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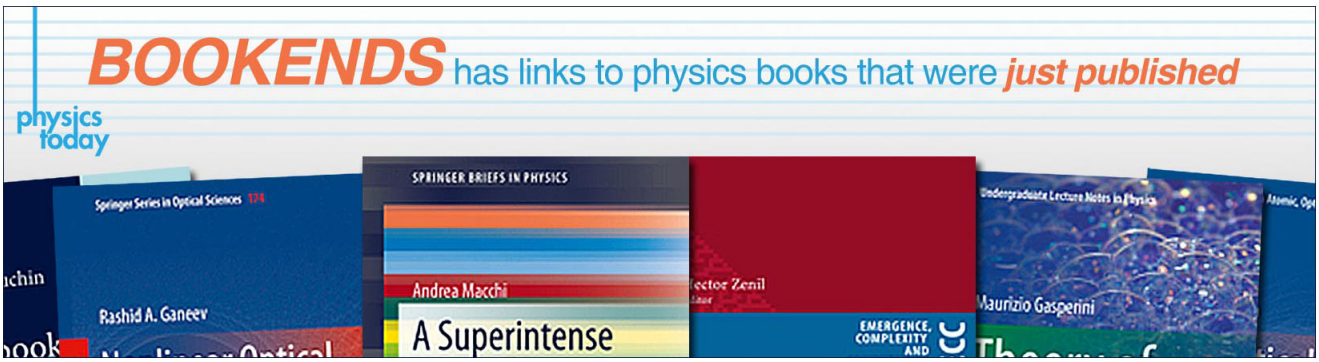

# Cathodoluminescence of electron irradiated opal-based nanocomposites

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Synthetic opals infilled with silicon (opal-Si) and with Si and Pt (opal-Pt-Si) have been irradiated in a scanning electron microscope under high excitation conditions. Electron irradiation-induced changes in the morphology and luminescent defect structure of both types of nanocomposites were assessed by scanning electron microscopy and by cathodoluminescence (CL) microscopy and spectroscopy. Irradiation causes strong morphological changes in the ordered structure of the matrix and quenching of the nanocrystals-related CL emission in the opal-Si samples. On the contrary, such effects are not observed in the opal-Pt-Si nanocomposites. In both types of samples, electron irradiation induces the appearance of a CL band centered at 2.95 eV, attributed to complex centers involving oxygen vacancies in the silica spheres forming the matrix. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1390307]

Due to continuous scaling of solid-state electronics technology towards smaller and faster devices, three-dimensional (3D) assemblies of semiconductor nanostructures with a high volume density of active elements could be used in the near future. Synthetic opal has a regular sublattice of channels and voids that can be infilled with different materials in order to create 3D nanostructures which can form the basis of objects for microelectronics, e.g., solid state devices with $p$-$n$ junctions or Schottky diodes.[1,2] Opal matrices infilled with semiconducting materials are also a subject of interest in optoelectronics due to the application of these composites as photonic crystals.[3,4]

Opals are made of closed-packed amorphous submicron silica spheres forming a face centered cubic lattice. It is known that the defect structure of $SiO_2$ is sensitive to ionizing radiation.[5,6] Many $SiO_2$-based devices must be operated in radiation environments. Therefore the characterization of the radiation sensitive defect structure of opals is of great importance to optimize device performance and applications. In this work, synthetic opals infilled with silicon (opal-Si) and opals infilled with Si and Pt (opal-Pt-Si) have been irradiated in a scanning electron microscope (SEM) under high excitation conditions. Electron beam irradiation effects on the morphology and luminescence properties of the samples have been assessed by SEM in the secondary electron mode and by cathodoluminescence (CL) microscopy and spectroscopy. In particular, we have investigated the influence of electron irradiation on the luminescent defect structure of the opal matrix as well as on the emission related to Si nanocrystals which are present in the nonirradiated samples. Luminescence of Si-based heterostructures and Si nanocrystals are subjects of increasing interest due to potential integration of this material in optoelectronic devices.

Opals consisting of amorphous silica spheres of about 250 nm diameter have been investigated in the present work. The opals were prepared by sedimentation of synthetically grown monodispersed spherical $SiO_2$ globules.[7] The silica spheres consist of several closed-packed spheres of smaller diameter ($\sim$ 40 nm), which in turn are made of particles of about 10 nm in size.[8] After sedimentation, the opals are hardened by hydrothermal annealing. During this process most of the smaller globules become partially coagulated, and a porous disordered structure appears inside the silica spheres.[9] About 26% of the total matrix volume is accessible for filling with other substances. Incorporation of silicon into opal by a thermal chemical vapor deposition technique and the procedure for embedding Pt in the opal matrix have been previously described.[2,10] Opal-Pt-Si composites were prepared embedding the opals first with platinum and then with silicon. These treatments lead to opal structures with the interstitial region partially filled, due to coating of the spheres, with Si or both Pt and Si, respectively. Irradiation was performed in the SEM at room temperature with an accelerating voltage of 30 kV and a beam current of $6\times10^{-7}$ A. The samples were irradiated until a final saturation condition, referred to as morphological, total CL intensity, and CL spectral changes, was reached. The morphology of the samples after irradiation was investigated in a Leica Stereoscan 440 SEM. CL observations were carried out in the 300–1800 nm spectral range using a Hitachi S-2500 SEM. Details of the experimental setup used for CL images and spectra acquisition have been reported elsewhere.[11] CL measurements presented in this work were performed at 80 K with an accelerating voltage of 20 kV and a beam current of 20 nA. No infrared CL was observed in both types of samples after irradiation.

Scanning electron microscopy observations of the infilled opals before irradiation revealed compact and well-ordered layers of $SiO_2$ spheres of about 250 nm of diameter. Figure 1 shows a SEM image of an opal-Si sample irradiated for 50 s. The image shows bending and the formation of cracks in the surface layers, while the opal layers underneath

 

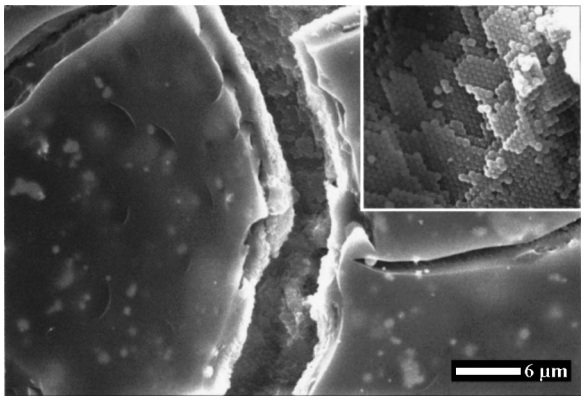


FIG. 1. Secondary electron SEM micrograph of an irradiated opal-Si sample. The inset image ($10\times 9\ \mu m^2$), taken inside the central crack, shows the original ordered structure of the composite.

retained their original ordered structure, as shown in the inset of Fig. 1. Similar structural changes have been previously observed in opal samples after ion implantation and annealing.[12] Both electrical and thermal stresses, respectively associated to electron beam-induced charge trapping and heating, are considered to be responsible of these morphological alterations. Our results agree with previous observations of permanent volume changes induced by electric fields related to electron irradiation in amorphous and crystalline $SiO_2$ samples.[6,13] On the other side, the role of thermal stresses is enhanced by the low thermal conductivity and density of the opal samples, as compared with bulk silicon oxide.[8] We have previously reported the CL properties of the samples used in this work before electron irradiation.[14] Emission bands observed at about 1.9 eV, 2.2–2.4 eV, and 2.7 eV are related to the defect structure of the silica spheres forming the opal matrix, while bands near 3.4 eV and in the 1.50–1.75 eV range were proposed to be related to Si nanocrystals. Representative CL spectra from the opal-Si samples before and after electron irradiation are presented in Fig. 2. Besides an overall CL intensity increase, irradiation induces a significant decrease of the relative intensity of the 1.9 eV band, attributed to nonbridging oxygen hole centers (NBOHC) defects.[5,15] In addition, a clear enhancement of the CL output can be appreciated on the high energy side of the visible spectrum. Gaussian deconvolution of the spectrum

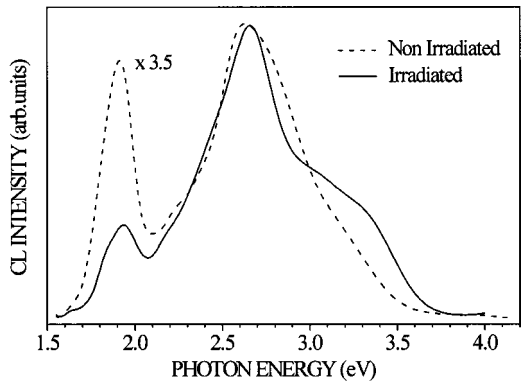


FIG. 2. CL spectra of opal-Si nanocomposites before (dashed line) and after (solid line) electron irradiation.

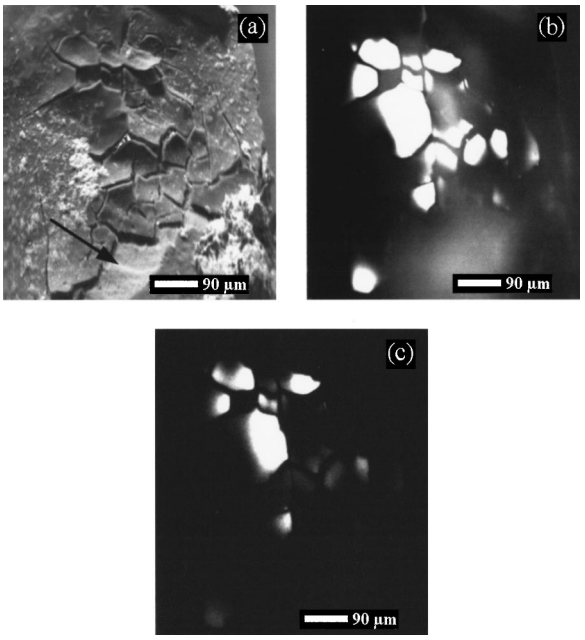


FIG. 3. (a) SEM image of an irradiated opal-Si composite. The arrow marks a nonirradiated region of the sample. (b) Corresponding panchromatic CL image. (c) Monochromatic CL image, acquired at 2.95 eV, of the same area.

has shown that this intensity increase is due both to a slight enhancement of the 3.4 eV band, assigned to twofold coordinated Si defects located at the interface between Si nanocrystals and the silica spheres,[16] and the appearance of a new emission band centered at 2.95 eV. The CL emission related to Si nanocrystals that was observed centered between 1.57 and 1.59 eV in some regions of the opal-Si composites[14] is not detected after electron irradiation. Figure 3(a) shows a secondary electron SEM image of an opal-Si composite irradiated for 55 s. The lower part of the image corresponds to a nonirradiated region. A panchromatic CL image of the same area and a monochromatic CL image acquired at 2.95 eV are, respectively, shown in Figs. 3(b) and 3(c). Both CL images were recorded under the same excitation parameters in the SEM and signal amplification electronic settings. The spectral width of the monochromatic image is about 15 nm. The CL intensity shows an inhomogeneous spatial distribution, but a luminescence enhancement can be observed in the irradiated region. The monochromatic micrograph reveals the appearance of the 2.95 eV emission only in the irradiated material, in agreement with the results presented in Fig. 2.

Contrary to the opal-Si case, irradiation does not alter the opal-Pt-Si nanocomposites' morphology. Actually, no topographical changes have been observed after irradiating the samples for times up to 2 h, which can be explained by the higher electrical and thermal conductivity of these samples, due to the presence of Pt, as compared with that of the opal-Si samples.[2] CL spectra recorded after irradiation substantially differ from those obtained in nonirradiated areas (Fig. 4). Electron irradiation also induces in the opal-Pt-Si samples the appearance of the 2.95 eV CL band, which becomes the dominant emission. Due to the contribution of the 3.4 eV emission the spectra in this region show a peak at about 3.0 eV. Besides, irradiation induces a strong decrease,

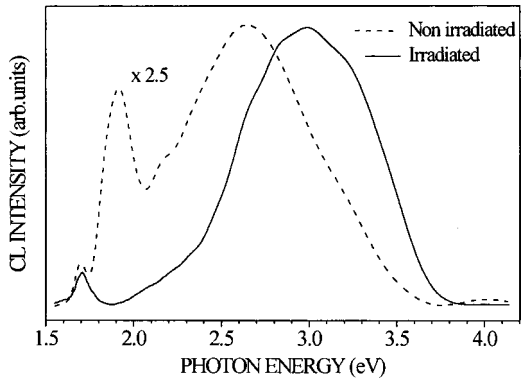


FIG. 4. CL spectra of an opal-Pt-Si sample before (dashed line) and after (solid line) electron irradiation.

or even a complete quenching, of the 1.9 eV CL band, as in the spectrum shown in Fig. 4. Suppression of the 1.9 eV luminescence has been previously reported in ion-bombarded[17] and electron irradiated[13] silica samples due to defects related to radiation damage. In addition, Fig. 4 shows that electron irradiation does not influence the Si nanocrystal-related CL band, centered at about 1.70 eV in the opal-Pt-Si composites.[14] Hence structural changes caused by irradiation in the opal-Si samples appear to modify the defect states at the interface between Si nanocrystals and the silica spheres, which are considered to be responsible of the CL observed between 1.57 and 1.70 eV.[14,18] However, this defect structure is preserved in the opal-Pt-Si nanocomposites where the effect of thermal and electrical stresses is less pronounced. Another significant effect of electron irradiation on the luminescence of the samples is the appearance of the strong emission band centered at 2.95 eV. A CL band centered at 2.93 eV has been observed[19] in crystalline $SiO_2$ and attributed to an irradiation produced intrinsic defect. On the other hand, Kohketsu *et al.*[20] observed a photoluminescence band centered at 3.0 eV in silica melted under vacuum, and attributed it to oxygen divacacies or trivacancies. Our results are consistent with the possibility that electron irradiation under the vacuum conditions of the SEM chamber favors the creation of oxygen vacancy complexes in the opal-based composites. Radiolytic processes leading to the formation of different types of mobile charged oxygen defects in silica have been previously reported.[5,21] Nevertheless, it should be mentioned that the formation of neutral molecular oxygen due to such processes seems in our case not to take place, as suggested by the absence of infrared CL near 0.97 eV.[21]

In summary, electron irradiation in the SEM induces different changes in the morphology and luminescent defect structure of opal-Si and opal-Pt-Si nanocomposites. CL related to Si nanocrystals observed near 1.70 eV is preserved in the irradiated opal-Pt-Si samples, which also retains the ordered structure of the opal matrix. On the contrary, irradiation causes strong morphological changes and quenching of the nanocrystals-related emission in the opal-Si samples. In both types of nanocomposites electron irradiation induces the appearance of an intense CL emission band centered at 2.95 eV, probably related to complex centers involving oxygen vacancies in the silica spheres forming the opal matrix.

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[1] C. Díaz-Guerra, J. Piqueras, V. G. Golubev, D. A. Kurdyukov, A. B. Pevtsov, and M. V. Zamoryanskaya, Appl. Phys. Lett. **77**, 3194 (2000).
[2] V. N. Bogomolov, N. A. Feoktisov, V. G. Golubev, J. L. Hutchison, D. A. Kurdyukov, A. B. Pevtsov, R. Schwarz, J. Sloan, and L. M. Sorokin, J. Non-Cryst. Solids **266–269**, 1021 (2000).
[3] Yu. A. Vlasov, V. N. Astratov, O. Z. Karimov, and A. A. Kaplyanskii, Phys. Rev. B **55**, R13357 (1997).
[4] H. Miguez, A. Blanco, F. Meseguer, C. López, H. M. Yates, M. E. Pemble, V. Fornes, and A. Mifsud, Phys. Rev. B **59**, 1563 (1999).
[5] M. A. Stevens Kalceff, Phys. Rev. B **57**, 5674 (1998).
[6] M. A. Stevens Kalceff, M. R. Phillips, and A. R. Moon, J. Appl. Phys. **80**, 4308 (1996).
[7] W. Stöber, A. Fink, and E. Bohn, J. Colloid Interface Sci. **26**, 62 (1968).
[8] V. N. Bogomolov, D. A. Kurdyukov, L. S. Parfenieva, A. V. Prokofiev, S. M. Samoilovich, I. A. Smirnov, A. Jezowski, J. Mucha, and H. Misiorek, Phys. Solid State **39**, 341 (1997).
[9] V. N. Bogomolov, L. M. Sorokin, D. A. Kurdyukov, T. M. Pavlova, and J. L. Hutchison, Phys. Solid State **39**, 1869 (1997).
[10] V. N. Bogomolov, V. G. Golubev, N. F. Kartenko, D. A. Kurdyukov, A. B. Pevtsov, A. V. Prokofiev, V. V. Ratnikov, N. A. Feoktisov, and N. V. Sharenkova, Tech. Phys. Lett. **24**, 326 (1998).
[11] C. Díaz-Guerra and J. Piqueras, Physica C **275**, 37 (1997).
[12] M. Ajgaonkar, Y. Zhang, H. Grebel, and C. W. White, Appl. Phys. Lett. **75**, 1532 (1999).
[13] M. A. Stevens Kalceff, G. J. Thorogood, and K. T. Short, J. Appl. Phys. **86**, 205 (1999).
[14] C. Díaz-Guerra, D. A. Kurdyukov, J. Piqueras, V. I. Sokolov, and M. V. Zamoryanskaya, J. Appl. Phys. **89**, 2720 (2001).
[15] L. N. Skuja, A. R. Silin, and A. G. Boganov, J. Non-Cryst. Solids **63**, 431 (1984).
[16] H. Z. Song, X. M. Bao, N. S. Li, and X. L. Wu, Appl. Phys. Lett. **72**, 356 (1998).
[17] M. R. Khanlary, P. D. Townsend, and J. E. Townsend, J. Phys. D **26**, 371 (1993).
[18] Y. Kanemitsu, Phys. Rev. B **49**, 16845 (1994).
[19] M. A. Stevens Kalceff and M. R. Phillips, Phys. Rev. B **52**, 3122 (1995).
[20] M. Kohketsu, K. Awazu, H. Kawazoe, and M. Yamane, Jpn. J. Appl. Phys., Part 1 **28**, 615 (1989).
[21] M. A. Stevens Kalceff, Phys. Rev. Lett. **84**, 3137 (2000).