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Annealing characteristics of Si doped amorphous silica films by rf sputtering

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Si doped amorphous silica films were prepared by rf magnetron sputtering technique. As-deposited films which had relatively low Si dopant were annealed in inert atmosphere, and spectroscopic analyses were performed for as-deposited and all the annealed samples by infrared (IR) absorption, X-ray fluorescence analysis, X-ray photoelectron spectroscopy (XPS) and ^{29}Si magic angle sample spinning nuclear magnetic resonance spectroscopy (^{29}Si MAS-NMR). When the sample was annealed at 800 °C, the IR absorption peak located at 1080 cm^{-1} shifted to slightly higher wave number. On the other hand, the decrease of Si clusters or Si–Si bonds in as-deposited film was deduced from X-ray fluorescence and XPS spectra for the sample annealed at 800 °C. These annealing characteristics of the films prepared in this study were discussed based on the random bonding model of SiO_x film, and the spectral variations with thermal annealing were interpreted by the rearrangement of Si and O atoms in as-deposited films, rather than the simple clustering of excess Si atoms. © *1999 Kluwer Academic Publishers*

1. Introduction

A silicon dioxide film on silicon has been a very useful device for a surface-protective layer, a good insulator and an antireflecting coating. Silica films prepared via vapor phase by various methods are highly pure and widely used in the electronics and optoelectronics industries. On the other hand, non-stoichiometric silicon oxide films (SiO_x, $0 < x < 2$), which are called silicon-rich oxide films, are known to be interface layers between silicon substrates and silica films. SiO_x films with various chemical compositions can be prepared by some deposition methods [1–5], and it is possible that the variation of x values causes the change in electrical and optical characteristics for SiO_x films. Since SiO_x films are generally annealed in the course of their processing, it is of interest to investigate the preparation process and the annealing characteristics of SiO_x films.

Recently, Si derivative new materials, such as porous silicon and Si low-dimensional materials are of much interest for new optical devices. A new controversial phenomenon is blue photoluminescence from porous silicon after rapid thermal oxidation [6–8], which is attractive for displays and fast optoelectronics devices. The origin of this phenomenon is still unclear. Several authors have suggested that the blue photoluminescence originates from the inside of smaller Si clusters than those in red luminescent PS [6, 7]. However, other factors such as defects in a silica glass [9] or the surface states of silicon clusters [10] cannot be ruled out. Regardless of the exact origin of the photoluminescence, it may be related to the existence of Si–O chemical bonds or the oxygen-related Si microstructure. The characterization of SiO_x films which have various distribution of Si–Si bonds and Si–O bonds will be more important for detailed investigations of the above Si derivative materials.

In this study, Si doped amorphous silica films were successfully prepared by the rf sputtering technique. For as-deposited and annealed samples, spectroscopic analyses were performed by infrared (IR) absorption, X-ray fluorescence analysis, X-ray photoelectron spectroscopy (XPS), and ^{29}Si magic angle sample spinning nuclear magnetic resonance spectroscopy (^{29}Si MAS-NMR). The variations of these spectra with thermal annealing were discussed in terms of the change in arrangement of constituent Si and O atoms in the films.

TABLE I Sputtering conditions

Sputtering gas	Ar (100%)
Gas pressure	0.67 Pa
Rf power	200 W
Substrate material	Si wafer, Al_2O_3, Cu
Substrate temperature	About 100 °C
Substrate-target distance	60 mm
Target	Si chips on SiO_2 glass
Number of Si chips	9
Sputtering time	40 min, 5h

2. Experimental

Si doped amorphous silica films were prepared with rf magnetron sputtering equipment (ULVAC SH-350). The target was a pure SiO_2 glass plate of 4 inches in diameter on which 9 Si single-crystal chips ($10 \times 10 \times 0.65$ mm^3) were placed symmetrically with respect to the center. The co-sputtering was performed under the conditions of Table I. Sample films were deposited on Si single-crystal wafers for IR and XPS measurements, on polycrystalline alumina plates for X-ray fluorescence analysis and on copper substrates for ^{29}Si MAS-NMR measurement. The film thickness was controlled by sputtering time, and it was determined from a steplike change of film edge, which was detected by a surface texture measuring instrument (Surfcom 112B Tokyo Seimitsu Corp.). For as-deposited samples, an annealing treatment was carried out under N_2 3×10^2 Pa atmosphere after five gas substitutions in a vacuum furnace, which was evacuated to about 3 Pa.

IR transmission spectra were recorded using a Fourier transform IR spectrophotometer (Horiba FT-310). The contribution from the silicon substrate was removed from the data using a differential method. For an X-ray fluorescence analysis for Si K_β line, an electron probe micro analyzer (Shimadzu EMX-SM) was used, and Si K_β emission spectra were excited by means of an electron beam (accelerating voltage and sample current were 20 kV and 1 μA, respectively). XPS measurements were performed by an X-ray photoelectron spectrometer (ULVAC PHI Inc.) using a Mg K_α X-ray source (300 W) at a constant analyzer pass energy of 35.75 eV. The calibration of the binding energy of Si 2p core level was made by fixing C 1s core level. For an NMR measurement, free standing films were prepared by stripping the films from copper substrates. A ^{29}Si MAS-NMR spectrum was measured at room temperature on a JEOL JNM-GX400 spectrometer operating at 79.3 MHz for the ^{29}Si resonance. The spinning rate was ~6 kHz. The short pulses (1 μs) were used with a 40 s time delay between pulses, and the spectrum was accumulated 8086 times. Chemical shifts of ^{29}Si relative to TMS (tetramethylsilane) were determined by using the peak at −34 ppm of PDMS (polydimethylsilane) as an external reference.

3. Results

3.1. IR absorption properties

No diffraction peak of Si microcrystals was observed for as-deposited and all the annealed samples by X-ray diffraction measurements. As-deposited samples were 1.3 μm and 9 μm in thickness for 40 min and 5 h sputtering, respectively.

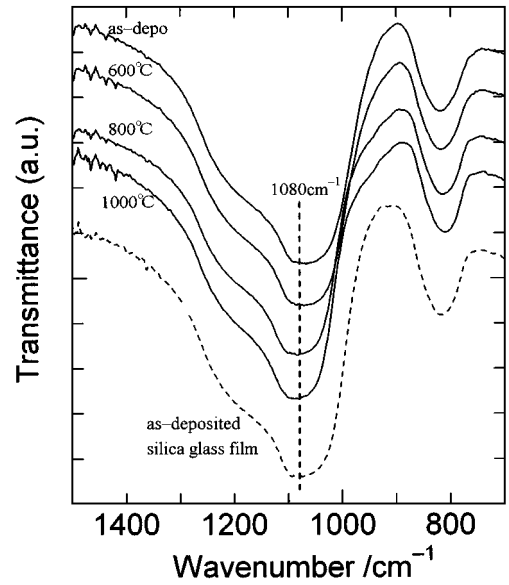

Figure 1 The variation of IR transmission spectra with annealing temperature.

Fig. 1 shows the variation of IR transmission spectra with annealing temperature. The samples were annealed in N_2 atmosphere for a constant annealing time, 3 h. A spectrum for silica glass film is also displayed in the figure. This silica glass film was prepared on a Si wafer by the same sputtering condition. The IR absorption peak around 1100 cm^{-1} region is related to the mode of Si–O–Si stretching vibration, and a small peak around 800 cm^{-1} is due to the Si–O–Si bending vibration [11, 12]. With the increase of annealing temperature, the main peak attributed to the Si–O–Si stretching vibration mode shifts to a slightly higher wave number. The wave number of the main peak for the silica glass film is 1080 cm^{-1}. For as-deposited SiO_x film, IR absorption maximum is located at 1065 cm^{-1}. From the relationship between IR peak position and x in SiO_x [1], the x value in the SiO_x film was roughly estimated at 1.7.

3.2. X-ray fluorescence analysis

Fig. 2 shows the X-ray emission spectra of Si K_β line for a thicker sample on an alumina substrate. The thicker sample on the alumina substrate was employed for the sake of excluding the effects of the substrate. The sputtering conditions for a sample preparation are identical with that for the sample shown in Fig. 1 except for the substrate material and sputtering time. For comparison, X-ray emission spectra of Si K_β line for a bulk silica glass and a Si wafer are also shown with them. Si K_β spectra for a silica glass and a Si wafer represent electronic transitions from the valence band of silica glass to Si 1s core level and from the valence band of Si crystal to Si 1s core level, respectively [13]. The difference between Si K_β spectrum for as-deposited sample and that for the bulk silica glass is clearly observed around the higher energy shoulder. It would be due to

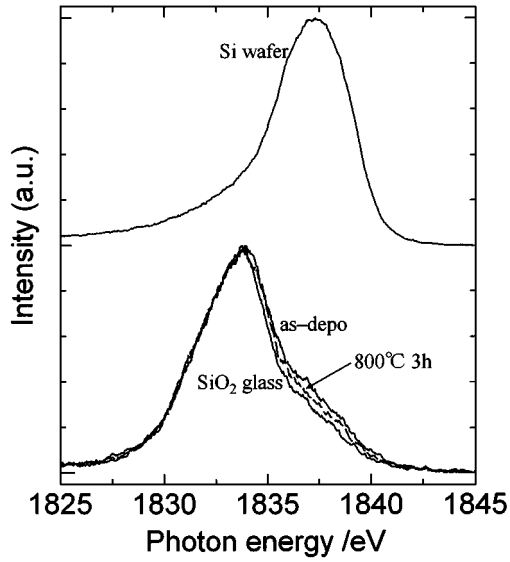

Figure 2 X-ray emission spectra of Si K_β lines.

Si clusters or Si–Si bonds in the film. The shoulder of spectrum after thermal annealing is a little smaller than that of as-deposited sample. This result shows that thermal annealing makes the number of Si clusters or Si–Si bonds in as-deposited sample decrease, but a small number of Si–Si bonds are still present even after thermal annealing.

3.3. X-ray photoelectron spectroscopy

Si 2p core level spectra are shown in Fig. 3. The sample shown here is the sample as shown in Fig. 1. Si 2p deeper core level energy depends greatly on the nearest neighbors of Si atoms. If some oxygen atoms of a stoichiometric SiO_2 glass network, where all Si atoms are surrounded by four oxygen atoms, are replaced by silicon atoms that are less electronegative than oxygen atoms, the Si 2p core level will shift to lower binding energy. Rochet *et al*. [14] reported that the binding energy of the Si^0 state corresponding to Si atoms having no oxygen neighbors was about 99 eV, and that of the Si^{4+} state corresponding to Si atoms having four oxygen neighbors was about 103.5 eV.

The dashed lines in Fig. 3 represent the Gaussian curves corresponding to the Si^{4+} state, where Si atoms are surrounded by four oxygen atoms. A slight peak of the Si^0 state is observed for the as-deposited sample. Thermal annealing at 800 °C makes the intensity of this peak smaller, and the profile of the spectrum asymmetric, resulting from the decrease of Si^0 components and the increase of Si atoms in the intermediate oxidation states, such as Si^{2+} and Si^{3+}. However, annealing at 1000 °C causes the increase of the signal intensities at lower binding energies, which corresponds to the increase of Si^0 and Si^{1+} components. This anomalous change of the XPS spectrum on annealing will be discussed later.

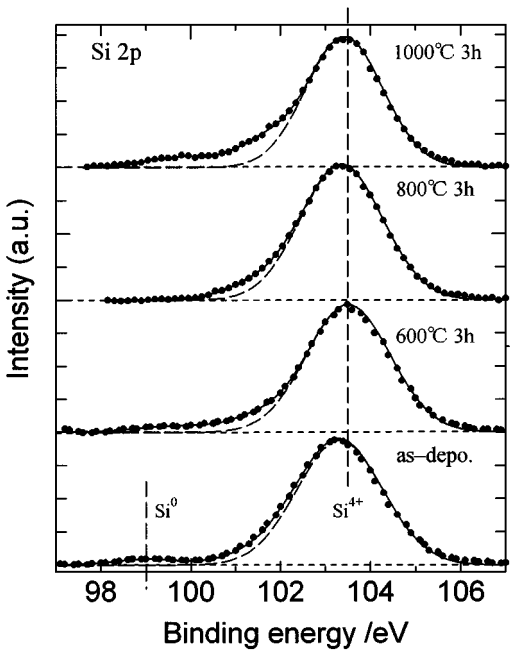

Figure 3 The variation of Si 2p core level spectra with annealing temperature.

3.4. ^{29}Si MAS-NMR measurement

Fig. 4 shows the ^{29}Si MAS-NMR spectrum for free standing films. The sputtering conditions are identical with those for other samples with the exception of copper substrates. Sample films on copper substrates were peeled off and annealed at 800 °C for 3 h. The ^{29}Si MAS-NMR chemical shift has been known to be very sensitive to the change in the first coordination sphere of the Si atom. Philipp [1] proposed that SiO_x had a structure made up of Si tetrahedral units, Cn, Si-($O_n Si_{4-n}$), where n took a value among 0, 1, 2, 3 and 4, and that each Si tetrahedral unit was distributed randomly in a statistical sense. From this random bonding model, Dupree *et al*. [15] estimated the peak position of the central Si atom in each tetrahedron. They performed ^{29}Si MAS-NMR measurements for three commercial SiO powders, and carried out a least-squares fit of their spectra to a sum of five Gaussians. As the result, they found that chemical shifts with the least

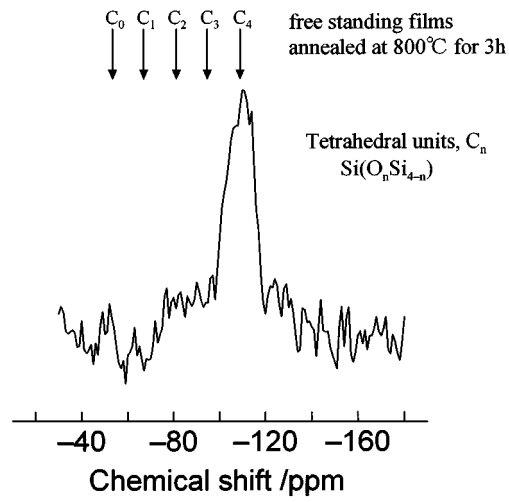

Figure 4 ^{29}Si MAS-NMR spectrum obtained at 79.3 MHz, 8086 s cans, 1 μs pulses, 40 sec delay. Chemical shifts referenced to TMS.

uncertainty were −67 and −109 ppm. Referring to ^{29}Si chemical shifts of vitreous SiO_2 and a-Si, it was determined that these values corresponded to the chemical shifts of C_1 and C_4 tetrahedral units. Taking these values as fixed points and assuming a linear variation of chemical shifts, the peak position of the central Si atom in each tetrahedron was estimated. These peak positions are indicated in the figure. It is found that the sample annealed at 800 °C has C_2 or C_3 units in which Si atoms are in the intermediate oxidation states, but a quantitative discussion is difficult for very weak signal intensity.

4. Discussion

The change of spectra for IR absorption, X-ray fluorescence and XPS upon thermal annealing will be interpreted based on the random bonding model mentioned above. IR peak shift to higher wave number by annealing has been explained by the following two suppositions. Firstly, the macroscopic reaction

$$2SiO_x \rightarrow xSiO_2 + (2-x)Si \qquad (1)$$

by thermal annealing can be expected to take place. This phase separation has already been proposed [3, 14] to take place on SiO_x film with $x < 1.5$ in the absence of oxidation. As the result of this reaction, various kinds of Si tetrahedral units in the film ultimately turn into C_0 and C_4 units, that is to say, Si-(Si_4) and Si-(O_4). Needless to say, C_0 units don't contribute to Si–O–Si stretching vibration mode, thus IR peak position of this mode shifts to higher wave number. The second supposition is the oxidation of the film on thermal annealing. The oxidation of the film transforms Si tetrahedral units with small n values into the units with larger n values because of the intrusion of oxygen atoms in the film. That causes the peak shift of Si–O–Si stretching mode. In this experiment, the annealing treatment was performed under N_2 3×10^2 Pa atmosphere after five gas substitutions. Although the possibility of oxidation is not excluded blindly, the influence of oxidation can be almost neglected. Additionally, the anomalous change in the XPS spectrum by annealing cannot be explained by the oxidation process. Therefore, IR peak shift to higher wave numbers by annealing would be caused by the increase of C_4 units through the phase separation process. However, IR spectra do not directly indicate the variation of the number of C_0 units with annealing, and Si–Si vibrations cannot be detected by IR spectroscopy. The variation of the number of C_0 units with annealing will be discussed below by using the other spectroscopic data.

The results of X-ray fluorescence and XPS showed the decrease of the number of C_0 units by annealing at 800 °C. Without being affected by the oxidation process, this decrease would originate not from the phase separation but from the dissolution of small Si clusters. The dissolution means that C_0 units in as-deposited samples turn into the units with larger n values because of their instability. The Si 2p core level spectrum for the sample annealed at 800 °C also indicated the decrease of the number of C_0 units, compared with that for the as-deposited sample. However, the Si 2p core level spectrum for the sample annealed at 1000 °C indicated the increase of the components with lower binding energy as compared with the sample annealed at 800 °C. This result supports that the change of the XPS spectrum by thermal annealing must be explained not only by the phase separation but also by the rearrangement of Si and O atoms in as-deposited film, which includes the dissolution of small Si clusters. Probably, depending on annealing conditions and on excess Si content in the film, either the phase separation or the dissolution would be dominant through the thermal annealing process. In this study, thermal annealing at temperatures below 1000 °C would cause the dissolution of small Si clusters, instead of the phase separation into the formation of Si microcrystals. For annealing at 1000 °C, on the other hand, a small amount of silicon clustering would take precedence over the dissolution of Si cluster mentioned above. The increase of C_0 and C_1 units by annealing at 1000 °C as observed in Fig. 3 also supports a small amount of clustering of excess silicon atoms in as-deposited films.

Based on the random bonding theory, SiO_x film is composed of five different tetrahedral units, C_n, Si-(O_nSi_{4-n}) ($n = 0, 1, 2, 3, 4$). The rearrangement of Si and O atoms can be defined as the exchange Si atoms and O atoms between different tetrahedral units without changing the ratio of O to Si atoms. This is expressed by the equilibrium reaction,

$$2C_n \rightleftharpoons C_{n-1} + C_{n+1} \qquad (n = 3, 2, 1). \qquad (2)$$

On the other hand, the elementary reaction of the dissolution process would be assumed by the following reaction between five tetrahedral units,

$$C_0 + 4C_n \rightarrow C_1 + C_{n-1} + 3C_n \qquad (n = 3, 2). \qquad (3)$$

If the equilibrium reaction of Equation 2 (n = 3) proceeds to the right and the reaction of Equation 3 takes place, the increase of C_4 units and the decrease of C_0 units by annealing are achieved simultaneously. If only a small number of C_0 units exist in the as-deposited film, this rearrangement will be the origin of the IR peak shift to higher wave number for the sample annealed at 800 °C. The rearrangement into the dissolution of small Si clusters (Equation 3) would cause the depression of the shoulder for the X-ray fluorescence spectrum by annealing at 800 °C and the decrease of Si^0 and Si^{1+} components by annealing at the temperature below 1000 °C as shown in Figs 2 and 3. This model for the rearrangement of Si and O atoms gives a satisfactory explanation for the spectral variation of the film with fewer excess Si atoms by annealing.

Surely, this supposition based on a simple model will not be perfectly consistent with the real structural change of the sample. However, this is a possible mechanism of an annealing process for Si doped amorphous silica films with fewer excess Si atoms. The result of the ^{29}Si MAS-NMR measurement, where the existence of C_2 units rather than C_0 units were observed, also

shows that thermal annealing at 800 °C for this sample does not cause the macroscopic phase separation. The phase separation and the dissolution process by thermal annealing successfully account for annealing characteristics of Si doped amorphous silica films. For more quantitative understanding of the annealing characteristics of SiO_x films with x value approaching 2, theoretical calculations and thermodynamic studies will be required.

5. Conclusion

Si doped amorphous silica films were prepared by the rf magnetron sputtering technique, using 9 Si chips on a silica glass target. For as-deposited and annealed samples, spectroscopic analyses were performed by IR absorption, X-ray fluorescence, XPS and ^{29}Si MAS-NMR. When the sample was annealed up to 1000 °C, IR absorption peak shifted to a slightly higher wave number. On the other hand, the binding energy of the Si 2p core level varied anomalously with annealing temperature. These spectral variations of the films on thermal annealing were interpreted by the rearrangement of Si and O atoms in as-deposited films. For Si doped amorphous silica films with fewer excess Si atoms, thermal annealing at temperatures below 1000 °C would cause the dissolution of small Si clusters, rather than the phase separation into the formation of Si microcrystals.

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