ECS Transactions, 6 (3) 523-529 (2007)
10.1149/1.2728817, ©The Electrochemical Society

A Comparison of the Effects of Silicon Oxide and Silicon Nitride Host Matrices on the Photoluminescence from Si Nanocrystals after High Temperature Annealing

T. Roschuk, O. H. Y. Zalloum, J. Wojcik, H. Zhang, and P. Mascher

Department of Engineering Physics and Centre for Emerging Device Technologies, McMaster University, Hamilton, ON L8S 4L7 Canada

Si nanoclusters embedded in two different dielectric matrices, silicon oxide and silicon nitride, have been formed through annealing of Si-rich silicon oxide (SRSO) and Si-rich silicon nitride (SRSN) thin films. The light emitting properties of these materials have been analyzed through room temperature UV-excited photoluminescence (PL) experiments. Features of the PL spectra from both types are presented and the nature of light emission from Si-nanoclusters is discussed on the basis of the results from these two different host environments.

Introduction

The progress of integrated photonics based on Si as a platform material is inhibited by the lack of a Si based emitter. Bulk Si itself is a poor light emitting material due its indirect bandgap and the presence of non-radiative recombination pathways, such as free carrier absorption, making it an unsuitable candidate. When the dimensions of Si are reduced down to a few nanometers, however, the efficiency of light emission is greatly enhanced due to quantum confinement effects (1). The observation of light emission in quantum confined Si systems has driven research in areas aimed at understanding the mechanisms of the emission process and at developing a Si-based light source.

Various types of quantum confined Si - such as porous Si and Si nanoclusters/nanocrystals (Si-ncs) - have been extensively explored due to their potential for creating a Si-based laser (2,3). In particular, Si-ncs formed in oxide based systems have received considerable attention due to the observation of gain in these materials (4). Such Si-nc based systems may be fabricated by the formation of Si rich silicon oxide, either through ion implantation into SiO_2 or during the thin film growth process itself, followed by a high temperature anneal to induce cluster formation and, at sufficiently high temperatures, crystallization of some of the Si clusters (5). While the oxide interface serves to provide stability and passivation of the Si-ncs, as well as a high energy barrier for confinement, it also poses a considerable problem for carrier injection into the nanocrystals themselves and presents one of the major barriers to the development of a Si-based laser using SRSO materials. Furthermore, while quantum confinement is acknowledged to play a considerable role in the enhanced emission process, there remains debate as to the exact role of interface states and defects related to the surrounding host matrix. In particular, the oxide interface has been shown to have a significant effect on the emission process of Si-ncs (6). Also, SRSO thin films subjected to an anneal under the presence of hydrogen have been previously shown to exhibit an increased PL intensity, an effect attributed to the passivation of dangling bonds at the nanocrystal interface, which can serve to suppress radiative recombination from the Si-ncs (7,8).

While a large portion of the literature is focused on Si-ncs formed in an oxide host, there have also been reports on the formation of Si-ncs within silicon nitride based materials presenting a number of interesting results (9-11). From a material science perspective, Si-ncs may be fabricated under similar processing conditions, however, the use of SRSN thin films removes the proposed influence of interface states related to the oxide host matrix, which as mentioned above, can have a large effect on the light emission from Si-ncs. Furthermore, in spite of some reports on the topic, the exact role of the nitride interface in the emission process has not yet been studied to the same degree as the oxide interface (9,12). From a device perspective, it has been suggested that the nitride host matrix may be more suitable for the development of a Si-nc based light emitter due to its smaller bandgap than SiO_2, making the electroluminescence process more efficient (13). Recently, Sung *et al.* have reported on the fabrication of LED structures based on Si quantum dots embedded in silicon nitride, an encouraging result showing the potential of these materials (14).

In this paper we present first results of our study of the light emitting behavior of Si-ncs formed in nitride host matrices through the analysis of photoluminescence spectra and compare the results to the typical PL emission observed from Si-ncs formed in an oxide. Additionally, the effect of introducing hydrogen into the anneal process on the PL observed from SRSN thin films is briefly discussed.

Experimental Details

SRSO and SRSN thin films have been grown on crystalline Si substrates through inductively coupled plasma chemical vapor deposition (ICP-CVD) using Ar diluted silane (SiH_4), O_2, and N_2 source gases. Different film compositions were obtained by varying the oxygen and nitrogen gas flow rates. During the deposition process the substrate was heated to a temperature of 120°C. No oxygen was introduced into the chamber during the deposition of the SRSN samples; however, preliminary Rutherford backscattering (RBS) analysis indicates the presence of some oxygen in some of the films. The thicknesses and refractive indices of the films were monitored *in-situ* during the growth process through spectroscopic ellipsometry using a J.A. Woollam ellipsometer operating from 600 to 1100 nm. Post-deposition, the refractive indices and thicknesses were verified to within 5% at 632.8 nm using a laser ellipsometer. Full details of the ICP-CVD deposition system will be discussed elsewhere. A calibration set of SRSO samples were grown on carbon substrates in order to accurately determine the film compositions through RBS. A similar calibration run is currently being performed for the SRSN samples.

Following their deposition, samples were annealed in a quartz tube furnace under flowing Ar and Ar + 5% H_2 at temperatures ranging from 600 to 1200 °C for 60 minutes.

Photoluminescence experiments were performed using a HeCd laser operating at 325 nm along with an Ocean Optics spectrometer. Full details of the PL system have been previously discussed (15). A transmission electron microscopy image, used to illustrate the presence of Si-ncs in a SRSO film, was obtained using a Philips CM12 electron microscope.

Results and Discussion

A typical set of PL spectra for Si-ncs formed in SRSO thin films is shown in Figure 1 for samples annealed at different temperatures. Luminescence in SRSO samples is attributed to the formation of Si-ncs in the film leading to quantum confinement effects. Figure 2 shows a TEM image illustrating the presence of Si-ncs within a SRSO film. The crystallinity of similar films has been previously studied through X-ray diffraction (16). Quantum confinement of the Si-ncs leads to a widening of the bandgap from that of bulk Si and thus a blue-shift of the emission wavelength. The emission wavelength may be tuned by controlling the average nanocrystal size through the film composition, as well as through the anneal conditions (temperature and time). Increasing the anneal temperature (as shown in Figure 1) and time can modify the nucleation and growth rates of the nanocrystals leading to changes in the observed PL intensity and an observed red-shift of the peak emission wavelength (16,17).

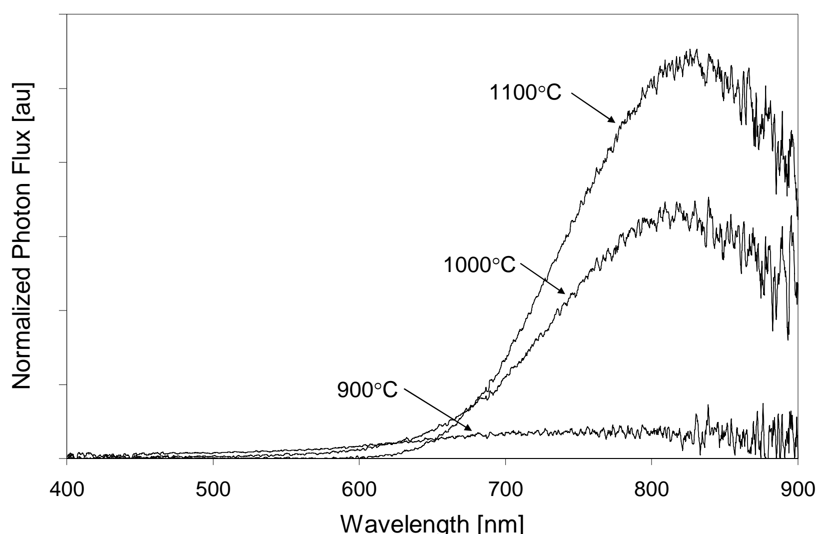

Figure 1. PL Spectra for a SRSO sample grown with 42% Si and annealed at the temperatures shown.

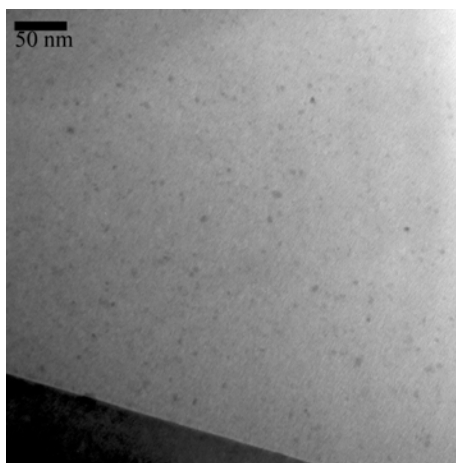

Figure 2. A TEM image illustrating the presence of Si-ncs (dark spots) in a SRSO thin film having 39% Si annealed at 1100 °C for 2 hrs under Ar.

While quantum confinement is acknowledged to play a dominant role in the emission process of Si-ncs, it is also known that oxide related defects can greatly affect the

emission properties. In particular, the Si=O double bonds have been found to play a significant role, resulting in a red-shift of the emission wavelength from what is often expected from quantum confinement alone for small nanocrystals and restricting the ability to tune the emission wavelength (6).

In contrast to SRSO thin films, which display no significant PL until having been subjected to annealing treatments at temperatures above 900 °C, SRSN thin films have been found to exhibit luminescence in the as-deposited samples. Figure 3 shows the PL spectra for a set of samples having refractive indices from 1.75 to 2.29, corresponding to films having 38 to 53% Si. The low refractive index of the least Si-rich samples is attributed to the presence of some oxygen in the samples. While the deposition chamber was subjected to a cleaning process prior to the film growth and no oxygen was intentionally introduced during the growth process, residual oxygen in the gas delivery lines and within the chamber is considered as the source of the oxygen within the samples. Estimates of as much as 25% oxygen have been found for samples having the least Si while more Si-rich samples appear to have significantly less oxygen. It should be noted that a large error margin exists in these initial compositional estimates. As the Si content is increased, there is a shift of the emission peak to lower energies, a result that appears to correlate well with the expected behavior from quantum confinement. Additionally, the decrease in peak intensity would seem to support this conclusion, as once the Si-ncs grow beyond the quantum confinement regime their behavior approaches that of the bulk and the emission efficiency decreases. Reports on the formation of Si-ncs within as-deposited SRSN thin films grown through PECVD have shown the ability to control the emission peak from the near IR (NIR) to the UV in such samples (14,18). However, we note here that annealing treatments below 900 °C (not shown) have been found to partially quench the as-deposited PL for our samples and more information is needed on the film structure before any final conclusions can be drawn related to the actual nature of the as-deposited PL observed here.

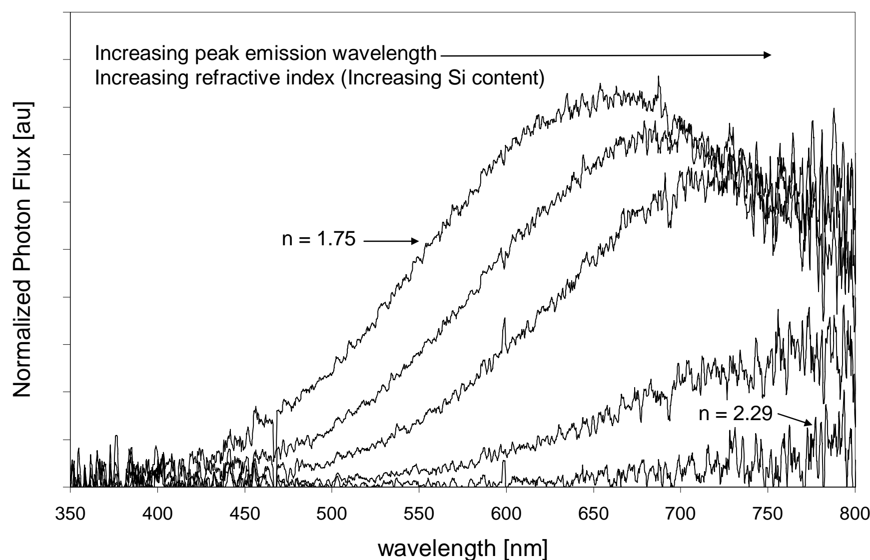

Figure 3. PL Spectra for a set of as-grown SRSN samples. For films with the highest Si content a significant reduction in the PL peak intensity is observed, leading to the significant amount of noise observed in their spectra.

Figure 4 shows the PL spectra for a SRSN sample annealed under Ar at the indicated temperatures. While the PL from SRSO thin films subjected to similar anneals is found to be centered in the 700 - 900 nm wavelength range, SRSN thin films have been found to emit over a wider range, extending from ~375 nm into the NIR. Furthermore, the PL results clearly indicate the presence of at least two luminescent emission bands, which can be seen to be centered between 400 - 500 nm and 650 - 750 nm, with peaks at ~450 - 470 and 680 nm, respectively. While some oxygen has been found to be present in the film, the NIR PL emission peak typically observed in SRSO thin films (as shown in Figure 1) is not clearly present. Oxide related emissions may play a role in the broad nature of the spectra, extending the observed PL into the NIR. However, similarly broad spectra have been reported for SRSN thin films grown by ion beam sputtering and subjected to a different annealing process (19).

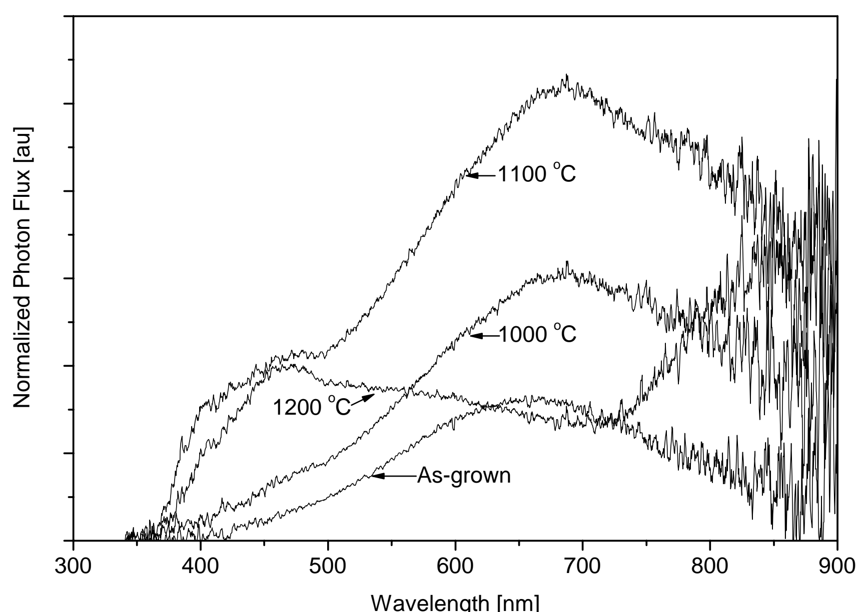

Figure 4. PL spectra for a SRSN sample annealed at the temperatures shown. A refractive index of 1.75 was measured for the as-deposited film. The low value is partially attributed to the presence of some oxygen in the film.

Interestingly, the change in anneal temperature from 1000 to 1100 °C has little effect on the position of the 680 nm peak, with the only observable change being an increase in intensity. Likewise, doubling the anneal time leads to an increase in the emission intensity (by a factor of ~1.3 for this sample), without a shift in the emission wavelength. These results are indicative of the formation of more common luminescent centers at the higher anneal temperature but contrast with results seen for SRSO thin films and expected from quantum confinement. Preliminary results of studies of the effects of changing the film composition do show a shift in the peak emission wavelength, as expected for confined structures. Furthermore, it is evident from the PL spectra that annealing at 1200°C results in a significant modification of the emission behavior in the SRSN samples. While the PL emission at 470 nm is still present, the 680 nm peak is absent, or at a minimum drastically reduced, and another emission band becomes apparent beyond 750 nm. Due to limitations in the current setup details of this NIR

emission are not considered at this time. The origin and nature of the PL in these SRSN materials remain unclear and are currently an active area of research.

Finally, the effects of incorporating hydrogen into the anneal process are briefly considered. Figure 5 shows the PL spectra for a SRSN sample annealed both with and without the presence of hydrogen in the anneal process. For the sample annealed under the presence of hydrogen an increase of a factor of ~2.6 is observed in the peak intensity. This increase in the observed PL intensity is considered to arise due to a similar effect as that for the case of SRSO samples. The introduction of hydrogen to the anneal process allows hydrogen atoms to incorporate into the sample where they serve to passivate dangling bonds at the nanocrystal interface, eliminating non-radiative recombination pathways (7). Currently, samples are being prepared for Fourier transform infrared spectroscopy experiments in order to provide a better understanding of the incorporation of hydrogen into the films to further clarify this effect.

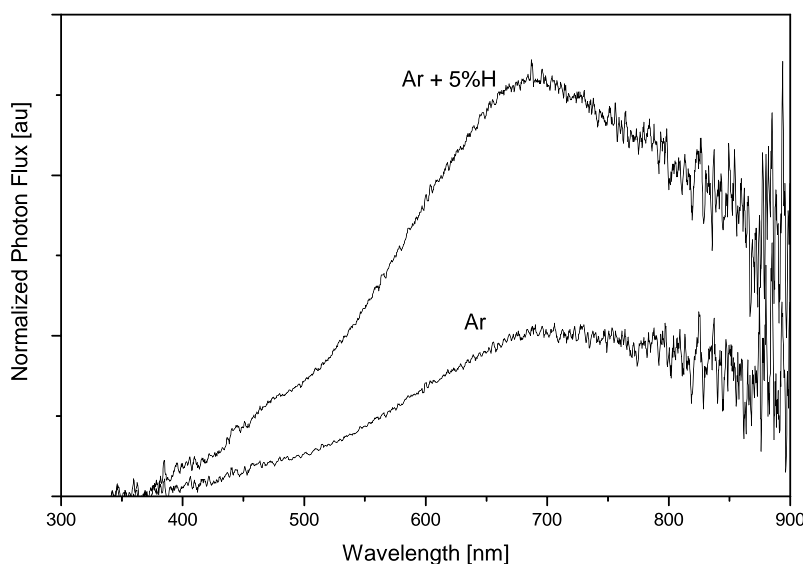

Figure 5. PL spectra for a SRSN sample annealed at 1000 °C under Ar and Ar + 5%H for 60 minutes.

Conclusions

Light emitting silicon nanoclusters have been formed in SRSO and SRSN thin films. Photoluminescence from the SRSO thin films is observed in the IR and can be attributed primarily to quantum confinement in the nanocrystals with a significant influence on the observed emission wavelength from the oxide matrix. A broad visible emission spectrum is observed for SRSN thin films with multiple peak emissions being present. The different nature of the PL emissions suggests that differing processes related to the dielectric interface play a significant role in the luminescence of these films. However, the influence of quantum confinement and potential defects on the PL of SRSN thin films remains unclear. Experiments are currently underway to more accurately determine the origin and nature of the PL in these materials.

Acknowledgments

This work has been supported by the Ontario Research and Development Challenge Fund (ORDCF) under the auspices of the Ontario Photonics Consortium

(OPC) and by the Centres for Photonics and Materials and Manufacturing, divisions of Ontario Centres of Excellence Inc (OCE).

References

1. S. Ossicini, L Pavesi, and F. Priolo, *Light Emitting Silicon for Microphotonics*, Springer, Berlin (2003).
2. L. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).
3. L. Pavesi and D. J. Lockwood (editors), *Silicon Photonics*, Springer, Berlin (2004).
4. L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzò, and F. Priolo, *Nature* **408**, 440 (2000).
5. F. Iacona, G. Franzò, and C. Spinella, *J. Appl. Phys.* **87**, 1295 (2000).
6. M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, and C. Delerue, *Phys. Rev. Lett.* **82**, 197 (1999).
7. D. Comedi, O. H. Y. Zalloum, and P. Mascher, *Appl. Phys. Lett.* **87**, 213110 (2005).
8. D. Comedi, O. H. Y. Zalloum, E. A. Irving, J. Wojcik, and P. Mascher, *J. Vac. Sci. Technol.* **A24**, 817 (2006).
9. S. V. Deshpande, E. Gulari, S. W. Brown, and S. C. Rand, *J. Appl. Phys.* **77**, 6534 (1995)
10. A. Aydinli, A. Serpengüzel, and D. Vardar, *Sol. Stat. Commun*. **98**, 273 (1996).
11. M. Molinari, H. Rinnert, and M. Vergnat, *Appl. Phys. Lett*. **77**, 3499 (2000).
12. M. Molinari, H. Rinnert, M. Vergnat, and P. Weisbecker, *Mat. Sci. Eng.* **B101**, 186 (2003).
13. L. Dal Negro, J. H. Yi, L. C. Kimerling, S. Hamel, A. Williamson, and G. Galli, *Appl. Phys. Lett.* **88**, 183103 (2006).
14. G. Y. Sung, N.-M. Park, J.-H. Shin, K.-H. Kim, T.-Y. Kim, K. S. Cho, and C. Huh, *IEEE J. Selected Topics Quantum Electron.* **12**, 1545 (2006).
15. O. H. Y. Zalloum, M. Flynn, T. Roschuk, J. Wojcik, E. Irving, and P. Mascher, *Rev. Sci. Instrum*. **77**, 023907 (2006).
16. D. Comedi, O. H. Y. Zalloum, E. A. Irving, J. Wojcik, T. Roschuk, M. J. Flynn, and P. Mascher, *J. Appl. Phys.* **99**, 023518 (2006).
17. F. Iacona, C. Bongiorno, C. Spinella, S. Boninelli, and F. Priolo, *J. Appl. Phys.* **95**, 3723 (2004).
18. T.-Y. Kim, N.-M. Park, K.-H. Kim, Y.-W. Ok, T.-Y. Seong, C.-J. Choi, and G. Y. Sung, *Mat. Res. Soc. Symp. Proc.* **817**, L4.3.1, (2004).
19. M.-S. Yang, K.-S. Cho, J.-H. Jhe, S.-Y. Seo, J. H. Shin, K. J. Kim, and D. W. Moon, *Appl. Phys. Lett.* **85**, 3408 (2004).