DEFECT-FREE BAND-EDGE PHOTOLUMINESCENCE IN SiGeC STRAINED LAYERS GROWN BY RAPID THERMAL CHEMICAL VAPOR DEPOSITION

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ABSTRACT

The defect-free band-edge photoluminescence at both 30K and 77K was observed for the first time in Si/SiGeC/Si quantum wells. The SiGeC samples were prepared by rapid thermal chemical vapor deposition (RTCVD) by using methylsilane as carbon source added in a dichlorosilane and germane mixture. Deep photoluminescence around 0.8 eV, previously reported by Boucaud et al., was no longer observed under any excitation conditions. Compared to control Si/SiGe/Si quantum wells, the initial effect of adding the C is to decrease the bandgap of the host SiGe layers, despite the fact that the diamond has a large bandgap.

INTRODUCTION

Recently, the SiGe technology has significant progress to fabricate Si/SiGe heterojunction bipolar transistors (HBT) with f_T and f_{max} of 117GHz[1] and 120GHz[2], respectively. However, further applications of the strained SiGe technology is limited due to the critical thickness[5] constraint on pseudomorphic growth of SiGe on Si. For the thickness larger than the critical thickness, the SiGe layers may generate dislocations at the Si and SiGe interface, which has detrimental effect on device performance. The strain, therefore, will restrict applications of SiGe technology such as super graded bases of HBTs and i-layers of the pin detectors, where high Ge content or large thickness is required. To overcome the strain limitation, the incorporation of C into SiGe layers attracts much 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 increases the thickness of pseudomorphic SiGeC layers on Si[4]. The C incorporation may also have effects on the band structure of new SiGeC layers, especially the bandgap.

Molecular beam epitaxy (MBE)[3], solid phase epitaxy[6], and RTCVD[4] have been reported to fabricate SiGeC alloys. However, no electrical results have been obtained from the alloys of previous work. Boucaud et al.[7] reported photoluminescence(PL) measurements of SiGeC alloys grown by RTCVD at 550°C. However, there were deep level transitions in the PL spectra, indicating some imperfect crystallinity in their SiGeC films. In this paper, we study the incorporation of C into SiGe layers on Si substrates by RTCVD and report the first defect-free band-edge photoluminescence of the Si/SiGeC/Si quantum wells. The electrical measurement of Si/SiGeC HBTs will be reported elsewhere[8].

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GROWTH

All the SiGeC 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 accurately measured on all samples by infrared transmission with the estimated error of ±5°C[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 100 sccm for the germane mixture (0.8 % in hydrogen). The methylsilane flow varied from 0 to 12 sccm. For samples characterized by photoluminescence, the SiGeC layers were capped with ~ 50Å of silicon. The Si cap layers were grown at 550°C by flowing 100-sccm silane mixture (2% in hydrogen) and 3-slpm 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.
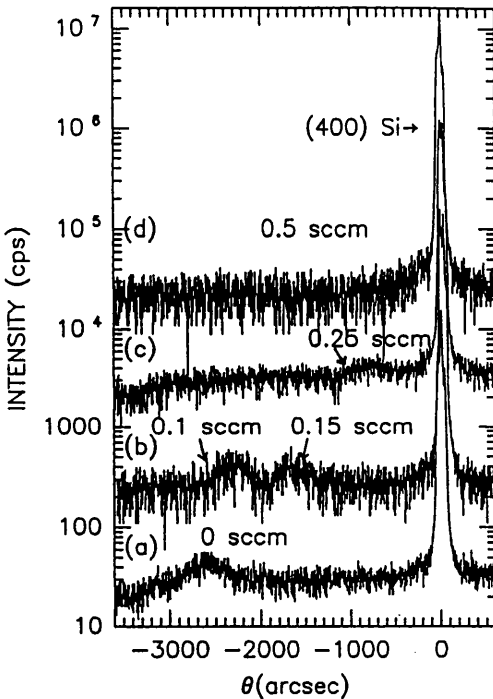

Fig.1 The double crystal X-ray rocking curves of SiGeC alloy layers. The addition of methylsilane leads to the shift of SiGeC (400) peaks towards the Si (400) peaks up to a methylsilane flow of 0.25 sccm. This indicates the strain in the SiGeC alloy is reduced. From the shift, the C concentration in (c) can be estimated as high as 2%. Further increase of the methylsilane flow to 0.5 sccm leads to amorphous layers. Note that the sample (b) had two layers of SiGeC alloys.

To study the reduction of compressive strain of SiGe by adding substitutional C, a set of samples with different methylsilane flows were grown, while the other flows were maintained at the same conditions. The thicknesses of these SiGeC films were 40 nm, characterized by sputter Auger profiling. No dislocation lines were observed in any of these films by defect etching[10]. The double crystal X-ray diffractometer was used to obtain the rocking curves around (400) diffraction peaks of Si substrates. The films without any methylsilane flow revealed a Ge content of 0.25, estimated from separation of (400) peaks between Si and SiGe in the X-ray rocking curves(Fig.1(a)). The addition of methylsilane led to the shift of SiGeC peaks towards the Si (400) peaks up to a methylsilane of 0.25

sccm(Fig.1 (b) and (c)). This indicates the strain in the SiGeC was reduced. Note that the samples in Fig.1(b) has two SiGeC layers. The broad and weak SiGeC peaks were due to the small thickness (40 nm) of those films. Assuming the Ge content is the same for the addition of small amount of C, and using the compensation ratio of 1%C to 8%Ge[4], we can estimate the C concentration in these SiGeC layers. The maximun C concentration obtained was 2 % for the methylsilane flow of 0.25 sccm(Fig.1(c)). The calibrated Secondary Ion Mass Spectrometry (SIMS) of the same sample also confirms that the C concentration is about 2%. The Fourier Transform Infrared Spectroscopy (FTIR, not shown here) of a similar sample with the same 0.25 sccm methylsilane flow exhibited a sharp vibration peak at 600 cm^{-1}, characteristic of substitutional carbon. For SiGeC layers with the methylsilane flow of 0.5 sccm, there is no diffraction peak besides the Si substrate peak in the rocking curve(Fig1.(d)), indicating amorphous growth.

Two quantum well samples were grown for the PL measurements. One is the 60 Å Si/Si$_{0.75}$Ge$_{0.25}$/Si quantum well, which is the control sample. The other one is the 60Å Si/Si$_{0.73}$Ge$_{0.27}$C$_{0.003}$/Si quantum well. The thicknesses of these two quantum wells were measured by high resolution transmission electron microscopy (HRTEM) in cross-sectional configuration and showed no SiC precipitates in plan view or cross section. Both quantum wells were defect free on the scale of HRTEM. The thickness variation in both well is about 10 %, although the interface is not atomically abrupt. Using this thickness and the integrated atomic areal density of Ge from Rutherford Backscattering Spectroscopy (RBS) and assuming that atomic density of SiGeC is a linear function of Ge content (since the C content is so small) , the Ge contents in the quantum wells were obtained. Calibrated SIMS was used to measure the C concentration. The SiGeC is clearly present in Fig.2. The C concentration of 0.3 % was obatined for the Si/SiGeC/Si sample, after substracting the background from the surface peak.
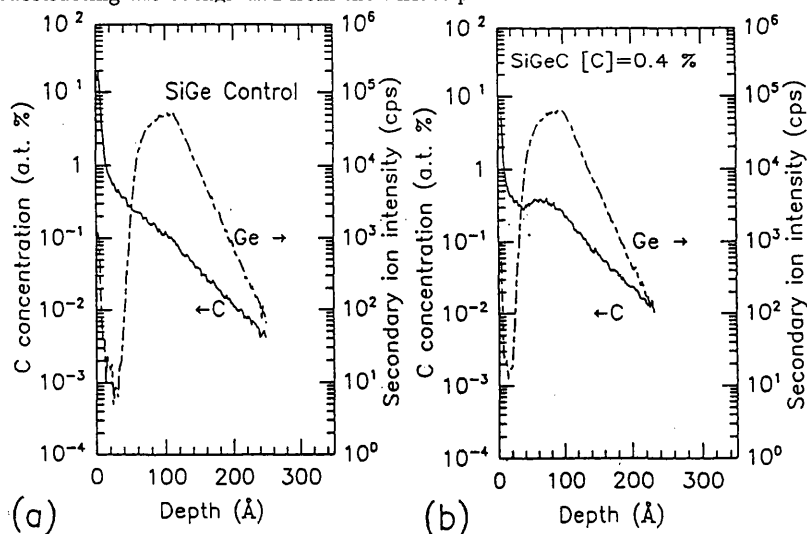

Fig.2. SIMS plots of (a) a control Si quantum well and (b) a Si/SiGeC/Si quantum well. The bump on the C profile in (b) indicates the C concentration in SiGeC is about 0.3%.

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PHOTOLUMINESCENCE

The photoluminescence (PL) was taken with an Ar^+ ion laser and a Ge detector. At 77K and a power density of 1 W/cm^2, the PL spectrum of the Si/SiGeC/Si and quantum wells is qualitatively similar to that of Si/SiGe/Si quantum wells (Fig.3), and presumably due to band-edge electron-hole plasma recombination[11, 12]. The strongest peak in the spectrum is the no-phonon (NP) transition due to the lattice disorder (alloy fluctuations, interface roughness, and impurities) which relaxes the momentum conservation requirement. Another peak on the low energy side of the NP line is the overlap of the transverse optical (TO) phonon replicas. The the deep level transition at 0.8 eV and D$_3$ dislocation lines, previously reported by Boucaud et al.[7], do not exist in the spectra at the power density from 0.1 W/cm^2 to 10 W/cm^2. This is the first time that such defect-free PL of SiGeC has been demonstrated. 0.1 W/cm^2 is the lowest pump power density for which band-edge SiGeC PL has been reported. In previous work[7], band-edge PL (always with D$_3$ lines) was observed only for the power density over 25 W/cm^2(spot size: 0.5 mm in diameter). At power density under 42 W/cm^2 (spot size: 3mm in diameter), only deep PL was observed.
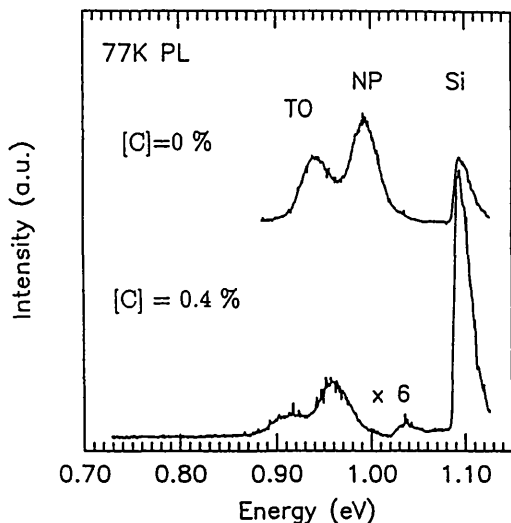

Fig.3 77K PL spectra of a Si/SiGe/Si quantum well and a Si/SiGeC/Si qunatum well. The deep transition at 0.8 eV and D$_3$ dislocation lines are not observed in the spectrum of the SiGeC sample.

30K PL spectra of these two quantum well samples (Fig.4) are similar to those at 77K, with no deep PL or D-lines. No PL was observed at 4K. This origin is not clear, but may be related to the impurities in the SiGeC quantum wells due to the impure methylsilane source. For the power density from 0.5 to 10 W/cm^2, the peak energy of of SiGeC sample is on average 36 meV lower than that of SiGe control sample, with similar power dependence[13]. The slightly lower Ge content of SiGeC sample, compared to SiGe control sample (27 % vs 25 %), contributes 15 meV of the 36 meV red shift. Note that the uncertainty of the quantum confinement energy due to the uncertainty in the quantum well thickness is within 5 meV, based on our previous study[14]. The bandgap decrease of SiGeC wells is, therefore, about 21 meV solely due to the carbon incorporation, after the

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correction of Ge content difference. The error bars on this number are ±30meV, primarily from the uncertainty in measuring exact Ge content in the quantum wells.
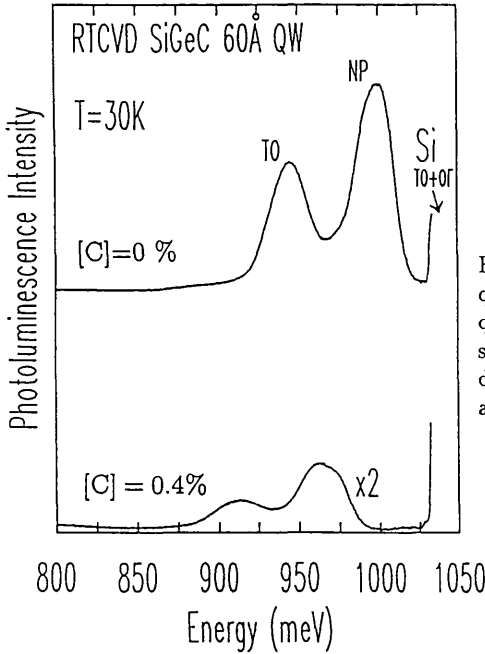

Fig.4 30K PL spectra of (a) a Si/SiGe/Si quantum well and (b) a Si/SiGeC/Si quantum well. The spectra are very similar to the 77K PL spectra. No deep transition and D_3 dislocation lines are observed.

The carbon incorporation into SiGe on Si has two effects on the bandgap. One is the strain relaxation (the C compensates the compressive strain of Ge), which would increases the bandgap of the SiGeC quantum wells. The 0.3 % C can compensate 2.4% Ge. The compressive strain of Ge in the SiGe layers grown on Si causes the decrease of bandgap by 4.5 meV/%Ge[15]. Thus, the 0.3%C in the SiGeC layers would be expected to increase the bandgap by 11 meV solely due to strain relaxation. The other one is bulk alloy effect of SiGeC material, which gives the bandgap shift of relaxed SiGeC layers after addition of C without any strain. Assuming that these two effects are additive, the bulk alloy effect of the 0.3% C incorporation would decrease the bandgap by 32±30 meV (-21-11 meV) in the relaxed $Si_{0.75}Ge_{0.25}C_{0.003}$ alloys. Our results that C incorporation decreases the bandgap of relaxed SiGeC by 106±110 meV/%C for small amount of C are consistant with the theoretical calculation of Demkov and Sankey[16], which predict a bandgap decrease about 110 meV/%C for the dilute C in $Si_{1-y}C_y$ alloys. This implies an initial downward bowing in the bandgap vs lattice constant curve as C is addeded into SiGe alloys. This observation is not unique in alloy semiconductors, especially for the alloys with large misfit between the constituents. For example, in III-V semiconductors of InAs-InSb system (InSb has the lower bandgap), the bandgap of InSb also decreases with the small addition of As.

SUMMARY AND ACKNOWLEDGEMENTS

We have successfully fabricated single crystalline SiGeC alloys with C content up to 2 % using the methylsilane as C source in our RTCVD reactor. We also present the defect-free band-edge PL at both 30 and 77K of Si/SiGeC/Si quantum wells for the first time. After correcting for Ge concentration variation and strain relaxation, the effect of C incorporation into relaxed SiGeC alloys appears to initially decrease the bandgap, not to increase it. The carbon incorporation into SiGe can provide another degree of freedom to design novel Si-based devices.

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