silicon.

REFERENCES

[1] L. T. Canham, *Appl. Phys. Lett.*, **57**(1990), 1046.

[2] Tsutomu Shimizu-Iwayama, Katsunori Fulita, Setsuo Nakao, Kazuo Saitoh, Tetsuo Fujita, and Noriaki Itoh, *J. Appl. Phys.*, **75**(1994), 7779.

[3] Lin Chi-huei, Lee Si-chen and Chen Yang-fang, *Appl. Phys. Lett.*, **63**(1993), 902.

[4] H. R. Philipp, *J. Phys. Chem. Solids*, **32**(1971), 1935.

[5] P. Brüsch, Th. Stockmeier, F. Stucki and P. A. Buffat, *J. Appl. Phys.*, **73**(1993), 7677.

[6] H. Watanabe, K. Haga and T. Lohner, *J. of Non-Cryst. Solids*, **164-166**(1993), 1085.

[7] Ma Zhi-xun, Liao Xian-bo, He Jie, Yue Guo-zhen, Wang Yong-qian, Cheng Wen-chao and Kong Guang-lin, *Solid State Commun.*, **104**(1997), 587.

[8] J. S. Lannin, N. Maley, and S. T. Kshirsagar, *Solid State Commun.*, **53**(1985), 939.

[9] M. H. Brodsky, M. Cardona and J. J. Cuomo, *Phys. Rev.*, **B16**(1977), 3556.

[10] V. K. Malinovsky and A. P. Sokolov, *Solid State Commun.*, **57**(1986), 757.

[11] I. H. Campbell and P. M. Fauchet, *Solid State Commun.*, **58**(1986), 739.

[12] D. V. Tsu, G. Lucovsky and B. N. Davidson, *Phys. Rev.*, **B40**(1989), 1795.