Effect of Carbon on the Valence Band Offset of $Si_{1-x-y}Ge_xC_y$/Si Heterojunctions

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Abstract

We have grown pseudomorphic single crystal $Si_{1-x-y}Ge_xC_y$ layers on Si (100) substrates by Rapid Thermal Chemical Vapor Deposition with up to 2.5% substitutional carbon. Capacitance-voltage as well as admittance spectroscopy measurements have been used to study the effect of carbon on the valence band offset of compressively strained $Si_{1-x-y}Ge_xC_y$ / (100) Si heterojunctions. The valence band offset of $Si_{1-x-y}Ge_xC_y$/Si decreased by 25-30 meV as 1% carbon was added. Previous studies showed that 1% carbon increased the bandgap of strained $Si_{1-x}Ge_x$ alloys by 21-26 meV, indicating that all the change in bandgap of $Si_{1-x}Ge_x$ as carbon was added is accommodated in the valence band.

Introduction

The strain in pseudomorphic $Si_{1-x}Ge_x$ layers on Si substrates and resulting critical thickness imposes a severe limit on the engineering of Si-based heterostructures. It has been shown that the addition carbon to form $Si_{1-x-y}Ge_xC_y$ alloys reduces the strain, with each carbon atom compensating the strain of 8-10 Ge atoms [1-2]. In addition to reducing the strain, C causes a slow increase in bandgap of $Si_{1-x}Ge_x$. Photoluminescence (PL) measurements on $Si_{1-x-y}Ge_xC_y$ as well as transport studies of heterojunction bipolar transistor (HBT) with $Si_{1-x-y}Ge_xC_y$ as the base showed that the addition of 1% C increases the bandgap of $Si_{1-x}Ge_x$ by 21-26 meV[3-5]. Given the bandgap increase, it implies a change of valence and/or conduction band offset of the $Si_{1-x}Ge_x$ / (100) Si heterostructures when carbon is added into the $Si_{1-x}Ge_x$ layers. In this paper, we report the measurement of the valence band offset of $Si_{1-x-y}Ge_xC_y$/Si as a function of C concentration by capacitance-voltage and admittance spectroscopy techniques. While C causes a slow increase in bandgap of $Si_{1-x}Ge_x$, we have found that reducing the strain in $Si_{1-x}Ge_x$ by adding C increases the bandgap less than does reducing the strain by merely removing Ge. Figure.1 is the plot of bandgap versus biaxial compressive strain for both pseudomorphic $Si_{1-x}Ge_x$ on Si (100) and experimental $Si_{1-x-y}Ge_xC_y$ data points. As C is added to $Si_{1-x}Ge_x$ and Ge content is held fixed, the strain decreases and bandgap increases, but the bandgap increase is much less than it would be if the strain was reduced simply by removing Ge without adding C. That is, for a given bandgap, $Si_{1-x-y}Ge_xC_y$ has less misfit strain and therefore allows a greater critical thickness than does C-free $Si_{1-x}Ge_x$. This point is further illustrated in Fig. 2, where we calculated and plotted the equilibrium critical thickness for $Si_{1-x-y}Ge_xC_y$ films. Therefore, by growing $Si_{1-x-y}Ge_xC_y$, significant improvements can be made in the trade-off between bandgap and critical thickness.

Experiments

All the samples were grown by Rapid Thermal Chemical Vapor Deposition (RTCVD). The chamber pressure was kept at 6 torr. Dichlorosilane ($Si_2H_2Cl_2$), germane (GeH_4) and methylsilane ($SiCH_6$) were used as the precursors of Si, Ge, and C, respectively. Details of our growth system are available elsewhere[6]. The flow rates were 26 sccm for dichlorosilane, 1-4.5 sccm for germane, and 0-0.35 sccm for methylsilane, resulting in [Ge] = 20%-39.5%, and [C] = 0% -2.5%. All $Si_{1-x-y}Ge_xC_y$ layers were in-situ doped with diborane. P^+ $Si_{1-x-y}Ge_xC_y$ / p^- Si heterostructures and p^- type Si/$Si_{1-x-y}Ge_xC_y$/Si structure were grown for capacitance-voltage and admittance spectroscopy measurements, respectively. The devices were formed by a single-mesa, two mask process. First the mesas were created by plasma etching in SF_6 and then the Ti/Al metallization was patterned by lift-off. The mesa area is 320 x 180 μm^2 and the top contact area is 160 x 130 μm^2.

Results and Discussions

Fig. 3 shows the (400) x-ray diffraction (XRD) performed on strained $Si_{1-x-y}Ge_xC_y$ layers with 39.5% Ge and various C concentrations. The concentration of Ge was obtained by measuring the XRD peak relative to that of the Si substrate. This value is consistent with the Ge concentration obtained by PL . As C is added, the peak starts shifting toward the Si peak, indicating decreased lattice constant, i.e., reduced strain. Broad peaks of $Si_{1-x-y}Ge_xC_y$ are indication of Scherer broadening in the thin films which becomes more prominent as more C is added. Assuming that the Ge content was unchanged by the addition of methylsilane at a constant germane flow, the C content was quantified by measuring the relative shift of the XRD peak of $Si_{1-x-y}Ge_xC_y$ layers with respect to that of $Si_{1-x}Ge_x$ and use the Ge:C strain compensation ratio of 8.3[2]. Results of XRD show good single crystal quality wit substitutional levels of up to 2.5% C. High resolution transmission electron microscopy (HRTEM) images of the sample with 1.2% C show good interface quality and no evidence of dislocations or SiC precipitates. Fig. 4 shows the

band structure of a p^+ $Si_{1-x-y}Ge_xC_y$ / p^- Si heterojunction. From the band diagram , ΔE_v can be expressed as

$$\Delta E_v = E_{F(SiGeC)} + qV_{bi} + E_{F(Si)}$$

where $E_{F(SiGeC)}$ is the position fermi level relative to the valence band of $Si_{1-x-y}Ge_xC_y$, qV_{bi} is the built-in voltage of the junction, $E_{F(Si)}$ is the position of the valence band of Si relative to the Fermi level. E_a is defined as the activation energy.

In theory, ΔE_v may be measured by thermal activation of the leakage current[7]. However, the leakage current for the entire device can be easily dominated by non-ideal sources at a few local defects. Therefore, we used capacitance-voltage technique to measure the band offset [8] which was found to have more reliable sample to sample repeatability and far less scatter among devices on the same wafer than the leakage current measurement. The capacitance of the device was measured as a function of reverse bias at 100 K. The AC frequency used in this measurement ranged from 10 KHz to 4 MHz, and the amplitude was set at 30-50 mV. Much like a Schottky barrier or one sided pn junction, the capacitance per unit area C is given by

$$\frac{1}{C^2} = \frac{2(V_{bi} - V)}{q\varepsilon N_A}$$

here V is the DC bias and N_A is the doping concentration on the Si side of the heterojunction. By plotting $1/C^2$ vs. applied DC voltage, V_{bi} and N_A can be obtained. Fig. 5 shows the capacitance-voltage characteristics of the samples containing 39.5% Ge and various C content. It is observed that the C-V data points are linear over the range of applied voltages. Values of N_A were obtained from the slopes of the fitted lines and found to be in the range of $10^{17}/cm^3$. These values are in good agreement with those measured by spreading resistance tests. Based on N_A , we calculated $E_{F(Si)}$ at 100K. By extrapolating $1/C^2$ to zero, we obtained the built-in voltages with different C levels. The Built-in voltage decreases as more C is added. To extract ΔE_v, we also need the doping concentrations in $Si_{1-x-y}Ge_xC_y$ layers to calculate $E_{F(SiGeC)}$[9]. Note that the boron incorporation in $Si_{1-x-y}Ge_xC_y$ layers does not depend on the C level, as shown by the measurement of secondary ion mass spectroscopy (SIMS). Figure 6 presents the valence band offsets of $Si_{1-x-y}Ge_xC_y$/Si plotted as a function of C content with different Ge concentrations and dopings. The figure shows a consistent decrease in the valence band offset of $Si_{1-x-y}Ge_xC_y$/Si as C is added. The slopes are nearly parallel; scatter in the data is minimal, and growth temperature has no significant effect on the ΔE_v. From the slopes of the fitted lines, we found that the valence band offset of $Si_{1-x-y}Ge_xC_y$/Si decreased by 25-30 meV/ %C. We also found that the **absolute** ΔE_v measured by the capacitance-voltage technique varied slightly with different AC frequencies (within 15 meV from 10 KHz to 1 MHz). However, the C effect on the change of ΔE_v was negligibly influenced by the measurement frequency (< 4 meV/%C). Comparison to the total bandgap change of 21-26 meV/%C indicates that nearly all of the change in bandgap as C is added to strained $Si_{1-x-y}Ge_xC_y$ is accommodated in the valence band.

The valence band offset was also measured in some cases by admittance spectroscopy. This technique has previously been applied on $Si_{1-x}Ge_x$/Si structures[10]. Our structures were similar, except that Al/Ti Schottky diodes were used instead of pn junctions to provide the surface depletion. Figure 7 is the band diagram of the structure, together with the equivalent circuit. The capacitance C_d corresponds to the depletion region of the metal/Si Schottky junction. G_u and C_u are the conductance and capacitance of the two Si/$Si_{1-x-y}Ge_xC_y$/Si junctions which are outside of the Schottky barrier depletion region. Figure 8 and Figure 9 are the capacitance and conductance of Si/$Si_{1-x}Ge_x$/Si and Si/$Si_{1-x-y}Ge_xC_y$/Si heterostructures as functions of temperature for various frequencies. Assuming C_u and C_d are independent of temperature, the capacitance of the sample is equal to the capacitance of C_d in series with C_u at low temperatures. The total capacitance increases to C_d at high temperatures. The transition occurs when the AC excitation frequency resonates with the thermal emission rate of holes from the $Si_{1-x-y}Ge_xC_y$ quantum well to the Si valence band, which also gives rise to maximum conductance. Since the emission rate is proportional to $\exp(-E_a/kT)$, we expect the peak of conductance to occur at higher temperatures for larger excitation frequencies. Given the same excitation frequency, the conductance peak will occur at a lower temperature for a smaller valence band offset. This is indeed the case by comparing Fig. 8 and Fig. 9. By studying the temperature dependence of capacitance and conductance at different frequencies, the activation energy can be obtained, as shown in Fig. 10. Measurements showed a 39 meV reduction in valence band offset for 1.6% C, corresponding to 25 meV/%C, in good agreement with results obtained by capacitance-voltage technique.

Eberl et al [11] reported ΔE_v measurements of $Si_{1-x-y}Ge_xC_y$/ (100) Si from PL of $Si_{1-x-y}Ge_xC_y$/Si and $Si_{1-x-y}Ge_xC_y$/$Si_{1-y}C_y$ quantum wells. Their results were consistent with ours for $y \leq 0.008$. But for $y > 0.01$, they inferred a opposite sign of ΔE_v . Since their $Si_{1-x-y}Ge_xC_y$ samples contained low Ge concentrations, it may be that higher C content makes the $Si_{1-x-y}Ge_xC_y$ layers approach tensile strain, which would radically alter the band alignment.

Conclusion

We have shown that, by the capacitance-voltage technique, the valence band offset of $Si_{1-x-y}Ge_xC_y$/ (100)Si decreases by 25-30 meV/%C for films which are still substantially compressively strained. The resulting band structure with large ΔE_v and negligible ΔE_c is similar to that of pseudomorphic SiGe on (100) Si. Admittance spectroscopy measurement gives good agreement. We have also demonstrated that, by RTCVD, as much as 2.5% substitutional C can be incorporated into the single crystal $Si_{1-x}Ge_x$ layers.

Acknowledgments

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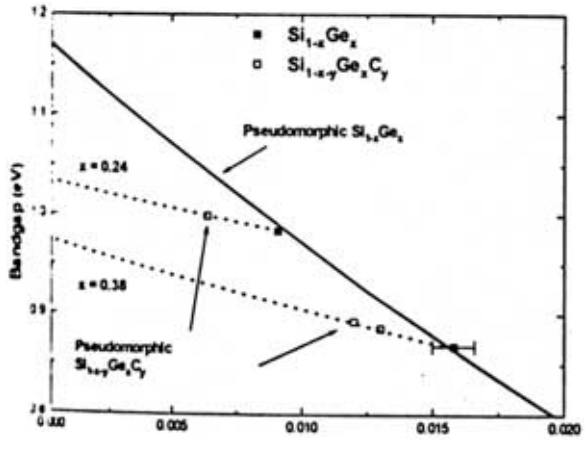

Fig. 1 Bandgap as function of strain for pseudomorphic films on Si (001)

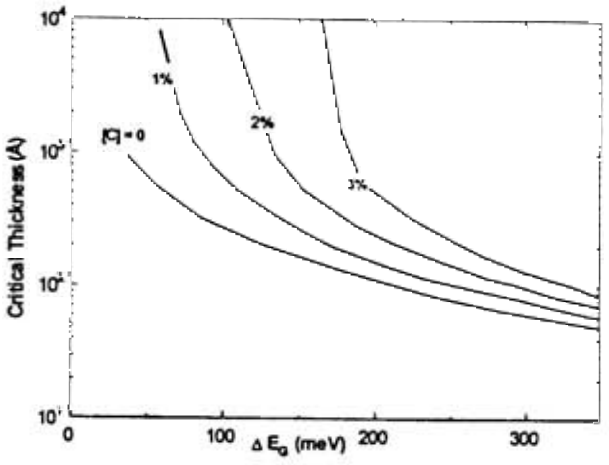

Fig.2 Comparison of critical thickness/bandgap trade-off for $Si_{1-x}Ge_x$ and $Si_{1-x-y}Ge_xC_y$ on Si (100) substrate. the critical thickness is from the Matthews-Blakeslee equilibrium model, assuming that the elastic properties of $Si_{1-x-y}Ge_xC_y$ are the same as those of $Si_{1-x}Ge_x$.

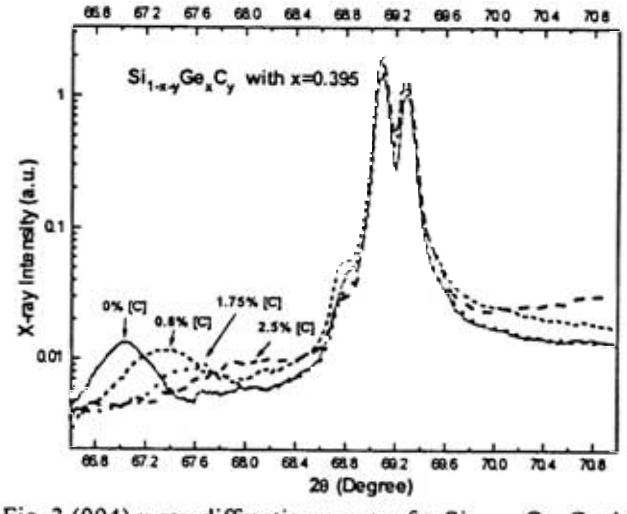

Fig. 3 (004) x-ray diffraction spectra for $Si_{1-x-y}Ge_xC_y$ thin films on Si (001). Two Si substrate peaks are due to Cu $K_{\alpha 1}$ and $K_{\alpha 2}$ x-ray lines

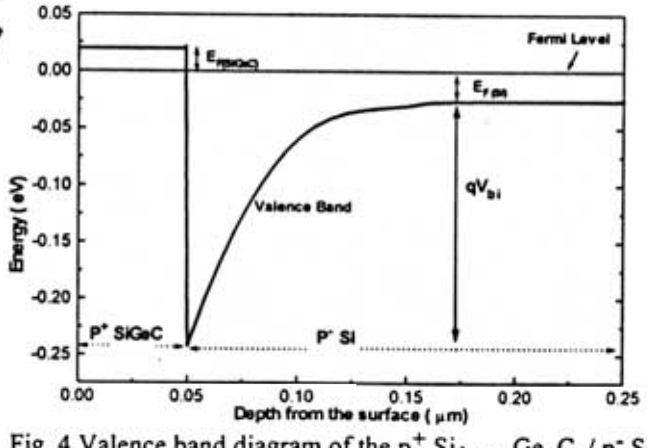

Fig. 4 Valence band diagram of the p^+ $Si_{1-x-y}Ge_xC_y$/ p^- Si

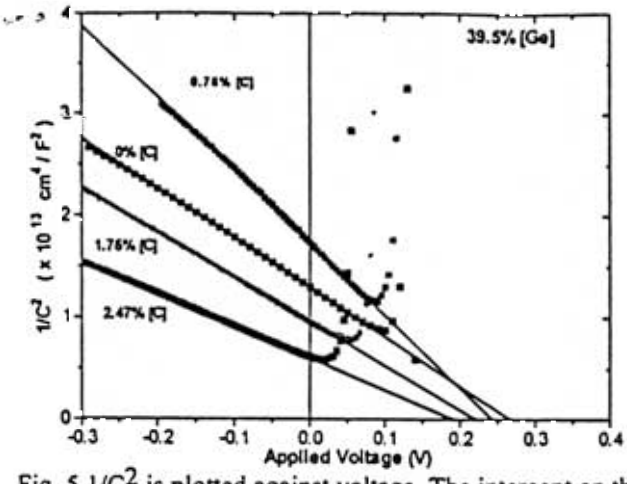

Fig. 5 $1/C^2$ is plotted against voltage. The intercept on the voltage axis is the built-in voltage. The measurement frequency is 100 KHz

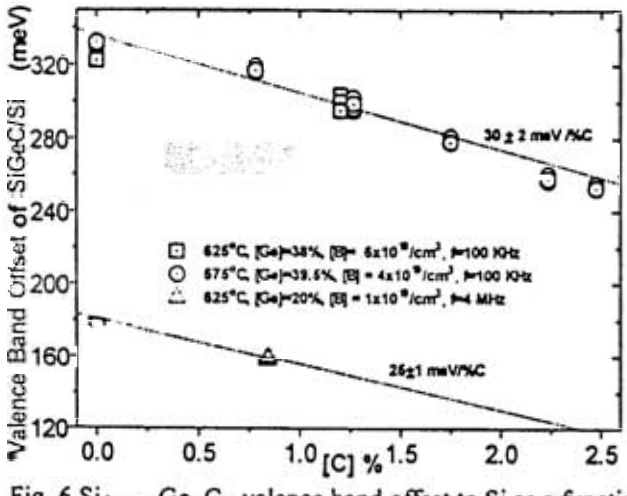

Fig. 6 $Si_{1-x-y}Ge_xC_y$ valence band offset to Si as a function of C content.

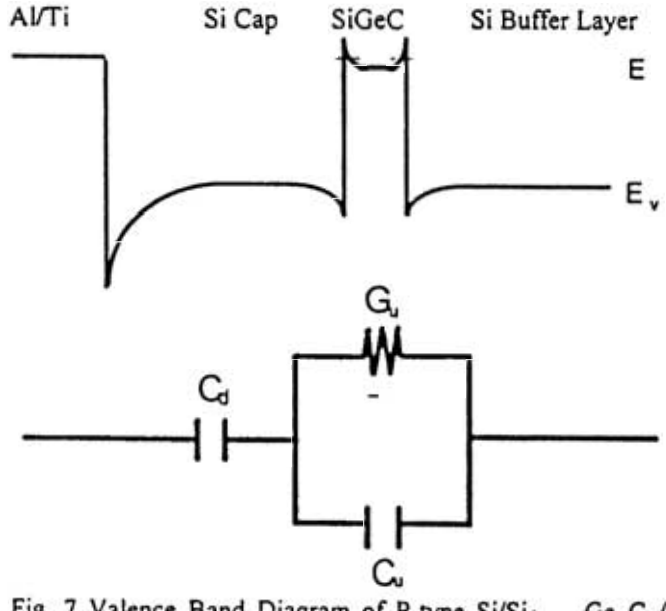

Fig. 7 Valence Band Diagram of P-type $Si/Si_{1-x-y}Ge_xC_y/Si$ admittance structure

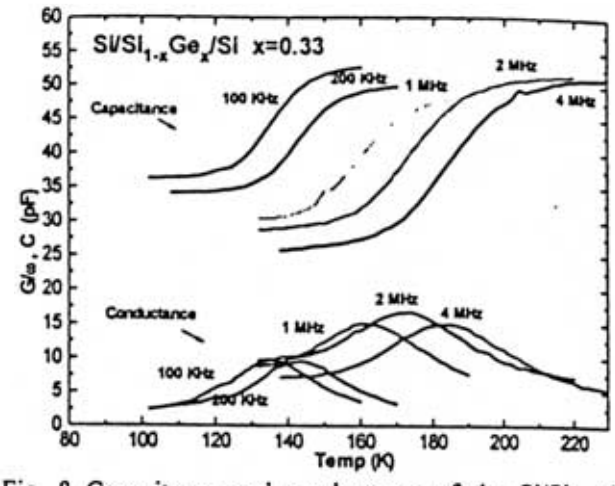

Fig. 8 Capacitance and conductance of the $Si/Si_{1-x}Ge_x/Si$ heterostructures as a function of temperature for various frequencies measured under zero bias condition , with 33% Ge concentration.

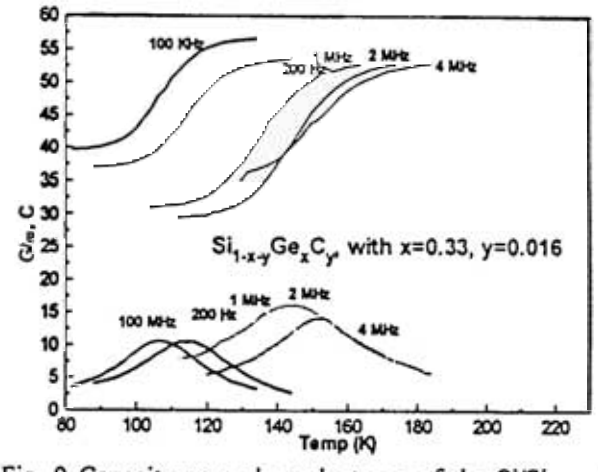

Fig. 9 Capacitance and conductance of the $Si/Si_{1-x-y}Ge_xC_y$ /Si heterostructures as a function of temperature for various frequencies measured under zero bias condition. C content is 1.6% and Ge concentration is 33%.

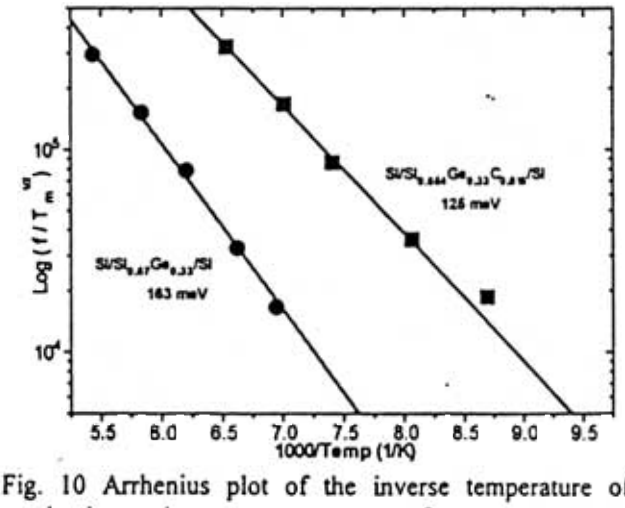

Fig. 10 Arrhenius plot of the inverse temperature of the conduction peaks versus measurement frequency.