Effect of Annealing Temperature on 1.5 μm Photoluminescence from Er-Implanted 6H-SiC

A.J. STECKL and J. DEVRAJAN

Department of Electrical and Computer Engineering, University of Cincinnati, Cincinnati, OH 45221-0030

W.J. CHOYKE, R.P. DEVATY, and M. YOGANATHAN

Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA 15260

S.W. NOVAK

Evans East, Plainsboro, NJ 08536

The effect of post-implantation anneal on erbium-doped 6H-SiC has been investigated. 6H-SiC has been implanted with 330 keV Er^+ at a dose of 1×10^{13} /cm^2. Er depth profiles were obtained by secondary ion mass spectrometry (SIMS). The as-implanted Er-profile had a peak concentration of $\sim 1.3 \times 10^{18}$/cm^3 at a depth of 770Å. The samples were annealed in Ar at temperatures from 1200 to 1900°C. The photoluminescence intensity integrated over the 1.5 to 1.6 μm region is essentially independent of annealing temperature from 1400 to 1900°C. Reduced, but still significant PL intensity, was measured from the sample annealed at 1200°C. The approximate diffusivity of Er in 6H SiC was calculated from the SIMS profiles, yielding values from 4.5×10^{-16} cm^2/s at 1200°C to 5.5×10^{-15} cm^2/s at 1900°C.

Key words: Diffusivity, erbium, implantation, ions, photoluminescence (PL), SiC

INTRODUCTION

Optical fiber communications require light sources emitting in the vicinity of the 1.54 μm silica fiber attenuation minimum. The first report[1] of 1.5 μm photoluminescence (PL) from erbium-implanted Si and III-V semiconductors was published approximately a decade ago. Er and other rare earths (RE) impurities take the trivalent electronic state when incorporated in a host material. Sharp line photoluminescence results from internal electronic transitions of the 4f states. The energy of these transitions is relatively independent of the host material since the 4f electrons are well shielded by the outer electrons. The finding by Ennen et al.[1] has led to investigations by several groups on how to optimize the performance of Er-doped semiconductors. This includes control of anneal temperature and time[2] in Er-doped GaAs, InP and GaP, in-situ Er doping during molecular beam epitaxial growth of GaAs,[3] and impurity co-implantation in Er-implanted Si.[4] An important advance in the PL efficiency of Si:Er through the introduction of oxygen was first reported by Favennec et al.[5] This has resulted in significant gains toward the goal of high efficiency room temperature operation of Si:Er devices.[6–9] An alternative approach toward the same objective has been identified by Favennec et al.,[10–11] who observed that PL emission efficiency at a given temperature increases with the band-gap of the host semiconductor, thus indicating the advantage of using a wide band-gap semiconductor[12] as the host. Based on this idea, the Er-doping of several III-V and II-VI semiconductors has been investigated: ZnTe,[11] CdS,[11] $In_{1-x}Ga_xP$,[13] GaP,[14] GaN, and AlN.[15]

Er-doped 6H-SiC has recently been reported[16] to have a high photoluminescence efficiency at wave-

(Received August 2, 1995; revised November 16, 1995)

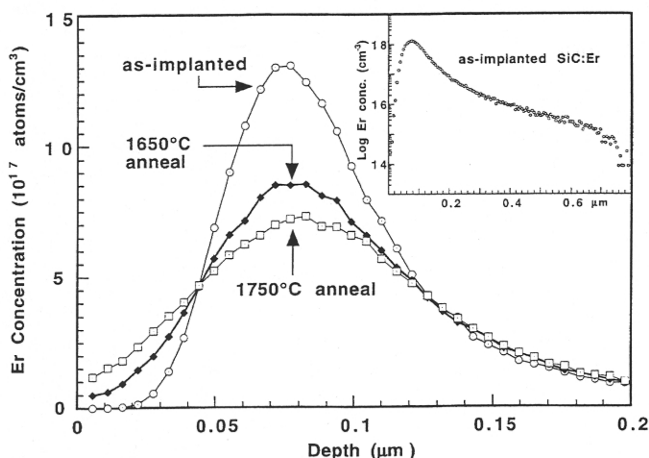

Fig. 1. Er depth profiles (SIMS) in 6H-SiC as function of annealing temperature. Inset contains as-implanted Er profile to a depth of 1 μm.

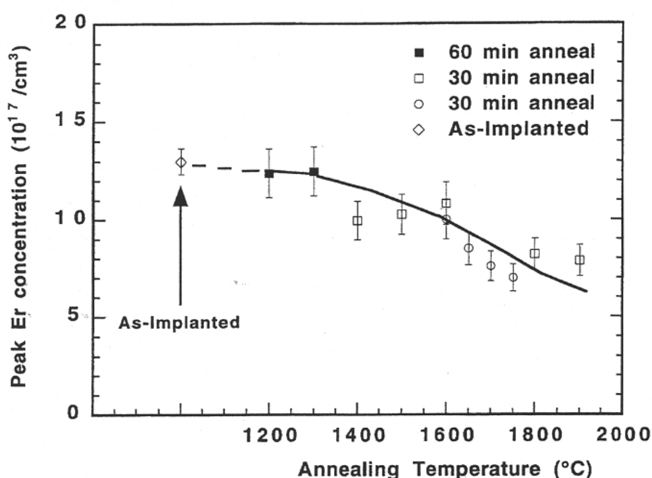

Fig. 2. Effect of anneal temperature on peak Er concentration in 6H-SiC.

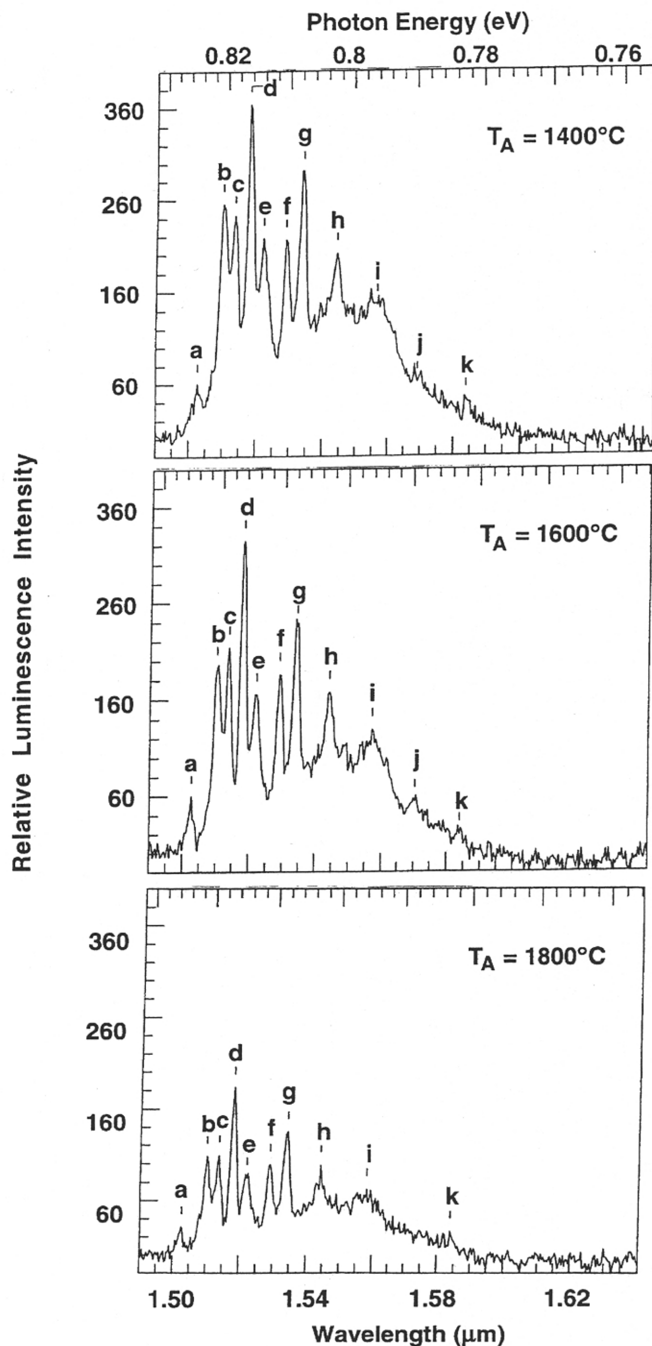

Fig. 3. Relative luminescence intensity measured at 293°K from 6H-SiC:Er samples annealed at several temperatures: (a) 1400, (b) 1600, and (c) 1800°C.

lengths in the 1.5–1.56 μm region when measured at temperatures as high as 150°C. This is a very exciting prospect as it would enable the operation of optical communications systems at the higher temperatures generated by higher bandwidth or higher power. In this paper, we report on the effect of anneal temperature on near-infrared (IR) PL in Er-implanted 6H SiC. We also report Er diffusivity values obtained from the modification of the implanted depth profile as a function of anneal temperature.

EXPERIMENTAL CONDITIONS

The samples used in these experiments consisted of <0001> 6H SiC substrates with an off-axis angle of 3.5±0.5°. The substrates were n-type as-grown, with a carrier concentration of 3×10^{17} to 2×10^{18}/cm^3. The Er was introduced by a single implantation perpendicular to the substrate surface at 330 keV with a dose of 1×10^{13}/cm^2. These conditions were chosen based on results[17] with Er-implanted Si, which indicated that at an implantation energy of 330 keV, a dose of 1×10^{13} Er/cm^2 resulted in a maximum PL emission at 1.54 μm. This is in contrast to conditions previously used[16] in Er-doped SiC where multiple implants at several energies (from 1 MeV to 40 keV) were used to obtain a roughly square Er profile. After implantation, isochronal anneals were performed in ultra-high purity Ar under the following conditions:

- Set A: for 60 min at temperatures from 1200 to 1350°C;
- Set B: for 30 min at temperatures from 1400 to 1900°C; and
- Set C: for 30 min at temperatures from 1600 to 1750°C.

Sets B and C were annealed and characterized at different times. The as-implanted Er concentration profile in the 6H SiC samples and the effect of anneal on the Er concentration was obtained by secondary ion mass spectrometry (SIMS) depth profiling with a 6 keV O_2^+ beam. Photoluminescence spectra were obtained primarily at room temperature using 46 mW HeCd laser excitation, a grating monochromator and a North Coast liquid-nitrogen cooled Ge detector.

RESULTS AND DISCUSSION

As shown in the SIMS depth profile of Fig. 1, the as-implanted concentration has a Gaussian profile with a peak concentration of $\sim 1.3 \times 10^{18}/cm^3$ at a depth of 770Å. From the exponential tail seen in the semi-log plot of the Fig. 1 inset, it is clear that the off-axis orientation angle of the substrate was not sufficient to prevent the occurrence of ion channeling. However, the projected range compares very favorably with predicted values.

Several Er depth profiles obtained after annealing at different temperatures are compared with the as-implanted profile in Fig. 1. As expected, annealing causes Er out-diffusion from the implanted profile toward the surface and the bulk of the 6H SiC substrate. The values of the peak Er concentrations in the 6H SiC are plotted as a function of anneal temperature from 1200 to 1900°C in Fig. 2.

The 6H-SiC:Er photoluminescence in the 1.5 to 1.6 μm region obtained at 293°K from 6H-SiC:Er samples is shown in Fig. 3 for samples annealed at 1400 to 1800°C. A complex, multi-line spectrum is observed, containing approximately ten well-defined peaks (labeled a through k) between 1.5 and 1.58 μm, and several additional less distinct peaks. The wavelength associated with each peak does not vary (within experimental error) with annealing temperature. The relative intensities of the peaks do not change significantly with anneal temperature, resulting in spectra with very similar patterns.

The six-line segment (peaks labeled b, c, d, e, f, g) from 1.51 to 1.53 μm appears to be the characteristic signature of the 6H-SiC:Er PL spectrum, appearing in all samples measured at room temperature. This sextuplet is also observed in samples annealed at temperatures as low as 1200°C. No single peak dominates, but peaks d and g at 1.5183 μm (816.4 meV) and 1.5343 μm (807.9 meV) consistently exhibit the highest amplitude.

While our main purpose in this study is the investigation of the operation of 6H SiC:Er at room temperature or above, we have measured low tem-

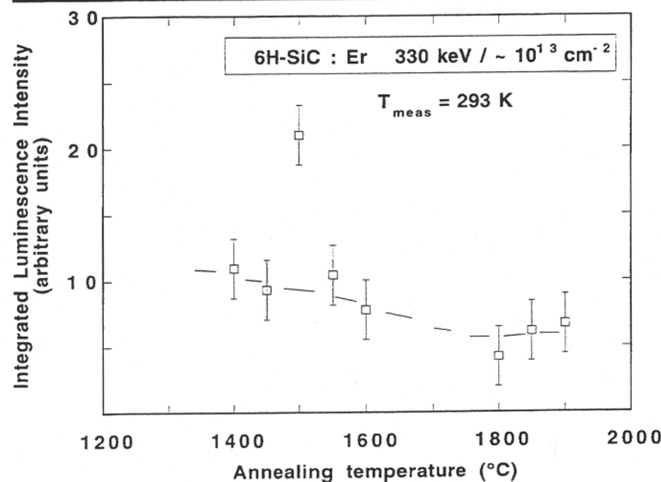

Fig. 4. Integrated (1.5–1.6 μm) luminescence intensity measured at 293°K from 6H-SiC:Er samples annealed at 1400–1900°C.

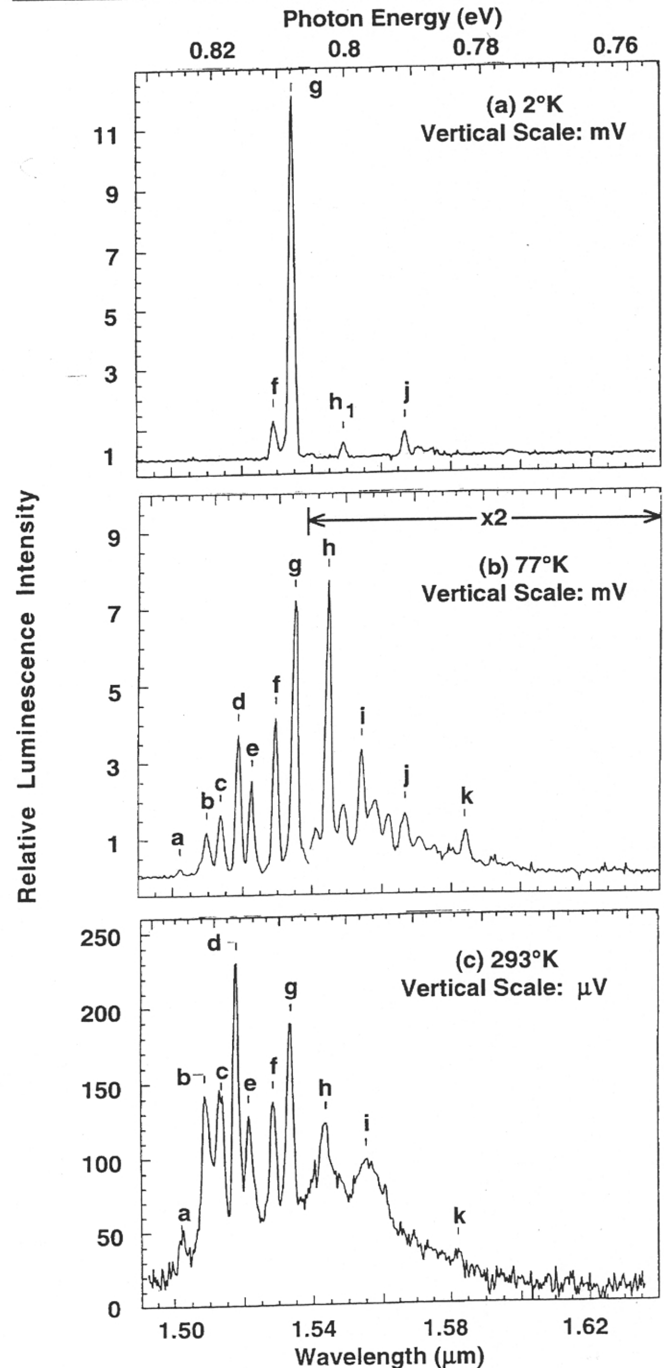

Fig. 5. Relative luminescence intensity measured from an 6H-SiC:Er sample annealed at 1600°C and measured at (a) 2, (b) 77, and (c) 293°K.

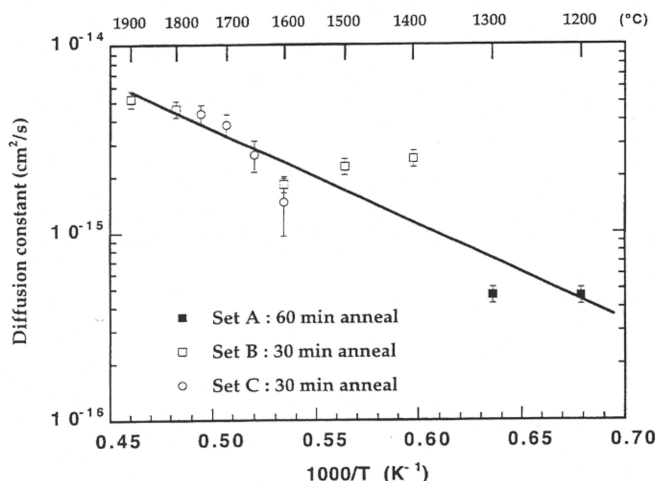

Fig. 6. Er diffusivity in 6H-SiC as a function of anneal temperature.

perature PL spectra for comparison purposes. As shown in Fig. 5, the same sextuplet observed at 293°K is also present at 77°K. However, at 2°K, there is only one major emission peak (the g-line) at 1.5345 (807.8 meV). The energy difference between adjacent peaks ranged from 1.9 to 3.8 meV. It is possible that other peaks with much lower intensity are present. The origin of the multiple peak emission is due to the crystal field splitting of each of the free Er^{3+} energy levels into multiple sublevels arrayed in the vicinity of the original energy level.

In the wavelength range of interest, the transitions to be considered are from substates of the $^4I_{13/2}$ level to substates of the $^4I_{15/2}$ level. Interestingly, the emission wavelength of most of the lines are essentially constant with both anneal temperature and measurement temperature. This indicates that in SiC as in other semiconductors the nature, but not the intensity, of the Er emission is independent of the host material.

The integrated luminescence intensity (from 1.5 to 1.64 μm) was obtained from data taken under identical circumstances at 293°K to insure equivalent conditions of incident excitation light for Er-implanted 6H-SiC samples annealed at temperatures from 1400 to 1900°C. As plotted in Fig. 4, it can be seen that an approximately constant integrated luminescence is obtained over this temperature range, with a slight trend toward decreasing luminescence with increasing temperature. The integrated luminescence intensity obtained after annealing at 1500°C does not follow the trend, being approximately two times larger than for samples annealed at temperatures 50°C higher and lower.

The photoluminescence value at 1500°C was confirmed by repeating the measurement. Possible explanations for this effect include variation in surface conditions (affecting the percentage of reflected vs absorbed light) or a higher Er dose being inadvertently being implanted in this particular sample. In order to fully establish whether there is indeed a sharp increase in luminescence intensity after annealing at 1500°C, the entire set of experiments (implantation and annealing) needs to be repeated. Finally, annealing at temperatures below 1400°C (down to the lowest temperature investigated—1200°C) resulted in the integrated luminescence decreasing rapidly.

Very little published information[18] exists on the diffusivity of impurities (mainly B, Al, and N) in 6H-SiC and no information exists on the diffusivity of rare earth elements. The effect of diffusion on the implanted concentration profile[19] is given by

$$N(x,t) = \frac{Q}{[2\pi(\Delta R_p^2 + 2Dt)]^{1/2}} \exp\left\{-\frac{(x - R_p)^2}{2(\Delta R_p^2 + 2Dt)}\right\} \quad (1)$$

where Q is the ion dose, R_p is the projected range, ΔR_p is the straggle, D is the diffusivity, and t is the anneal time. This relation assumes that the initial implanted depth profile can be approximated by a Gaussian distribution. We have calculated the Er diffusivity by fitting the Er concentration in the Gaussian region after each anneal to Eq. (1). We estimate an error of ±5% in fitting the experimental data to the simulated profile.

Values of Er diffusivity from 4.5×10^{-16} cm²/s at 1200°C to 5.5×10^{-15} cm²/s at 1900°C were obtained by this technique. An activation energy (E_a) of 0.98 eV for Er diffusivity in 6H-SiC is obtained from the diffusion constant vs inverse temperature plot in Fig. 6. The values of ^{167}Er diffusivity obtained from the fit is in agreement with the few reports of impurity diffusivity in 6H-SiC available in the literature, roughly decreasing with the mass of the element: (a) ^{11}B - 6×10^{-13} cm²/s at 1850°C reported by Vodakov et al.;[20] (b) ^{14}N - 5×10^{-9} cm²/s at 2447°C reported by Slack and Scace;[21] (c) ^{27}Al - 2×10^{-12} cm²/s at 1800°C reported by Chang et al.;[22] and 8×10^{-13} cm²/s at 1850°C reported by Vodakov et al.;[20] (d) ^{52}Cr - 2.2×10^{-13} cm²/s at 1750°C reported by Griffiths.[23]

SUMMARY AND CONCLUSIONS

The effect of annealing on Er-implanted 6H-SiC has been investigated at temperatures from 1200 to 1900°C. Anneal temperatures in the 1400 to 1900°C range produced strong room temperature PL at 1.5 to 1.6 μm wavelengths. Annealing 6H-SiC:Er at temperatures as low as 1200°C provides near-infrared luminescence with substantial intensity and with the same characteristic lines as observed from samples annealed at higher temperatures.

These findings have several important technological implications: (a) annealing of 3C-SiC:Er can be performed in the conventional quartz tube furnaces which are widely utilized by the semiconductor industry; (b) structures consisting of 3C-SiC:Er films grown on Si may be feasible, since the anneal temperature required for Er activation is lower than the Si melting point. In turn, this lays open the possibility of integrating efficient room temperature 1.5 μm emitters in 3C-SiC:Er with Si microelectronics technology for on-chip control, signal processing, and memory capabilities.

REFERENCES

1. H. Ennen, J. Schneider, G. Pomrenke and A. Axman, *Appl. Phys. Lett.* 43, 943 (1983).
2. G.S. Pomrenke, H. Ennen and W. Haydl, *J. Appl. Phys.* 59, 601 (1986).
3. R.S. Smith, H.D. Müller, H. Ennen, P. Wennekers and H. Maier, *Appl. Phys. Lett.* 50, 49 (1987).
4. J. Michel, J.L. Benton, R.F. Ferrante, D.C. Jacobson, D.J. Eaglesham, E.A. Fitzgerald, Y.-H. Xie, J.M. Poate and L.C. Kimerling, *J. Appl. Phys.* 70, 2672 (1991).
5. P.N. Favennec, H. L'Haridon, D. Moutonnet, M. Salvi and M. Gauneau, *Jpn. J. Appl. Phys.* 29, L524 (1990).
6. F.Y.G. Ren, J. Michel, Q. Sun-Paduano, B. Zheng, H. Kitagawa, D.C. Jacobson, J.M. Poate and L.C. Kimerling, *Mater. Res. Soc. Symp. Proc.* 301, 87 (1993).
7. S. Lombardo, S.U. Campisano, G.N. van den Hoven, A. Cacciato and A. Polman, *Appl. Phys. Lett.* 63, 1942 (1993).
8. G. Franzo, F. Priolo, S. Coffa, A. Polman and A. Carnera, *Appl. Phys. Lett.* 64, 2235 (1994).
9. T. Kimura, A. Yokoi, H. Horiguchi, R. Saito, T. Ikoma and A. Sato, *Appl. Phys. Lett.* 65, 983 (1994).
10. P.N. Favennec, H. L'Haridon, M. Salvi, D. Moutonnet and Y. Le Guillou, *Electron. Letts.* 25, 718 (1989).
11. P.N. Favennec, H.L'Haridon, D. Moutonnet, M. Salvi and M. Gauneau, *Mater. Res. Soc. Symp. Proc.* 301, 181 (1993).
12. For a recent review of wide band-gap semiconductors see H. Morkoç, S. Strite, G.B. Gao, M.E. Lin, B. Sverdlov and M. Burns, *J. Appl. Phys.* 76, 1363 (1994).
13. A.J. Neuhalfen and B.W. Wessels, *Appl. Phys. Lett.* 60, 2657 (1992).
14. X.Z. Wang and B.W. Wessels, *Appl. Phys. Lett.* 64, 1537 (1994).
15. R.G. Wilson, R.N. Schwartz, C.R. Abernathy, S.J. Pearton, N. Newman, M. Rubin, T. Fu, and J.M. Zavada, *Appl. Phys. Lett.* 65, 992 (1994).
16. W.J. Choyke, R.P. Devaty, L.L. Clemen, M. Yoganathan, G. Pensl and Ch. Hässler, *Appl. Phys. Lett.* 65, 1668 (1994).
17. D. Moutonnet, H. L'Haridon, P.N. Favennec, M. Salvi, M. Gauneau, F. Arnaud D'Avitaya, and J. Chroboczek, *Mater. Sci. & Engin.* B4, 75 (1989).
18. D.Y. Yarbrough, *Solid State Techn.* 23 (Nov. 1968).
19. T.E. Seidel, *VLSI Technology*, ed. S.M. Sze, (New York: McGraw-Hill, 1983), ch. 6.
20. Ya.A. Vodakov, E.N. Mokhov and M.B. Reifman, *Sov. Phys.-Solid State*, 8, 1040 (1966).
21. G.A. Slack and R.I. Scace, *J. Chem. Phys.* 42, 805 (1965).
22. H. Chang, C.Z. LeMay and L.F. Wallace, *Silicon Carbide*, ed. J.R. O'Connor and J. Smiltens, (Pergamon Press Ltd., 1960), p. 496.
23. L.B. Griffiths, *J. Appl. Phys.* 36, 571 (1965).
24. A.J. Steckl and J.P. Li, *IEEE Trans. Electron. Dev.* 39, 64 (1992).
25. C. Yuan, A.J. Steckl and M.J. Loboda, *Appl. Phys. Lett.* 64, 3000 (1994).