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Influence of sample oxidation on the nature of optical luminescence from porous silicon

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Site-selective luminescence experiments were performed upon porous-silicon samples exposed to varying degrees of oxidation. The source of different luminescence bands was determined to be due to either quantum confinement in nanocrystalline silicon or defective silicon oxide. Of particular interest is the defective silicon-oxide luminescence band found at 2.1 eV, which was found to frequently overlap with a luminescence band from nanocrystalline silicon. Some of the historical confusion and debate with regards to the source of luminescence from porous silicon can be attributed to this overlap. © 2000 American Institute of Physics. [S0003-6951(00)01330-9]

The discovery of intense visible luminescence at room temperature from porous silicon caused considerable interest in the possibility of creating silicon-based optoelectronic devices. Quantum confinement in nanocrystalline silicon accounts for one particular luminescence band whose emission wavelength is tunable over a wide range (red–blue) by altering sample preparation conditions and postpreparation treatments that alter the size of the nanocrystalline-silicon features, making this particular luminescence band very desirable for end applications. This luminescence band has been observed in both oxidized and nonoxidized samples. Other luminescence bands, most commonly observed in the blue region of the visible spectrum and in the UV, are attributed to defective silicon oxide that forms on porous silicon when the sample is exposed to ambient or other oxidative conditions. Sample oxidation and postpreparation treatments will clearly be important factors to be considered in the generation of porous-silicon devices. The synchrotron techniques of x-ray excited optical luminescence (XEOL) and optical x-ray absorption fine structure (XAFS) have made valuable contributions to the study of porous-silicon luminescence. These techniques have been utilized in the past to rule out potential porous-silicon luminescence mechanisms, find previously unreported luminescence bands from porous silicon, and determine the average size of luminescent features in porous silicon in relation to the average size of features as a whole. The power of these techniques lies in the ability to create selectivity by distinguishing between sites in a sample that do and do not produce luminescence. When the photon energy used for sample excitation is tuned to a specific absorption edge or even a specific feature of a particular absorption edge, specific elements or chemical states of the sample absorb the greatest fraction of the incoming photons, and the mechanism of luminescence related to those specific sites will generate more luminescence. The optical luminescence can also be used as a measure of yield for absorption spectra. If this experiment is carried out in an emission-wavelength-specific fashion, then the absorption spectrum will reflect only the sites of the sample responsible for optical luminescence at that specific wavelength. Due to the state selectivity, this experiment can extract useful information even in cases where broad luminescence bands of differing origin significantly overlap.

In this letter, we report the XEOL and optical XAFS results for a series of porous-silicon samples exposed to varying degrees of oxidation, which will aid in understanding porous-silicon luminescence by monitoring the luminescence from the samples as a function of this oxidation. Of greatest interest is the orange luminescence band found at 2.1 eV (590 nm) that can be attributed to defective silicon oxide in oxidized samples. The energy of this 2.1 eV defective oxide band in relation to commonly reported energies for the luminescence band produced by quantum confinement indicates that this band may have contributed in the past to confusion and debate with regards to the origin of luminescence from porous silicon due to misidentification and overlap.

Three porous-silicon samples were prepared using anodic etching from a p-type (B-doped, 1–10 Ω cm) Si(100) wafer for 20 min with a 1:1 mixture of 48 wt % HF and absolute ethanol, and a current density of 20 mA/cm². One sample was stored in ambient conditions, while another sample was refreshed with HF to remove the silicon oxide just prior to introduction to the vacuum chamber. The third sample was dipped into a 0.0001 MAgNO₃ solution immediately after preparation, resulting in a REDOX reaction. The silver is reduced to metallic form and deposited as nanoclusters averaging 10 nm in diameter upon the surface of the porous silicon, and the surface of the porous silicon became heavily oxidized as a result.

Experiments were performed both at the Canadian Synchrotron Radiation Facility (CSRF) double-crystal monochromator (DCM) beamline at the Synchrotron Radiation Center (nonoxidized samples), and the high-resolution intermediate x-ray spectroscopy beamline (2-ID-C) (Ref. 14) at

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the Advanced Photon Source (oxidized samples). In both cases, a photon bandwidth of $\sim 0.8$–$0.9$ eV was used. Optical luminescence was measured with the use of a JY H-10 optical monochromator coupled to a cooled Hamamatsu 943-02 photomultiplier tube. Optical XAFS were collected either in total luminescence yield (TLY) mode with the optical monochromator set to pass all optical emission (200–850 nm) or in partial luminescence yield (PLY) mode with the optical monochromator set to a specific emission wavelength with a bandpass of 1 nm. Total fluorescence yield (TFY) and total electron yield (TEY) measurements were also collected for each sample using a photodiode and sample drain current, respectively. Since TFY and TLY both have micron-scale sampling depths at these energies, small nanoclusters of silver upon the surface of one sample does not hinder the acquisition of data.

Figure 1(a) shows the TEY and luminescence (TLY) absorption spectra for the HF-refreshed porous-silicon sample. The near-edge features observed in these spectra are identical to those observed for a clean Si(100) wafer. Figure 2(a) shows the luminescence spectrum for this sample taken with an excitation energy of 1880 eV. As expected, only one luminescence band is observed at 600 nm (1.9 eV), which is consistent with past studies of nonoxidized porous-silicon samples that show a nanocrystalline-silicon origin to the luminescence. Absorption spectra for the ambient-oxidized porous-silicon sample are shown in Fig. 1(b). Differences are immediately evident in the TFY spectrum as compared to the nonoxidized sample [Fig. 1(a)]. An absorption edge jump at 1840 eV related to nonoxidized silicon is still present in this sample, but two new spectral features at 1844 and 1847 eV have emerged due to the exposure to ambient conditions. The feature at 1844 eV can be attributed to silicon suboxides and hydroxides, while the feature at 1847 eV can be attributed to SiO$_2$. Silicon-oxide features were even more pronounced in the surface-sensitive TEY spectra for oxidized samples (not shown). The TLY spectrum in Fig. 1(b) for the ambient-oxidized sample shows spectral features related to both silicon and silicon oxide, indicating sources of luminescence in this sample related to both silicon and silicon oxide. Figure 2(b) shows the luminescence spectra for this sample taken at excitation energies below the oxide features (1843 eV) and at the most intense oxide feature (1847 eV). Multiple peaks are now present in these spectra indicating the presence of multiple luminescence bands in this sample. The position of the lesser peak at 450 nm (2.7 eV, blue) is consistent with previous results that observed a blue luminescence band in oxidized porous-silicon samples and defective silicon-dioxide glasses. Figure 1(b) shows the partial luminescence yield spectrum for this sample when the optical monochromator is set to the 700 nm (1.8 eV) maximum in Fig. 2(b). Since these detection techniques only probe luminescence sites in the sample, the fact that both silicon and silicon-oxide features are observed indicates that this peak is produced by two overlapping bands of differing origin. If one compares the relative intensity of the silicon-oxide and silicon spectral features of the total and partial luminescence yields [Fig. 1(b)], clearly the silicon feature is considerably more intense in the partial yield taken at 700 nm as compared to that in the total luminescence yield. The nanocrystalline-silicon luminescence band is a large contributor to the luminescence peak at 700 nm, which is confirmed by the intensity of the peak as a function of the excitation energy. When the excitation energy is tuned to 1847 eV, the silicon-oxide sites of the sample should preferentially absorb a greater fraction of the incoming photons. The peak intensity at 700 nm drops by a factor of 2 as the excitation...
energy is tuned to 1847 eV, confirming the assertion that a luminescence band from nanocrystalline silicon is a large contributor.

Figure 1(c) shows the absorption yield spectra for the porous-silicon sample that was rapidly oxidized by exposure to AgNO₃ solution. The silicon-oxide feature at 1847 eV is now much more intense than in previous samples, and the spectral feature at 1844 eV observed in Fig. 1(b), which is attributed to incomplete oxidation products, is absent. These results indicate that the oxidation of the porous-silicon sample by immersion into the AgNO₃ solution is more complete than oxidation by exposure to ambient conditions. The effect of this oxidation treatment is even more apparent in the TLY spectrum [Fig. 1(c)]. From the relative intensities of the Si and SiO₂ peaks, the silicon oxide is now clearly the major source of luminescence. Figure 2(c) shows the XEOL spectra for this sample at excitation energies below the absorption threshold (1830 eV), at the silicon absorption threshold (1840 eV), and at the silicon-oxide feature (1847 eV). The fact that no significant change occurs as the excitation energy is scanned across 1840 eV also indicates that luminescence from nanocrystalline silicon is now a very small contributor to the total luminescence from the sample. Changing the excitation energy to 1847 eV shows a marked increase in the intensity of the spectrum, as well as the emergence of a weak ultraviolet (UV) luminescence band at approximately 310 nm (4.1 eV), consistent with previous results on UV emission from oxidized porous-silicon samples and defective silicon dioxide. The most intense peak of the XEOL spectra at 590 nm (2.1 eV, orange) is found at an energy that is in agreement with luminescence bands reported for defective silicon dioxides. Figure 1(c) also shows the partial luminescence spectra taken at 340 and 650 nm, respectively. The PLY spectrum at 340 nm clearly shows that the luminescence bands in the blue and UV regions can be entirely attributed to defective silicon dioxide. The PLY at 650 nm shows that although the major contributor to the luminescence in this sample is defective silicon oxide, a small amount of luminescence is detected from the nonoxidized porous silicon deep under the heavily oxidized surface of the sample.

The defective oxide luminescence band at 2.1 eV, in particular, provides some interesting insight into the historical debate and confusion over the source of luminescence from porous silicon. Some of the strongest opposition to the quantum-confinement model of luminescence came from models that proposed silicon oxide as the source of luminescence from porous silicon. A series of articles by Prokes and co-workers in particular, where oxidized porous-silicon samples producing orange-red luminescence were studied, presented a very strong argument against luminescence via quantum confinement and in favor of silicon-oxide-related luminescence. This study shows, however, that luminescence bands in the orange-red region of the spectrum can be produced both by overlapping bands from nanocrystalline silicon and from defective silicon oxides. We have also seen that a change in the level of oxidation of the sample will have a large affect on the relative contributions of these two sources of luminescence to the total luminescence spectrum. Previous studies where the affect of ambient oxidation upon sample luminescence was examined often appear inconsistent with respect to the affect of oxidation upon the luminescence efficiency. This is likely explained by different preparation conditions resulting in porous-silicon samples with differing sensitivities to ambient oxidation. It is clear that the conditions under which porous-silicon samples are prepared, stored, and treated need to be carefully documented. In cases where samples have been exposed to oxidizing conditions, the possibility of luminescence from both nanocrystalline silicon and defective silicon oxides must be considered.

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