Phase-separated Si nanoclusters from Si oxide matrix grown by laser-assisted chemical vapor deposition

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Recently, silicon-based materials are now playing an important role in microelectronic devices. But their applications in optical integrated circuits are severely handicapped by the indirect band gap properties of bulk crystalline Si (c-Si). In order to achieve integration with other Si-based electronic circuits and optical integrated circuits, substantial efforts have been undertaken to investigate the characteristics of Si nanostructures. In our previous work, we utilized a laser-assisted chemical vapor deposition (LACVD) system to grow Si nanoclusters embedded in silicon oxide and silicon nitridematrices at low temperature and without a post-annealing process. In this work, the structural and related optical properties of LACVD deposited Si nanocluster embedded Si oxide films were investigated, and two phase mixture model was proposed to investigate the mechanism of the films and the relevant properties of the Si oxide films grown by the LACVD method.

The LACVD system, consisted of an external CO_2 laser and a conventional plasma-enhanced chemical vapor deposition (PECVD) system. The CO_2 laser beam was guided into the chamber of the PECVD system through ZnSe window with anti-reflection coating. The pyrolytic decomposition of SiH_4 gas resulted from the high absorptivity of the laser at a wavelength of 10.6 μ m. Figure 1(a) shows the measured FTIR spectra of the Si oxide films grown by both the LACVD system at room temperature and the PECVD system at various substrate temperatures. It can be seen from the spectra that the peak position of the Si–O stretching vibration mode of the Si oxide films grown by the LACVD system at room temperature is $1057 cm^{-1}$, while the peak positions for films grown by the PECVD system at room temperature, 150, 200, and 300˚ C are 1050, 1037, 1028, and $1021 cm^{-1}$, respectively. The differences in peak position imply some differences in chemical composition and structure of the films. A mixture model is proposed, which considers the film as a mixture of two phases: a pure Si phase and a pure SiO_x phase. The peak position of the Si–O stretching vibration mode (f_{Si-O}) in the FTIR spectra of a homogeneous SiO_x varies linearly with the oxygen-to-silicon atomic O/Si ratio or the stoichiometric value of the Si oxide. This relation can be expressed as follows:

$$x = 0.02 \times f_{Si-O} - 19.3 \tag{1}$$

where f_{Si-O} was measured in units of wavenumber. Using this equation, we can estimate the O/Si ratio of a homogeneous single phase SiO_x when its mode frequency is measured. Figure 1(b) shows the actual composition O/Si ratio measured by EDS and the stoichiometric value estimated from the Si–O stretching vibration peak position of the FTIR spectra for films grown by LACVD with a CO_2 laser power of 40 W and by PECVD with various substrate temperatures. For the Si oxide films grown by the conventional PECVD system under various substrate temperatures, the actual composition ratio of the whole film measured by EDS and the atomic ratio x of the SiO_x phase estimated from FTIR data are nearly the same. This fact indicates that the Si oxide films grown at various substrate temperatures by the PECVD system are homogeneous single phase Si oxides. The fact that the ratio decreases with the substrate temperature implies that a higher substrate temperature favors the decomposition of SiH_4 and hence increases the Si content in the grown film.
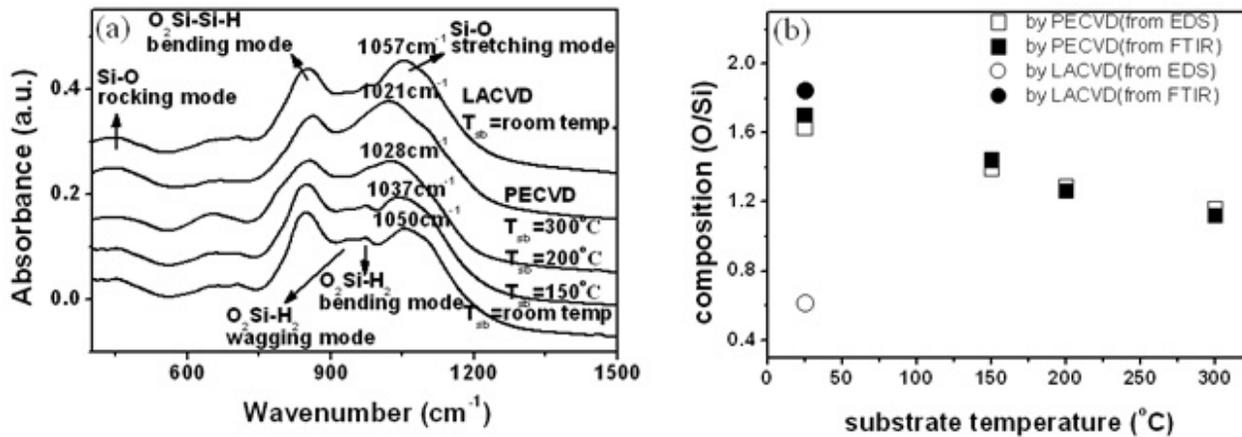
FIG. 1. (a) FTIR spectra of the films grown by LACVD at room temperature and by PECVD at various substrate temperatures; (b) Comparison of O/Si atomic ratio measured from EDS and theoretically calculated from Si-O stretching mode of FTIR.

A prominent feature for the Si oxide films grown by the LACVD system can be noted. There is an obvious inconsistency between the EDS measured actual O/Si ratio and the stoichiometric value estimated from FTIR results. Noting that the EDS result is for the whole film and the FTIR estimated stoichiometry is only for the single phase oxide, we can conclude that the Si oxide films grown by the LACVD system can be described by the two phase mixture model, consisting of a pure Si phase and an Si oxide phase. According to the model, the composition ratios of the two phases in the films grown by the LACVD system with a CO_2 laser power of 40 W can be represented as follows:
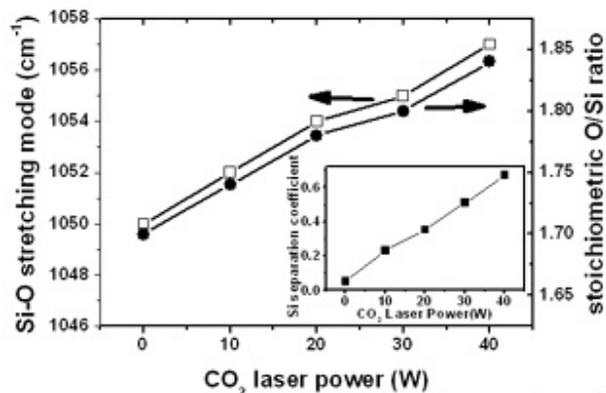
$$SiO_{0.61} \rightarrow aSi + bSiO_{1.84} \tag{2}$$

Fig. 2. Wavenumber of Si-O stretching and the stoichiometric O/Si ratio as a function of the CO_2 laser power in the LACVD system.

where a and b are called the Si separation coefficient and Si oxide matrix coefficient, respectively. The actual chemical composition ($SiO_{0.61}$) of the films was determined by the EDS results, and the O/Si ratio of the Si oxide phase ($SiO_{1.84}$) was estimated from the Si–O stretching vibration mode frequency of the FTIR spectra. According to the measurement results, we can deduce that the CO_2 laser assistance in the deposition process induces the phase separation of an Si nanocluster phase and an oxygen-richer Si oxide phase ($SiO_{1.84}$). The absorption peak position of the Si–O stretching vibration mode and the correspondingly estimated stoichiometric O/Si ratio of the Si oxide phase of the films grown by the LACVD method at various CO_2 laser powers are shown in figure 2.

Table 1 shows the EDS measured chemical composition, the O/Si ratio of Si oxide matrix estimated from FTIR, the Si phase separation coefficient a, and the Si oxide matrix coefficient b for Si oxide films grown by LACVD with various CO_2 laser powers. The Si content in the film increases with the assisted CO_2 laser power, which is attributed to the increase in the decomposition rate of SiH_4 as mentioned above. The dependence of the Si separation coefficient on the assisted CO_2 laser power is also shown in the inset of figure 2. The Si separation coefficient obviously increases with respect to the increase of the CO_2 laser power. Therefore, we conclude that the CO_2 laser assistance can effectively promote not only the decomposition of SiH_4 but also the formation of Si nanoclusters.

Figure 3 shows the Raman spectra of the Si oxide films grown by the LACVD system with a CO_2 laser power of 40 W at room temperature and by PECVD at various substrate temperatures. A distinct feature of the Raman spectra of LACVD grown samples, different from that of PECVD grown samples, is the presence of two broad bands centered at 150 and 480 cm^{-1}, which are assigned to the transverse acoustic phonon mode and the transverse optical phonon mode of amorphous Si. The a-Si related signals of LACVD grown samples confirm the existence of the Si nanoclusters embedded in the Si oxide matrix.
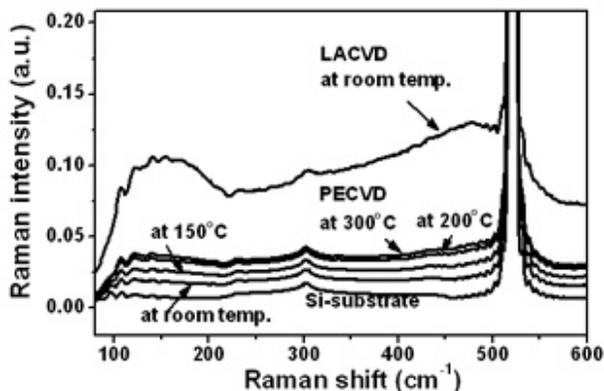

FIG. 3. Raman spectra of the Si oxide films grown by LACVD at room temperature and by PECVD at various substrate temperatures.
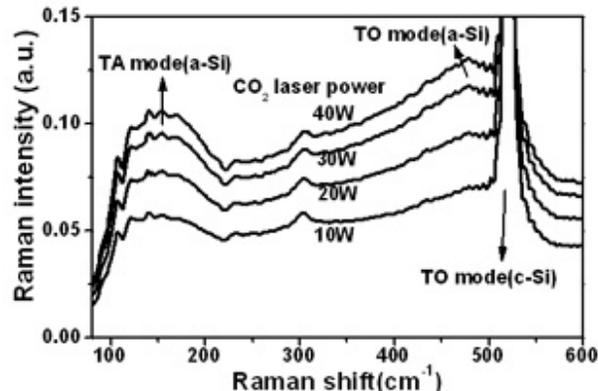
FIG. 4. Raman spectra of Si oxide films grown by LACVD with various CO_2 laser powers at room temperature.

Figure 4 shows Raman spectra of the Si oxide films grown by the LACVD system with various CO_2 laser powers at room temperature. The intensity of the broad band around 150 cm^{-1} of the TA mode of a-Si increases with the CO_2 laser power, which indicates that the amount of the separated Si nanoclusters increases with the CO_2 laser power. The photoluminescence (PL) measurements also confirm the existence of nano-sized Si domains in the films grown by the LACVD system. No PL light emission was observed for the Si oxide films grown by the PECVD with various substrate temperatures. However, the films grown by the LACVD system show strong PL signals, as shown in figure 5 (a). The corresponding PL peak energy and intensity as a function of the assisted laser power are shown in figure 5(b). As shown in figure 5(b), the peak energy shifts toward a lower photon energy with increase of the CO_2 laser power used in the deposition. According to the quantum confinement effect, the PL peak energy increases with the decrease of the dimensions of Si nanoclusters. The red-shift of the PL peak can thus be attributed to a larger particle size of the Si nanoclusters in the films deposited with a higher laser power. The increase of PL intensity implies a higher density of Si nanoclusters in the film during the deposition process when a higher CO_2 laser power was used.
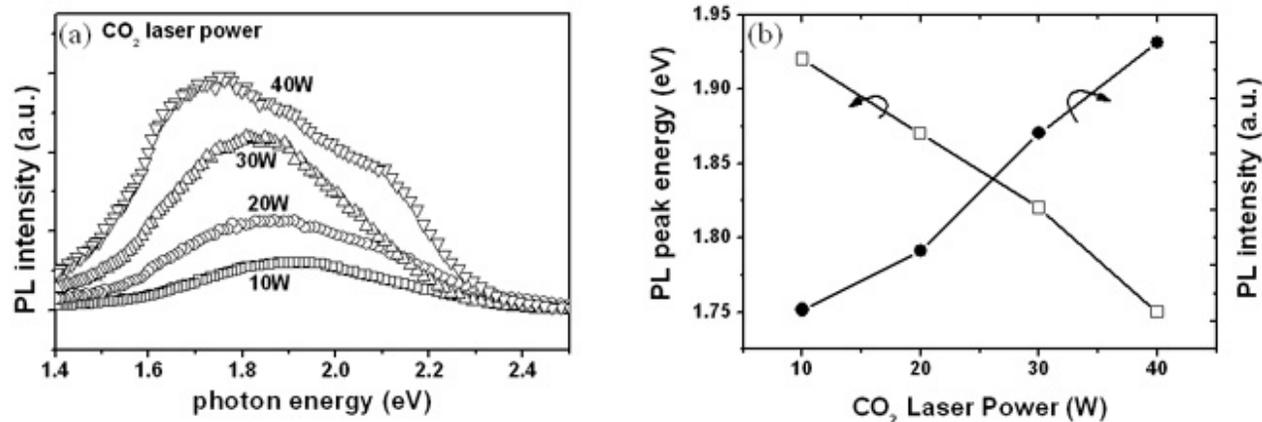

FIG. 5. (a) PL spectra of Si oxide films grown by LACVD with various CO_2 laser powers at room temperature, and (b) PL peak energy and intensity as a function of CO_2 laser power.

The refractive indices of the Si oxide films grown by the LACVD with various laser powers were investigated. For a mixture of Si nanoclusters and Si oxide matrix, the equivalent refractive index Neq of the grown Si oxide film can be deduced from the following equation:

$$N_{eq} = V_{Si} \times N_{Si} + V_{matrix} \times N_{matrix} \tag{3}$$

where N_{Si} and N_{matrix} are the refractive indices of Si nanoclusters and Si oxide matrix, respectively. V_{Si} and V_{matrix} are the volume fractions of Si nanoclusters and the Si oxide matrix, respectively. To determine the optical properties of the grown films, we use the following parameters: (i) the refractive index of Si is 3.4; (ii) the atomic densities of Si and SiO_2 are 5×10^{22} and 6.6×10^{22} cm^{-3}, respectively. The atomic density of the Si oxide matrix can be obtained using the interpolation method. The volume fraction of the Si and Si oxide matrix (V_{Si} and V_{matrix}) for films of known phase separation parameters a and b can be deduced. Figure 6 shows the measured equivalent refractive indices of the grown Si oxide films and the calculated refractive indices of the Si oxide matrix

FIG. 6. The measured refractive indices (N_{eq}) of the Si oxide films and the calculated refractive indices (N_{matrix}) of the Si oxide matrix as a function of CO_2 laser power.

portion of the films as a function of the laser power used for film growth. The calculated refractive indices of the Si oxide matrix of stoichiometric value 1.7–1.84 (i.e. $SiO_{1.7}$–$SiO_{1.84}$) range from 1.5–1.44, in good agreement with the theoretically calculated value. This result also supports the proposed two phase mixture model for Si oxide films grown by the LACVD method.
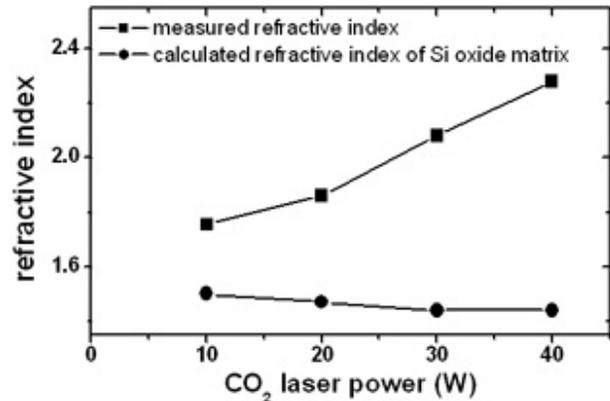
In this study, Si oxide films grown by the PECVD system at various substrate temperatures and by the LACVD system with different CO_2 laser powers were investigated. In comparison with the PECVD grown film, the LACVD grown film exhibited some interesting features. The results of EDS and FTIR analyses indicated that a phase-separated Si nanocluster phase existed in the films grown by the LACVD system at room temperature, which was also confirmed by the Raman spectra of the film. The PL spectra shifted to a longer wavelength and the intensity increased for films grown with a higher laser power. This behavior implies that the size of the Si nanoclusters becomes larger and the number of Si nanoclusters increases for the films grown with a higher laser power. Based on these properties, it is expected that the phase-separated Si nanoclusters embedded in Si oxide grown by the LACVD system may be interested in the future optoelectronic applications.

Table I Experimental values of actual chemical composition of grown Si oxide films measured from EDS, O/Si ratio of Si oxide matrix estimated from FTIR, Si phase separation coefficient a, and Si oxide matrix coefficient with various CO_2 laser powers.

CO_2 laser power	actual chemical composition (from EDS)	Si oxide matrix (from FTIR)	coefficient a	coefficient b
0W (PECVD)	1.63	1.7	0.05	0.95
10W	1.38	1.74	0.23	0.77
20W	1.15	1.78	0.35	0.65
30W	0.83	1.8	0.51	0.49
40W	0.61	1.84	0.67	0.33