A Luminescence Study of Porous Diatoms

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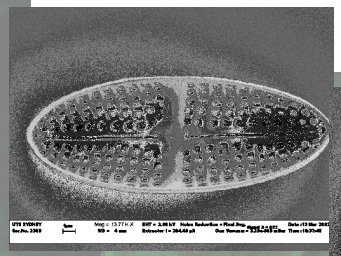
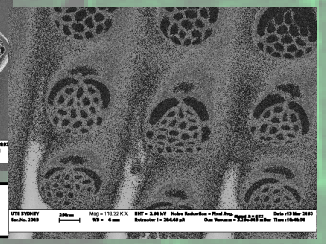
What are diatoms? Diatoms are a small plant like creature that live in aqueous environments. They have been studied for well over two centuries by biologists, and their remains have been found in large deposits of diatomaceous earth, which is mined for water filtration and housing insulation, among other uses. One of the more unusual properties of these diatoms is that they produce an amorphous silica shell or "frustule" which is ***nano-porous***. There are thousands of diatom species with a commensurate variety of frustule form and pore type. The pores in diatom valves range in diameter from > 1µm to < 10 nm [1]. Figures 1,2 and 3 show example secondary electron micrographs of some of the diatoms examined here.





Figures 1 and 2 (above): SEM secondary electron images of cultured Achmanthes Subsessilis diatom

Why study diatoms? Interest in porous semiconductor and insulating materials has developed from the realisation that porous silicon luminesces efficiently in the visible region when irradiated with ultraviolet light [2]. Porous silica was originally investigated in an attempt to elucidate the mechanism of luminescence for porous silicon. However, porous silica has since been found to have its own unique properties and is now used in a number commercial applications [3-6]. In particular we note that porous silica has been used for novel optical fiber based photonic devices [7] and more recently as a matrix for high quantum efficiency nanoparticle luminescence devices [8,9]. Diatoms are another form of porous silica. The equivalent potential of diatoms for optoelectronic and photonic device applications is examined here by studying the luminescence properties of a number of different types of diatom. These include fresh water benthic diatoms collected from streams, and cultured diatoms from the University of Ghent.

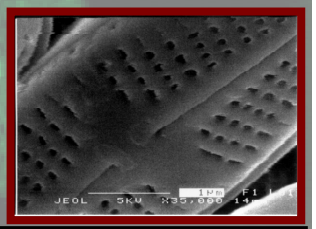
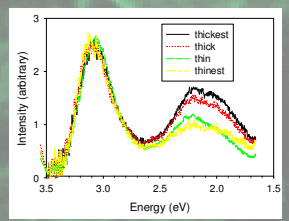
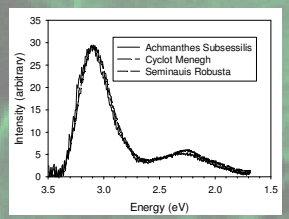


Figure 3: SEM secondary electron micrograph of a fresh water benthic diatom.



Figures 4 (above): Photoluminescence spectra of benthic fresh water diatoms at different positions

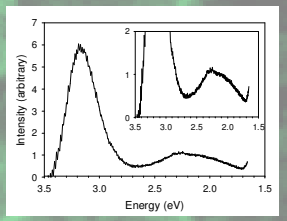


Figures 5 (above): Photoluminescence spectra of cultured diatoms.

Photoluminescence (PL): The 325 nm line of a Kimmon Electric He-Cd continuous wave laser was used as an excitation source. The spectra were collected using a Jobin Yvon-SPEX Triax 320 monochromator with a 600 line/mm grating and an Oriel 77438 photomultiplier.

Strong blue and yellow luminescence could be distinguished by eye. The spectral results for fresh water stream collected benthic diatoms (figure 4) and cultured diatoms (figure 5), may be compared to the spectrum for fused silica (figure 7). The spectra of all three figures show the same three broad bands, though with the benthic diatoms having notably stronger relative luminescence in the yellow-red area. The origin of the peak at 2.15 eV is often attributed to smaller dimensional structure.

The spectra of figure 4 were taken at different positions for the same sample, in areas of different thickness.



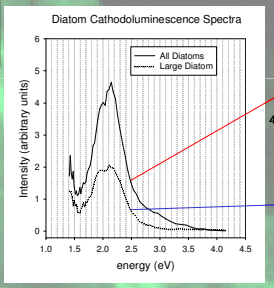
Figures 6 (to left): Photoluminescence spectra of fused silica.

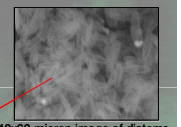
Cathodoluminescence (CL): The CL system used here was an Oxford Instruments MonoCL cathodoluminescence imaging and spectral analysis system housed in a Joel JSM-35C SEM. The system had a monochromator with a 1200 line/mm grating blazed at 500 nm, and was capable of collecting wavelength-dispersed spectra in the wavelength range from 300 to 900 nm using a photomultiplier. The electron beam was kept at 25 kV for these measurements.

Figure 7 shows CL images collected at a wavelength of 560 nm. Extremely good spatial resolution was obtained from the CL images. Figure 7 also shows the luminescence spectrum for a single large diatom (the analysis area is also shown in the figure) and another spectrum for a group of smaller diatoms, which may include particulate impurities. The spectra have the same features indicating that any particulate included in the larger area image did not contribute noticeably to the main features of the spectrum.

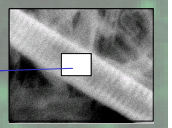
From figure 7 it is apparent that the diatom CL spectra show two main peaks at approximately 620-640 nm (2.0 - 1.95 eV) and 580 nm (2.15 eV). The peak at 2.0 eV is identical with literature values related to defects for amorphous or microcrystalline silica [8-10]. The peak at 2.15 eV appears to be consistent with a smaller dimensional structure.

No blue emission is evident in figure 7, however figure 8 shows that localised emissions in this wavelength region were present.





40x60 micron image of diatoms



16x12 micron image of diatoms

Figure 7 (above): CL spectra for fresh water benthic diatoms.

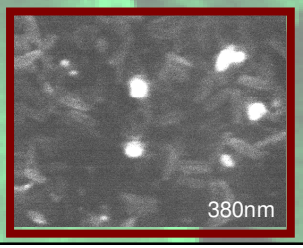


Figure 8 (above): CL image of fresh water benthic diatoms taken at 380 nm.

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Acknowledgments: We would like to acknowledge the support of the Australian Institute of Nuclear Science and Engineering. K. S. A. Butcher would also like to acknowledge the support of an Australian Research Council Fellowship and a Macquarie University Research Grant.