

Growth and photoluminescence of high quality SiGeC random alloys on silicon substrates

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We report chemical vapor deposition growth of SiGeC layers on $\langle 100 \rangle$ Si substrates. At the growth temperature of 550 °C, the C concentration as high as 2% can be incorporated into SiGe (Ge content $\sim 25\%$) to form single crystalline random alloys by using low flow of methylsilane (0.25 sccm) as a C precursor added in a dichlorosilane and germane mixture. For intermediate methylsilane flow (0.5 sccm – 1.5 sccm), the Fourier transform infrared spectroscopy (FTIR) absorption spectra indicate the growth of amorphous layers. For the layers with high flow of methylsilane (12 sccm), there are silicon-carbide-like peaks in the FTIR spectra, indicating silicon carbide precipitation. The films were also characterized by x-ray diffraction, high resolution transmission electron microscopy, secondary ion mass spectroscopy, and Rutherford backscattering spectroscopy to confirm crystallinity and constituent fractions. The defect-free band-edge photoluminescence at both 30 K and 77 K was observed in Si/SiGeC/Si quantum wells, even at power densities as low as 0.5 W/cm² and 1 W/cm², respectively. Deep photoluminescence around 0.8 eV and luminescence due to D_3 dislocations at 0.94 eV were not observed under any excitation conditions. © 1996 American Institute of Physics. [S0021-8979(96)02217-7]

I. INTRODUCTION

There has been remarkable progress in recent years in Si/SiGe technology, with heterojunction bipolar transistor (HBT) performance of f_T (cutoff frequency) and f_{\max} (maximum frequency of oscillation) of 117 GHz¹ and 160 GHz,² respectively, having been reported. Further applications of the material system are limited, however, by the critical thickness constraints of strained layers. To overcome this limitation, the incorporation of carbon into random Si_{1-x}Ge_x has attracted great interest. Because the lattice constant of cubic carbon (diamond) is 52 % smaller than that of Si,³ the substitutional incorporation of C can compensate the compressive strain of SiGe on Si and can increase the thickness of pseudomorphic SiGe layers on Si.⁴ On the other hand, the C incorporation may also have an effect on the material quality of new SiGeC layers, because of interstitial C incorporation and silicon carbide precipitation. We have therefore investigated the incorporation of C into SiGe layers on Si substrates to form such SiGeC random alloys. We report the growth and characterization of such single crystalline SiGeC random alloys.

The main challenge in fabricating such alloys is to incorporate C atoms in substitutional sites instead of forming the thermodynamically favored precipitates of SiC. Several

techniques have been reported to fabricate SiGeC alloys. Eberl *et al.*³ used molecular beam epitaxy (MBE) to grow SiGeC at the temperature of 400–550 °C. Im *et al.*⁵ used solid phase epitaxy to grow SiGeC at 800 °C following implantation of C and Ge into Si. However, no optical results and very limited electric results⁶ have been obtained from the alloys grown by these two techniques. Our group⁷ and others⁸ have observed band-edge photoluminescence (PL) in films grown by rapid thermal chemical vapor deposition (RTCVD), but only at pump power levels of ≥ 25 W/cm², and often defect levels were also observed.⁸

In this paper, we report the observation of defect-free band-edge photoluminescence at a power density as low as 1 W/cm². This indicates a very low nonradiative impurity density in our SiGeC films.

II. GROWTH AND STRUCTURAL MEASUREMENTS

All samples reported in this paper were grown on 100-mm (100) Si wafers by RTCVD. The SiGeC layers were grown at 550 °C using methylsilane as C source. The growth temperature was measured on all samples by infrared transmission.⁹ The growth pressure was 6 Torr. The gas flows were 3 standard liters per minute (slpm) for a hydrogen carrier, 26 sccm for dichlorosilane, and 0.8 sccm for germane. This yields SiGe layers with a nominal Ge fraction of 0.25. The details of the RTCVD reactor can be found in Ref. 9.

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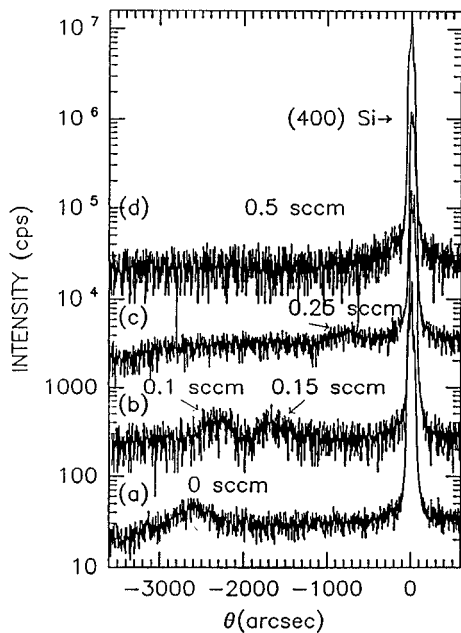


FIG. 1. Double crystal x-ray rocking curves of SiGeC alloys with Ge fraction of ~ 0.25 . The addition of methylsilane led to the shift of SiGeC (400) peaks. Further increase of methylsilane flow of 0.5 sccm yielded amorphous layers. Note that sample(b) had two layers of SiGeC alloys and thicknesses of these films were about 400 Å.

As small amounts of methylsilane were added to the source gases, we observed a shift in the (400) x-ray diffraction peak of the resulting 400 Å $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ layers away from that of a similar layer without C (Fig. 1). The largest shift ($\Delta\theta$ of 1800 ± 200 arcsec) was observed for a methylsilane flow of 0.25 sccm [Fig. 1(c)]. Assuming a compensation ratio of 1% C to 8% Ge,⁴ this corresponds to $2 \pm 0.2\%$ C. The broadening of the diffraction peaks with FWHM of ~ 400 arcsec was due to the thin layers (400 Å) and was close to the estimated value of 430 arcsec using the Scherrer formula.¹⁰ Growth rate with no methylsilane flow was 4 Å/min. Methylsilane flow had little effect on growth rate at these flow rates. The SIMS (secondary ion mass spectroscopy) profile of the same sample also confirmed a C concentration of 2% (Fig. 2) with flat C and Ge profiles. The SIMS also revealed that the Ge fraction was not substantially changing as C was introduced so that the change of x-ray diffraction was not due to a reduction in the Ge content. Fig. 3 shows the estimated C concentration vs methylsilane flow. Further increase of the methylsilane flow to 0.5 sccm yielded layers with no extra crystalline peaks [Fig. 1(d)], indicating possible growth of amorphous layers. Note that the sample with 0.5 sccm methylsilane flow was also extensively studied by XRD for the θ value from 0 to +3600 arcsec (not shown here), but no diffraction peak was observed. However, it is still possible that the SiGeC peak was hidden under the (400) Si peak. To study the material structure of the SiGeC layers formed with high methylsilane flow, the FTIR (Fourier transform infrared spectroscopy) absorption measurements were performed. Three distinct types of FTIR spectra (Fig. 4) were observed, depending on the methylsilane flow. At low flow (0.25 sccm), the FTIR [Fig. 4(a)] showed a sharp absorption

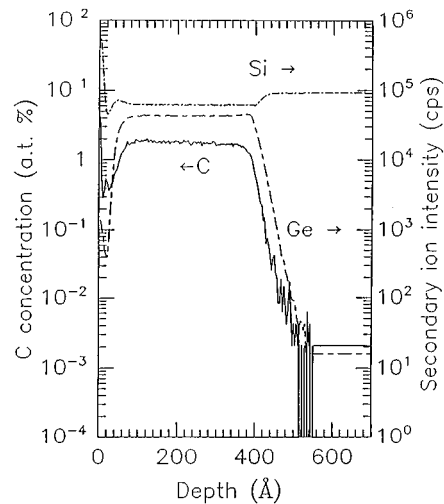


FIG. 2. SIMS plots of a SiGeC alloy to confirm the C fraction of 2%.

peak at 600 cm^{-1} , which is characteristic of vibration frequency of substitutional C in Si.¹¹ This is consistent with the x-ray diffraction results, indicating a single crystalline layer. At intermediate flow (1.5 sccm), a broad peak from 600 cm^{-1} to 840 cm^{-1} was observed [Fig. 4(b)], very similar to the absorption spectrum of amorphous silicon carbide.¹² This is again consistent with x-ray diffraction results that no diffraction peak was observed for samples with similar methylsilane flow. At high flow (12 sccm), there were two new absorption peaks around 800 cm^{-1} and 960 cm^{-1} [Fig. 4(c)]. These are consistent with the TO and LO phonon vibrations, respectively, of various silicon carbide polytypes.^{13,14} This indicates the possible formation of polycrystalline SiC precipitates. The $\sim 2\%$ substitutional C obtained in SiGe using low temperature CVD with methylsilane in this work is consistent with the limit observed by other groups using similar techniques.¹⁵

Two $\text{Si}/\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}$ quantum well samples (well thickness ~ 60 Å) were grown for PL measurement, with $y=0$ (no methylsilane, sample 1604) as a control sample and with $y=0.003$ (sample 1607). Because the methylsilane flow for 1607 was very small (less than 0.1 sccm) and not repeat-

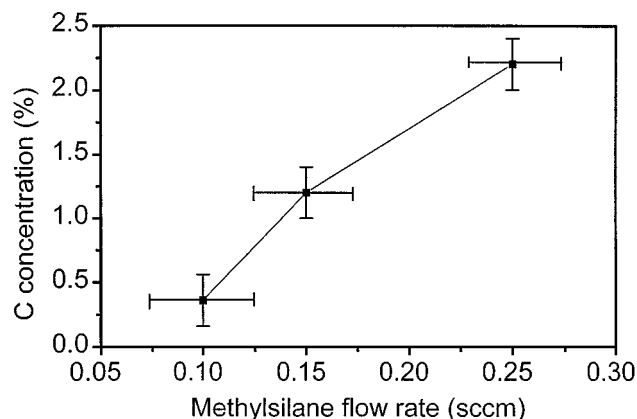


FIG. 3. Carbon concentration as a function of the methylsilane flow.

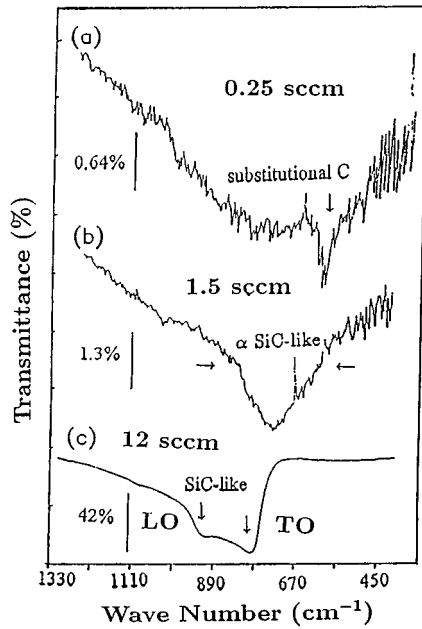


FIG. 4. FTIR spectra of SiGeC samples with different methylsilane flows. Three distinct types of spectra are observed, depending on the methylsilane flow. A substrate without epilayers was used as a reference sample to remove substrate absorption modes. Estimated SiGeC layer thicknesses are 200 Å. Note that scales are different for each spectrum.

able with our mass flow controller, an exact methylsilane flow cannot be reported. The thicknesses of these two quantum wells were measured by high resolution transmission electron microscopy (HRTEM) in cross-sectional configuration. Neither samples showed evidence of SiC precipitates or other defects in plan view or cross section. Fig. 5 shows the cross-sectional HRTEM image of the SiGeC quantum well. The interfaces were not atomically abrupt, yielding a thickness variation in both wells of about 10%. Using this thickness and the integrated atomic areal density of Ge (with $\pm 5\%$ error bar) from Rutherford backscattering spectroscopy (RBS), the Ge contents in the quantum wells were

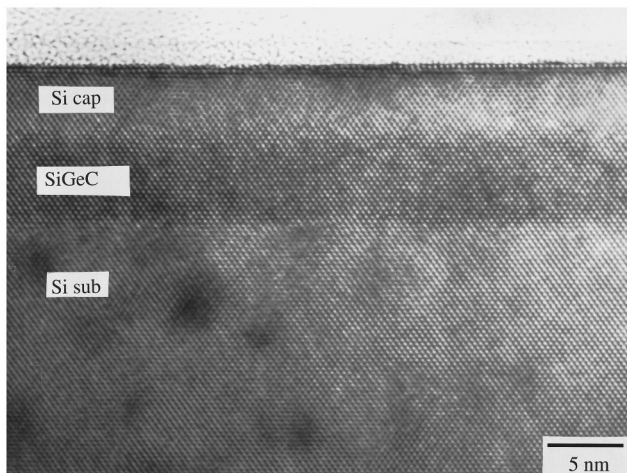


FIG. 5. High resolution cross-section TEM of a 60 Å Si/Si_{0.73}Ge_{0.27}C_{0.003}/Si quantum well.

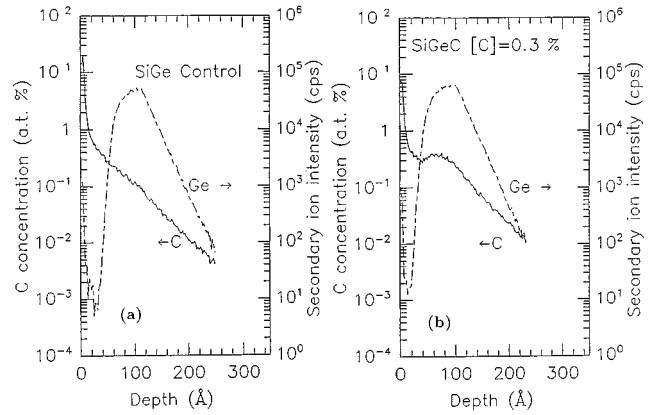


FIG. 6. SIMS plots of (a) a control Si/SiGe/Si quantum wells and (b) a Si/SiGeC/Si quantum well with a C content of 0.3%.

obtained: $x=0.25\pm 0.04$ (1602) and $x=0.27\pm 0.04$ (1607) were found. Calibrated secondary ion mass spectroscopy (SIMS) was used to measure the C concentration and SIMS profiles are presented in Fig. 6. After subtracting the background from the surface peak, a C concentration of 0.3% was found for sample 1607. The Si_{1-x-y}Ge_xC_y layers were capped with ~ 50 Å of silicon grown at 550 °C using 2 sccm silane and 3 slpm of hydrogen. Previous experiments on SiGe samples in our lab have shown that a Si cap increases the photoluminescence intensity by over an order of magnitude, presumably due to a decrease in surface recombination.¹⁶

III. PHOTOLUMINESCENCE

Photoluminescence (PL) measurements were performed with an Ar⁺ ion laser and a liquid N₂ cooled Ge detector. At a sample temperature of 77 K and a pump power density of 0.5–5 W/cm², the PL spectra of the Si/SiGeC/Si and Si/SiGe/Si quantum wells were qualitatively similar (Fig. 7). The PL appears consistent with emission from the band-edge

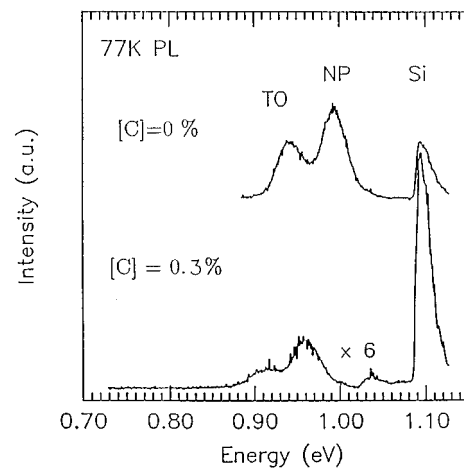


FIG. 7. 77 K photoluminescence spectra of a control Si/SiGe/Si quantum well and a Si/SiGeC/Si quantum well. The deep transition at 0.8 eV and D₃ dislocation line are not observed in the spectrum of the SiGeC sample.

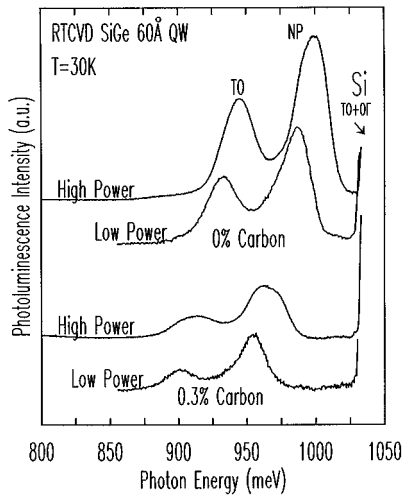


FIG. 8. 30 K photoluminescence spectra of a control Si/SiGe/Si quantum well and a Si/SiGeC/Si quantum well at power densities of 1 (low power) and 10 (high power) W/cm^2 .

recombination of electron-hole plasma.^{17,18} In Ref. 17, the expression of electron-hole plasma recombination gives an excellent fit to the line shapes. Other than the Si peak at 1.10 eV, the strongest peak is the no-phonon (NP) transition due to the lattice disorder (alloy fluctuations and interface roughness), which relaxes the momentum conservation requirement. The peak on the low energy side of the NP line is the overlap of the transverse optical (TO) phonon replicas. Note that the peak at 1.04 eV of SiGeC PL spectra is the two-phonon replica of bound exciton emission (one TO to conserve the momentum, and the other TO at Γ point) from Si.¹⁹ In the previous report of band-edge PL in $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ layers (with $x=0.15$ and $y=0.005$),⁸ at a pump power density of $\sim 1 \text{ W}/\text{cm}^2$ range, no band-edge PL was observed, and only a deep PL near 800 meV was seen. At a pump power density of $\sim 25 \text{ W}/\text{cm}^2$, band-edge PL was observed, but defect luminescence (the D_3 dislocation line) was also seen, suggesting some defects and strain relaxation in the samples. We observed band-edge luminescence already at a pump density of $0.5\text{--}5 \text{ W}/\text{cm}^2$, and deep luminescence or dislocation lines were not observed under any conditions. In other samples grown at 575°C , our group has previously reported defect-free luminescence, but only at much higher pump power ($\sim 50 \text{ W}/\text{cm}^2$) than those used here. This is the first time that such defect-free band-edge luminescence in SiGeC layers at such low pump power has been reported and indicates the high quality and lack of non-radiative recombination traps in the samples.

More complete measurements were made at 30 K at power densities from 0.5 to $10 \text{ W}/\text{cm}^2$ to examine the effect of power densities on bandgap. The spectra (Fig. 8) are similar to those at 77 K , with no deep transitions or D -lines under any excitation conditions. No PL was observed at 4 K for these samples grown at 550°C , however. Note that PL down to 2 K was observed for the SiGeC samples grown at 575°C .⁷ From 1 to $10 \text{ W}/\text{cm}^2$, peak energies of both samples show similar power dependence and SiGeC quantum wells have a lower bandgap than SiGe quantum wells (Fig. 9). The

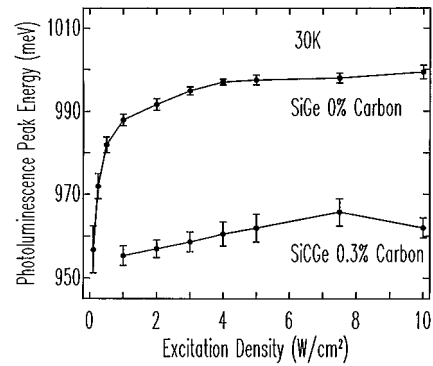


FIG. 9. Peak photoluminescence position vs pump power at 30 K for quantum wells with and without C.

blueshift of NP peak with increasing power density is due to the band-filling effect.¹⁷ Because of the large uncertainty in Ge content from sample to sample and in the quantum well width, the cause for the lower bandgap in the 0.3% C sample can not be ascribed to the C incorporation. Other work by our group and others shows the effect of initial C incorporation on band-edge PL is to raise the peak position by $21 \text{ meV}/\% \text{ C}$.^{7,8} The theoretical predictions of the effect of small C incorporation on relaxed $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ and $\text{Si}_{1-x}\text{C}_x$ bandgap vary from $+18 \text{ meV}/\% \text{ C}$ ²⁰ to $-100 \text{ meV}/\% \text{ C}$.²¹ Because of the strain in the SiGeC wells, these values cannot be compared directly to experimental results. Details can be found in Ref. 7.

The linewidth (FWHM) of the NP peaks was 35 meV at 77 K for the 0.3% C sample, similar to the SiGe samples in our lab grown at 625°C . The broadening may be due to the band filling and thermal broadening.¹⁷ The linewidth of 0.3% C sample became narrower at low pump power than at high pump power at 30 K spectra. At the same pump power, the 0.3% C sample had consistently a slightly wider linewidth ($\sim 5 \text{ meV}$ wider) than the control sample. The quantitative model of the linewidth is still not well understood.

IV. CONCLUSIONS

We have reported band-edge photoluminescence without defect lines in $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ layers at a power density as low as $\sim 1 \text{ W}/\text{cm}^2$. Substitutional carbon concentrations as high as 2% have been incorporated into SiGe to form single crystalline random alloys by using low flow of methylsilane (0.25 sccm). For the intermediate flow of methylsilane ($0.5\text{--}1.5 \text{ sccm}$), an amorphous layer was formed. At a flow of 12 sccm methylsilane, silicon carbide precipitates were observed. We also observed band-edge photoluminescence without defect lines in a $\text{Si}/\text{Si}_{0.73}\text{Ge}_{0.27}\text{C}_{0.003}/\text{Si}$ quantum well at a power density as low as $\sim 1 \text{ W}/\text{cm}^2$, the lowest power density reported so far, indicating the high quality of the SiGeC samples.

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- ¹E. Crabbe, B. S. Meyerson, J. M. C. Stork, and D. L. Hareme, *Tech. Dig. Int. Elec. Dev. Mtg.* 83 (1993).
- ²A. Schuppen, U. Erben, A. Gruhle, H. Kibbel, H. Schumacher, and U. Konig, *Tech. Dig. Int. Elec. Dev. Mtg.* 743 (1995).
- ³K. Eberl, S. S. Iyer, S. Zollner, J. C. Tsang, and F. K. LeGoues, *Appl. Phys. Lett.* **60**, 3033 (1992).
- ⁴J. L. Regolini, F. Gisbert, G. Dolino, and P. Boucaud, *Mater. Lett.* **18**, 57 (1993).
- ⁵S. Im, J. Washburn, R. Gronsky, N. W. Cheung, Y. M. Yu, and J. W. Ager, *Appl. Phys. Lett.* **63**, 2682 (1993).
- ⁶W. Faschinger, S. Zerlauth, G. Bauer, and L. Palmethofer, *Appl. Phys. Lett.* **67**, 3933 (1995).
- ⁷A. St. Amour, C. W. Liu, J. C. Sturm, Y. Lacroix, and M. L. W. Thewalt, *Appl. Phys. Lett.* **67**, 3915 (1995).
- ⁸P. Boucaud, C. Francis, F. H. Julien, J.-M. Lourtioz, D. Bouchier, S. Bodnar, B. Lambert, and J. L. Regolini, *Appl. Phys. Lett.* **64**, 875 (1994).
- ⁹J. C. Sturm, P. V. Schwartz, E. J. Prinz, and H. Manoharan, *J. Vac. Sci. Technol. B* **9**, 2011 (1991).
- ¹⁰B. D. Cullity, *Elements of X-ray Diffraction*, 2nd ed. (Addison-Wesley, Reading, MA, 1978), p. 102.
- ¹¹K. Eberl, S. S. Iyer, J. C. Tsang, M. S. Goorsky, and F. K. Legoues, *J. Vac. Sci. Technol. B* **10**, 934 (1992).
- ¹²T. Fukazawa, K. Sasaki, and Furukawa, in *Amorphous and Crystalline Silicon Carbide II, Springer Proceedings in Physics*, edited by M. M. Rahman, C. Y.-W. Yang, and G. L. Harris (Springer, Berlin, 1988), Vol. 43, p. 49.
- ¹³Z. C. Feng, W. J. Choyke, and J. A. Powell, *J. Appl. Phys.* **64**, 6827 (1988).
- ¹⁴W. J. Choyke, D. R. Hamilton, and L. Patrick, *Phys. Rev.* **133**, A1163 (1964).
- ¹⁵J. Mi, P. Warren, P. Letourneau, M. Judelewicz, M. Gailhanou, M. Dutoit, C. Dubois, and J. C. Dupuy, *Appl. Phys. Lett.* **67**, 259 (1995).
- ¹⁶J. C. Sturm, X. Xiao, P. V. Schwartz, and C. W. Liu, *J. Vac. Sci. Technol. B* **10**, 1998 (1992).
- ¹⁷X. Xiao, C. W. Liu, J. C. Sturm, L. C. Lenchyshyn, and M. L. W. Thewalt, *Appl. Phys. Lett.* **60**, 1720 (1992).
- ¹⁸C. W. Liu, J. C. Sturm, Y. Lacroix, M. L. W. Thewalt, and D. D. Perovic, *Appl. Phys. Lett.* **65**, 76 (1994).
- ¹⁹J. C. Sturm, A. St. Amour, Y. Lacroix, and M. L. W. Thewalt, *Appl. Phys. Lett.* **64**, 2291 (1994).
- ²⁰R. A. Soref, *J. Appl. Phys.* **70**, 2470 (1991).
- ²¹A. A. Demkov and O. F. Sankey, *Phys. Rev. B* **48**, 2207 (1993).