Time-resolved photoluminescence spectra of strong visible light-emitting SiC nanocrystalline films on Si deposited by electron-cyclotron-resonance chemical-vapor deposition

S. J. Xu[a]
Department of Physics, The University of Hong Kong, Hong Kong, China

M. B. Yu, Rusli, and S. F. Yoon
School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore

C. M. Che
Department of Chemistry, The University of Hong Kong, Hong Kong, China

SiC nanocrystalline films on Si substrates deposited using advanced electron-cyclotron-resonance chemical-vapor deposition exhibit intense visible light emission at room temperature under laser excitation. Continuous-wave and time-resolved photoluminescence measurements for these SiC films were carried out at room temperature. The photon energy of the dominant emission peaks is higher than the band gap of cubic SiC. Room-temperature optical absorption measurements show a clear blueshift of the band gap of the samples with a decrease of the average size of the nanoclusters, indicating an expected quantum-confinement effect. However, the emission spectra are basically independent of the size. Temporal evolution of the dominant emissions exhibits double-exponential decay processes. Two distinct decay times of ~200 ps and ~1 ns were identified, which are at least two orders of magnitude faster than that of the bound-exciton transitions in bulk 3C–SiC at low temperature. Strong light emissions and short decay times strongly suggest that the radiative recombinations may be from some direct transitions such as self-trapped excitons on the surface of the nanoclusters. © *2000 American Institute of Physics.* [S0003-6951(00)04618-0]

Silicon carbide (SiC) is an ''old'' but important semiconductor material. In recent years, there is an overall renewed interest in this material due to development of new growth techniques.[1–3] SiC light-emitting diodes (LEDs) are one of its optoelectronic device applications. However, due to the intrinsic indirect-band-gap character, the quantum efficiency of the best SiC LED reported so far[4] is still as low as about 10^{-4}. Visible photoluminescence (PL) and electroluminescence (EL) of hydrogenated amorphous SiC(a-SiC:H) films were observed in 1978 (Ref. 5) and 1983,[6] respectively. Shortly thereafter, a so-called a-SiC:H thin-film LED made of a-SiC:H $p–i–n$ junctions was demonstrated.[7] Although the brightness of this a-SiC:HLED is high enough to be observed by the eye, it is still too low for any practical application as a display panel.[8] Microcrystalline SiC alloys deposited by electron-cyclotron-resonance chemical-vapor deposition (ECRCVD) were utilized as carrier injection layers to improve the performance of a-SiC:H LEDs.[8] Recent research work[9,10] in ECRCVD SiC coating technology has demonstrated the potential for fabricating high-quality SiC x-ray mask membranes. Furthermore, the microstructure of SiC films on Si deposited by the ECRCVD technique was found to be an amorphous matrix embedded with nanosized crystalline particles.[9,10] On the other hand, obviously inspired by the discovery of porous Si emitting strong luminescence, some groups reported PL and EL spectra of porous SiC fabricated using single-crystal SiC polytypes such as 3C, 4H, and 6H.[11–14] However, there has been little work on the luminescence properties of nanocrystalline SiC films deposited on Si using the ECRCVD technique. In this letter, we report the steady-state and transient luminescence characteristics of SiC nanocrystalline films grown on Si using ECRCVD. SiC films emit intense visible light at room temperature under excitation of a short-wavelength laser. The measured two luminescence decay time constants are ~200 ps and 1 ns. The strongly enhanced luminescent efficiency may be due to direct optical transitions.

The SiC films investigated here were deposited on Si (100) substrates using the ECRCVD technique. Details of the growth will be published elsewhere.[15] Here, we focus on the luminescent properties of two typical samples.

In the steady-state PL measurement, an argon-ion laser with a wavelength of 351 nm and output power of 5 mW was used as the excitation light source. The emission signal was dispersed in a double 0.25 m monochromoter and was detected by a photomultiplier tube using a standard lock-in amplification technique. For time-resolved PL measurements, the excitation light was ~2 ps pulses with a wavelength of 400 nm from frequency doubling of a 800 nm line of a mode-locked Ti:sapphire laser. The transient luminescence signal was dispersed in a 0.25 m monochromoter and was captured by a streak camera. The overall temporal resolution of the whole system is about 15 ps. Atomic-force microscopy (AFM) observation on the morphology of the samples was performed in a Digital Instruments NanoScope III with tapping mode.

Figures 1(a) and 1(b) show the AFM pictures of samples D and E, respectively. Both samples were grown under the
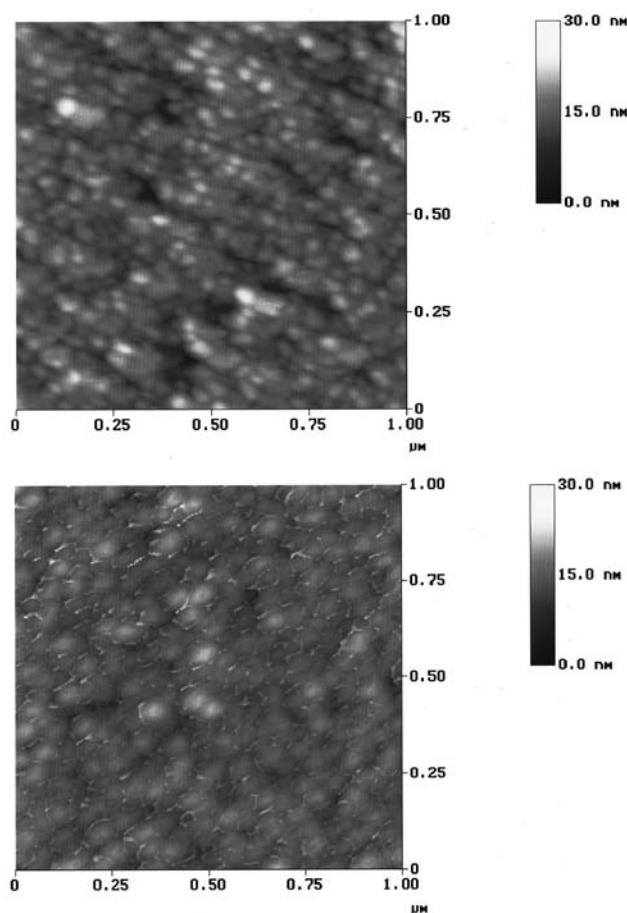
[a]Electronic address: sjxu@hkucc.hku.hk

Appl. Phys. Lett., Vol. 76, No. 18, 1 May 2000

Xu *et al.* 2551

FIG. 1. AFM pictures of the SiC nanocrystal films of samples D (a) and E (b).

FIG. 2. Room-temperature optical absorption and steady-state PL spectra of samples D and E.

same conditions except for the gas flow ratio of the reaction gases. For sample D, the flow ratio of H_2:SiH_4:CH_4 is 100:10:3, while for sample E, the flow ratio is 100:5:1. The nanosized clusters embedded in the films can be clearly seen in Fig. 1. Compared with that of sample D, the average diameter of the SiC clusters of sample E is larger. Moreover, the surface roughness of sample E is smaller than that of sample D. From the absorption spectra shown below, the size-dependent effect of the band gap of the SiC nanocrystals can be demonstrated. Figure 2 shows the room-temperature PL spectra and absorption spectra of samples D and E. We first discuss the absorption spectra of the SiC nanocrystals. Like porous Si, the SiC nanocrystals exhibit unstructured optical absorption spectra due to the large distribution of the cluster size. The minimum indirect-band gap of cubic SiC (also called 3C–SiC) is the energy separation between Γ_{15V} and X_{1C}.[16] Its value is about 2.2 eV at room temperature.[17] Above this transition the absorption coefficient α should follow the well-known law of $\sqrt{\alpha(\hbar\omega)} \propto (\hbar\omega - E_{g1})$ for indirect-band-gap semiconductors.[18] For an allowed direct transition, a photon energy dependence of the absorption coefficient should be expected as $\alpha(\hbar\omega)^2 \propto (\hbar\omega - E_{g2})$.[19] Following Ben-Chorin *et al.*'s work[19] on Si nanocrystals, indirect band gaps extrapolated from measured absorption spectra are $\sim$2.32 and $\sim$2.12 eV for samples D and E, respectively, which are close to the minimum indirect band gap of 3C–SiC. Possible direct band gaps of $\sim$3.5 and $\sim$2.94 eV are deduced for samples D and E, respectively.
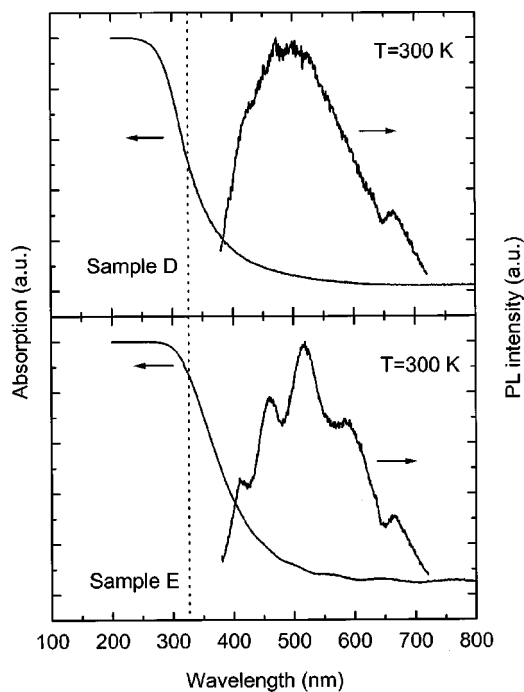
The large difference between the possible direct band gaps of samples D and E shows clear evidence for quantum confinement. However, the emission spectra of samples D and E exhibit independence of the cluster size, as shown in Fig. 2. Indeed, this is a quite puzzling problem, which also occurs in Si nanocrystals.[20] Like Si nanocrystals, all SiC nanocrystals display broad emission spectra even covering the whole visible light region. Most of the peaks in the PL spectrum of sample E stem from optical interference between the top surface of the films and the top surface of the Si substrates. We also found that the luminescent characteristics of the samples are very stable. For example, we did not observe any degradation of the emission intensity eight months after the samples were stored in air. This characteristic is very important for practical applications of SiC nanocrystals in optoelectronic devices.

Figure 3 shows the time evolution of the luminescence intensity of the dominant emissions from samples D and E at room temperature. The solid lines show the biexponential fitting results to the experimental data. Two decay time constants of 166, and 772 ps were obtained for sample D, while decay time constants of 246 and 974 ps were identified for sample E. It should be noted that the decay times of about 1 ns are at least two orders of magnitude faster than that of the bound-exciton transitions of bulk 3C–SiC at low temperature.[21] The biexponential decay implies that multi-levels may be involved in radiative recombination. A more interesting phenomenon is that SiC nanocrystals at room temperature have comparable PL decay times with high-quality bulk direct-band-gap semiconductors[22,23] and their low-dimensional structures such as quantum wells[24,25] and quantum dots[25,26] at low temperature. Recently, Wilcoxon and Samara[27] reported a radiative lifetime of $\sim$1 ns of the blue light emission of crystalline Si nanosized particles in the size of $\sim$2 nm. They attribute the transition to direct recombination at the Brillouin-zone center. The observed intense
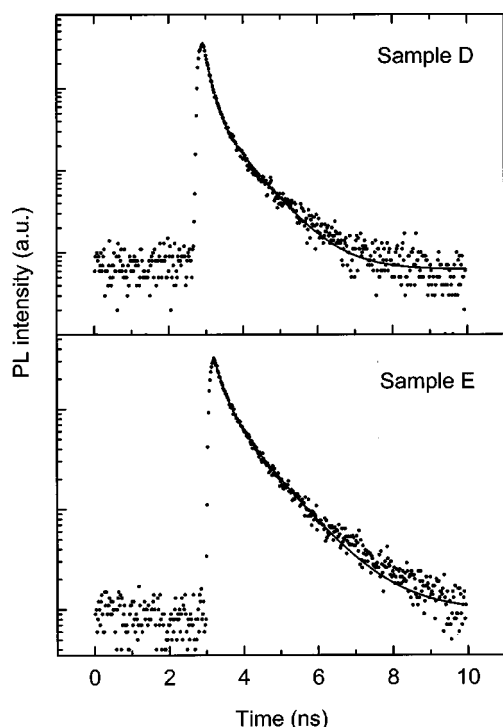
FIG. 3. Room-temperature PL decay curves of the dominant emission peaks of samples D and E. The solid circles represent the experimental data while the solid lines show the biexponential fitting results.

photon emission and 1-ns-level PL decay time strongly suggest that the dominant radiative recombinations in the SiC nanocrystals are from direct optical transitions. It is known that the surface states play a core role in the influence of the optical and electrical properties of nanoclusters because of such a high surface-to-volume ratio.[28] Koch, Petrova-Koch, and Muschit[29] suggested that surface states may act as luminescent centers in Si nanocrystals. Recently, Allan, Delerue, and Lannoo[30] theoretically demonstrated the stability of the self-trapped exciton state at the surface of a Si nanocrystal using semiempirical and *ab initio* local-density calculations. According to their calculations, these luminescent surface states are obtained for dimer bonds passivated, for instance, by hydrogen atoms or by silicon oxide. They also found that the light emission from such trapped excitons is basically independent of cluster size. In this regard, it is noted that we use highly pure hydrogen gas as the diluting agent of SiH_4 and CH_4 in the synthesis. Therefore, it is quite possible that our SiC nanoclusters are terminated by hydrogen. Significant reduction of the nonradiative rate due to termination of dangling bonds at the nanocrystal surface was addressed previously.[28] Allan *et al.*[30] also pointed out that the self-trapped exciton model is likely to be valid for all types of semiconductor nanocrystals. It is interesting that the lifetime of self-trapped excitons in the Si nanocluster calculated by them is close to 1 ns. We are thus led to conjecture that the dominant optical transition in SiC nanocrystals is due to the surface self-trapped excitons proposed by Allan, Delerue, and Lannoo.[30]

In summary, we have grown nanocrystalline SiC films on Si using ECRCVD. These SiC films emit intense visible light at room temperature under excitation of a short-wavelength laser. The steady-state and ps time-resolved PL spectra of these samples were measured at room temperature.

It was found that the PL decay time in the nanosecond scale is at least two orders of magnitude faster than that of the bound-exciton transitions in bulk 3C–SiC at low temperature. Direct optical transitions, such as surface self-trapped exciton transitions, should be responsible for the dominant emissions with a decay time of ~1 ns. This nanocrystalline SiC film emitting strong visible light should be a promising material for fabrication of white-light LEDs.

[1] G. L. Harris, *Properties of Silicon Carbide* (INSPEC, London, U.K., 1995).
[2] G. Pensl, H. Morkoç, B. Monemar, and E. Janzén, *Silicon Carbide, III-Nitrides and Related Materials: Parts I and II* (Trans. Tech., Switzerland, 1998).
[3] *SiC Materials and Devices*, Semiconductors and Semimetals Vol. 52, edited by Y. S. Park (Academic, London, U.K., 1998).
[4] L. Hoffman, G. Ziegler, D. Theis, and C. Weyrich, J. Appl. Phys. **53**, 6962 (1982).
[5] D. Engemann, R. Fischer, and J. Knecht, Appl. Phys. Lett. **32**, 567 (1978).
[6] H. Munekata and H. Kukimoto, Appl. Phys. Lett. **42**, 432 (1983).
[7] D. Kruangam, T. Endo, W. Guang-Pu, H. Okamoto, and Y. Hamakawa, Jpn. J. Appl. Phys., Part 2 **24**, L806 (1985).
[8] D. Kruangam, in *Amorphous and Microcrystalline Semiconductor Devices: Optoelectronic Devices*, edited by J. Kanicki (Artech House, 1991), Chap. 6.
[9] S. Y. Lee, K. C. Song, J. Kim, J.-H. Son, and J. Ahn, Jpn. J. Appl. Phys., Part 1 **37**, 6841 (1998).
[10] A. R. Shimkunas, P. E. Mauger, L. P. Bourget, R. S. Post, L. Smith, R. F. Davis, G. M. Wells, F. Carrina, and R. B. McIntosh, J. Vac. Sci. Technol. B **9**, 3258 (1991).
[11] T. Matsumoto, J. Takahashi, T. Tamaki, F. Futagi, H. Mimura, and Y. Kanemitsu, Appl. Phys. Lett. **64**, 226 (1994).
[12] H. Mimura, T. Matsumoto, and Y. Kanemitsu, Appl. Phys. Lett. **65**, 3350 (1994).
[13] A. O. Konstantinov, A. Henry, C. I. Harris, and E. Janzén, Appl. Phys. Lett. **66**, 2250 (1995).
[14] L. S. Liao, X. M. Bao, Z. F. Yang, and N. B. Min, Appl. Phys. Lett. **66**, 2382 (1995).
[15] M. B. Yu, Rusli and S. F. Yoon (unpublished).
[16] S. Yoshida, in *Properties of Silicon Carbide*, edited by G. L. Harries (INSPEC, London, U.K., 1995), p. 76.
[17] K. Järrendahl and R. F. Davis, in *SiC Materials and Devices*, Semiconductors and Semimetals, Vol. 52, edited by Y. S. Park (Academic, London, U.K., 1998), p. 14.
[18] R. J. Elliot, Phys. Rev. **106**, 1384 (1957).
[19] M. Ben-Chorin, B. Averboukh, D. Kovalev, G. Polisski, and F. Koch, Phys. Rev. Lett. **77**, 763 (1996).
[20] D. J. Lockwood, Solid State Commun. **92**, 101 (1994).
[21] J. P. Bergman, E. Janzén, S. G. Sridhara, and W. Choyke, *Silicon Crabide, III-Nitrides and Related Materials: Part I* (Trans. Tech., Switzerland, 1998), p. 485.
[22] G. W. 't Hooft, W. A. J. A. van der Poel, and L. W. Molenkamp, Phys. Rev. B **35**, 8281 (1987).
[23] O. Brandt, J. Ringling, K. H. Ploog, H.-J. Wünsche, and F. Henneberger, Phys. Rev. B **58**, R15977 (1998).
[24] J. Feldmann, G. Peter, E. O. Göbel, P. Dawson, K. Moore, C. Foxon, and R. J. Elliott, Phys. Rev. Lett. **59**, 2337 (1987).
[25] P. Lefebvre, J. Allègre, B. Gil, A. Kavokine, H. Mathieu, W. Kim, A. Salvador, A. Botchkarev, and H. Morkoç, Phys. Rev. B **57**, R9447 (1998).
[26] M. Colocci, A. Vinattieri, L. Lippi, F. Bogani, M. Rosa-Clot, S. Taddei, A. Bosacchi, S. Franchi, and P. Frigeri, Appl. Phys. Lett. **74**, 564 (1999).
[27] J. P. Wilcoxon and G. A. Samara, Appl. Phys. Lett. **74**, 3164 (1999).
[28] See, for example, A. P. Alivisatos, Science **271**, 933 (1996).
[29] F. Koch, V. Petrova-Koch, and T. Muschit, J. Lumin. **57**, 271 (1993).
[30] G. Allan, C. Delerue, and M. Lannoo, Phys. Rev. Lett. **76**, 2961 (1996).