

OPTICAL CHARACTERISTICS OF POROUS SILICON CARBIDE BY PHOTOLUMINESCENCE SPECTROSCOPY

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Abstract – We have been prepared the porous silicon carbide (PSC) by electrochemical etching of silicon carbide single crystals. Samples of PSC have been studied by the methods of scanning electron microscope (SEM) and photoluminescence (PL). Two PL bands attributed to the blue and green light emission were observed in this study. According to the anodization conditions, the main source of emission in the oxidized layers of PSC lies in the different surface defect centers which consist of different geometrical structures due to the polytypes. It means that origin of these PL bands may be existed in different size pores simultaneously. The present results indicate that the high energy band comes from the top porous layers while the low energy band comes from the lower porous layers.

INTRODUCTION

Still nowadays, light-emitting semiconductor devices are fabricated almost absolutely from direct-band gap semiconductors such as gallium arsenide and indium phosphide. In the fall of 1990, however, Canham reported that one could obtain visible photoluminescence (PL) from porous silicon (PS) layers formed on the surface of an indirect-band gap silicon wafer at room temperature¹. Afterwards, the PL of PS has been studied for several years and the range of PL bands has been extended from red¹, green², blue³ through recently ultraviolet^{4,5} regions. The blue light is one of the three primary colours in nature including red and yellow. The display technologies require red, green, and blue devices but shorter wavelength region like blue devices has not been established completely. Therefore, it is important for realizing a full-colour display. Much of the investigation has concentrated on the stable blue light emission material. However, there exist the problems of the stability and the optical efficiency of PS. When the as-grown PS was illuminated or stored in air, its PL has been degraded with time.^{6,7}

Silicon carbide (SiC) is known as a very interesting material which has the prospects of fabrication of intense blue-green light-emitting diodes (LED).^{8,9} SiC has many crystal structures, that is, polytypes, which are classified by the stacking sequence and cycle along the c-axis direction.¹⁰ One of polytypes is due to long unit cells, many inequivalent sites

existing for 4H, 6H, and 15R SiC. These inequivalent sites are divided into two kinds. One is a cubic-like arrangement of first-and second-neighbor atoms, B atom in the sequence of ABC in the close-packed structure and the other is a hexagonal-like arrangement, B atom in the sequence of ABA.¹⁰ The crystals studied were α -SiC of several hexagonal and rhombohedral polytypes of 4H, 6H, and 15R. To our best knowledge, there is no report on the formation of porous polytype SiC structures using the electrochemical etching techniques with and without light similar to those for porous Si, although there have been some reports on the photo-electrochemical etching of 6H-SiC¹¹ and β -SiC.^{12,13}

In this paper, we report that the fabricated porous SiC has been produced a homogeneous pore size in spite of its polytype structures. And the blue light emission with the maximum around 460 nm and the green light emission with the maximum around 540 nm were observed for each condition of photo-assisted etching (PA) and dark-current mode (DCM).

MATERIALS AND METHODS

The samples used were purchased from Elektroschmelzwerk Kempten GmbH in Germany. These samples consisted of α -SiC, crystal polytypes 4H, 6H, and 15R. The initial SiC wafers cut into small pieces (1 cm \times 1 cm or 5 mm \times 5 mm) and Ag for a good ohmic contacts were deposited on the back side of SiC samples. External platinum wires were attached to the contacts. The SiC electrode was placed into a teflon electrochemical cell, along with a Pt wire counter electrode in a solu-

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tion of 25%vol. (HF:H₂O:C₂H₅OH=1:1:2) HF. Two samples were anodized at a current density, 30 mA/cm² for 30 min. But the different experimental conditions in this case were used. In sample A, anodization was carried in the dark. In sample B, anodization was carried out with light irradiation using a 150 W Xenon UV lamp with 220~400 nm wavelength range (power 15mW/cm²).

Scanning electron microscopy (SEM) has been used to characterize the pore formation on the porous SiC layer.

Photoluminescence excitation (PLE) and PL spectra were recorded by a SLM8100 spectrofluorometer with a 450 W Xe arc lamp light source and 4 nm bandpass excitation and emission monochromators. The fluorescence of a rhodamine B solution was used as a reference to correct a variation of the Xe light source with time and wavelength.

RESULTS AND DISCUSSION

Figure 1 shows the SEM images of sample A and B, respectively. The sample A and B have the localized etching non-uniformities occurred along the defect. However, the existence of pores is confirmed by the bright areas which are devoid of any matter. The material prepared under dark-current conditions, labeled sample A has a variable morpholo-

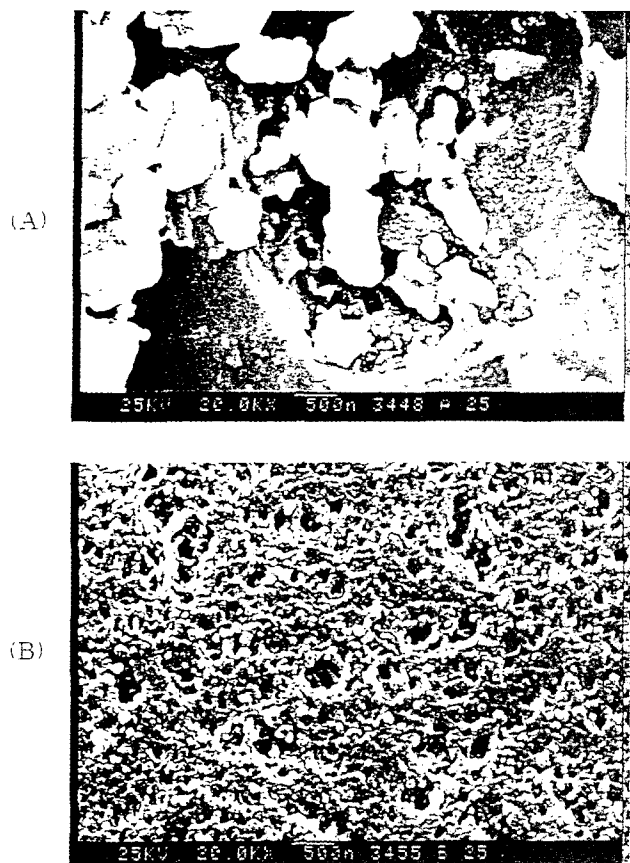


Figure 1. SEM images of samples A and B, respectively.

gy dominating nm size, whereas for material obtained in the photoassisted process, labeled sample B has much more homogeneous relative to sample A. And the pore size of B is much smaller and thickness is much less than observed in A. However, the comparison of two porous silicon carbides (PSCs : sample A and B) with bulk SiC have shown that the pore morphology varied somewhat across the surface of sample. It will be indicated that may be due to variations in the pore morphology as a function of thickness of porous layer and may be attributed to non-uniformities in the photochemical process, such as the UV intensity or the localized electrode potential.¹⁴

In addition, it is likely that the preferential dissolution of nearest neighbor pore leads to the pore-pore overlap when the porous α -SiC is fabricated by means of electrochemical anodization as shown in Figure 1. These results indicate that the substrate's porous layer has shown a possibility to form multi-layers such as superlattice.

Figure 2 shows the PL spectra taken from samples formed under various preparation conditions. The spectra have been measured at room-temperature using an ultraviolet (340 nm) excitation light. A two-band spectra structure is obtained for an atmospheric stored PSC samples. The two spectra are quite similar in the emission wavelength range and they are well distinguished by the main two bands, respectively. On the other hand, the PL peak values of sample A are 494 and 534 nm and the PL peak values of sample B are 455 and 522 nm, respectively. These luminescence peak positions observed are below the band gap (430 nm) of the SiC crystal. For sample B, the integration ratio of the shorter wavelength blue band (380 ~ 510 nm) and the longer wavelength green band

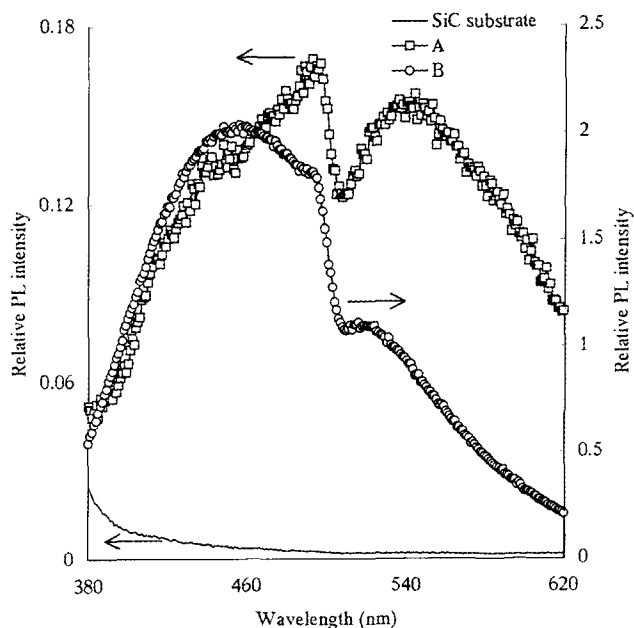


Figure 2. PL spectra of samples A and B, respectively, at excitation wavelength 340 nm.

(510 ~ 620 nm) is almost the same. However, the integration ratio of two bands in sample A is quite different, that is, the blue band is 5 times larger than that of the green band. Also, the blue band of sample A is one order larger than that of sample B. This implies not only a difference in 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 spectrum is due to the PSC layer because the initial sample has not shown the spectrum in the same range at room temperature. This is quite similar result with that of porous silicon.¹⁵ Xie et al. reported that the PL of porous silicon exhibits a broad Gaussian spectrum with a bandwidth of which range from 180 to 200 nm (FWHM), possibly due to a structural inhomogeneity.¹⁵

The presence of more than one emission band in the PL spectrum of a molecule is indicative that emission is occurring from more than one chemical species and/or different pore sizes. Most often, impurities account for extraneous emission bands. But it is not the case, that is, the two-band phenomenon observed in PL spectrum suggests that there are two main different luminescent objects on the corresponding different size distribution, one is lower energy band due to excitation of inner crystallites. Because the removal of porous layer has been disappeared high-energy band (data not shown). The other one is that higher energy band seems to be hydrogenated amorphous silicon carbide by oxidation with the much smaller pore sizes during the electrochemical treatment.

Zhang *et al.*¹⁶ reported that high energy band in the PL spectra of PS is due to oxidation in atmospheric storage and low energy band is probably related to the size of the remnant Si in PS. It was pointed out that the PS energy gap is widened by quantum confinement effect (QCE) and increases rapidly when the size of Si is less than 5 nm.¹⁷

Comparing the results of the present study with those of previous work,^{12,18} our PL spectra were similar to previously published steady-state PL spectra obtained at room temperature.¹⁸ However, our energy band shifted 20 nm to higher energy band comparable to Konstantinov *et al.* results¹⁸. They concluded that the origin of the PL as related to surface defect centers introduced by the reaction of HF at the surface of SiC.

To investigate the factor affecting the PL spectra, we obtained the PLE spectra of sample A and B at the emission wavelength, 540 nm, as shown in Figure 3. It can be seen that PLE spectra consist of two main bands, that is, the 380~500 nm region of the lower excitation band with the maximum around 380 nm (sample B) and 440 nm (sample A) respectively, and the 300~380 nm region of the higher excitation band with the maximum around 335 nm (sample A) and 330 nm (sample B), respectively. In sample B, the

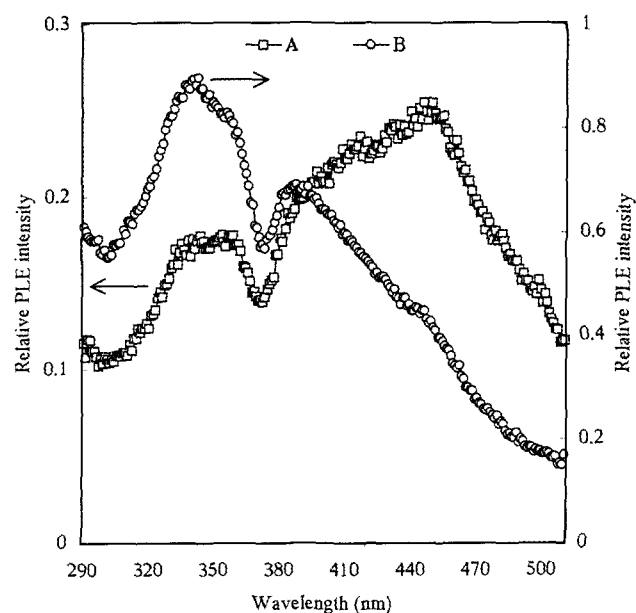


Figure 3. PLE spectra of samples A and B, respectively, at emission wavelength 540 nm.

higher excitation band is smaller than that of the lower excitation band, while the higher excitation band is larger than of the lower excitation band in sample A. And the large Stokes shift observed in the PLE spectrum result. It indicates that the luminescent emission primarily occurs via relaxed electronic states, i.e., the states that have the largest absorptive oscillator strength are not the states through which the photoexcited electron-hole pairs radiatively recombine.¹⁵ We can confirmed that the shapes and intensity of PLE spectra depend on the etching condition. Therefore, the different appearance in the PLE spectra of sample A and B is primarily due to different sizes of their absorbing medium occurring with anodized etching. Generally the fluorescence emission spectrum appears to be a mirror image of the absorption spectrum, specifically the absorption representing the S_0 to S_1 transition. In many molecules these energy levels are not significantly altered by the different electronic distributions of S_0 and S_1 . But it is not shown the symmetry behavior in this case. Such deviations from the mirror image rule may be reflected a different geometric arrangement of nuclei in the excited state as compared to the ground state or the different size distribution of interquantum dots. Of course, this behavior is considered in semiconductor quantum crystallites and amorphous semiconductor luminescence as well.

As described above, the PLE spectra show the nonmonotonic character between PLE and PL of sample A and B, respectively. Two possible assumptions are suggested in this study. One can be assumed that it may be due to the overlapping between the long wavelength edge of excitation and the short wavelength edge of emission band. The other one can be assumed that a different peak excitation energy

is reflected in the porosity differences of the samples due to the polytypes.

From the point of view on the porosities, our results suggest that the average nanocrystal size in the top layers must be smaller than the average size in the lower layers with similar to porous silicon.¹⁹ We conclude that there is correlation between the different size of pores and the optical properties of the PL and the two bands of the PL excitation spectrum correspond to two different main absorption centers. That is, the high energy band (blue region) comes from the top porous layers while the low energy band (green region) comes from the lower porous layers. However, further work is needed to determine why the PL spectra should cause changing according to the etching conditions.

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