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Edge-jump inversion in the Si $L_{3,2}$-edge optical XAFS of porous silicon

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We present a study of the progressive inversion of the edge jump of the Si $L_{3,2}$-edge XANES (X-ray Absorption Near Edge Structures) recorded with photoluminescence yield (PLY) for a series of porous silicon samples with varying thickness. It is found that edge jump inversion occurs as the thickness of the film increases from the thin to the thick regime.

Keywords: Si $L_{3,2}$-edge, porous silicon, optical XAFS

1. Introduction

Yield spectroscopy has been widely used to record X-ray absorption fine structures (XAFS) for specimens not suitable for transmission measurements (XAFS IX Proceedings, J. Phys. IV France, 1997). The general assumption is that the yield closely resembles the absorption spectrum. For total electron yield (TEY) (Erbil etal. 1988; Kasrat et al. 1996) and fluorescence yield (FLY) (Kasrai et al. 1996; Rosenberg et al. 1992), this assumption is generally valid. However, yields closely resembled the absorption spectrum cannot always be obtained in photoluminescence (PLY) measurements (Bianconi et al. 1978; Goulon et al. 1983; Pettifier & Bourdilon 1987; Murata et al. 1993; Jiang et al. 1993; Coulthard et al. 1998).

This study concerns the edge-jump behaviour in optical XAFS (X-ray absorption monitored by PLY). It has been documented that if the sample is thin the optical XAFS will exhibit a normal edge jump and if the sample is thick, the edge jump will be inverted (Jiang et al. 1993). Here, we report an investigation of this behavior using a series of porous silicon samples.

Porous silicon (PS) is a sponge-like crystalline Si network containing Si crystallites of nm size. PS emits visible light at room temperature upon synchrotron light irradiation (a quantum confinement effect) in contrast to bulk Si (Cullis et al. 1997). By controlling the preparation conditions, we can vary the thickness of the luminescent layers (Coulthard 1998). Thus a series of PS samples with varying thickness provides a good testing ground for the edge-jump inversion behavior in optical XAFS. The results in turn will shed some light on the distribution of nanostructures within the PS film.

2. Experimental

Porous silicon samples were prepared by electrochemical etching of a p-type Si(100) wafer at current densities varying from 5 mA/cm^2 to 500 mA/cm^2 for 20 minutes. This range covers etching (<100 mA/cm^2) and polishing conditions (>100 mA/cm^2) (Coulthard 1998). Scanning Electron Microscopy (SEM) shows that the thickness of the PS layer varies linearly at low current density and flattens out at high current density (>100 mA/cm^2) (Coulthard 1998). The thickness of a 20 mA/cm^2-20 min sample is typically several μm, depending on the resistivity of the specimen.

X-ray absorption experiments were performed at the Canadian Synchrotron Radiation Facility (CSRF) at the Synchrotron Radiation Center (SRC), University of Wisconsin-Madison. The Canadian grasshopper beamline was used to record the Si $L_{3,2}$-edge XAFS in both TEY (specimen current) and PLY mode. PLY was recorded with a JY H10 monochromator equipped with a Hamamatsu photon multiplier (R943-02). All PS specimens were refreshed with HF to remove the oxide prior to the measurements. The optical XAFS was obtained with the optical monochromator set at zero order. A set of luminescence spectra is shown in Fig.1. All yields are normalized to photon flux.

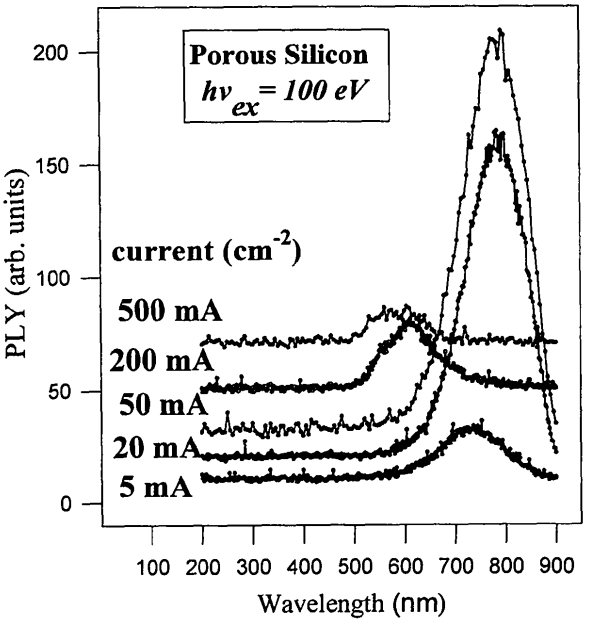

Figure 1
Luminescence spectra for a series of porous silicon samples.

3. Results and Discussions

Figures 2 and 3 show the Si $L_{3,2}$-edge XANES obtained in TEY and PLY, respectively, for a series of PS samples. The vertical line marks the resonance maximum. Several features are noteworthy. First, we see in Fig. 2 that the TEY XANES are essentially the same for all PS samples as expected for HF refreshed porous silicon (Coulthard et al. 1999). A small dip is seen at the rising edge (~ 99.7 eV) in the high current density samples. This dip is attributed to the effect of differential charging resulting from an abrupt increase in the absorption coefficient (hence an abrupt decrease in sampling depth) across the edge. It is found from photoemission that PS charges up significantly relative to bulk Si because of its relatively poor electron transport properties (Coulthard 1998, Jacob et al. 1998). Second, the PS edge threshold (Fig. 2) is blue-shifted relative to Si(100) and the spectral features broaden due to quantum confinement and disorder, respectively (Jiang et al. 1993). Finally, Fig. 3 exhibits the most interesting feature: edge jump inversion as the thickness of porous silicon increases.

We see that edge jump inversion occurs going from 20 mA/cm^2 to 50 mA/cm^2. Qualitatively, this immediately indicates that the former is optically thin while the latter is becoming optically thick (inversion). The explanation for this can be found in the abrupt change in absorption coefficient across the edge. As the luminescent layer gets thicker, (e.g. > three absorption lengths, 95% absorption above the edge), a small increase in photon energy from below to

out a fraction of luminescent sites that were probed when the photon energy was below the edge.This immediately results in a drop in the luminescence quantum yield and an inversion in the edge jump.

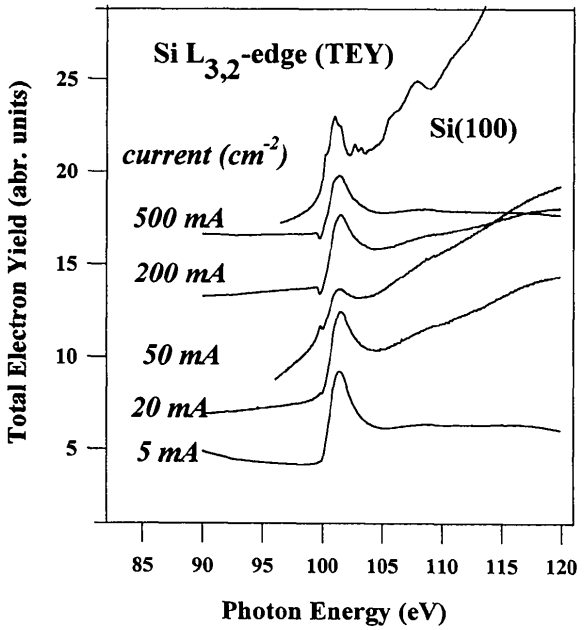

Figure 2
Si $L_{3,2}$ -edge XANES (TEY) for a series of porous silicon samples together with that of an ambient Si(100) wafer.

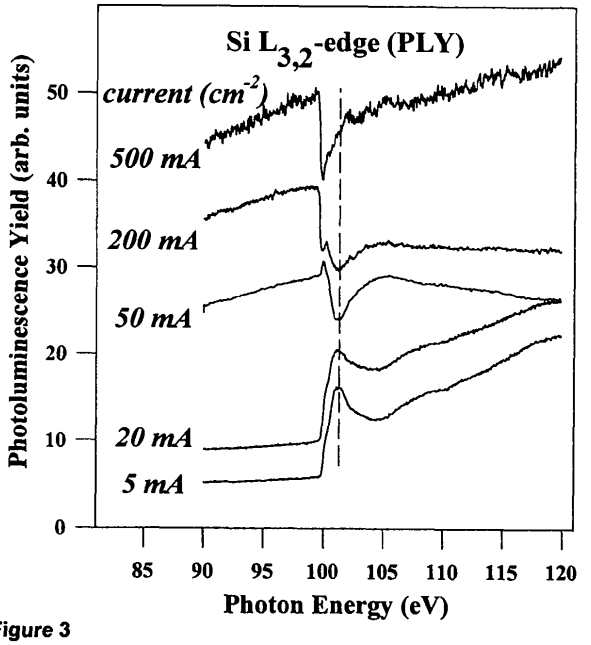

Figure 3
Si $L_{3,2}$-edge XANES (PLY) for the PS described in Fig.2.

At the Si $L_{3,2}$ -edge (~100 eV), the one-absorption length below and above the edge with a typical porosity of 80% (range of porosity in PS : 65-90%) accounted for is ~23 and 0.25 μm respectively (Henke et al. 1982). The attenuation length of optical photon in Si is typically ~ 1 μm (5 μm with porosity accounted for), much longer than the X-ray absorption length above the edge. Thus the behavior of optical XAFS for porous silicon in this photon energy range is primarily determined by the absorption length of the soft X-ray photons, in contrast to hard X-ray studies and TEY where the attenuation of the yield often determines the appearance of the XAFS.

We now compare these absorption lengths with the thickness of the PS film. SEM results indicate that the thickness of the 20 mA/cm^2 and 50 mA/cm^2 samples used in this study are ~10 and ~23 μm, respectively significantly greater than the three-absorption lengths of 0.75 μm in PS for absorption above the Si $L_{3,2}$-edge. The PS thickness for this series increases with current density linearly and reaches a plateau of ~ 20 μm at 100 mA/cm^2. The fact that a ~10 micron film exhibits a normal edge jump instead of the expected inversion immediately indicates that the luminescence sites must be distributed near the nominal surface of the PS layer. Thus a thicker layer (higher current density) does not necessarily increase the luminescence as already borne out in Fig.1. Finally, we note that an intermediate optical thickness is seen in the 500 mA/cm^2 sample (Coulthard 1998). The PLY XANES bears no resemblance to the TEY spectrum. More details for the intermediate cases will be discussed elsewhere.

4. Conclusion

Using a series of porous silicon samples with variable thickness, we have shown that inversion of the Si $L_{3,2}$ -edge optical XAFS occurs when the thickness of the specimen increases from the thin sample regime to the thick sample regime confirming some of the notions proposed earlier. These results also indicate that there exist a concentration gradient of luminescence sites which concentrate very closely to the more open upper surface of porous silicon.

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