A p-$Ge_{1-x}C_x$/n-Si Heterojunction Diode Grown by Molecular Beam Epitaxy

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***Abstract*—We report on the fabrication and characterization of the first p-n diode made from a heterojunction of epitaxial p-type $Ge_{0.998}C_{0.002}$ on an n-type Si substrate. Epitaxial $Ge_{0.998}C_{0.002}$ was grown on a (100) Si substrate by solid source molecular beam epitaxy. The p-GeC/n-Si junction exhibits diode rectification. The I-V characteristics of the p-GeC/n-Si diode indicate a reasonable reverse saturation current of 89 pA/μm^2 at -1 V and a high reverse breakdown voltage in excess of -40 V. Photoresponse from the $Ge_{0.998}C_{0.002}$ p-n diode was observed from 1.3-μm laser excitation resulting in an external quantum efficiency of 1.4%.**

I. INTRODUCTION

GROUP IV semiconductor alloys have attracted intense studies over the last decade for their potential applications in electronic as well as optoelectronic integrated circuits on Si [1]–[2]. Due to the 4.2% lattice mismatch between Si and Ge, most investigations have involved SiGe heterostructures with limited Ge concentration ($\leq$30%) to enhance device performance [3]. The formation of the ternary alloy $Si_{1-x-y}Ge_xC_y$, by adding C to the SiGe system, makes it possible to reduce the strain within the SiGeC system about the lattice matching condition for Si substrates while allowing adjustable bandgaps [4]–[6] by altering the Ge:C ratio. The binary alloy $Ge_{1-x}C_x$ also provides the same flexibility from pure Ge under compressive strain (4.2% misfit) to diamond under tensile strain (−34.3% misfit) and has been studied by a number of groups [7], [8]. Osten *et al.* [7] showed that inclusion of C into Ge delays the onset of strain relaxation, and does not behave identically to Ge with an artificially reduced strain.

Group IV alloy materials research is beginning to spawn device applications, such as strain compensated SiGeC base layers in heterojunction bipolar transistors [9]. Our own investigations have begun to explore materials issues [10] and processing issues [11] of the GeC binary alloy, and have now expanded to investigate novel devices. In this letter, we report on the fabrication and characterization of the first p-n diode made from a heterojunction of molecular beam epitaxial (MBE) p-type $Ge_{1-x}C_x$ epilayer with 0.2% carbon on an n-type Si substrate which demonstrates rectification and photoresponsivity.

One issue which hinders the investigation of Group IV alloys, however, is the limited solubility of C in Ge and Si. Scace and Slack [12] reported the solubility of C in Ge as 10^8 atoms/cm^3 at the melting point of Ge. Also, a theoretical investigation by Sankey et al. [13] approximation indicated that GeC is thermodynamically unstable in solid state form, decomposing into its segregated components, under zero pressure. But, far from thermodynamic-equilibrium growth techniques have been successful in synthesizing $Ge_{1-x}C_x$ alloys with small percentages of carbon, like MBE (under 3% C) [8] or chemical vapor deposition (CVD) with highly reactive precursors (under 5% C) [14].

II. EXPERIMENTS

The $Ge_{1-x}C_x$ epilayer was grown on a (100) n-Si wafer with a carrier concentration of 10^{15} cm^{-3} by MBE in an EPI 620 system without a buffer layer. Details of the $Ge_{1-x}C_x$ growth are described elsewhere [8]. The substrate temperature during growth was kept at 400 °C to minimize outdiffusion of the B dopant into the Si substrate. The measured thickness of the GeC epilayer was 0.6 μm. The C concentration was 0.2%, as determined by the growth condition, calibrated from samples with higher C concentrations.

The $Ge_{0.998}C_{0.002}$ epilayer was doped p-type by a concurrent boron flux, using an effusion cell loaded with pure boron in a pyrolytic graphite crucible during the MBE growth. From Hall effect measurements, the electrically active B concentration was about 4×10^{18} cm^{-3}. The $Ge_{1-x}C_x$ epilayer was also examined in a Philips 400T transmission electron microscope (TEM) in cross sectional views. The TEM specimen was prepared by mechanical thinning followed by Ar ion milling at a voltage of 4 kV.

Heterojunction p-n diodes were fabricated and a schematic is shown in the insert of Fig. 1. Circular GeC mesas were formed by photolithography and then etching down to the Si substrate, using a $H_3PO_4 : H_2O_2 : H_2O$ etchant solution [15]. The diameter of the p-n diode mesas was 106 μm. Standard liftoff technology was used to form e-beam deposited Au ohmic contacts on the GeC mesas. The n-Si ohmic contact was formed by e-beam evaporation of Ti/Au on the entire backside of the substrate. The samples were annealed at 350 °C in a forming gas (15% H_2-N_2) ambient for 3 min. The upper Au contacts were determined to be ohmic [11] using transmission line method (TLM) test structures with a measured contact resistance of only 5.6×10^{-6} $\Omega\cdot$cm^2.

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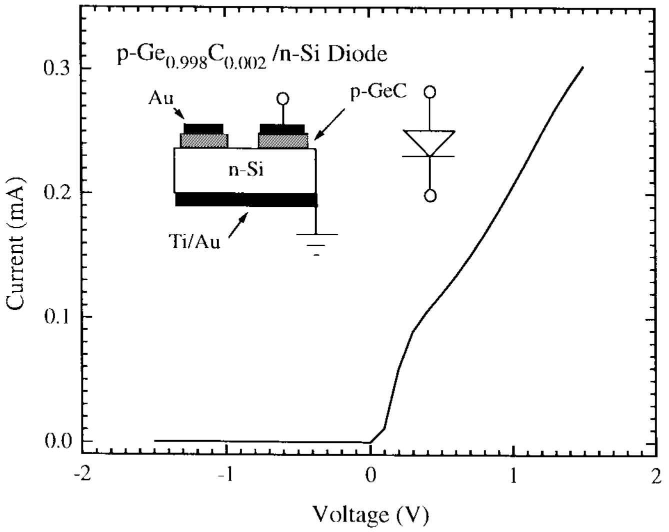

Fig. 1. The measured $I-V$ characteristics of the p-$Ge_{0.998}C_{0.002}$/n-Si diode at reduced bias. The insert depicts the fabricated diode structure used in this study.

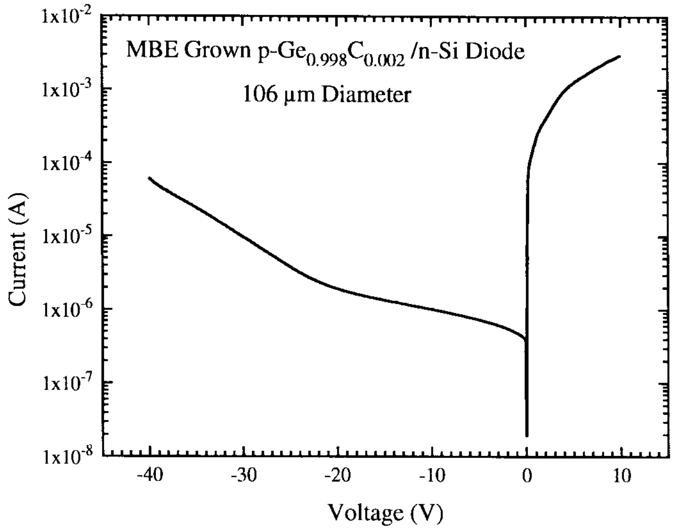

Fig. 2. The measured log $I-V$characteristics of the p-$Ge_{0.998}C_{0.002}$/n-Si diode.

III. Results and Discussion

The GeC epilayer on Si (~4% misfit) exceeds the critical thickness, which is only a few monolayers. TEM analysis reveals that the epitaxial $Ge_{0.998}C_{0.002}$ used in this study is a single crystal. The epilayer is continuous and uniform with a flat surface, and a high density of dislocations threading to the free surface. The interface between the GeC epilayer and Si substrate is abrupt with visible strain contrast and a large quantity of defects and dislocations. Similar, thick dislocated $Ge_{1-x}C_x$ epilayers on Si have demonstrated bandedge luminescence [10].

The $I-V$ characteristics of the p-GeC/n-Si diode were measured and are shown in Figs. 1 and 2. The GeC/Si structures exhibit diode rectification. There are three possibilities for the rectified $I-V$ characteristics: 1) a Schottky Au/p-GeC contact on the top surface, 2) the p-GeC/n-Si heterojunction itself, and/or 3) the n-Si/Ti-Au contact on the backside of the substrate. But, measurements confirm ohmic behavior of the Au/p-GeC junction [11], as discussed above, and the n-Si/Ti-Au backside contact is also expected to be ohmic, since the contact area is over the full surface. This results in a very low current density which even if Schottky-like would simulate an ohmic contact through defect-related tunneling on the unpolished substrate backside. In addition, a p-GeC/n-Si contacted in series to a n-Si/Ti-Au Schottky would behave as two back-to-back diodes. The measured $I-V$ characteristics do not support this supposition. Therefore, diode rectification is believed to be solely influenced by the p-GeC/n-Si heterojunction.

The $I-V$ curve, shown in Fig. 1, exhibits a low turn-on voltage of only 0.15–0.2 V. At low bias, the measured ideality factor is about 1.29. As the bias voltage is increased, see Fig. 2, the $I-V$ curve bends over to a smaller slope, which is probably caused by the high series resistance associated with the low-doped n-Si substrate. There is also a slight s-shape, or kink, under small forward bias, see Fig. 1. The serpentine $I-V$ curve suggests that some tunneling current is taking place but which is superimposed upon a much larger forward biased diffusion current. The reverse saturation current, shown in Fig. 2, is reasonable, and exhibits a reverse breakdown voltage in excess of -40 V. At -30 V, the measured reverse saturation current is 1.2 nA/μm^2, and falls to 89 pA/μm^2 at -1 V. This is comparable to a reported leakage current density of 70 pA/μm^2 for a 800 Å SiGeC p-i-n photodetector [16] and about 100 pA/μm^2 at -1 V for a Ge p-i-n photodetector on Si [17] which used $a \geq 2$ μm buffer layer.

For a low C concentration in the $Ge_{1-x}C_x$ epilayer, the conduction-band discontinuity is estimated as 0.05 eV, obtained from the electron affinity of Si (4.05 eV) and of pure Ge (4.0 eV) [18], while the valence-band discontinuity is 0.51 eV. Alternatively, the band offsets of SiGe heterojunctions have been well studied and predict a valence-band offset of 0.68 eV [19] for a pseudomorphic Si/Ge interface. However, the band discontinuities are well defined only if the in-plane lattice parameter is continuous across the interface [19]. This is not the case here due to partial or complete relaxation of the epilayer. However, both models predict a type II heterojunction for Si/GeC with low C%.

Calculation from the proposed band diagram indicates that the built-in voltage should be about 0.37 eV. The discrepancy between the theoretical and the measured turn-on voltage of 0.15–0.2 eV could be caused by 1) poor crystalline quality of the GeC/Si interface which has a large number of dislocations, 2) bandgap narrowing in the GeC epilayer due to residual strain at the GeC/Si heterojunction interface, or 3) bandgap narrowing due to highly doped GeC. The dislocations can act as trapping centers and allow defect-assisted tunneling of electrons from the conduction band of Si to these trapping centers within the bandgap of GeC and subsequent emission of electrons from these states to the conduction band of GeC. Therefore, the initiation of the turn-on voltage is obscured and leads to the slight s-shape in the $I-V$ curve at low bias.

Photoresponsivity was observed for the GeC/Si heterojunction diodes. Lasers with wavelengths of 1.3 μm (h$\nu >$

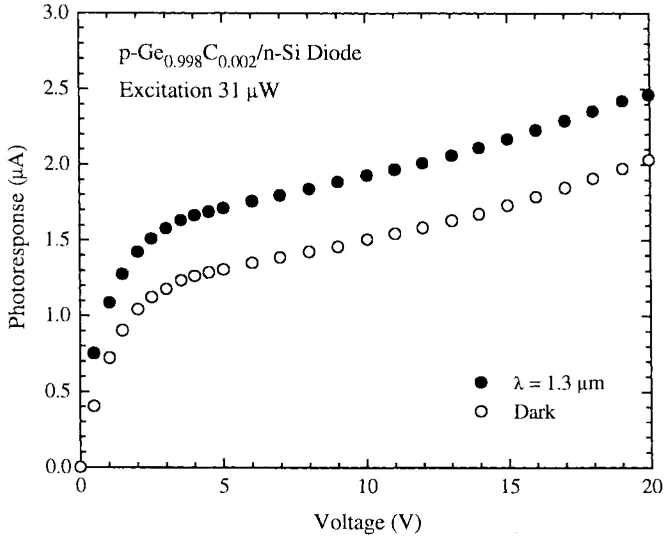

Fig. 3. The dark current (○) and photoresponse (●) of the reverse-biased p-Ge$_{0.998}$C$_{0.002}$/n-Si diode under laser excitation($\lambda = 1.3$ μm) of photon energy above the GeC bandgap but below the bulk Si bandgap.

GeC only) and 0.78 μm (h$\nu >$ GeC and Si) were used to measure photoresponsivity. An appreciable photoresponse was measured using 0.78 μm laser excitation. This is to be expected if photons are absorbed in the surrounding bulk Si, around the mesa perimeter, and then photo-induced carriers diffuse to the p-n heterojunction. However, photoresponsivity was also observed when excitation was switched to below the Si bandgap ($\lambda = 1.3$ μm). The small laser spot was able to be focused between the periphery of the mesa and the upper metal contact. A photocurrent of 0.45 μA was measured, as shown in Fig. 3, which corresponds to a responsivity of 1.45×10^{-2} A/W and an external quantum efficiency (EQE) of 1.4%. These results are significant because the diode did not have an anti-reflection (AR) coating and the light collection region is confined to a narrow region (tens of angstroms) at the p$^+$-GeC/n$^-$-Si junction. This leads to a much shorter path length within the p$^+$-GeC depletion region than a previous normal incidence 800 Å SiGeC p-i-n photodetector which reported EQE ~1% at 1.3 μm [16].

IV. CONCLUSION

In conclusion, the first p-n diode made from a heterojunction of epitaxial p-type Ge$_{0.998}$C$_{0.002}$ on an n-type Si substrate was demonstrated. The $I-V$ curve of the p-GeC/n-Si diode indicated reasonable reverse saturation current (89 pA/μm^2 at -1 V) and high reverse breakdown voltage in excess of -40 V. Some evidence in the $I-V$ curves suggests a small tunnel current was combined with a large forward biased diffusion current. Despite the large number of dislocations and defects at the heterojunction, a photoresponse from the Ge$_{0.998}$C$_{0.002}$ epilayer was observed by 1.3-μm laser excitation with a measured EQE of 1.4%.

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