OPTICAL PROPERTIES OF SILICON NANOSTRUCTURED THIN FILMS

Yeong Wai Woon, Yussof Wahab, Karim Deraman and A. Magentharau

Physics Department, Faculty of Science,
Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor.

ABSTRACT

Optical properties of Silicon (Si) nanostructures were investigated. Amorphous Si-rich silicon oxide (Si-rich SiO_x) films were grown on intrinsic Si wafer and quartz substrates by using the reactive Radio Frequency (RF) magnetron sputtering technique. Oxygen and argon gas were fed into the vacuum chamber during the deposition to form a mixture of oxygen and argon plasma. High temperature post annealing produced the Si nanocrystals embedded in Si oxide. Photoluminescence (PL) spectra of samples before and after post-annealing in air were compared. The PL intensity increased after annealing. Strong ultraviolet (UV) and blue emission have been observed from the annealed sample. The blue emission was related to the neutral oxygen vacancies from the SiO_x films, and the UV emission was ascribed to luminescence centers at the interface between the Si nanocrystals and the SiO_2 matrix. Raman scattering was employed to monitor the chemical changes before and after high-temperature annealing.

INTRODUCTION

Silicon, as the leading material in the commercial microelectronics, has been considered unsuitable for light emitting devices due to its indirect band-gap which limits its efficiency as a light-emitter [1]. However, the light emission from low dimensional silicon (porous Silicon, silicon nanocrystals, Si/SiO_x quantum wells, Si nanopillars) has attracted a strong interest since the Canham's report [2] on the strong visible photoluminescence from porous Si at room temperature. The relaxation of the k-selection rule due to the spatial confinement in low-dimensional Si nanostructures is a promising approach to overcome the indirect nature of the optical transition in Si, and thus causes the band-gap widening and the increase of the radiative efficiency at room temperature. The great development in communication technology has resulted in an increased demand for the integrated devices combining of electrical and optical interconnections. The application of Si based nanostructures for nanoelectronics and integrated light-emitters has a promising potential as they keep the positive properties of Si and is technological compatibility with present Si integrated circuits [3].

In the past few years, Si nanocrystals (Si-NCs) embedded in amorphous silica matrix has been extensively studied due to their unique optical properties and the simplicity of producing them, as well as the technological compatibility with present Si integrated circuits [4]. Compare with the porous Si, the Si-rich silicon oxide (SiO_x, x<2) is a more robust material which exhibits similar optical properties to porous silicon but is

Corresponding Author : cloud.wen@gmail.com

significantly less susceptible to damage. Several mechanisms have been proposed and still being discussed, to explain the PL properties of the room-temperature photoluminescence of Si-rich SiO_x thin films. The mechanisms suggested including the defects either within the SiO_2 [5-7] or at Si/SiO_2 interface [7-9], or radiative recombination of confined excitons within the Si-NCs [10,11]. Today, we believe that the electronic states of Si nanostructures and thus their optical properties are influenced mainly by the quantum confinement effects and the enhanced role of states and defects at the surface.

Here, we report our investigation on the optical properties of Si-rich silicon suboxide (Si-rich SiO_x) thin film prepared by reactive RF magnetron sputtering. Effect of thermal annealing in air on the Si-rich SiO_x films was studied. We summarize the optical data accumulated so far.

EXPERIMENTAL DETAILS

Si-rich SiO_x thin films was fabricated by RF magnetron sputtering with a silicon (99.999% purity) target arranged in a distance of 34mm from the substrate holder. The substrates used in this study were Si wafers (for ellipsometry and Raman measurements) and quartz plates (for PL and FTIR measurement). The Si wafers and quartz were ultrasonically cleaned in acetone, acid hydrofluoric, and then de-ionized water. Before starting the deposition process, the vacuum chamber was pumped down to a base pressure of 8×10^{-6} Torr. A mixed atmosphere of argon (50%) and oxygen (50%) gas was fed into the vacuum chamber during deposition, with a sputtering pressure of 5×10^{-2} Torr. The c-Si target was oxidized by the plasma and sputtering occurred from this oxidized surface. This mode of sputtering wherein chemical reaction occurs between the target and plasma molecules is called reactive sputtering. After deposition, the samples were annealed at various temperatures for half an hour in air. The fabrication parameters of samples are summarized at Table 1.

Table 1: List of samples used in this study.

Sample	RF power (W)	Flow rate	Deposition time	Film thickness (nm)
A	150	8 sccm	6 min	~ 390
B	50	8 sccm	30 min	~ 40

The PL spectra were measured by using Perkin-Elmer LS55 Luminescence Spectrometer with a pulsed-xenon flash lamp as the excitation source (20kW). Excitation wavelength is tunable within 200nm to 800nm. Raman scattering measurements were carried out to monitor the chemical changes of Si-rich SiO_2 films, by using Perkin Elmer Spectrum GX Raman FTIR spectrometer. All spectra have been measured at room temperature.

Corresponding Author : cloud.wen@gmail.com

RESULTS AND DISCUSSION

Figure 1 shows the room-temperature PL spectra of Si-rich SiO$_x$ films on quartz substrates, before and after thermal annealing. The two highest peaks (400nm and 600nm) in the graph of both annealed and as-deposited samples are not emission but the excitation peaks. Very weak PL in visible range at 450nm to 545nm was observed in all the as-deposited SiO$_x$ films. Furnace annealing at 1000°C gives rise to a remarkably intense UV emission peaked at ~370nm (3.35eV) and significantly increases the intensity of four blue PL peaked at 425nm (2.91eV), 458nm (2.71eV), 485nm (2.56eV), and 520nm (2.38eV) from the Si-rich SiO$_x$ films. The increase of PL intensity upon annealing can be explained by the effect of annealing in reducing the non-radiative centers in the as-deposited films, which resulted from dangling bonds, structural defects, etc.
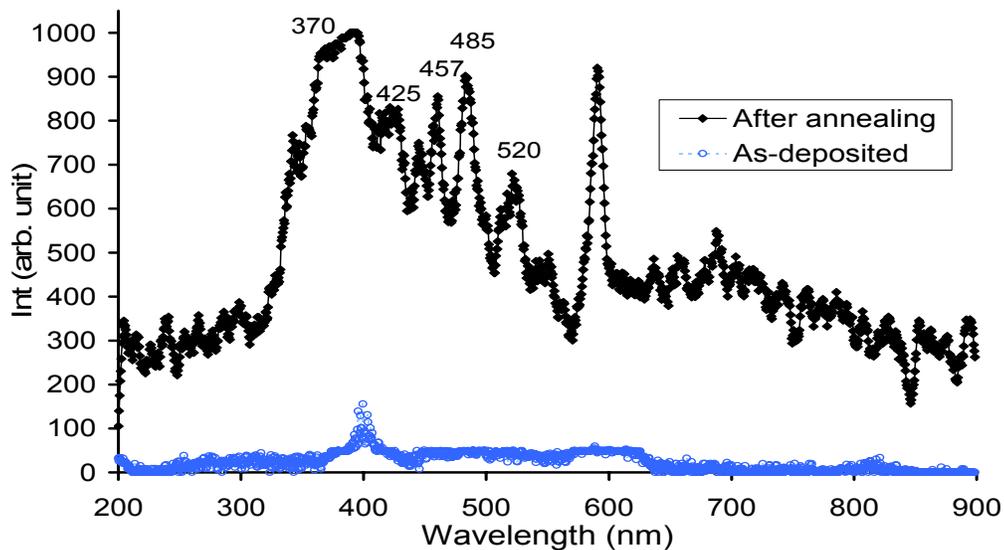

Figure 1: Room temperature PL spectra of the sputtered silicon oxide films (Sample A); as-deposited and annealed in air at 1000°C for 0.5 hour. The excitation wavelength is 200nm for all the spectra.

In order to study the effect of the excitation energy on the PL properties of those two bands stated above, we have measured the PL spectral in a range of excitation wavelength from 200 to 480nm at 20nm intervals. UV emission spectra taken at different excitation levels (200nm to 320nm) from one of the annealed samples are shown in Figure 2. Measurements were made at room temperature from the same location and spot size on the sample. The PL intensity increases rapidly while the bandwidth (FWHM) of UV emission reduces with increasing excitation photon energy. The UV emission only been observed at the high excitation energy (less than 320nm), but the blue emission was observed at all the excitation energies used. We believe that the UV emission requires ultraviolet excitation and thus cannot be observed when a

Corresponding Author : cloud.wen@gmail.com

visible range excitation is used. There was little or no change in the peak of the luminescence with different excitation energies.
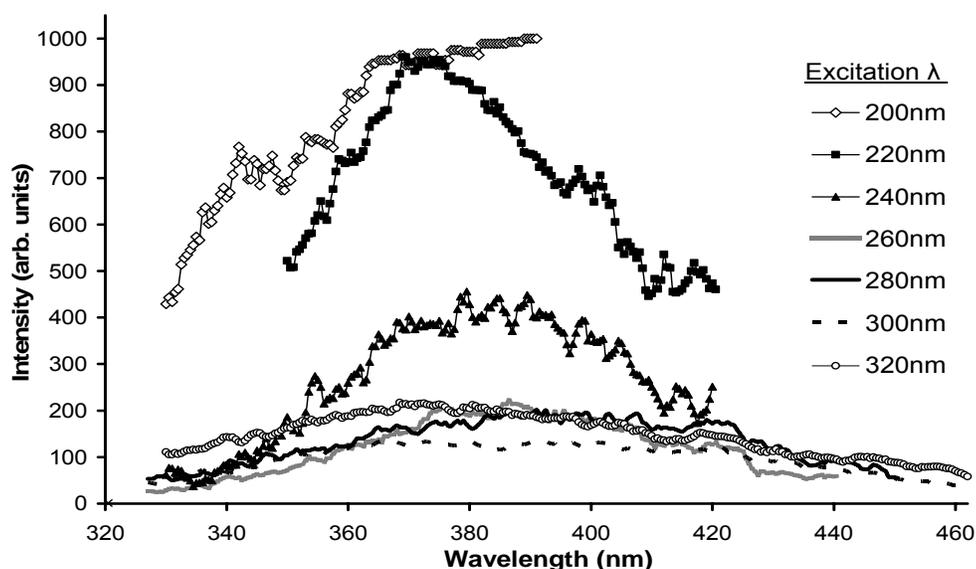

Figure 2: Room temperature PL spectra of Sample A (after annealing in air at $1000^{o}C$ for 0.5 hour) at various excitation wavelength from 200nm to 320nm. All the data are taken from the same spot on the sample.

We used Raman spectroscopy for the structure analysis. For the as-deposited sample, the typical Raman peak of amorphous SiO_2 (a-SiO_2) at ~410-420cm^{-1} was observed [12], indicating majority of the Si in as-deposited sample was in the amorphous phase. After annealing, the intensity of a-SiO_2 band decreased, but a crystalline Si band at ~520cm^{-1} with higher intensity was observed. High temperature annealing of SiO_x films in air leads to decomposition of suboxide into SiO_2 and aggregates of Si [13]. However, since the a-SiO_2 band still occurred in the Raman spectra of annealed sample, we believe that some a-Si still existed after annealing. The changes in the Raman spectra are consistent with the decomposition reaction described above.

The blue emission at ~2.5-2.9eV has been frequently observed in high-purity silica glass and ion implanted SiO_2, and was associated to the well known B_2 band in SiO_2. The B_2 band is induced by neutral oxygen vacancies ($O_3 \equiv Si-Si \equiv O_3$) arising from the presence of excess Si. These oxygen deficiency induced defect centers, which are radiative recombination centers either present as isolated defects in the silica matrix or exist at the Si/SiO_2 interface, exhibit an excitation band at around 5.0eV and emission bands around 2.7eV [5]. The position of the blue peak and excitation energies used in our measurements provides good fit to the results. Hence, we assume that the blue emission from the Si-rich SiO_x films is caused by neutral oxygen vacancies. As the as-deposited samples also exhibited weak blue emission under UV excitation, we believe that the oxygen vacancies in the films were induced during the reactive RF sputtering.
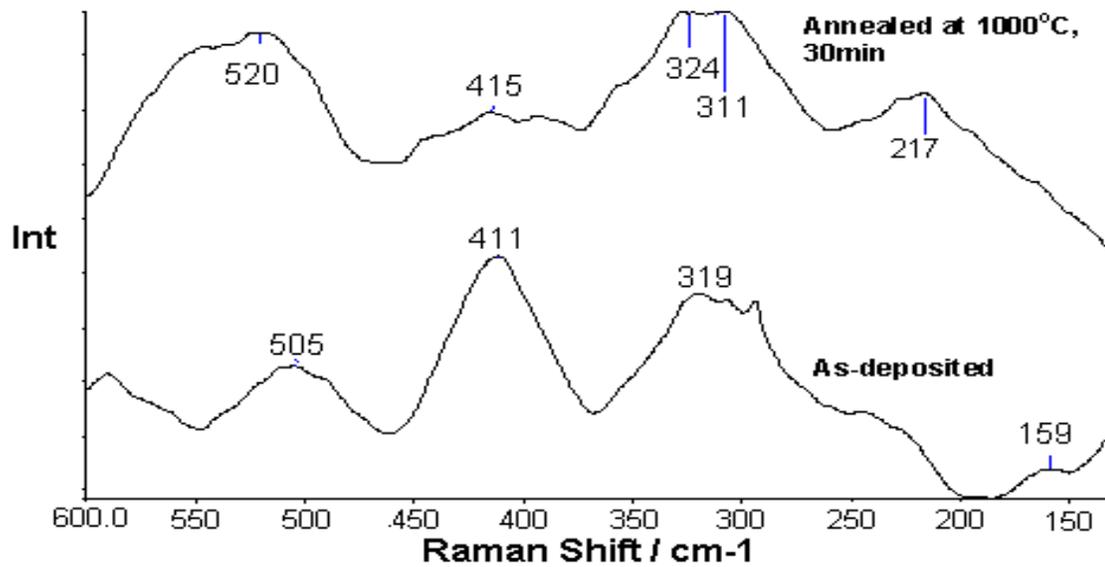
Corresponding Author : cloud.wen@gmail.com

Figure 3: Raman spectra of Sample E; as-deposited (bottom) and after annealing in air at 1000^oC for 0.5 hour (top).

The same UV luminescence has been reported by other researchers. Kim *et al.* [14] observed a weak UV emission at 365nm from Si-rich oxide layers, and ascribed it to the hole-trapped E' centers ($O_3 \equiv Si\cdot$). Soon after that, Song et al. [15] observed a strong UV emission at 370nm from the high temperature annealed silicon oxide films fabricated by magnetron sputtering, which was believed to be originated from the luminescence centers at the interface between the Si-NCs and the SiO_2 matrix. It is plausible that the UV band observed in our works is originated from the luminescence centers at the Si/SiO_2 interface also. However, more experimental works are required to extract a conclusion for the origin of the UV and blue-light emission bands observed, though their possibility has been discussed here.

CONCLUSION

We have demonstrated that UV band at ~370nm was observed from Si-rich SiO_x films prepared by reactive radio-frequency magnetron sputtering. We believed that the UV emission, which gains intensity after the films were annealed in air at high temperature is associated with the luminescence centers at the interface between the Si-NCs and the SiO_2 matrix. Under the high energy excitation, we also observed blue emission from Si-rich SiO_2 films, which is ascribed to neutral oxygen vacancies in the films. The UV and blue light emitted from the Si-rich SiO_2 films can be utilized as the light source for optical data storage, which desires a shorter wavelength to realized higher storage density.

Corresponding Author : cloud.wen@gmail.com

ACKNOWLEDGEMENT

REFERENCES

[1].   Pavesi, L., Negro, L.D., Mazzoleni, C., *et al*. (2000); *Nature*. **408**, 440.
[2].   Canham, L.T. (1990); *Appl. Phys. Lett.* **57**, 1046.
[3].   Iacona, F., Franzo, G. and Spinella, C. (2000); *J. Appl. Phys.* **87**, 1295.
[4].   S. Zhang, W.Zhang, J.Yuan. (1998); *Thin Solid Film.* **326**, 92.
[5].   Seifarth, H., GroÈtzschel, R. *et al*. (1998); *Thin Solid Films*. **330**, 202.
[6].   Ternon, C., Gourbilleau, F. *et al*. (2003); *Physica E*. **16**, 517.
[7].   Torchynska, T.V. et al. (2003); *J. Lumin*. **102-103**, 557.
[8].   Shirai, H., Tsukamoto, T., Kurosaki, K. (2003); *Physica E*. **16**, 388.
[9].   Kanemitsu, Y. (1996); *J. Lumin*. **70**, 333.
[10].   Zhang, Bayliss, S.C., Hutt, D.A. (1995); *Appl. Phys. Lett*. **66**, 1977.
[11].   Kenyon, A.J., Trwoga, P.F., Pitt, C.W. (1996); *J. Appl. Phys*. **79**, 9291.
[12].   Kanzawa, Y., Hanashi, S., Yamamoto, K. (1996); *J. Phys. Condens. Matter*. **8**, 4823.
[13].   Hayashi, S. and Yamatomo, K. (1996); *J. Lumin*. **70**, 352.
[14].   Kim, K., Suh, M.S. *et al*. (1996); *Appl. Phys. Lett*. **69**, 1908.
[15].   Song, K.Z., Bao, X.M. *et al*. (1998); *Appl. Phys. Lett*. **72**, 356.

Corresponding Author : cloud.wen@gmail.com