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We introduce visible photoluminescences (PL) of violet (432 nm) and yellow (561 nm) at room temperature from thermally treated silicon dioxide thin films. These luminescences were very strong with a near infinite degradation time. At an oxide layer thickness less than 200 nm, these luminescences were not seen, even with high temperature annealing at about 1000 °C. As a result of photoluminescence, x-ray photoelectron spectroscopy, Fourier transform infrared, and high-resolution transmission electron microscopy measurements, we conclude that the violet PL originates from the nanocrystalline silicon formed in the silicon oxide film by the thermal strain effect between the silicon substrate and the silicon dioxide film, while the yellow PL originates from the radiative decay of self-trapped excitons that are confined to oxygen sufficient structures. © *1996 American Institute of Physics.* [S0003-6951(96)03248-2]

Despite the superiority of III–V and II–VI compound materials in optoelectronic devices, the application of silicon materials to optical devices has been very energetic during the past few years. One of these efforts is the study for porous silicon that emits visible luminescence (600–800 nm) at room temperature. The mechanism for this light emission has been the subject of some controversy and several models have been suggested. Recently, the observation of blue and red emission from porous silicon annealed in an oxygen ambient was reported.[1] According to previous reports, the visible emission in porous silicon came from the nanocrystalline silicon and oxygen-related complexes.[2–6] However, the origin of the blue emission from oxidized porous silicon is not clear yet. Also, Zhao *et al.* observed a luminescence band at 2.8 eV, which is ascribed to the size effect by the formation of nanocrystalline silicon (*nc*-Si) in amorphous silicon (*a*-Si) thin films during the rapid thermal annealing (RTA) process.[7] It is known that some bulk SiO_2 (such as high-purity silica glasses) can exhibit a 2.7 eV band at low temperatures, but the 2.7 eV band was not seen in the thermal dioxide.[8] Also, Liao *et al.* recently reported that a fairly stable blue emission (~2.7 eV band) was observed from Si^+-implanted SiO_2 films thermally grown on a Si substrate under an ultraviolet excitation of 5.0 eV at room temperature.[9]

In this letter, we report the observation of violet and yellow luminescence bands at wavelengths of 432 nm (~2.87 eV) and 561 nm (~2.21 eV) at room temperature from silicon dioxide (SiO_2) thin films that were annealed by the RTA method. Without thermal treatment, the luminescence from the oxide layer is very weak and fades during

laser illumination. On the other hand, the luminescences from thermally treated silicon dioxide films were very strong and stable despite laser illumination and long air exposure times. Also, the color of luminescence from oxide layers depended on the thickness of the silicon dioxide films, the temperature, and the time of the annealing process.

The structure of samples used was silicon oxide thin film grown by thermal oxidation at 1100 °C with a wet method on a (100) silicon substrate. The thickness of the silicon oxide thin films ranged from 10 to 500 nm. The thermal treatment for prepared samples was performed by the rapid thermal annealing method in a nitrogen ambient. The temperature and time of the thermal treatment were in the range of 500–1000 °C and 1–20 min, respectively. Before and after the RTA process, the samples were studied using photoluminescence (PL) spectra, Fourier transform infrared (FTIR) spectrometry, and high-resolution transmission electron microscopy (HRTEM) measurements. The PL measurements were carried out using a 364 nm line Ar ion laser as the excitation source at room temperature. The PL spectra were detected using a photomultiplier and a GaAs detector.

Figure 1 shows the dependence of the PL spectra with respect to the temperature of thermal treatment with a silicon oxide layer thickness of 350 nm. In our PL measurements, two dominant peaks were observed at 432 and 561 nm in all samples. At temperatures below 700 °C, the luminescences were very weak and faded during laser illumination. However, at temperatures higher than 800 °C with an annealing time of 10 min, the luminescences were very strong and did not degrade for a long time. Also, with increasing thermal treatment temperature, the 432 nm peak showed minimal increase in intensity while the relatively smaller 561 nm peak showed a dramatic increase, eventually surpassing the 432 nm peak. In other words, the color from the sample varied from blue to yellow with increases in temperature and time

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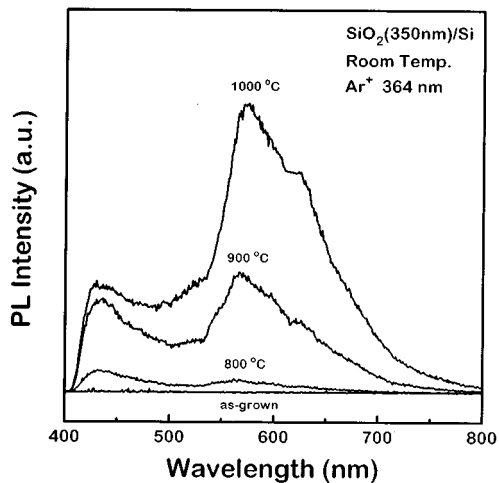
FIG. 1. PL spectra of samples annealed for 10 min at 800, 900, and 1000 °C, respectively.

FIG. 2. XPS spectra of samples before and after thermal treatment for 10 min at 1000 °C.

of thermal treatment. More specifically, at 800 °C, the color from the sample was blue, while at 1000 °C, the color from the sample was yellow. With the change of oxide film thickness, the peak positions were unchanged while the relative intensities of the two peaks showed change. However, when the thickness of the oxide layer was thinner than 200 nm, these luminescences were not seen under any conditions (annealing temperature and time, etc.). On the other hand, the samples annealed by a furnace at the same conditions as those of RTA showed also a similar trend in the PL signal (not shown here). This suggests that the effect of the thermal strain between the silicon substrate and silicon oxide film is correlated with the origin of the luminescence phenomena in our samples.

Recently, the origin of the 2.2 eV emission was reported by Itoh et al.[10] They ascribed this emission to the radiative decay of self-trapped excitons in a-SiO_2 that was irradiated by an electron pulse. A self-trapped exciton is considered to be an interstitial–vacancy pair, of which the interstitial takes the form of an O_2 molecule, and the interstitial–vacancy pair is confined to a SiO_2 tetrahedron. Also, the Si–O–Si bridging bond angle between the SiO_4 tetrahedra is largely reduced. That is, silicon atoms neighboring an oxygen vacancy are asymmetrically relaxed by thermal treatments. In the thermally treated oxide layer, the evidence of the structural deformation of the SiO_2 layer was confirmed by x-ray photoelectron spectroscopy (XPS) analysis (Fig. 2). After thermal treatment, the O 1 s (532.33 eV) peak originating from the SiO_2 structure decreased, while two peaks, an oxygen sufficient structure (~533 eV) and an oxygen deficient structure (~531 eV), were newly generated.[11] With increasing temperature, the oxygen sufficient peak increases causing the oxygen deficient peak to decrease. In comparison with PL data, these results indicate that the oxygen sufficient structures were related to the origin of yellow luminescence. In other words, due to thermal strain, oxygen sufficient structures become the dominant structure rather than SiO_2. Furthermore, these results are also consistent with the results of an infrared transmission experiment as shown by Fig. 3.
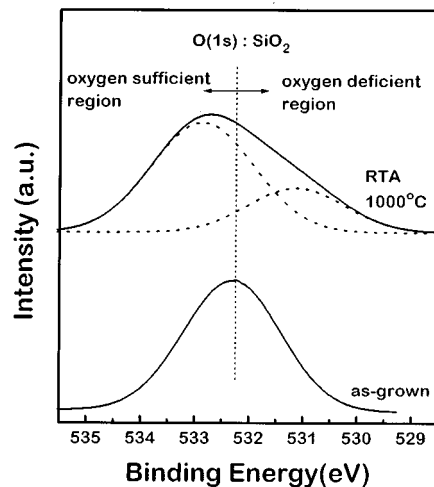
Figure 3 shows FTIR spectra measured at room tempera-

ture on as-grown silicon oxide film [Fig. 3(a)] and on an annealed silicon oxide film at 900 °C [Fig. 3(b)] and 1000 °C [Fig. 3(c)], respectively. This spectra display the presence of two types of bonded oxygen. The strong peak at 1070 cm^{-1} indicates the Si–O–Si stretching mode while the weak peak at 460 cm^{-1} shows the Si–O–Si bending mode. After 10 min of thermal treatment at 1000 °C, the number of Si–O–Si bending modes (460 cm^{-1}) rapidly increased, while the Si–O–Si stretching mode (1070 cm^{-1}) did so only slightly. This FTIR result indicates that the deformations of the Si–O bond occurred in the silicon oxide film during thermal treatment. Furthermore, the increase in the Si–O–Si bending mode is comparable with that of the 561 nm (yellow) band in the PL spectra (Fig. 1). Also, we observed that the position of the Si–O–Si stretching mode shifts to a higher energy by about 30 cm^{-1}. the reason for this shift of the peak position is not clear and further studies are needed to clarify this phenomenon.

Results obtained by Tohmon et al. using as-manufactured silica glass showed a 460 nm (2.7 eV) emission peak from oxygen-deficient glass and defined the origin
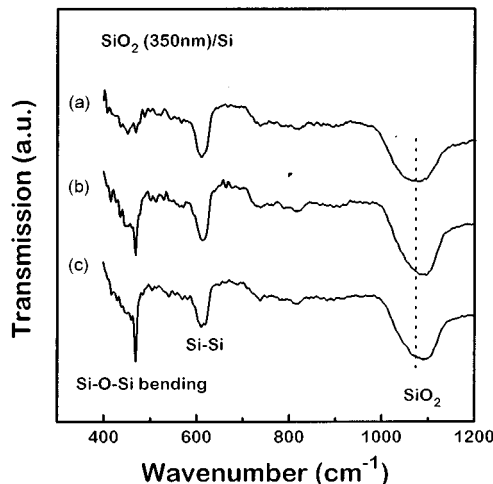

FIG. 3. FTIR signals of the SiO_2 thin film that was (a) as-grown, (b) annealed at 900 °C, 10 min, and (c) annealed at 1000 °C, 10 min.
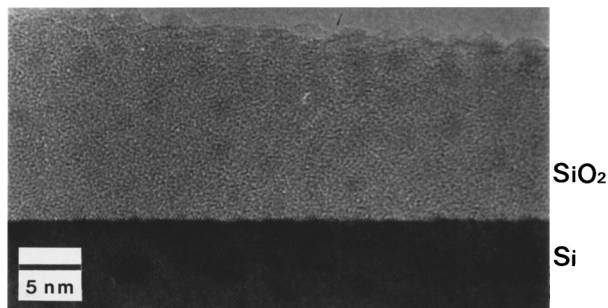
Appl. Phys. Lett., Vol. 69, No. 22, 25 November 1996

Choi et al.   3403

FIG. 4. Cross-sectional HRTEM micrograph showing ultrafine crystallites of the annealed SiO$_2$ thin film at 1000 °C, 10 min.

of this emission as that from a neutral oxygen-vacancy defect (≡Si—Si≡).[12] However, in our PL measurement, a slightly higher emission (in comparison with oxygen-deficient glass) of 432 nm was obtained. Figure 4 shows the TEM micrograph of a 10 min thermally treated sample at 1000 °C. This shows Si nanocrystals distributed randomly throughout the amorphous silicon oxide layer with an average size of 2 nm in diameter and the size distributed within a range of 1–3 nm. The calculation of the exciton energy from the average nanocrystal size was done using the pseudopotential method[13] and empirical tight binding with a variety of implicit bases.[14] Comparison of this calculation and that of the calculated exciton energy from measured photoluminescence energy (432 nm) is very reasonable.

From these results, we can consider the following: (1) The 432 nm emission is from nanocrystalline silicon that is formed in the silicon oxide layer by thermal energy and thermal strain. The intensity of the 432 emission is gradually increased with temperature and seems to be saturated at 1000 °C, with a new luminescence band appearing in the range of 450–530 nm. At 800 °C, the neutral oxygen-vacancy defects are generated by thermal strain and form the ultrafine crystallites in the oxide layer. By increasing the temperature of the thermal treatment, the number of oxygen sufficient structures is increased and the correlation among the neutral oxygen-vacancy defects (≡Si—Si≡) is very active. Therefore, the size of the silicon crystallites is larger. (2) The 561 nm light emission is from the radiative decay of self-trapped excitons. A self-trapped exciton is considered to be an interstitial–vacancy pair that is confined to oxygen sufficient structures such as SiO$_3$ or a SiO$_4$ tetrahedron. The oxygen sufficient structures are formed at an interfacial region between nanocrystalline silicon and amorphous silicon oxide by thermal energy and thermal strain. By increasing the temperature of the thermal treatment, the number of nanocrystalline silicon increases causing the interfacial region to increase while the change of structure from amorphous SiO$_2$ to oxygen sufficient structures is accelerated. Thus, the intensity of this emission is rapidly increased with increasing temperature.

In summary, we introduced visible photoluminescence that was obtained from thermally grown silicon dioxide films followed by thermal annealing. Two dominant luminescences at 432 and 561 nm, were measured. The relative intensity of the two luminescences varied with respect to the change of the thickness of the silicon dioxide film, temperature, and the time length of thermal treatment. By increasing the temperature above 800 °C, a new luminescence center was generated between a wavelength range of 450–530 nm. Thus, we can consider the 432 nm emission to be from nanocrystalline silicon formed in the oxide layer by thermal energy and thermal strain and the 561 nm light emission to be from the radiative decay of self-trapped excitons confined to oxygen sufficient structures.

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