

Study of Photoluminescence and Morphology for Porous Amorphous Silicon Carbide

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Porous amorphous silicon carbide (aSiC) was prepared by electrochemical etching/anodization method. Photoluminescence (PL) spectra of the samples were measured at room temperature. The surface morphology of the samples was studied by an atomic force microscope (AFM). We observed clear dependence of PL spectra on fabrication condition and surface morphology.

I. Introduction

Two decades ago, Canham first established the visible room temperature PL spectra from porous silicon (PSi)¹. It has paved a way to observe the visible PL from the indirect band gap materials. In comparison with Si, SiC has unique properties, such as wide band gap, high melting point, high thermal conductivity, large breakdown voltage, which allow it to work in extremely harsh conditions and environments. Recently, it was found that PSiC exhibits a strong visible PL and it has attracted much research interest due to its possible applications in blue-green light-emitting diodes or photo-detectors².

Many papers have reported on the PL spectra and the mechanism of the strong visible PL from the material^{3,4}. In this research work, we report the results of a systematic study concerning the dependence of the PL spectra on the fabrication process and on the surface morphology of the porous structures. We also proposed an emitting mechanism for the visible PL of porous aSiC (P-aSiC).

II. Experimental

P-aSiC thin films in this work were obtained by electrochemical etching/anodization from aSiC thin films in the hydrofluoric acid (HF) aqueous electrolyte with the aid of H₂O₂ or Triton surfactants⁵. The aSiC thin films were fabricated by plasma-enhanced chemical vapor deposition (PECVD) at 400°C on the standard Si crystal substrate. We used three main types of samples: intrinsic P-aSiC, n-doped P-aSiC and p-doped P-aSiC. The film thickness is 3 micrometers. All the samples were anodized by using a voltage constant source, which output voltage (260V for all samples) is

applied to the load consisting of a sample connected in series with a 180 kΩ resistor. All the anodization processes were carried out in 30 minutes.

III. Results and Discussion

PL measurements were performed at room temperature using 325nm line of a He-Cd laser. The samples showed very broad PL spectra in the visible and near-infrared region. Figure 1 shows PL spectra of intrinsic P-aSiC samples with different HF concentration. The PL spectra are comprised of two main bands with the peak energies of 1.7 and 2.3 eV. Interference modes in the PL spectra correspond to thickness of aSiC films.

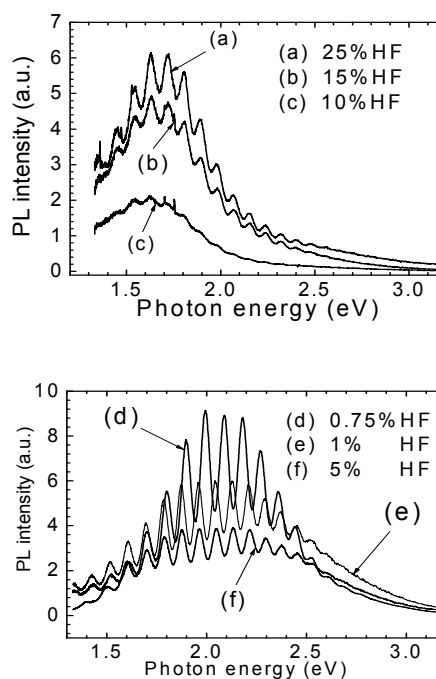


FIG. 1: HF concentration dependence PL spectra of intrinsic P-aSiC

Systematic evaluations of PL dependence on the different concentrations of HF in the electrolyte were taken. The results indicated

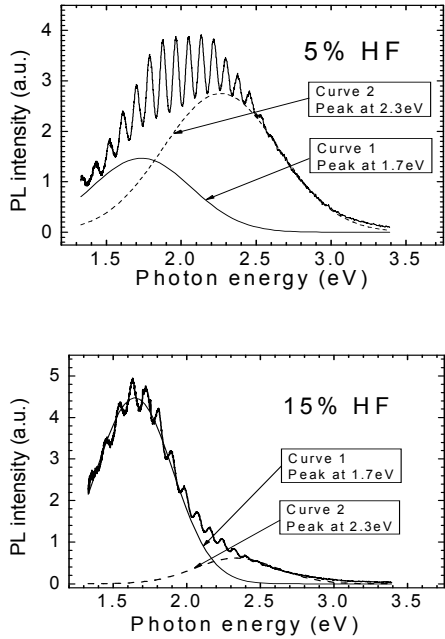


FIG. 2: Fitting results of PL spectra of intrinsic P-aSiC with 5% and 15% HF. Both were fitted with two Gaussian functions with the peak energies of 1.7 and 2.3 eV.

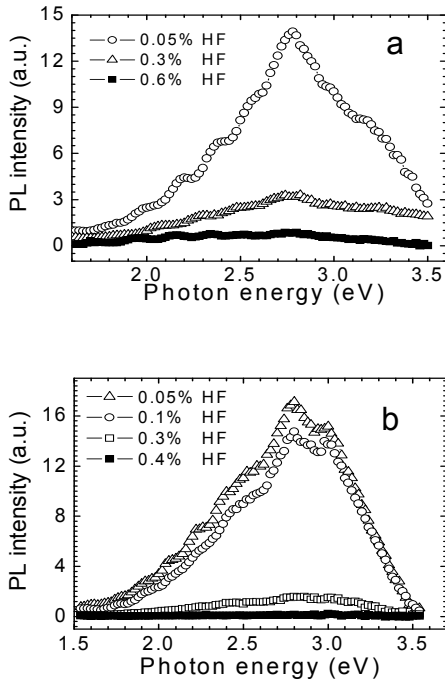


FIG. 3: HF concentration dependence PL spectra of n-type P-aSiC (a) and p-type P-aSiC (b).

that the PL intensity depends strongly on the amount of HF. The two bands showed different tendencies for a change in the concentration of HF. In particular, for a range of the HF concentration less than 5%, the more dilute HF, the higher PL intensity at 2.3 eV was observed. In contrary, the PL band at 1.7 eV was observed only with the samples which were etched in the solution with the concentration of HF larger than 10%, and the PL intensity increased with increasing amount of HF. In order to identify two observed bands, the PL spectra were fitted into two Gaussian functions represented by Curve 1 and Curve 2 as seen in Fig. 2. Figure 3 shows the PL spectra of n-type and p-type P-aSiC samples. Those samples showed the same PL behavior as the intrinsic P-aSiC for a change in the HF concentration, which is, the PL intensity increases in visible region for samples doped with the HF concentration less than 1%. In addition, the peak energy shifted to 2.8 eV.

To examine the relations between the PL intensity, the HF concentration and the morphology of the porous layer, the atomic force microscope (AFM) measurements were performed. The AFM images showed that pore diameter varies from several tens nanometers to several hundreds nanometers, pore depth varies between ten nanometers to several ten nanometers. With decreasing the HF concentration, diameter and depth of pores increased with lower pore density as shown in

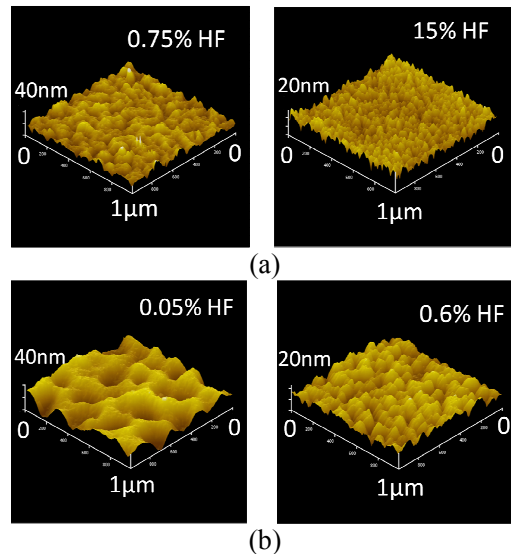
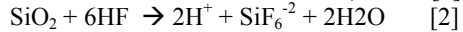
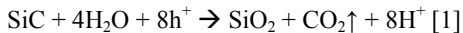


FIG. 4: AFM images of intrinsic P-aSiC (a) and n-type P-aSiC (b)

Fig. 4. That means the low density of the wide pores will result in the strong visible green-blue band. It indicates that the surface nanostructure plays an important role in the variation of the PL intensity of P-aSiC. Concerning the influence of doping on the surface morphology of P-aSiC, in principle, doping helps reducing the resistance of bulk SiC. Consequently it helps the anodization process to occur much easier. Comparing the AFM images of intrinsic and doped samples, we found that the doped P-aSiC showed larger pore diameter than the intrinsic P-aSiC. It implies that doping effects directly on the pore formation and the surface structures of SiC.

The origin of PL of P-aSiC up to now is still unclear. Regard to the origin of visible PL from PSi, the quantum confinement effect is believed to be the main reason. But no explicit evidence of quantum confinement has been observed in our samples because the PL photon energy is constant for a change in HF concentration. If fine nanostructure showing quantum confinement effect, the PL photon energy might be changed by changing etching process. So the emitting mechanism of PSiC is predicted to be very different from PSi. Most of reports on PL of PSiC agree with the idea that PL arises from surface states, which are generated during anodization process^{3,4,6}. In this report, we propose an emitting mechanism of P-aSiC related to surface states and surface regions in the point of view of surface species. In order to understand how the etching process could help generate strong visible PL spectra from a weak luminescence material, we paid attention to the fabrication process in more details. The chemical reaction throughout the electrochemical etching process is believed to be as follows⁷:



From those reactions, we infer that first of all, a SiO₂ layer was formed on the surface of material. This layer then interacted with HF to form the porous structure along with producing H⁺ ion on the surface of sample. Several percents of HF are needed to dissolve the entire amount of SiO₂. From those evaluations, we propose a PL mechanism of P-aSiC, that is, the surface-related compounds are possibly the origin of the strong visible spectra from P-aSiC. The PL band at 2.3 and

2.8 eV is believed to originate from oxygen-related bonds. In particular, for the samples with small amount of dilute HF (less than 5%), strong green-blue PL bands at around 2.3 or 2.8 eV were observed. Reaction [2] indicates that the less amount of HF, the more amount of SiO₂ remains, and conversely, increasing the HF concentration will deoxidize the oxide layer. The results demonstrate a clear correlation between surface chemistry and PL peak energy. The relative PL intensities of the two bands depend on the ratio of the amount of surface species. This correlation can also be found in previous studies⁸. The hypothesis is also consistent with the PL results in Fig.1 and Fig.3 for both intrinsic and doped samples, as well as PL spectra fitting curves in Fig. 2. Figure 5 illustrates the dependence PL intensities of two PL bands with different HF concentrations. Regarding the PL of SiO₂, it was reported that SiO₂ showed very broad PL in visible region and several bands were identified, including bands at 1.9, 2.2 and 2.7 eV⁹. Those evidences reinforce our prediction that PL spectrum at the peak of 2.3 and 2.8 eV emerges from Si-O related compounds. Meanwhile, the origin of PL spectra from near infrared PL band at 1.7 eV is still difficult to understand. PL examination of the bulk SiC

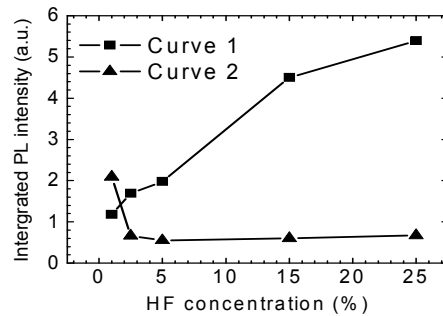


FIG.5: Integrated PL intensity of Curve 1 and Curve 2 in Figure 2 as a function of HF concentration.

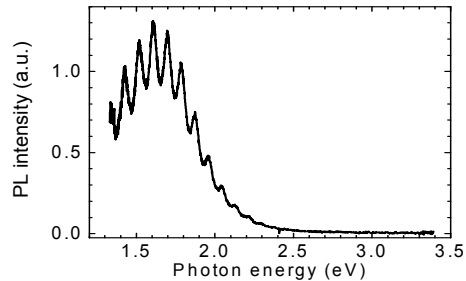


FIG. 6: PL spectrum of bulk aSiC

indicated that bulk aSiC also showed very weak near infrared PL at 1.7 eV (Figure 6), which is believed to result from oxidation in air. So we suggest that the PL band at 1.7 eV originates from some unknown chemical bonding after storing samples in air for a long period of time. On the blue-shift of doped samples in comparison with intrinsic one, it has been unclear that how the doping process effect the electronic structures of samples. The AFM images indicate that the pore diameter changes significantly in the case of the doped samples in comparison with non-doped samples. We have pointed out that PL intensity of P-aSiC depends on the variation of pore diameter. But the doped and intrinsic samples studied in this research were etched at different HF concentrations, the behavior of PL spectra of doped samples at higher HF concentration is still unknown. So further investigations on the samples etched at higher concentration of HF are needed in order to understand sufficiently the blue-shift of PL peak photon energy of doped samples.

For better understanding of electronic structure and PL mechanism of P-aSiC, photoluminescence excitation (PLE) measurement was performed. A Xenon lamp connected with a monochromator was used as the excitation light source. The PL spectra were detected using a 30cm monochromator. The PLE spectra were plotted in Figure 7, all the spectra were normalized in order to emphasize the differences between emission regions. PLE spectra show an absorption peak at 3eV, which is larger than the emission peaks of every sample. The PLE spectrum is relatively independent on the PL energy. It excludes the possibility of quantum confinement effect as well as indicates that the

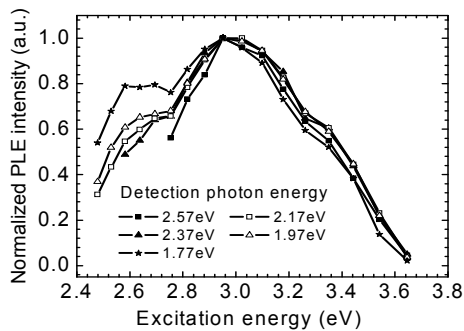


FIG.7: PLE spectra of 1%HF intrinsic P-aSiC

PL arises from recombination of a set of well-defined electronic energy levels, but its exact nature requires more investigation in the future.

IV. Conclusion

P-aSiC samples have shown the visible PL spectra at room temperature. The results indicated that PL spectrum depends strongly on the fabrication process, in particular, on the concentration of HF and the morphology of surface layer. The PL emission is found to contain two components with the PL peak at 1.7eV and 2.3eV, which correlates to the concentration of surface chemical elements in PSiC. From the results, we suggested that the PL band at 2.3 or 2.8 eV is originated from Si-O related bonds and PL band at 1.7eV originates from some chemical processes during the period of storing samples in air. For future research, we plan to measure the Raman scattering and the time-resolved PL measurements to verify our hypothesis and to clearly understand the relaxation mechanism of PSiC. Furthermore, we also plan to continue the research on the impact of doping on the PL properties of P-aSiC.

Acknowledgements

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Reference

- ¹L.T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
- ²S.I. Vlaskina, Semiconductor Physics, Quantum electronics & optoelectronics, **5**, 71 (2002).
- ³T. Matsumoto, J. Takahashi, T. Tamaki, T. Futagi and H. Mimura, Appl. Phys. Lett., **64**, 226 (1994).
- ⁴A.O. Konstantinov, A. Henry, C.I. Harris and E. Janzen, Appl. Phys. Lett., **66**, 2250 (1995).
- ⁵D.T. Cao, N.T.T. Ha, H.T. Ha, B. Huy, V.T. Thanh, C.T. Anh, P.T.M. Hoa and P.M. Sarro, Advances in Natural Sciences, **10**, 19 (2009).
- ⁶O. Jessensky, F. Muller, U. Gosele, Thin Solid Films, **297**, 224 (1997).
- ⁷J.Y. Fan, X.L. Wu, Paul K. Chu, Prog. Mat. Sci., **51**, 983 (2006).
- ⁸L. Tsybeskov and P. M. Fauchet, Appl. Phys. Lett. **64**, 1983 (1994).
- ⁹J. H. Stathis, M. A. Kastner, Phys. Rev. B, **35**, 2972 (1987).