Photoluminescence and Cathodoluminescence Studies of Diatoms – Nature's Own Nano-Porous Silica Structures

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Photoluminescence (PL) and cathodoluminescence (CL) data are presented for the silica frustules of some fresh water diatoms. The diatom frustules consist of a nano-porous silica structure that may possibly be exploited for optoelectronic or photonic applications. This work represents what we believe to be the first report of the CL and PL properties of this naturally occurring source of nano-porous silica.

1. Introduction

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 are 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 many different frustular forms and a variety of pore types. Figure 1 shows a secondary electron micrograph, collected using a field emission scanning electron microscope (FEG-SEM) of the diatoms examined for this study.

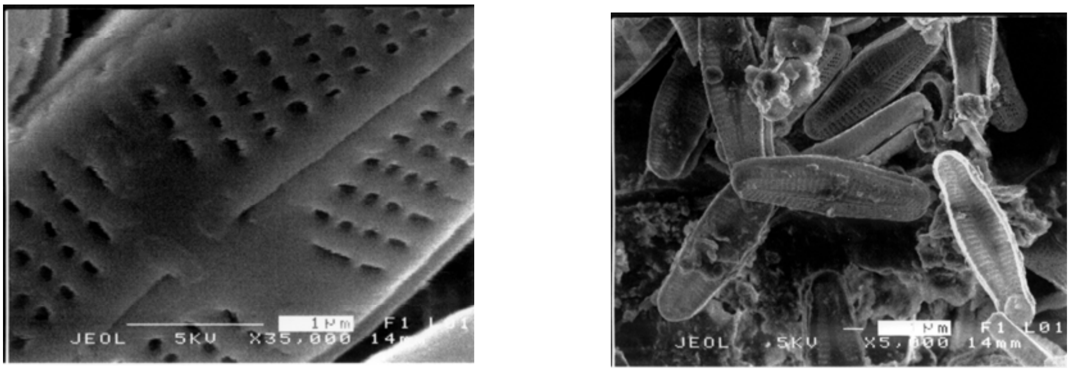

Fig. 1. SEM micrograph of a freshwater diatom frustule with organic residue removed (left). On the right is shown a group of frustules from the same sample.

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 [1]. 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. For instance porous silica can have a very low dielectric constant, almost approaching unity in extreme cases [2,3], and is therefore a potential "low k dielectric" for use in emerging copper-Si technology. There are also some reports that indicate that porous silica may be used as a gas sensor [4,5], and as a material for novel optical fiber based photonic devices [6]. It is the potential for optoelectronic and photonic devices that is of interest here.

Marine species typically have more elaborate shapes than freshwater species of diatoms. The complex architecture of diatom frustules is beautifully illustrated in the scanning electron micrographs of the 'Generic atlas' in [7]. The pores in diatom valves range in diameter from > 1μm to < 10 nm [7] and can be simple circular or elongate pores through thin siliceous plates, tube-like structures in more heavily silicified sections, or occur in complex multi-layered sheets with progressively finer pores sizes in each layer [7]. For this initial study we have elected to examine the more simply structured freshwater species shown in figure 1. We use as our tools photoluminescence (PL) and cathodoluminescence (CL). These were used to determine whether there is any unique signature for this form porous of silica, compared to other forms of silica that have been studied.

2. Sample preparation

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 Hamamatsu R943-02 photomultiplier. The electron beam was kept at 25 kV for all the measurements reported here. All CL spectra were corrected for the system response. The diatoms were taxonomically prepared [7; see pp10-11] and were settled in a liquid pool on a gold coated metal blank to a thickness of about 0.5 mm. The diatom frustules were lightly coated with graphite before being introduced into the SEM. PL measurements were carried out prior to the CL measurements. The 325 nm line of a Kimmon Electric He-Cd continuous wave laser was used as an excitation source, and a chopper was used to modulate the laser beam. A SPEX-270M monochromator with a 1200 line/mm grating and a Hamamatsu R446 photomultiplier were used for light collection.

3. Results

Under the 325 nm laser beam the sample emitted a strong blue photoluminescence that was clearly visible with the eye. The PL spectrum of the material was collected and was found to have a broad peak at 450 nm (2.75 eV). In contrast the CL emission is stronger at longer wavelengths, perhaps as a result of different excitation pathways. Figure 2 shows CL images collected at a wavelength of 560 nm. Extremely good spatial resolution was obtained from the CL images because the luminescence is produced in the thin wall of the hollow diatom shell so there is virtually no spreading of the electron beam compared with bulk silica. However, the skeletal structures themselves were extremely luminescent. Figure 2 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. The source of the spectral features is therefore the diatoms themselves.

From figure 2 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). CL peaks have been observed in these regions previously for fused silica. The 620-640 nm orange line has been linked most commonly with non-bridging oxygen hole centres (NBOHC) [8-11]. Though its been suggested that this emission band may also include a contribution from peroxy radicals [12]. The observation of this band for the diatoms would be consistent with the diatoms consisting of amorphous or microcrystalline silica [13]. The 2.15 eV emission appears to be of less certain origin, though it may also be due to an NBOHC formed from a different precuror [8] or hydrogen-related species [14]. A 2.28 eV emission has been observed for quartz due to the radiative recombination of self trapped excitons (STEs) in radiation induced amorphous silica outgrowths [8]. STE emissions have also been observed in the 2.6-2.8 eV range for crystalline silica and in the range of 2.2-2.4 eV for amorphous silica [8]. CL emission in the 2.15-2.45 eV range for opal has been tentatively attributed to STEs related to the formation of silicon nano-clusters in SiO_2 [15]. These possibilities all have a link to low dimensional silica based structures, the 2.15 eV emission observed here may therefore have some relation to the porous nanostructure of the diatom frustules.

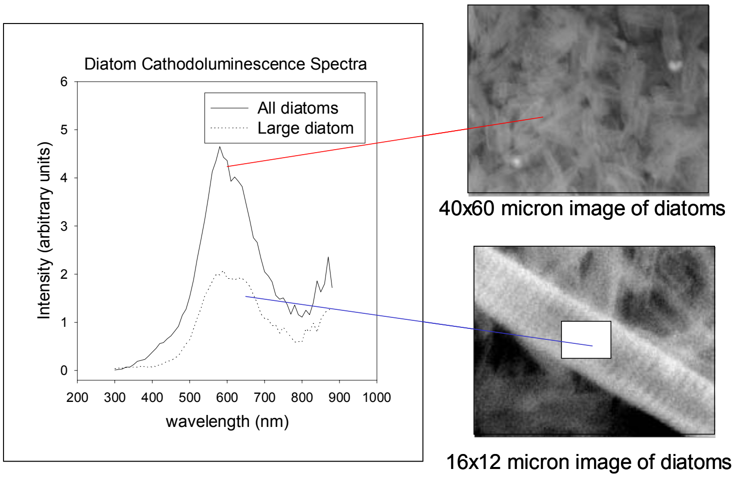

Fig. 2. CL spectra of freshwater diatoms, with CL images collected at 560 nm also shown.

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