Effect of Surface Passivants on the Photoluminescence from Si Nanocrystals

Moon-Seung Yang and Jung H. Shin
Department of Physics, Korea Advanced Institute of Science and Technology, Daejeon 305-701

Kyung Joong Kim∗
Nano Surface Group, Korea Research Institute of Standards and Science, Daejeon 305-600

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Room-temperature visible photoluminescence (PL) was observed in silicon oxide (SiO$_x$), silicon oxynitride (SiO$_x$N$_y$), and silicon nitride (SiN$_x$) films grown by ion beam sputter deposition. The amounts of oxygen and nitrogen in the films were controlled by using in-situ X-ray photoelectron spectroscopy (XPS). In the SiO$_x$ and the SiN$_x$ thin films, the PL energies showed blue-shifts due to the quantum-confinement effect with the decreased excess Si and the PL intensities showed maximum values near $x = 1.6$ and $x = 1.1$, respectively. We found another large blue-shift of about 0.6 eV in the PL energy between the SiO$_x$ and the SiN$_x$ films with similar excess Si due to surface passivation of Si nanocrystals. The increase of PL energy from SiO$_x$ through SiO$_x$N$_y$ to SiN$_x$ can be a direct evidence for a surface passivation effect, which is in agreement with the theoretical prediction. These results indicate that control of the nc-Si size and the surface passivant material are key parameters for enhancing the visible luminescence for a Si-based photonic device.

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I. INTRODUCTION

The visible luminescence from Si nanocrystals (Si-ncs) in silicon rich silicon oxide (SiO$_x$) has been studied seriously because of the possibility of their use as a Si-based optoelectronic device [1, 2]. Presently, light-emitting diodes, as well as optical gain, using SiO$_x$ have been reported [3–5]. Although the quantum-confinement effect plays a major role in determining the luminescence properties of SiO$_x$ films [6–9], luminescence in the overall visible region has proven to be difficult to obtain from Si-ncs in SiO$_x$ films even when they are small enough to have large bandgap energies. Moreover, the luminescence from Si-ncs is reported to be dominated by the interface state, and blue-green luminescence is impossible to obtain from oxide-passivated Si-ncs [10,11]. These results indicate that a new surrounding host material is required to control the luminescence energy from Si-ncs.

Recently, silicon-rich silicon nitride (SiN$_x$) has been proposed as a promising host material for visible luminescence from Si-ncs. SiN$_x$ can passivate nanocrystalline Si (nc-Si) without introducing oxygen-related deep states. Visible luminescence from amorphous Si nanoclusters in SiN$_x$ has already been reported in the blue-green range [12–14]. Furthermore, there are some reports about visible luminescence from nc-Si in a nitride matrix in the red and near-infrared regions [15–19]. However, the effects of stoichiometry and differences in surface passivation on visible luminescence have not been systematically studied for Si-ncs in SiO$_x$, SiO$_x$N$_y$, and SiN$_x$.

In this paper, we report the effect of stoichiometry on the visible luminescence due to the Si-ncs in SiO$_x$, SiO$_x$N$_y$, and SiN$_x$ thin films. The PL spectra of SiO$_x$ and SiN$_x$ thin films after post-annealing showed strong luminescence in the red and blue-green range due to the formation of Si-ncs. The small increase in the PL energy during the decrease of the excess Si from 12 % to 3 % could be explained by the quantum-confinement effect due to the decrease in the size of nc-Si. However, the PL energy of SiN$_x$ thin films showed a great difference from that of SiO$_x$ with similar excess Si. This can be understood by the effect of the surface states of Si-ncs, which shows that surface environment plays a major role in determining the PL energy. The variation of PL energy by Si-ncs in SiO$_x$N$_y$ films also supports the effect of surface passivation of Si-ncs.

II. EXPERIMENT

SiO$_x$, SiO$_x$N$_y$, and SiN$_x$ thin films were grown by ion beam sputter deposition (IBSD) using a Kaufman-type DC ion gun. The deposition chamber was evacuated to a...
pressure of $2.0 \times 10^{-8}$ Torr before introducing the argon gas into the system. The thin films grown in the deposition chamber could be transferred to a surface analysis chamber without exposure to air. Therefore, the oxygen content ($x$) of the silicon oxide film could be analyzed directly using in-situ X-ray photoelectron spectroscopy (XPS).

SiO$_x$ films were grown on p-type (100) Si wafers by IBSD of a Si target by an Ar$^+$ beam with an ion energy of 750 eV under oxygen flow. The relative sensitivity factors (RSFs) of Si and O were calculated from the areas of the Si 2p and O 1s peaks obtained by using in-situ XPS analysis of a stoichiometric SiO$_2$ thin film. Figure 1 shows the oxygen content of the SiO$_x$ thin films grown by IBSD as a function of the oxygen partial pressure at room temperature. Silicon started to be oxidized at a low oxygen partial pressure and saturated to a stoichiometric SiO$_2$ phase at high pressures above $2.0 \times 10^{-4}$ Torr.

Because N$_2$ gas is not so reactive, SiN$_x$ films were grown by using nitrogen ions as sputtering ions to form stoichiometric silicon nitride in the IBSD using Ar ion sputtering under a N$_2$ gas ambient. We used mixed ions of nitrogen and argon as the sputtering source to control the nitrogen content. In this case, nitrogen ions can act as a sputtering source and an ambient species to form silicon nitride by reaction with the adsorbed Si atoms. The nitrogen content ($x$) was controlled by varying the relative flow rates of the N$_2$ and the Ar gases introducing to the DC ion gun. The nitrogen content increases linearly with increasing N$_2$ flow rate from 1 to 9 sccm. SiN$_x$ films with enough excess Si content to form Si-ncs could be grown. The RSFs of Si and N were determined by dividing the areas of the Si 2p and N 1s peaks from in-situ XPS analysis by the relative compositions of Si and N measured by Rutherford backscattering spectroscopy (RBS) analysis of the same sample as shown in Figure 2.

Silicon oxynitride (SiO$_x$N$_y$) films were also grown by ion beam sputter deposition using nitrogen ions under oxygen ambient at room temperature. The relative ratio of nitrogen and oxygen was controlled by changing the oxygen partial pressure. Figure 3 shows the in-situ XPS spectra of the SiO$_x$N$_y$ films grown under various growth conditions. The relative compositions of nitrogen, oxygen, and silicon could be varied from 0 % to 52 %, 61 % to 0 % and 39 % to 48 %, respectively.
The excess Si content is very important for the formation of silicon nanocrystals and is defined as the excess portion of Si content under the hypothesis that the thin films are mixtures of pure Si and stoichiometric SiO$_2$ or Si$_3$N$_4$. The excess Si was controlled in the range from 3 \% to 12 \% in the SiO$_x$ and SiN$_x$ films. In the study of SiO$_x$N$_y$ films, the excess silicon remained constant at 9 – 10 \% for all films (A-F films in Figure 3) to keep the sizes of the Si-ncs in different matrices uniform. The layer thickness was controlled by the growth rate calibrated from the thickness measured by cross-sectional TEM images of reference films grown within a given time.

The thin films were annealed at 600 – 1100 $^\circ$C for 2 – 40 minutes in a pure nitrogen ambient by using a horizontal furnace to form Si-ncs. The samples were hydrogenated for 1 hour at 650 $^\circ$C under H$_2$ forming gas flow to passivate the Si dangling bonds. Photoluminescence spectra were measured at room temperature by using the 325-nm line of a He-Cd laser as the excitation source and a charge coupled device camera as the PL detector.

III. RESULTS AND DISCUSSION

PL emission is related with the phase of the nanostructure. Generally, as the annealing temperature increases, nanoclusters with amorphous phases are formed initially and then transformed to nanocrystals with a crystalline state at more elevated annealing temperatures. The annealing conditions for the optimum photoluminescence of SiN$_x$ films were investigated by using the PL spectra of SiN$_{x=1.1}$ after annealing under various temperatures as presented in Figure 4. The inset of Figure 4 shows that an isochronal annealing of 10 min is enough to the saturate the PL intensity. Although the as-deposited SiN$_x$ films do not show aN$_y$luminescence, the PL intensity increases greatly as the annealing temperature increases. An annealing temperature of 950 $^\circ$C was found to be the optimum annealing temperature for the maximum PL intensity. This result was reported to be sufficient for improving the intensity and for forming crystallites in SiN$_x$ [14].

The formation of nc-Si observed by high-resolution transmission electron microscopy (HR-TEM) in Figure 5 indicates that the photoluminescence originates from nc-Si. Also, the increases in PL energy and intensity of SiN$_x$ thin films at higher annealing temperature show that nano-crystalline Si is much more effective for the emission of PL than the amorphous nano-clusters formed at low annealing temperature. The SiN$_x$ films were annealed under the optimized annealing conditions (10 minutes at 950 $^\circ$C). The formation of 1- to 2-nm sized nc-Si in the annealed SiN$_{x=1.1}$ film was confirmed by using HR-TEM measurements, as shown in the upper side of Figure 5. The nc-Si in the right figure shows the 4 lattice fringes of (111) plane. The optimum annealing conditions for photoluminescence from SiO$_x$ films were 1100 $^\circ$C and 20 minutes. Much bigger Si-ncs of 2 – 3 nm were formed in SiO$_{x=1.64}$ thin films after annealing under the optimum conditions. This result indicates that Si-ncs are formed as a result of phase separation of a uniform amorphous phase of SiN$_x$ or SiO$_x$ during the rapid thermal process.

Generally, the Si dangling bonds in SiN$_x$ and SiO$_x$ thin films need to be passivated by hydrogenation to enhance the PL intensity [20,21]. Figure 6 shows the effect of hydrogenation of SiN$_x$ ($x=1.02, 1.1, 1.14$) and SiO$_x$ ($x=1.64$) films on the PL spectra. The whole PL spectra of hydrogenated and annealed films show Gaussian shapes. In the case of SiO$_x$, the PL intensities of the hydrogenated films are 10 times larger than those of the as-annealed films, and the PL energies show a red-shift [19]. The red-shift has been reported to originate from
the release of the surface defects of nc-Si, which is more sensitive to larger nc-Si. On the other hand, the PL intensity of SiN\(_x\) increases only slightly by hydrogenation. The change in the PL energy of SiN\(_x\) films after hydrogenation is smaller than that of SiO\(_x\) because the size of nc-Si in SiN\(_x\) films is smaller than that in SiO\(_x\), as shown in Figure 5. As a result, the visible luminescence of SiN\(_x\) films may originate from nc-Si rather than from defects.

Figure 7 (a) shows the room-temperature PL spectra of SiN\(_x\) films after annealing and hydrogenation. It shows broad PL spectra in the range of 1.7 – 2.7 eV. The PL peak energy increases (blue shift) from 2 to 2.34 eV as the excess Si content decreases from 12.4 to 5.9 at. %. In a similar way, the PL energy of SiO\(_x\) thin films increases from 1.4 to 1.7 eV as the excess Si content decreases from 11.5 % to 2.8 %, as shown in Figure 7 (b). The blue shift in this small energy range is believed to result from the quantum-confinement effect caused by the decrease in the size of the nc-Si. This result is in a good agreement with the previous reports on the effect of stoichiometry on the luminescence from nc-Si imbedded in a SiO\(_2\) matrix [7]. Furthermore, the luminescence at various wavelengths of visible light from SiN\(_x\) films could be observed even with the naked eyes.

The PL energies of the SiN\(_x\) and the SiO\(_x\) thin films are plotted as functions of the excess Si content in Figure 8. As the excess Si content decreases, the PL energy increases as a result of the quantum-confinement effect due to the decrease in the size of the nc-Si. The luminescence of SiO\(_x\) covers the red and the near-infrared range, and that of SiN\(_x\) includes the entire visible range. There is a big difference in the PL energy of about 0.8 eV
Fig. 9. Variation of the normalized PL intensities of SiNₓ (filled squares) and SiOₓ (open circles) with the excess Si content.

between the SiNₓ and the SiOₓ films with similar excess Si contents. This big difference is difficult to understand as a result of the quantum-confinement effect due to the decrease in the size of nc-Si. This result suggests that the surface environment of nc-Si, as well as the size of nc-Si, is an important factor for efficient luminescence. Figure 9 shows the normalized PL intensity of SiNₓ and SiOₓ thin films as functions of the excess Si content. The PL intensities of the SiNₓ and the SiOₓ thin films show maximum intensities at the excess Si of 8.2 % (x = 1.1) and 6.0 % (x = 1.64), respectively. There is similar tendency of the PL intensity between SiNₓ and SiOₓ with decreasing excess Si content. The optimum excess Si content is well correlated with the formation of Si ncs because the PL intensity is proportional to the number of Si-ncs. The amounts of nucleation and coalescence of the Si-ncs are important factors for the formation of nanocrystals. At a low excess Si content below the maximum PL intensity, the number of Si-ncs will decrease due to the inhibition of nuclei formation. At a high excess Si content above the maximum PL intensity, on the other hand, the number of Si-ncs will decrease again due to coalescence between adjacent small nanocrystals. This phenomenon indicates that the variation of PL intensity is well related with nucleation and coalescence of Si-ncs.

The effect of the matrix composition on the photoluminescence was studied by using SiOₓNᵧ films. The films were annealed at 1100 °C to precipitate nc-Si and were hydrogenated by 1-hr annealing at 650 °C in a forming gas to passivate the defects. The formation of nc-Si in the films was confirmed by HR-TEM, as shown in Figure 10. The micrographs in Figure 10 show Si-ncs in the four SiOₓNᵧ films (A, B, E, F), and display Si (111) lattice fringes. All films have similar-sized nc-Si of about 2 nm in diameter within a range of ±0.5 nm. Figure 11 shows the PL spectra of SiOₓNᵧ films. Sample A (SiOₓ) shows the typical, Gaussian-like PL spectrum of oxide-passivated nc-Si centered at 1.4 eV. Although the PL energy does not change, the PL intensity decreases nearly tenfold as the oxygen content is reduced from 61 % to about 30 % (samples A-D). However, a further reduction in the oxygen content to 19 % and a concomitant increase of the nitrogen content to 36 % (sample E) results in a clear blue-shift of the PL peak by 0.3 eV without a further decrease in the PL intensity. As the oxygen content is reduced down to zero (sample F), the PL peak again blue-shifts by an additional 0.3 eV, resulting in a PL peak centered near 2.0 eV. The PL intensity, on the other hand, remains the same as in samples D and E. The dependence of the PL energy on
the nitrogen content is summarized in the inset. The variation of the PL energy of SiO$_2$N$_y$ films is unlikely to be caused by the quantum-confinement effect because the sizes of the Si nc's are similar. The constant PL energy between samples A - D can be explained by the effect of oxygenation of the Si nc's. Oxygen double bonds surrounding Si nc's have been reported to lead to larger strain and a further reduction in the bandgap energy [11,22]. Therefore, the lack of change in the PL energy with the initial decrease in the oxygen content (A-D) can be related with the releasing of strain due to a decrease in the number of double bonds. Also, the sharp increase in the PL energy as the oxygen content is reduced close to zero (D-F) is consistent with the matrix effect. This qualitative agreement between the theoretical prediction and the experimental observation suggests that the increase in the PL energy is due to strain reduction caused by nitridation of the Si nc's surface. It also means that controlling the passivating dielectric layer can be an effective way to change the bandgap of nc-Si.

IV. CONCLUSIONS

SiO$_x$, SiO$_2$N$_y$, and SiN$_x$ films were fabricated by ion beam sputter deposition, and the stoichiometry of the films was successfully controlled by using in-situ XPS analysis. The PL energy could be tuned from red to blue by varying the size of nanocrystals and changing the host material. The PL spectra of the SiN$_x$ and the SiO$_x$ films showed small blue-shifts due to the quantum-confinement effect as the excess Si content decreased. However, the big difference in the PL energy of about 0.6 eV between the SiN$_x$ and the SiO$_x$ films with similar excess Si was well correlated with the surface-passivation effect. The effect of matrix passivation was confirmed again by comparing the PL energy variation and the relative composition of the SiO$_2$N$_y$ films. For Si-nc's with similar sizes obtained by exact control of the excess Si, the PL energy increased as the oxygen content decreased as a result of strain reduction. Consequently, the formation of nc-Si and surface control of the nc-Si are major parameters in determining the PL energy and intensity.

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REFERENCES