EFFECTS OF NANOCRYSTALLINE STRUCTURE AND PASSIVATION ON THE PHOTOLUMINESCENT PROPERTIES OF POROUS SILICON CARBIDE

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ABSTRACT

We present the results of an investigation of the dependence of the photoluminescence (PL) spectra on preparation conditions, the resulting microstructure, and post-anodization treatment of porous silicon carbide films which were formed from both p and n-type 6H-SiC substrates. Porous samples were prepared by anodic dissolution under different galvanostatic conditions, resulting in different porosities and crystallite sizes. Selected-area electron diffraction patterns taken on similarly prepared porous silicon carbide (PSC) samples confirmed that the films were monocrystalline. Transmission electron microscopy of as-anodized films revealed an isotropic porous network; a dependence of porosity and nanocrystallite size on porous layer formation current density was established. Some PSC samples were passivated using a short, thermal oxidation treatment. The effects of porosity and crystallite size, and of oxide passivation in these PSC films, on PL spectra and intensity were studied using a 365 nm Kr-ion laser as excitation. Under certain conditions, the spectrally integrated PL intensity of a passivated film is more than 450x that for the original bulk SiC substrate. PL spectra are presented, and possible mechanisms are discussed.

INTRODUCTION

Studies of the optical properties of porous Si (PS) fabricated by anodic dissolution in aqueous electrolytes have attracted considerable attention and interest since the discovery of the bright visible photoluminescence from this material in 1990.¹ The possibility of its use in optoelectronic applications has been advanced by the demonstration of electroluminescence (EL)²⁻⁵ and by improvements in the EL external quantum efficiency and longer-term device stability.⁶ While there remains considerable debate as to the origin of the bright luminescence in PS, which is generally peaked at energies higher than the bulk Si band gap,⁷ numerous authors have reported that the peak intensity and energy can be influenced by PS preparation conditions,⁸ substrate wafer doping level and dopant type,⁹ by aging¹⁰ and also by post-preparation surface treatments, including, quenching by solvents,¹¹ partial oxidation,¹² passivation by rapid thermal oxidation ^{13,14} and by rapid thermal nitridation in NH₃.¹⁵

Silicon carbide possesses a much wider energy gap ($E_g \sim 3.0 \text{ eV}$, 414 nm for the 6H polytype) than Si, and superior thermal conductivity, higher breakdown electric field, and higher saturation electron drift velocity. Nitrogen-aluminum donor-acceptor pair recombination in SiC has been the basis for a blue ($\lambda = 470 \text{ nm}$) light-emitting pn-junction diode,¹⁶⁻¹⁹ which has a small external quantum efficiency, ~10⁻⁴. While these LEDs have become commercially available,²⁰ the quantum efficiency remains low (~0.02-0.03%) and the peak emission energy is still well below the energy gap of bulk SiC. Based on developments in PS, it is believed that porous silicon carbide (PSC) is a possible candidate for more efficient and shorter wavelength light-emitting devices *vis-a-vis* those based on bulk SiC or porous Si.

There have been far fewer studies of PSC than PS. The formation of PSC by anodic dissolution of both *n*-type and *p*-type substrates was first reported by Shor, *et al.*^{21,22} Researchers have reported on PL and Raman scattering,²³⁻²⁶ and EL^{24,27} of PSC, electrical properties of PSC photoelectrochemically prepared from *n*-type substrates in UV light and in the dark,²⁸ and on the infrared reflectivity of PSC.^{26,29} We present here the first studies of the influence of the porosity and interpore spacing on the PL of PSC formed from *p*-type substrates by anodic dissolution. This also appears to be the first report on the effects of introducing a thin, passivating oxide layer onto the pore walls on the photoluminescent properties of PSC.

SAMPLE PREPARATION

Several PSC samples were prepared from aluminum-doped p-type 6H-SiC substrate wafer pieces (offaxis orientation of 3.5° +/- 0.5° off <0001> toward <1120>). The *p*-type SiC material is compensated with nitrogen atoms (donors) such that $N_A - N_D \sim 2 \times 10^{18}$ cm⁻³. First, ohmic electrical contacts were formed on each piece by the rapid thermal annealing of sputter-deposited films of titanium and platinum. An electrical lead was attached, and each sample was encapsulated in black wax, exposing a small area, typically on the order of 1-10 mm². The samples were placed in a solution of dilute hydrofluoric acid with ethanol. The ethanol served as a surfactant to minimize bubble formation, which could lead to a nonuniform current distribution across the surface of the semiconductor electrode. An anodic bias, referenced to a saturated standard calomel electrode, was applied to the samples for time periods ranging from one hour to more than twenty hours, depending upon the formation current density and resulting dissolution rate, forming thick porous layers. Several PSC samples were also prepared from similarly oriented n-type, nitrogen-doped, 6H-SiC wafers of compensated doping concentration $N_D - N_A \sim 4 \times 10^{18}$ cm⁻³. These pieces were anodized similarly, while being illuminated by a focused 1000 W Hg-Xe lamp. Free-standing PSC films with thicknesses greater than 50 µm were formed by an abrupt increase in the current density to greater than 500 mA/cm². Following the anodization, each sample was allowed to dry in air. Differences in the nature of the anodic etching between p-type and *n*-type SiC are discussed elsewhere.³¹

STRUCTURAL CHARACTERIZATION

Transmission electron microscopy (TEM) was performed on three PSC samples formed from p-type substrates at different anodic current densities. The samples were thinned by polishing and ion milling from the substrate side. Representative dark-field micrographs of samples prepared with J = 5 and 30 mA/cm² are shown in Figs. 1 and 2. Cross-section micrographs indicate that the microstructure of the PSC layer does not change with depth over the range of at least 1µm. The porosity and average interpore spacing depend on the formation current density (as shown in Table 1) in a manner which is qualitatively similar to observations in porous Si formed from p-type substrates.³² The porosity and mean crystallite diameters were tabulated directly from TEM micrographs.

Sample No.	Current Density (mA/cm ²)	Porosity (%)	Mean Crystallite Size (nm)
95P94-1	5	68	8.1
95 P 94-2	15	74	6.4
95P94-3	30	78	4.9

 Table 1

 Dependence of microstructure on formation current density for PSC formed from p-type SiC



PHOTOLUMINESCENCE MEASUREMENTS

The photoluminescence of a several similarly prepared PSC samples formed from *p*-type and *n*-type SiC substrates was measured at room temperature using the 365 nm line of the Kr-ion laser. The PL was dispersed by an 0.85m double spectrometer and detected by a cooled GaAs photomultiplier. The PL data were corrected for variations in spectral sensitivity of the optical apparatus by using a Xe lamp for spectral calibration. The spectral resolution was approximately 1.4nm, which is sufficient given the broad nature of the emission spectrum at room temperature. Free-standing and thick (>50 μ m) porous films on a bulk substrate had the same PL intensity and profile.

In Fig. 3, the room-temperature (RT) PL spectra of three as-anodized PSC films formed from a p-type substrate (p-PSC) at current densities of J = 5, 30 and 100 mA/cm² are shown. The integrated intensities of the samples prepared at J = 30 and J = 100 mA/cm² are ~2x and 8x that of the sample prepared at J = 5 mA/cm².

A similar behavior was observed for the as-anodized PSC films prepared from an *n*-type substrate (*n*-PSC), as shown in Fig. 4, along with the PL of bulk SiC for comparison. In this case, the integrated PL intensities of the films formed at $J = 30 \text{ mA/cm}^2$ and at $J = 60 \text{ mA/cm}^2$, are ~14x and 25x larger than that for the bulk SiC, respectively. A similar dependence of PL intensity on anodic current density in porous SiC films formed from *n*-type substrates has been observed by other investigators.^{23, 24}





PASSIVATED PSC FILMS

Following anodization, several of the *p*-PSC films which were formed at different current densities were placed into an oxidation furnace at 1150° C at atmospheric pressure for five minutes and were removed and allowed to cool in ambient. From the oxidation rates of crystalline SiC,³³ it is believed that an oxide of one or two monolayers will grow on the pore walls and will passivate at least a portion of the large internal surface area by reducing the number of surface states which act as trapping centers of nonradiative or slow radiative recombination. A comparison of the PL spectrum of unpassivated and passivated films formed at J = 5 mA/cm² is shown in Fig. 5. The integrated intensity of the oxidized PSC film is ~8x that of the as-anodized film.



The passivation of PSC films formed at a higher current density $J=30 \text{ mA/cm}^2$ yielded different PL results as seen in Fig. 6. Not only is the integrated intensity of the passivated film more than 20x greater than the as-anodized film, and more than 450x that of the bulk SiC, shown for comparison, but the PL is characterized by a broad, shorter wavelength emission.

The PL response of these films was observed to be nearly linear with Kr-ion laser excitation power up to 25 mW; however, the PL measurements of the oxidized PSC films were performed at lower excitation power than measurements on the as-anodized films and the bulk SiC substrate in order to obtain good signal-to-noise ratio in the weakly luminescent bulk SiC and to minimize the reduction of the PL signal from the oxidized PSC films due to heating at higher excitation power levels.

DISCUSSION

As mentioned earlier, the observation of an increase in the room temperature PL intensity in *n*-PSC with increased formation current density is in general agreement with other investigators.^{23, 24} Matsumoto, *et al*,²³ however, report that the peak of the luminescence blueshifts with increased formation current density (from 500 nm for J = 20 mA/cm² to 460 nm for J = 60 mA/cm²), and suggest that this is due either to quantum confinement as originally proposed in PS,¹ or due to luminescent surface states.³⁰ Our findings agree with those of Petrova-Koch²⁴ in that no spectral shifts were observed. Given that the microstructure of the *n*-PSC formed by photo-assisted electrochemical anodization exhibits an interpore spacing of ~30 nm and that all of the luminescence is due to quantum confinement. Petrova-Koch²⁴ proposed that the luminescence in both bulk and PSC is due to nitrogen-aluminum donor-acceptor pair recombination, and that the enhanced efficiency in PSC may be due to a geometrical confinement effect in which a photoexcited electron-hole-pair is highly localized due to the granular nature of the material, thereby suppressing nonradiative decay processes.

A similar increase in PL intensity is observed for as-anodized *p*-PSC which is also well below the bulk energy gap. Given the smaller characteristic dimension of this material, it is not clear whether quantum confinement is the basis for the enhanced PL. The enhanced PL could be due to localization of photoexcited carriers which limits nonradiative decay as proposed above, but also it could be due to distortion of the local band structure and/or a relaxation of the momentum selection rules, so that direct transitions are permitted.

Konstantinov, et al^{25} examined the effects of exposing *n*-PSC to oxygen ambient at 700°C for 1 hour. The result was a quenching of the blue-green PL, which was partially recoverable without the high energy component upon immersion in HF. In contrast, we observe that identically short, thermal oxidation treatments to the as-anodized p-PSC film further enhances the PL intensity for material of lower porosity and larger average interpore spacing (~8 nm), and there is an additional band of emission at energies higher than the original peak, extending into the bulk energy gap, in PSC of higher porosity and narrow average interpore spacing (~5 nm). The reason for this enhanced and blueshifted PL is not clear. One interpretation is that the oxidized highly porous PSC material consists of either further narrowed crystallites or local SiC clusters. A broad distribution of sizes and geometries of the remaining, passivated material could result in a virtual continuum of energy states. Another explanation, which is consistent with the first, is that a thermally grown oxide layer is passivating the large internal surface area of dangling bond sites. The striking difference could also be due to differences in the composition and properties of the surface layer of PSC following anodization at different current densities, and their associated oxidation kinetics. In contrast, the origin of the further enhancement of the PL and shorter wavelength emission could be due to the surface oxide film itself. It is clear that further work is required to characterize the structure, composition and properties adequately to explain the mechanism of PL in as-anodized and slightly oxidized p-PSC.

CONCLUSIONS

The room temperature PL efficiency of porous silicon carbide formed from p-type and n-type substrates is enhanced vis-a-vis that from the bulk substrate, and this enhancement is influenced by the preparation conditions. In addition, a further enhancement of the PL efficiency and short-wavelength emitting characteristics can be obtained by "passivating" the PSC using a short, thermal oxidation treatment. This leads to a room-temperature photoluminescence efficiency which, under certain circumstances, is more than 450x that for bulk SiC.

ACKNOWLEDGEMENTS

This work was supported at Kulite Semiconductor by a NASA Lewis Phase II SBIR Contract, No. NAS3-27247, and at Columbia University by the Joint Services Electronics Program Contract No. DAAH-4-94-G-0057. We gratefully acknowledge I. Grimberg of the Technion for performing TEM and electron diffraction studies.

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