Silicon Nanocluster-based Materials Studies on the SGM and PGM Beamlines

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Introduction

The efficiency of light emission in Si can be greatly enhanced by reducing the dimensions of Si down to the nanoscale and taking advantage of quantum confinement effects. Light emitting Si opens the possibility of developing Si-based light emitters suitable for integration with current CMOS microelectronics technology. The observed emission from Si-nanoclusters (Si-ncs), including both crystalline and amorphous nanoclusters, is strongly dependent on cluster size and the surrounding environment, with debate centering on the role of defects at the nanocrystal interface. Extensive efforts have, therefore, been devoted towards understanding the emission process in these materials in order to enhance their efficiency and to make a Si-based light emitter viable.

Science

Quantum confinement (QC) effects play a dominant role in the behavior of electrons and holes within Si-ncs, causing an increase in the observed emission energy with a reduction in size. Furthermore, the spatial confinement of electrons and holes within the Si-nc region leads to a spread in their momenta consistent with the predictions of the uncertainty principle, relaxing the need for phonon interaction in the recombination process and greatly enhancing the efficiency of the radiative recombination process in comparison with bulk silicon. While QC suggests that the emission energy should continue to increase with a reduction in size, in practice, the host environment of the nanocrystals, which can introduce defect and surface states, limits the observed emissions from Si-ncs.

Si-ncs were prepared by growing silicon rich thin films of silicon oxide (SRSO), nitride (SRSN), and oxynitride (SRSON) via electron cyclotron resonance plasma enhanced chemical vapour deposition or inductively coupled plasma chemical vapour deposition. Post deposition, the films were subjected to thermal annealing treatments at temperatures up to 1200°C. These annealing treatments promote a phase separation between the excess Si and a dielectric host (i.e. SiO_2 or Si_3N_4) leading to the formation of Si-ncs embedded within a dielectric matrix. Details related to the study of SRSO-based materials have previously been provided. [1]

Current work at McMaster University is focused on the analysis of structure in these films and the correlation with observed optical properties. The electronic structure and atomic bonding at the K and $L_{3,2}$ -edges of these materials is being analyzed using X-ray absorption spectroscopy (XAS) experiments at the SGM (11ID-1) and PGM (11ID-2) beamlines. Additionally, X-ray excited optical luminescence (XEOL) experiments are being utilized in order to excite Si atoms in different chemical states providing valuable information on the origin of the luminescence. In this report we focus on some of the preliminary results for the SRSN films obtained at the SGM beamline 11ID-1.

Discussion

Figure 1 shows the photoluminescence (PL) spectra for several SRSN thin films (where the increasing refractive index, n, corresponds to an increase in Si-content). While several sub-band defects associated with nitrogen bonds exist in the SRSN thin films a wider emission range as compared to SRSO has been observed.

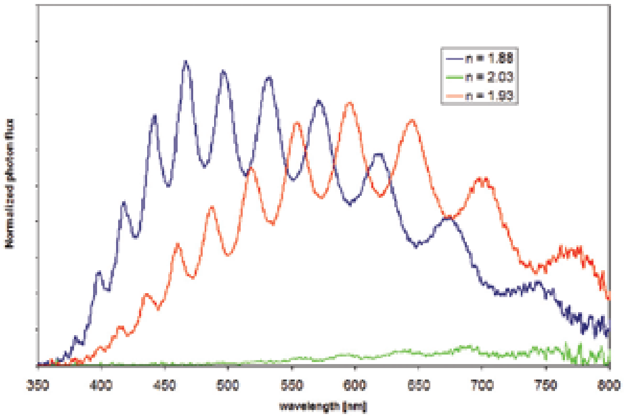

Figure 1: UV-PL spectra for SRSN thin films. The interference fringes are related to film thickness.

It is important to note that while nanocrystals have been observed through transmission electron microscopy (TEM) in the SRSO samples after high temperature annealing, the SRSN samples contain primarily amorphous nanoclusters, as confirmed by energy filtered TEM.

Figure 2 shows the total electron yield (TEY) spectra obtained at the Si K-edge for several of these samples as well as for reference samples of Si_3N_4 and a bare Si-wafer. The spectra show three primary absorption features at 1839, 1842, and 1847 eV corresponding to the edges of Si in Si, Si in Si_3N_4, and Si in SiO_2, respectively (small amounts of oxygen are observed in the SRSN samples although no oxygen was intentionally introduced during their growth). As the silicon content is increased the Si-N peak is observed to broaden and shift slightly to lower energies. The as-deposited SRSN samples show a featureless tail at 1839 eV.

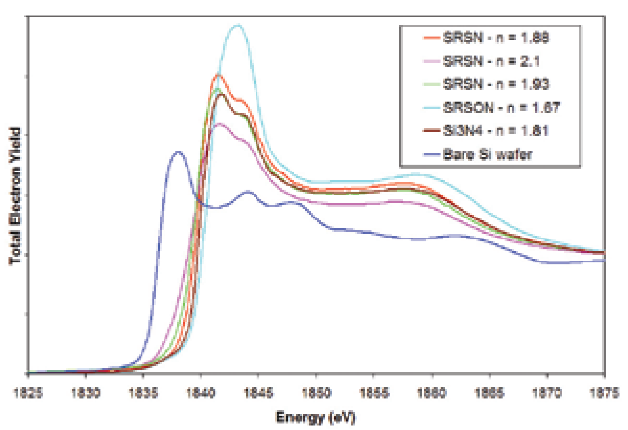

Figure 2: TEY spectra at the Si K-edge for as-deposited SRSN samples.

Figure 3 shows the TEY spectra for the sample having n = 1.88, as-deposited and annealed at the temperatures shown. After a high temperature anneal a small but distinct shoulder can be seen in the Si-Si region which is associated with the phase separation and clustering of Si. As these films contain only several atomic percent of Si in excess, the total volume fraction of the Si-ncs is small and the peak is of low intensity. In samples with greater Si concentrations this peak is first observed at lower annealing temperatures indicating a greater ease in Si-nc formation. The Si-N peak is observed to shift to higher energies, further indicative of the phase separation of these films.

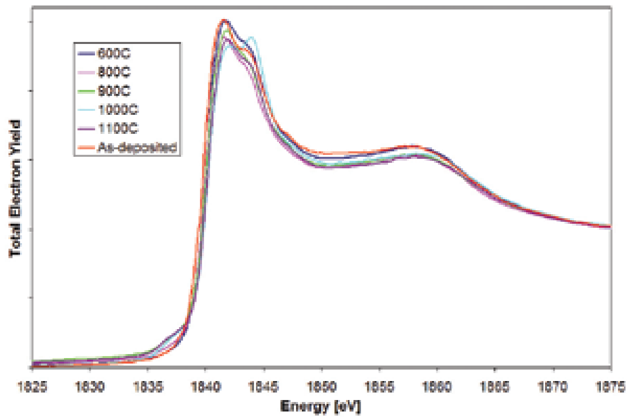

Figure 3: TEY spectra at the Si K-edge for an SRSN sample (n = 1.88) annealed at the temperatures shown.

While XEOL measurements show the excitation of an IR luminescence for SRSO samples at energies associated with Si-Si bonding, indicative of PL originating in the Si-ncs, no clear results have been observed for the SRSN films at the excitation energies associated with Si-Si, Si-N, or Si-O bonding. The origin of luminescence in these materials, therefore, remains an active area of study.

Results from the PGM beamline 11ID-2 have only been obtained recently and have not been sufficiently analyzed for inclusion in this report, however, they have yielded additional information concerning the Si $L_{3,2}$-edge in these samples. In Figure 4 we show the first XEOL results for a SRSO thin film doped with Tb and excited near the Si $L_{3,2}$-edge at 105 eV. The spectrum is characteristic of Tb and indicates the excitation of Si-ncs in these films followed by an energy transfer to the rare earth ions.

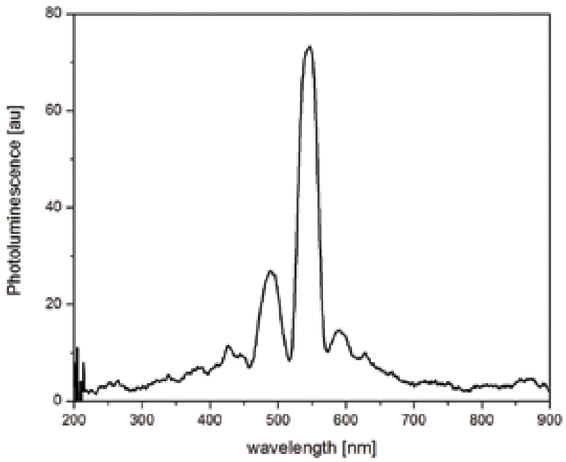

Figure 4: XEOL spectrum for a Tb-doped SRSO sample excited near the Si $L_{3,2}$ edge at 105 eV

Conclusion

Through the use of XAS details of the electronic structure and local chemical environment of Si-nc containing materials have been analyzed. The results are being correlated with the observed PL from these samples and a detailed analysis is planned for publication in the near future. Results from the PGM beamline are in the preliminary analysis stage. XEOL measurements have not yet provided conclusive evidence of the nature of luminescence in SRSN samples. Future studies will continue to examine the electronic structure of these materials and the nature of luminescence and will begin to analyze in more detail SRSN and SRSO samples doped with rare earth elements.

References

1. Comedi, D. et al.,2007. Study of Luminescence from Si-nanocrystal/Si-oxide Composites. CLS Activity Report 2005-2006, 29-30.

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