Articles

Photoluminescence and Photoluminescence Excitation from Porous Silicon Carbide

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Received September 20, 2000

The dependence of photoluminescence (PL) and photoluminescence excitation (PLE) on preparation conditions and the aging of porous silicon carbide (PSC) have been investigated. The fiber size of the material prepared under dark-current mode, labeled DCM, was larger than that of the photoassisted (PA) process. The intensity of the PL spectrum for the PA condition was higher than that of the DCM condition. The PA condition giving small fiber size exhibited a more prominent high-energy component but the emission bands of both conditions observed were rather similar. The origin of the PL may have played an important role in the surface defect center introduced by the reaction conditions of HF at the surface of the silicon carbide. Selective excitation of the PL bands using different excitation wavelengths has been used to identify distinct components within the PL bandwidth. Two main PL bands with peak wavelength of 494 and 534 nm were clearly resolved. On the other hand, selective emission of the PLE bands using different emission wavelengths has been used to identify distinct components within the PLE bandwidth. The higher energy band with peak wavelength of 338 nm and the lower energy bands involving 390, 451 and 500 nm were clearly resolved. According to the prolonged aging in air, PL spectra appeared as one band. This emission probably originated from states localized to the band-to-band recombination due to the oxidation on the crystallite surface.

Introduction

During the past several years silicon carbide (SiC) has attracted much interest because it exhibits wide band-gap (2.2 eV), high melting point (2,800), high thermal conductivity (0.255 W/cm) and a large breakdown electric field, allowing SiC to be used at ultra high temperature.[1-3] In addition, anodized porous SiC exhibits interesting optical properties, which are used in blue light emitting diodes and ultraviolet photodetectors.[4]

For other semiconductor materials, specifically Si, porous silicon has been studied in a number of papers.[5-7] The light visible luminescence efficiency observed in porous silicon-based light-emitting diodes has brought considerable attention to this phenomenon. However, this material lacks luminescence stability. Porous silicon carbide (PSC) is a candidate with higher band energies, wider band gap and better stability than porous silicon.[8]

To our best knowledge, there are no reports on the polytypes, 4H, 6H, 15R-α-SiC, where α is the hexagonal crystallographic structure, although there are several reports on the single crystalline β (cubic) SiC[9] and 6H-SiC.[4,10]

In this paper, we present the photoluminescence (PL) and the photoluminescence excitation (PLE) of PSC formed under various preparation conditions. We obtained intense blue-green luminescence of two orders of magnitude stronger than that produced by substrate SiC. Also, we obtained stable PL with PSC samples aged in ambient conditions for more than 1 year.

Experimental Section

The samples studied in this work were purchased from Elecktroschmelzwerk Kempten GmbH in Germany. These samples consisted of α-SiC, single crystal polytypes 4H, 6H and 15R. SiC takes the form of many different crystal structures (called polytypes), which are classified by the stacking sequence and cycle along the c-axis direction. The sample used is a stacking sequence 4H hexagonal (or α) (---ABCBABCB---), 6H hexagonal (---ABCACB---) and 15R rhombohedral (---ABCACBCABACABCB---).[11,12] We determined p-type (1×10^{-12} cm^{-3}) by a hall effect measurement by the Van der Pauw method. The crystal was cleaned first with trichloroethylene (99.5 wt.%) at temperature range 60-80 °C for 10 min. immediately followed by a N$_2$-gas (99.999%) drying and then rinsed with acetone before washing with water for 5 min. again followed by a N$_2$-gas drying.

The size of the samples were 10×10 or 5×5 with a squared shaped area of 100 mm^2 or 25 mm^2 exposed to the electrolyte. In order to achieve ohmic contact, Ag was sputtered on the back side of the SiC crystal. The sample was mounted in an electrochemical cell made from Teflon and connected to a potentiostat/Galvanostat (Hokuto Denko, HA-151) with a Pt wire as a counter electrode in 25 vol.% (HF : H$_2$O : C$_2$H$_5$OH =1 : 1 : 2) HF solution. The samples were anodized at a current density in the range 10-50 mW/cm^2, with the use of UV photo-assistance (PA, 220-400 nm, 15 mW/cm^2, 150W Xenon lamp with 200-400 nm band pass filter, sample name : B-25)

and in the dark-current mode (DCM, sample name : A-25) with etching time of period 30 min.

To investigate the pore formation of the surface layer we used electron microscopy (SEM, TOPCON, ABT-150F, Japan).

The PLE and PL spectra were recorded on a SLM8100 spectrofluorometer with a Xe arc lamp light source and 4 nm band pass excitation and emission monochromators. The fluorescence of a rhodamine B solution was used as a reference to correct for variation of the Xe light source for time and wavelength. Sample aging was in ambient conditions. The PLE and PL spectra of the aged samples were obtained exactly as in the fresh samples.

Results and Discussion

Figures 1 and 2 show the PL spectra obtained from the PSC of DCM and PA conditions, respectively. The two spectra are quite similar and are well distinguished by the two main bands. The PL peak values of the DCM condition are 494 nm and 534 nm, respectively. The PL peak values of PA condition are 493 nm and 522 nm, respectively. These luminescence peak positions are less than the band gap of the SiC crystal (430 nm). The integration ratio of bands differ significantly with the shorter-wavelength blue band being 5 times larger than that of the longer-wavelength green band in the PA condition. For the DCM condition the integration area of the shorter-wavelength blue band is similar to that of the longer-wavelength green band. In both conditions, the shorter-wavelength blue band of the PA condition is 2 times larger than that of the DCM condition.

This implies not only a difference in the basic physical nature of the excitation sources and emitters but also the importance of the surface formation relationship between
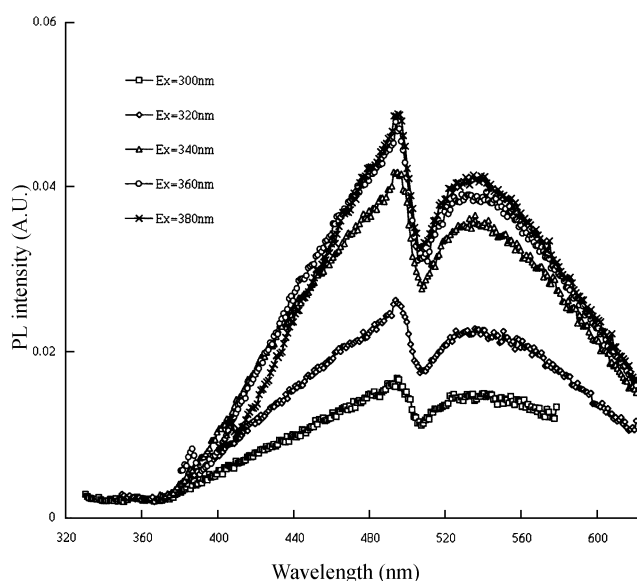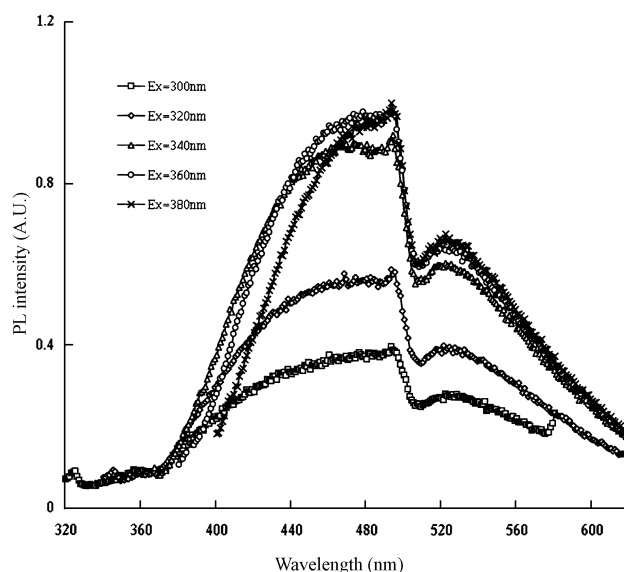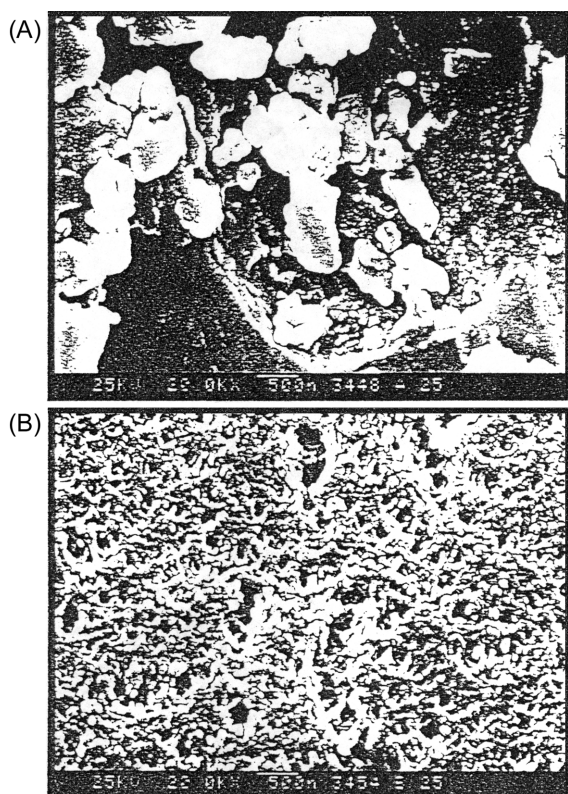

Figure 2. Photoluminescence spectra of B-25 porous SiC immediately after preparation for varoius excitation wavelengths at room temperature.

crystallite structures due to the different preparation conditions employed. It indicates that 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.

The origin of PL selective excitation of the PL bands using different excitation wavelengths has been used to identify distinct components within the PL band width. This variation in the excitation wavelength appears to be a useful tool for the selective excitation of PL bands and for the analysis of the spectra structure.

The two main PL bands with peak values of 493 and 522 nm in the PA condition are clearly resolved. The shapes of the PL spectra observed are independent of the excitation wavelength used, depending on only the excitation intensity. The PL of the PA condition has a relatively higher energy component compared to that of the DCM condition. This fact will be assumed for the higher energy component, which is enhanced under conditions that give a smaller pore size, as reported Konstantinov *et al.*[13] In fact, we have investigated the correlation between PL energy component and pore size of PSC. The SEM images of both samples of the PA and DCM conditions are shown in Figure 3. The images show a significant difference between the structures of the two conditions of material. It appears that the pore size of the PA condition is much smaller and the thickness is much less than that observed for the DCM condition. Also, our PL spectra observed are qualitatively similar to those reported by them.[13] However, the higher energy side of the emission with a peak value of 493 nm in the present study is blue shifted compared with that of the reported emission with a peak value of 510 nm. Their samples were different polytypes, 4H, 6H and 3C. This accounts for the difference between the band gap energy of this polytype and that of the different polytypes.

Figure 1. Photoluminescence spectra of A-25 porous SiC immediately after preparation for various excitation wavelengths at room temperature.

(A)

(B)

Figure 3. SEM images of PSC layers in DCM condition (A) and PA condition (B), respectively.

Figures 4 and 5 show the PLE spectra obtained from the PSC of the DCM and PA conditions, respectively, on the basis of an investigation of the PL spectra. These PLE spectra show an asymmetric shape, which indicates inhomogeneous broadening due to the mixed energy states of various fiber size pores.

We have resolved the dependence of the PLE band from 300 to 530 nm with the various emission wavelengths of
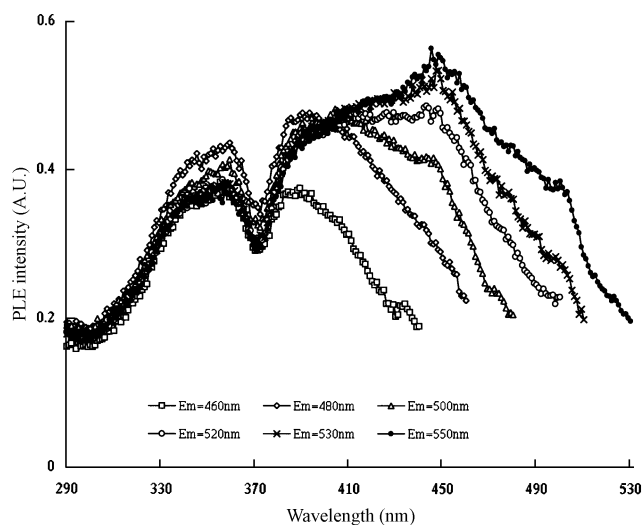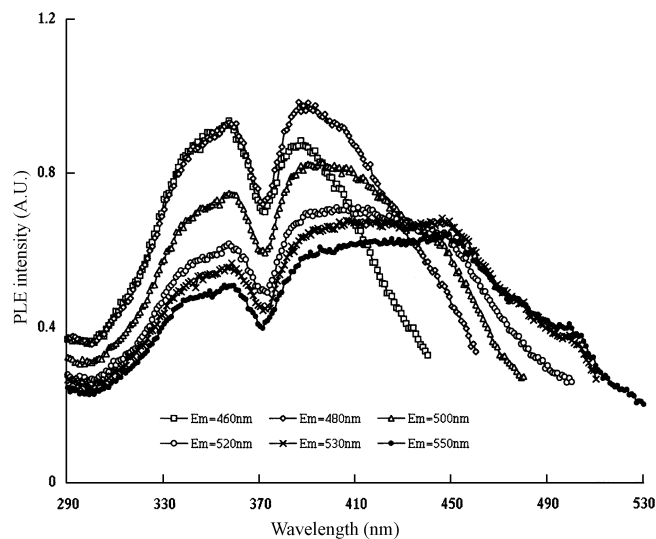
porous SiC, according to the conditions of material preparation. It consists of two main excitation bands: 500 nm-380 nm and 360 nm-330 nm. The shapes depend on the etching condition and the excitation intensity of the 360 nm-330 nm band in the PA condition is larger than that of the 500 nm-380 nm band in DCM. The 500 nm-380 nm band, including several sub-bands dependent on the emission energies of the sample in PA, is clearer and stronger than that of DCM. The 360 nm-330 nm band includes the two sub-bands, 338 nm and 358 nm, and the excitation intensity of the 338 nm band in the PA condition is larger than that of the 358 nm band in DCM. In both cases, PLE spectral peak positions tend to increase as the PL peak energy shifts to higher energies. This indicates that PL spectra from PSCs are a result of the separate excitation processes.

As one can see from the above results, the two main bands have several distinguishable sub-bands. Therefore, the origin of PL may play an important role on the surface defect center introduced by the reaction conditions of HF at the surface of silicon carbide. We have investigated the PL peak to determine whether its origin lies within the porous layer or stems from excitation of the SiC substrate underneath. In order to separate the contributions from the SiC substrate and the PSCs surface, we performed PL spectra measurement as shown in Figure 6. Figure 6 shows only the luminescence bands of PSC of both conditions. This indicates that the porosity on the surface states of PSC are related to the origin of PL.

Matsumoto *et al.*[4] concluded that the increase in luminescence intensity and the blue shift of the luminescence peak as a function of current density are related to the increase in porosity. That is, the surface region of porous SiC is responsible for the intense blue-green luminescence.

In addition, it is important in respect to stability that the change takes place in the PL spectra and the PLE spectra during aging of PSC samples in ambient conditions. How-

Figure 4. Photoluminescence excitation spectra of A-25 porous SiC immediately after preparation for various emission wavelengths at room temperature.

Figure 5. Photoluminescence excitation spectra of B-25 porous SiC immediately after various emission wavelengths at room temperature.
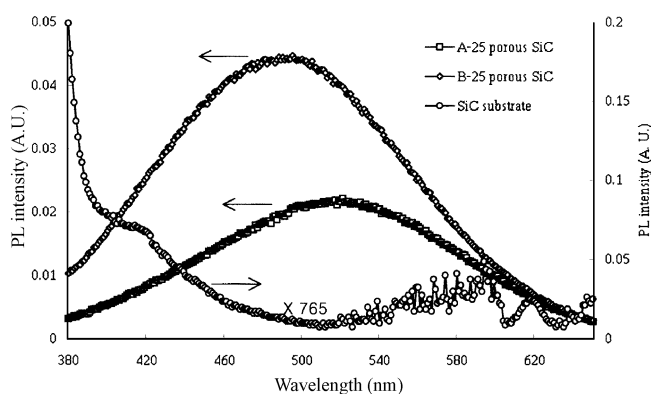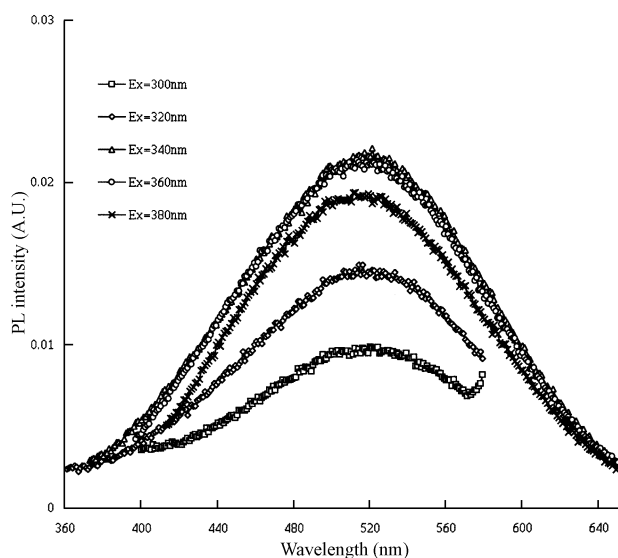
Figure 6. Photoluminescence spectra of A-25 porous SiC, B-25 porous SiC and SiC substrate, respectively, for excitation wavelength of 340 nm at room temperature.

Figure 8. Photoluminescence spectra of B-25 porous SiC after 1 year of aging in air atmosphere for various excitation wavelengths at room temperature.

ever, there has been no report concerning stability after aging for more than 1 year using PSC.
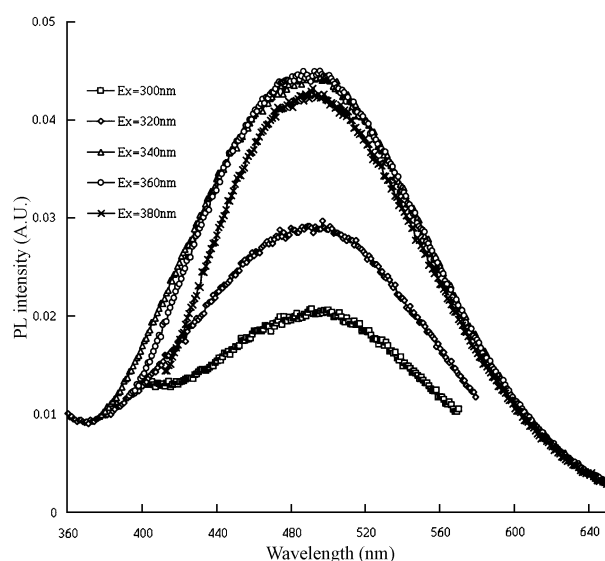
Figures 7 and 8 show the PL spectra for the process after 1 year of aging of the as-prepared same samples, conducted at room temperature in air atmosphere. It was found that the overall PL intensities decreased upon aging. Also, two main bands of the as-prepared samples have combined into one band, according to the aging.

The significant broadening of the spectrum following aging indicates the presence of oxidation by exposure of impurities to pore layer. This emission probably originates from states localized to band-to-band recombination due to the oxidation on the crystallite surface.

To identify distinct components within the PL bandwidth, PL spectra were obtained at different excitation wavelengths. In this case PL spectra still exhibited the same range of bands compared with that of fresh samples. We found that 1 year of aging under both conditions leads to a considerable

decrease in intensities in the 290 nm ~ 530 nm band range, which decreases about 20 times compared with the fresh samples. After 1 year of aging, emission band intensities of PA are 2 times higher than that of DCM in spite of the fact that the rate of decrease of PA is faster than that of DCM. We can resolved a number of sub-bands within the main band, according to the selective excitation wavelengths. This further indicates that the blue shift of the PL peak is related to the increase in porosity in the case of porous 6H-SiC.[4]

Figures 9 and 10 show the PLE spectra of the same samples after 1 year of aging at room temperature in air atmosphere. These PLE spectra are similar with that of fresh
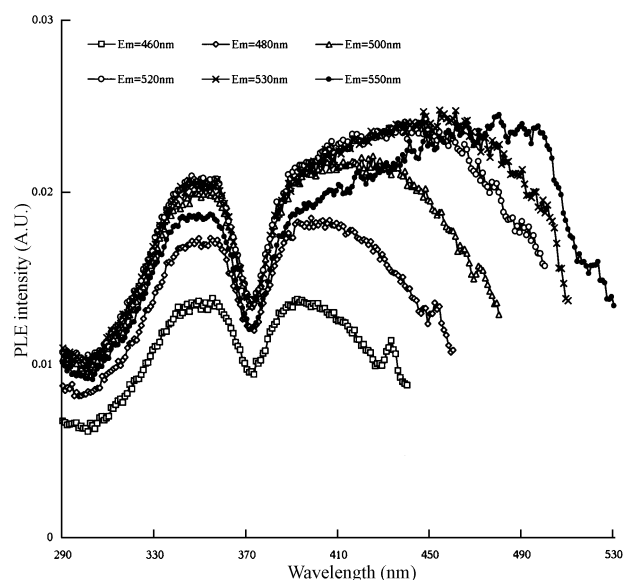

Figure 7. Photoluminescence spectra of A-25 porous SiC after 1 year of aging in air atmosphere for various excitation wavelengths at room temperature.
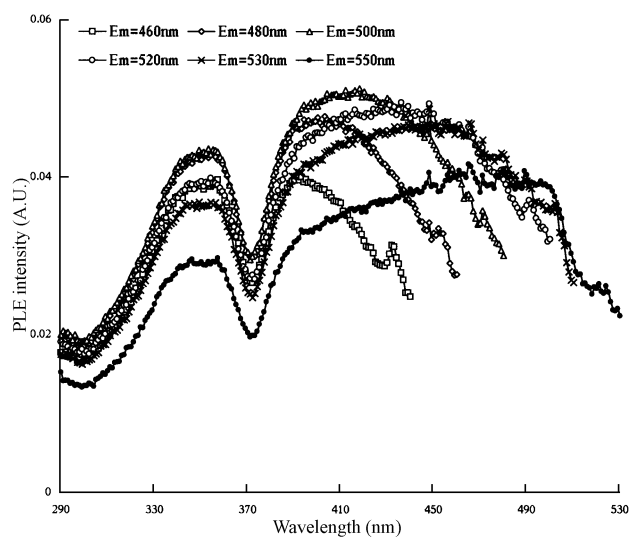

Figure 9. Photoluminescence excitation spectra of A-25 porous SiC after 1 year of aging in air atmosphere for various emission wavelengths at room temperature.

Figure 10. Photoluminescence excitation spectra of B-25 porous SiC after 1 year of aging in air atmosphere for various wavelengths at room temperature.

samples except for the overall decreases in intensities. In the porous silicon studies,[14-17] the PL intensity after aging was observed to decrease as a rule. It is explained by two factors.[18] One factor is an increase in the density of fast recombination centers (dangling silicon bonds), which form on desorption,[19] and the second factor is the destruction of the luminescing material on the surface of the silicon filaments, whose components are the desorbing complexes.[20] In our case, the chemical aspects of the electrochemical etching process in SiC were consistent with the procedure of the anodic etching system of Si. After prolonged aging in air, the PL spectra maintained the overall band range but combined into one band with a little decreasing. Of course, considering that our samples were exposed to air and stored a long period of time (1 year), it can be assumed that the PL intensity remained high. We ascertain that the properties of emission come from states localized to band-to-band recombination due to the formation of different pores sizes.

Conclusion

We investigated the optical properties of porous silicon carbide formed by electrochemical etching. According to the anodization condition, the main source of emission in the oxidized layers of porous SiC lies in the different surface defect centers, which consist of different geometrical structures. This indicates that the origin of these PL bands comes from the different sizes of porosity, simultaneously. We suggest that the different pores sizes can be the source of differ-ent emissions. That is, the increase in porosity is proportional to the increase in emission energies.

In the case of the aging process, the emission phenomenon is responsible for the band-to-band recombination due to the oxidation on the crystallite surface.

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