

Photoluminescence of Porous Silicon Carbide in Solvents

Ki-Hwan Lee*, Tae-Ho Lee, Ki-Seok Jeon, Seok-Won Yoon, Seung-Koo Lee,
Hae-Kwon Jeon and Chang-Shik Choi***
Department of Chemistry, Kongju National University, Kongju 314-701, Korea

The relationship between porous surfaces and photoluminescence (PL) behavior of porous silicon carbide (PSC) in various solvents has been studied. The porous surfaces of p-type silicon carbide can be fabricated by electrochemical anodization from the 6H, 15R, 4H- α -SiC substrates in dark-current mode (DCM) condition. We have been investigated the dependence of the PL spectra of PSC under the medium having the different dielectric constants. It has been found that PL depends sensitively on the environment surrounding the surface. The extent of chemically stability on the surface of PSC due to the various solvents was confirmed by reflectance Fourier transform infrared (FTIR) spectroscopy. Detailed IR experiments on the PSC samples were carried out before and after various solvents immersion. These results will be offered important information on the origin of PL in porous structure.

Key words: Photoluminescence, Porous silicon carbide, Dielectric constant

INTRODUCTION

Originally silicon carbide (SiC) has wide band-gap (3.2 eV), high melting point (2,800°C), high thermal conductivity (5.0 W/cm-K) and large breakdown electric field allowing SiC to operate at ultra-high temperature. In particular, SiC has attracted much interest due to its possible applications in blue light emitting diodes [1], ultra-violet photodetectors [2] and chemical sensor [3].

As a matter of fact, much effort has been directed to understanding the photoluminescence (PL) mechanism in porous silicon (PS) [4]. Because control of silicon surface chemistry is crucial to allow access to technologically interesting thin films for fabrication of new electronic devices [5].

Similarly to PS, modification and characterization of photoluminescent porous silicon carbide (PSC) surfaces has become a growing interest since Shor *et al.* [6] has been first reported the formation of porous silicon carbide (PSC) by subjecting a bulk n-type 6H-SiC crystal to electrochemical etching in 2% aqueous HF solution under UV illumination. The mechanism of visible light emission from PSC is currently under discussion. Danishevski *et al.* [7~9] were observed intense photoluminescence (PL) and polarization phenomenon of PSC by methods of vibrational and luminescence spectroscopy. In case of PS, Gelloz *et al.* [10]

proposed that the use of anodic oxidation of PS as a post-treatment has dramatically improved the electroluminescence (EL) external quantum efficiency and the stability from a device based on a thin transparent indium tin oxide contact on porosified n⁺-type silicon. It indicates that this particular kind of oxidation state can be played an important role of PL and EL of PS. The PL behavior of PSC was attributed to quantum confinement effect arising from isolated nanometer-size SiC features [4] as well as the chemical surface state of PSC [11]. The phonon-assisted hopping process could be a candidate too for PL of PSC [12, 13]. Buyanova *et al.* [14] proposed that the appearance of the given PL band is attributable to the absorption of light by a sensitizer on its (porous Si) surface and the subsequent transfer of excitation to luminescence centers. Many studies have been widely acknowledged that oxidation has been devoted to improving the efficiency and stabilizing the PL property. However, it is still required a deep understanding of the origin of PL. In case of PS, the PL of PS depends sensitively upon environment of the surface, especially when the material is immersed in a liquid electrolyte, has been recently reported [15]. In particular, this strong sensitivity of the photoluminescent PS surface presents the potential for application of this material in chemical sensors. However, we didn't find the report on the PL phenomenon of PSC in various solvents having dielectric constant. Thus we believe that the interaction between porous surface of PSC and dielectric solvents will be expected to contribute for the characterization of PL mechanism as well as the possibility of chemical sensors.

In this work, we have been demonstrated that the porous p-type silicon carbide can be fabricated by electrochemical anodization from the 6H, 15R, 4H- α -SiC substrates in dark-current mode (DCM) condition. We have been investigated

*To whom correspondence should be addressed.

E-mail : khlee@kongju.ac.kr

Received Dec. 15, 2005 Accepted Dec. 27, 2005

***Present address: Department of Oriental Medicine Resources,
Far East University, Emuseong 369-851, Chungbuk, Korea
TEL: (043)879-3708

E-Mail: cschoi@kdu.ac.kr

the dependence of the PL spectra on the dielectric constant of the embedding medium. The extent of chemical stability on the surface of PSC due to the various solvents was confirmed by reflectance Fourier transform infrared (FT-IR) spectroscopy. These results will be offered important information on the origin of luminescence in porous structures.

MATERIALS AND METHODS

The sample studied in this work was purchased from Elektroschmelzwerk Kempten GmbH in Germany. This sample consisted of α -SiC, crystal polytypes 6H, 15R and 4H. A silver contact was evaporated on the back side of the wafers. The anodization cell was made of Teflon, with a platinum wire as a cathode contact. The sample was anodized at a current density 30 mA/cm² with etching time period 30 min in 25 vol.% (HF : H₂O : C₂H₅OH = 1 : 1 : 2) HF solution in dark-current mode (DCM) condition. The PSC surface was rinsed with ethanol and dried under N₂ flow. As soon as the etching process finished, the samples were kept in darkness.

PL and PLE of porous silicon carbide were measured by spectrofluorometer (SLM8100, SIM AMINCO, USA) in atmosphere and various solvents; hexane, diethyl ether, isopropanol, acetone, ethanol, methanol, and water, respectively. Also, the reflectance infrared spectra of PSC were investigated before and after treatment with various solvent by FT-IR spectrometer (AVATAR360, Nicolet, USA).

RESULTS AND DISCUSSION

Figure 1 shows the PL spectra of PSC sample under various excitation wavelengths at room temperature. Two emission bands, a high energy band at about 492 nm and a low energy band at about 526 nm are observed. The PL band intensity strongly depends on the excitation wavelength, although the peak energy position does not change. These two dominant emission bands of PSC compared to initial sample are significantly different. This implies not only a difference in

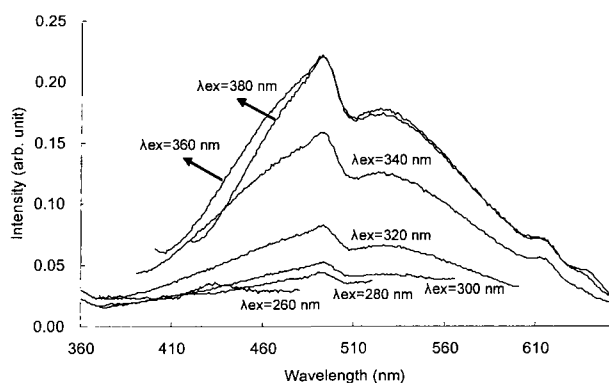


Figure 1. PL spectra of PSC sample under various excitation wavelengths at room temperature.

the basic physical nature of the excitation sources and emitters but also an importance of relationship between crystallite structures due to the different preparation conditions. Moreover, the results clearly indicate that the two-band PL spectra are due to the PSC porous layer because the initial sample has not shown the spectrum in the same range at room temperature [16].

To investigate the factor affecting the PL spectra, we obtained the photoluminescence excitation (PLE) spectra of the sample under various emission wavelengths as shown in Figure 2. The PLE spectra consist of two components—an ultraviolet component, which is represented by a structural maximum in the region 300–380 nm, and a visible component, which is represented by a section of broadening band with increasing emission wavelengths in the region 380–500 nm. The position of the PLE band maximum of the visible component depends on the wavelength of the emission light. It indicates that the PL is due to a superposition of two bands, one of which is excited in the visible range PLE band and the other one is excited in the ultraviolet band. In particular, the visible range PLE band is assumed that a different peak excitation energy is reflected in the different sizes and states of the nanostructured samples [17].

In order to observe the surface state of samples, we have been investigated the dependence of PL spectra in the presence of the liquid electrolytes having different dielectric constants. We have measured the PL spectra of samples in various organic solvents.

Figure 3 shows a plot of the PL quenching ratio (I/I_0) which was determined as the ratio of PL intensity before (I_0) and after (I) exposure to the solvent, at maximum emission wavelengths (blue band, 492 and green band, 526 nm, respectively), as a function of dielectric constants. The PL quenching ratio (I/I_0) of PSC sample drops by about three orders of magnitude when PSC is immersed in organic solvents of dielectric constants varying from 2 to 20. It indicates that PL depends sensitively upon surface environment. This quenching process may be ascribed to the creation of surface

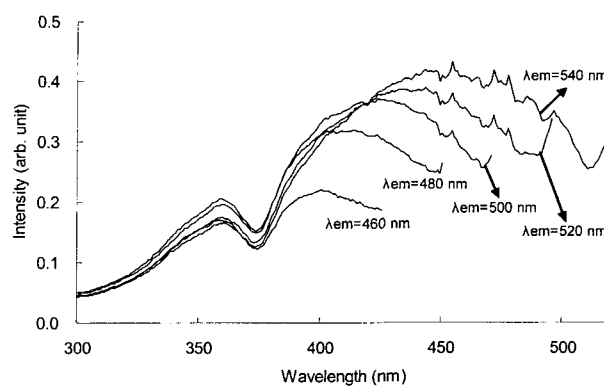


Figure 2. PLE spectra of PSC sample under various emission wavelengths at room temperature.

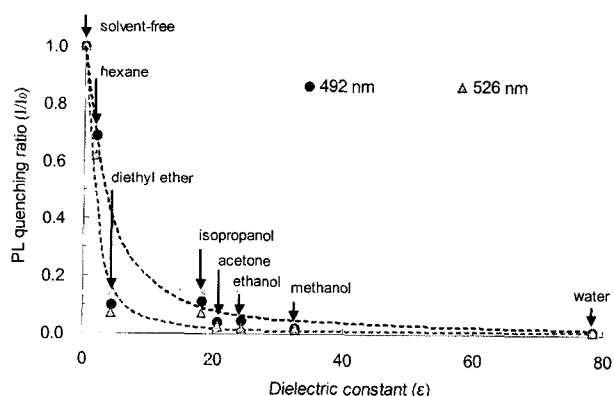


Figure 3. Plot of the PL quenching ratio (I/I_0) at maximum emission wavelengths, as a function of dielectric constants.

recombination centers by the adsorbed polar solvent molecules [18]. Thus, the electron and hole will recombine much more non-radiatively than the radiative recombination efficiency. Simultaneously, the PL quenching by electrolytes is stronger for the green region emission than that for blue region emission. Also, the profile of the quenching leads to nonlinear plot as a function of dielectric constant. It may be provided that the evolution of the PL is considered as an indication of a chemical modification, for example, partial dissolution, oxidation, or chemical substitution of the surface hydrogen of the porous layer at the liquid contact [15]. Therefore, we need to investigate the additional quenching due to the interaction of the solvent polar molecules with the surface.

From the IR study, we can see that PSC surfaces are considered as an indication of a chemical modification of PSC at the solvent contact. The IR spectrum has been shown that Si-C bond (760 cm^{-1}), which could be found from the initial substrate, can be easily broken when the etched process takes place (Figure 4). The surface becomes rich on C-H (960 and 990 cm^{-1}) [19], Si-O-Si (460 and 1190 cm^{-1}) [20] and O-Si-H

bond (2250 cm^{-1}), which are considered to increase in the oxygen component. It means a possibility for oxides to form during the sample washing and drying stage after electrochemical etching. Consequently, the PL characteristics of PSC can also change by influence of the creation of the reduced radiative recombination centers by the adsorbed polar solvent molecules containing oxygen. After the liquid electrolytes are evacuated, the Si-O-Si bond vibration has been disappeared on porous layer. Absorption bands associated with vibrations of S-H_x polysilanes bonds due to hydrogenation in the region $2300\sim 2400\text{ cm}^{-1}$ also increased. Thus, photoluminescence quenching may plausibly be ascribed to the creation of non-radiative recombination centers which is eliminated oxides by the adsorbed polar solvent molecules. Therefore, in case of blue and green regions of PL as shown in Figure 2, the origin of PL comes from the different kinds of mechanism. Thus it suggests that the PL of green region depends sensitively upon the oxidation state of porous surface as an indication of a chemical modification. Meanwhile, the origin of the blue PL band still lies within the nanostructured porous layer. In other words, PL spectra of PSC could be associated to the radiative recombination on the oxidation surface via the C-H and Si-O-Si bonds as well as quantum confinement effects depending on layer porosity.

In conclusion, we fabricated the porous surfaces of p-type silicon carbide by electrochemical anodization from the 6H, 15R, 4H- α -SiC substrates in dark-current mode (DCM) condition. In order to investigate the relationship between porous surfaces and photoluminescence (PL) behavior of porous silicon carbide (PSC) in various solvents, we were used the medium having the different dielectric constants. The dependence of PL spectra in the presence of the liquid electrolytes having different dielectric constants was shown that the profile of the quenching leads to nonlinear plot as a function of dielectric constant. These results allow us to conclude that PL of green region depends sensitively upon the

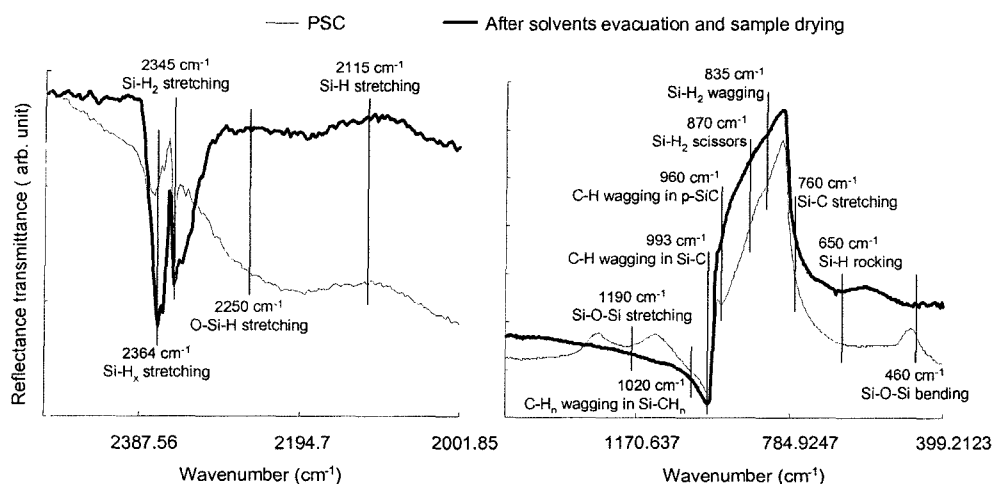


Figure 4. FT-IR spectra of as-prepared PSC and the same one after solvents evacuation and drying.

oxidation state of porous surface and PL of blue region depends on the quantum confinement effects due to the nanostructured porous layer.

ACKNOWLEDGMENTS

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (grant No. R05-2002-000-00946-0) and Kongju National University.

REFERENCES

- Mimura, H., T. Matsumoto and Y. Kanemitsu (1996) Light emitting devices using porous silicon and porous silicon carbide. *Solid State Electronics* **40**, 501-504.
- Powell, J. A., L. G. Matus and M. A. Kuczumski (1987) Growth and characterization of cubic SiC single-crystal films on Si. *J. Electrochem. Soc.* **134**, 1558-1564.
- Lin, V. S. Y., K. Motesarei, K. P. S. Dancil, M. J. Sailor and M. R. Ghadiri (1997) A porous silicon-based optical interferometric biosensor. *Science* **278**, 840-843.
- Canham, L. T. (1990) Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers. *Appl. Phys. Lett.* **57**, 1046-1048.
- Linford, M. R., P. Fenter, P. M. Eisenberger and C. E. O. Chidsey (1995) Alkyl monolayers on silicon prepared from 1-alkenes and hydrogen-terminated silicon. *J. Am. Chem. Soc.* **117**, 3145-3155.
- Shor, J. S., I. Grimberg, B. Weiss and A. D. Kurtz (1993) Direct observation of porous SiC formed by anodization in HF. *Appl. Phys. Lett.* **62**, 2836-2838.
- Danishevski, A. M., V. B. Shuman, A. Yu. Rogachev and P. A. Ivanov (1995) Investigation of porous silicon carbide by methods of vibrational and luminescence spectroscopy. *Semiconductors* **29**, 1106-1111.
- Danishevski, A. M., V. B. Shuman, E. G. Guk and A. Yu. Rogachev (1997) Intense photoluminescence of porous layers of SiC films grown on silicon substrates. *Semiconductors* **31**, 354-358.
- Danishevski, A. M., A. Yu. Rogachev, V. B. Shuman and E. G. Guk (1997) Polarization memory in an oxidized porous SiC layer. *Semiconductors* **31**, 1196-1199.
- Gelloz, B., T. Nakagawa and N. Koshida (1998) Enhancement of the quantum efficiency and stability of electroluminescence from porous silicon by anodic passivation. *Appl. Phys. Lett.* **73**, 2021-2023.
- Shin, W., W. Seo, O. Takai and K. Koumoto (1998) Surface chemistry of porous silicon carbide. *J. Electronic Mater.* **27**, 304-307.
- Rusli, G., A. J. Amaratunga and J. Robertson (1996) Polarization memory of photoluminescence in amorphous carbon. *Phys. Rev. B* **53**, 16306-16309.
- Masumoto, Y., H. Kunitimo, S. Shionoya, H. Munekata and H. Kukimoto (1984) Polarization memory of luminescence from photo-generated carriers in a-Si_xC_{1-x}:H (x~0.2). *Solid State Commun.* **51**, 209-212.
- Buyanova, I. A., I. A. Gorodetski, N. E. Korsunskaya, A. U. Savchuk and M. K. Shenkman (1996) Sensitized luminescence of porous silicon and its polarization characteristics. *Semiconductors* **30**, 797-801.
- Fellah, S., F. Ozanam, N. Gabouze and J. N. Chajalviel (2000) Porous silicon in solvents: Constant-lifetime PL quenching and confirmation of dielectric effects. *Phys. Stat. Sol. (a)* **182**, 367-372.
- Lee, K. H., Y. L. Du and T. H. Lee (1999) Optical Characteristics of Porous Silicon Carbide by Photoluminescence Spectroscopy. *J. Photoscience* **6**, 183-186.
- Lee, K. H., Y. L. Du and T. H. Lee (2000) Photoluminescence and Photoluminescence Excitation from Porous Silicon Carbide. *Bull. Korean Chem. Soc.* **21**, 769-773.
- Lauerhaas, J. M., G. M. Credo, J. L. Heinrich and M. J. Sailor (1992) Reversible luminescence quenching of porous silicon by solvents. *J. Am. Chem. Soc.* **114**, 1911-1912.
- Parkhutik, V. P., F. Namavar and E. Andrade (1997) Photoluminescence from thin porous films of silicon carbide. *Thin Solid Films* **297**, 229-232.
- Koropecski, R. R., R. D. Arce and J. A. J. Schmidt (2004) Infrared studies combined with hydrogen effusion experiments on nanostructured porous silicon. *J. Non-Cryst. Solids* **338-340**, 159-162.