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Ge layer transfer to Si for photovoltaic applications

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Abstract

We have successfully used hydrophobic direct-wafer bonding, along with H-induced layer splitting of Ge, to transfer 700-nm-thick, single-crystal Ge (100) films to Si (100) substrates without using a metallic bonding layer. The metal-free nature of the bond makes the bonded wafers suitable for subsequent epitaxial growth of triple-junction GaInP/GaAs/Ge solar cell structures at high temperatures, without concern about metal contamination of the active region of the device. Contact-mode atomic force microscopy images of the transferred Ge surface generated by hydrogen-induced layer-splitting reveals root mean square (rms) surface roughness of between 10 and 23 nm. Electrical measurements indicate ohmic *I–V* characteristics for as-bonded Ge layers bonded to silicon substrates with $\sim$400 Ω cm^{-2} resistance at the interface. Triple-junction solar cell structures grown on these Ge/Si heterostructure templates by metal–organic chemical vapor deposition show comparable photoluminescence intensity and minority carrier lifetime to a control structure grown on bulk Ge. An epitaxial Ge buffer layer is grown to smooth the cleaved surface of the Ge heterostructure and reduces the rms surface roughness from $\sim$11 to as low as 1.5 nm, with a mesa-like morphology that has a top surface roughness of under 1.0 nm, providing a promising surface for improved GaAs growth. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Compound semiconductor layered structures grown on bulk Ge substrates have been used to fabricate high-efficiency triple-junction tandem solar cells with efficiencies greater than 30% [1,2]. However, at present these are prohibitively expensive for all but space applications. The Ge substrate constitutes a large portion of the cell cost. Ge/Si heterostructures formed by wafer bonding and layer transfer of a thin crystalline Ge layer by H-induced exfoliation have the potential to reduce the product cost, while maintaining solar cell device performance. Significantly, this process enables formation of high quality Ge layers on Si without any epitaxial growth required. By transferring thin, single-crystal layers of Ge to a less expensive Si substrate and reclaiming the donor Ge wafer through a polish process, a single 300-μm-thick Ge wafer could serve as a source for transfer in excess of 100 thin Ge layers.

Tandem solar cells on Ge/Si require covalent bonding at the Ge/Si interface to ensure good thermal contact and mechanical strength, and to enable the formation of ohmic contact between the Si substrate and Ge layers. To accomplish this, hydrophobic Ge/Si wafer bonding has been employed, motivated by similar work for Si/Si bonding, in which the surface-terminating H atoms that facilitate van der Waals bonding can evolve from the interface at temperatures above 600°C, leaving direct covalent bonds between the two Si substrates [3,4].

2. Experimental details

Ge (100) wafers were implanted with H^{+} at 80 keV to a dose of 1.0×10^{17} cm^{-2} [5]. The wafer surface is rendered strongly hydrophobic by H^{+} ion implantation. Ge passivation consists of removal of adsorbed organic contamination, while maintaining the hydrophobic

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nature of the H-implanted Ge. Implanted Ge substrates were cleaned by acetone and methanol to remove organic contaminants, followed by a 1-min DI rinse and a subsequent 10-s dip in 5% HF and surface drying to remove any remaining oxide.

Si (100) wafers were passivated by a similar wet-chemical process sequence, followed by a deionized water rinse and a subsequent 30-s, 80°C 1:1:3 $H_2O_2/NH_4OH/H_2O$ (RCA1) cleaning process, followed by another deionized water rinse and a brief HF dip to remove the oxide grown. The RCA1 clean is included to further reduce the organic surface contamination and remove particles. Following surface passivation, both Si and Ge surfaces have rms roughness of less than 0.5 nm, as measured by atomic force microscopy (AFM). After passivation, the wafers were brought into contact at room temperature and bonding was initiated by 24 MPa of pressure applied over a 0.64-cm diameter region at the center of the wafer. The contact region was then propagated outwards using subsequent pressures of 6.1 MPa applied over a 1.3-cm diameter region and 1.5 MPa applied over a 2.5-cm diameter region. Bonded Ge/Si wafer structures were annealed at 175°C with an applied pressure of 930 kPa in a modified pressure cell to strengthen the bonding. Layer splitting was achieved by the formation of hydrogen-containing platelets that initiate the propagation of micro-cracks parallel to the Ge surface upon annealing in N_2 at a temperature greater than 350°C, with no external pressure on the wafers [5].

Metal–organic chemical vapor deposition (MOCVD) growth of triple-junction solar cell heterostructures on bonded Ge/Si substrates was performed using $(CH_3)_3Ga$ and AsH_3 precursors for GaAs cell growth and $(CH_3)_3Ga$, $(CH_3)_3In$ and PH_3 precursors for GaInP cell growth. The peak temperature during growth was 750°C and the structure consists of a GaAs buffer layer followed by pn junctions with two active base regions — a GaAs base and a GaInP base separated by tunnel-junction structures. Photoluminescence (PL) intensity and time-resolved photoluminescence (TRPL) minority carrier lifetime were measured in the heavily doped GaAs top contact layer in a control sample grown on bulk Ge and structures grown on Ge/Si heterostructures. PL measurements were performed with a pump laser operated at $\lambda = 457$ nm. Because the heavily doped GaAs contact layer was optically thick to the pump laser, photoluminescence was not observed in the GaInP base or the GaAs base region, both of which are expected to exhibit higher lifetime and superior material quality to the heavily doped GaAs contact layer. TRPL measurements were performed at NREL with a 600-nm pump laser operated at a repetition rate of 1000 kHz. The samples were maintained at 293 K during the measurement.

3. Discussion

3.1. Wafer bonding and layer transfer

Ge-to-Si direct wafer bonding and layer transfer has been achieved, but initial efforts were complicated by gas bubble formation at the bonded Ge/Si interface. These bubbles were likely caused by residual interface contamination present at the time of bonding, which subsequently evolved as gas trapped at the interface, either in the form of adsorbed water or organic contamination [6]. These bubbles have been eliminated by two methods.

The first method is by molecular beam deposition of a 40-Å amorphous Si layer on the H-implanted Ge substrate. In this case, a hydrophilic Si–Si wafer bond is formed using hydrophilic surface passivation on both the substrate and the a-Si layer deposited on the Ge wafer. The room-temperature bonding energy for hydrophilic Si surfaces is typically ~ 100 mJ cm^{-2} for Si/Si systems [4]. The Ge/Si heterostructures formed by Si/a-Si hydrophilic bonding show a strong reduction in the total number of interfacial bubbles. Bubble reduction is thought to be due to the increased hydrophilic bond strength at the Si/a-Si interface vs. the hydrophobic room-temperature bond strength of the Ge/Si interface in the previously mentioned Ge/Si hydrophobic bonding technique. The higher bond strength increases the bubble pressure required to separate the bonded surfaces and to deform the thin Ge transferred layer. Additionally, improved organic removal is made possible by the RCA1 clean of the a-Si layer.

The second method to eliminate bubbles at the interface is to use a 250°C pre-bonding anneal in N_2 following wet chemical cleaning, but prior to bonding the hydrophobic Ge and Si surfaces. This pre-bonding anneal is thought to desorb water and evolve organic contaminants, leaving a more perfectly H-terminated surface. This reduces the bubble defect density in transferred layers.

3.2. Ohmic electrical contact

The interface electrical properties were measured by defining Al on a Ge/Si heterostructure, prepared by a pre-bonding anneal in N_2 as described above, followed by a layer split anneal at 350°C. The Ge substrate was Ga-doped to 5×10^{17} cm^{-3} and the Si substrate was B-doped to 1×10^{18} cm^{-3} in an effort to minimize the junction depletion width formed at the heterojunction interface.

During initial application of a -10-V bias, the Ge/Si interface exhibited dielectric breakdown followed by ohmic *I–V* characteristics in subsequent scans (Fig. 1). These measurements indicate an interfacial resistance of 35–40 Ω over a total interfacial area of ~ 0.1 cm^2 for

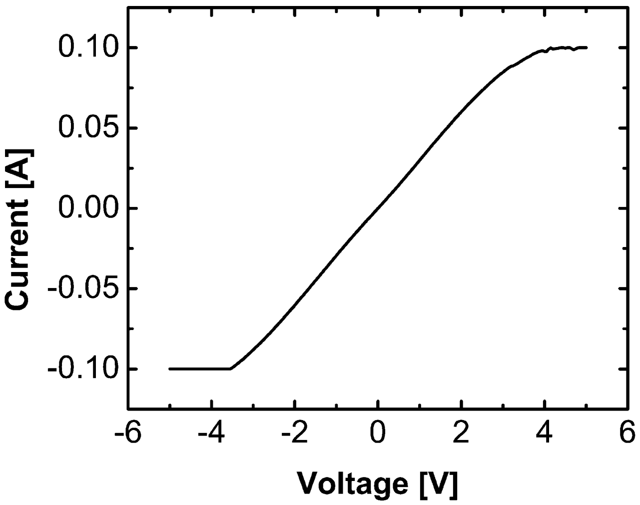

Fig. 1. Current–voltage curve for a P+Ge/P+Si heterostructure annealed to 350°C.

an areal interfacial resistance of ~400 Ω cm^{-2}. The Al contact and substrate resistances were determined to be negligible for overall structure resistance. The relatively high interface resistance is attributed to the fact that the bonded Ge/Si sample was annealed at a maximum temperature of 350°C, lower than the temperature required for covalent bond formation (600°C or greater in Si/Si) [3].

3.3. Triple-junction solar cell growth

Triple-junction solar cell structures were grown by metal–organic chemical vapor deposition on Ge/Si heterostructures fabricated by hydrophobic wafer bonding. Two of these Ge/Si heterostructures were used as templates for growth, labeled Sample 1 and Sample 2, while a control solar cell structure was also grown on bulk Ge in the same process. The rms surface roughness was measured by contact-mode atomic force microscopy; results are given in Table 1. Sample 1 exhibited rms surface roughness four-fold greater than that of the GaAs contact layer of Sample 2. These GaAs contact layer roughness values are uncorrelated to the exfoliated Ge surface roughness measured, a phenomenon that is not understood at present. Cross-sectional scanning electron micrographs of Sample 1 and the bulk Ge control structure are shown in Fig. 2. These images show the layer structure of the triple-junction solar cell and the morphology of the interfaces of the various layers and abrupt interfaces within the microscope resolution (~100 nm). Sample 1 exhibits a rough interface between the layers of the cell structure, with a maximum interface roughness of 0.3 μm located at the GaAs/GaInP interface.

Table 1
MOCVD triple-junction solar cell structure roughness measurements

Sample	Ge roughness (Å)	
	Pre-MOCVD	Post-MOCVD
Bulk Ge	<5	147
Sample 1	236	897
Sample 2	225	204

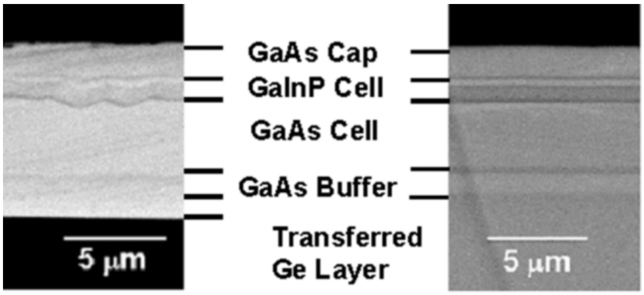

Fig. 2. Cross-sectional SEM image of MOCVD triple-junction solar cell structure as grown on a Ge/Si heterostructure template (left) and a bulk Ge substrate (right).

PL studies of the top GaAs contact layer indicate comparable GaAs band-edge emission at 880 nm for the bulk Ge control and Sample 2, the smoother epitaxial structure on Ge/Si, as indicated in Fig. 3. Sample 1 exhibits considerably lower PL intensity than Sample 2. The PL measurements demonstrate an inverse relationship between the GaAs contact layer surface roughness and GaAs contact layer band-edge photoluminescence intensity, suggesting an increased defect density in the samples with rougher GaAs contact surfaces.

TRPL measurements of the GaAs contact layer indicate short but comparable decay time constants of $\tau = 0.23$ ns for the bulk Ge sample and $\tau = 0.20$ ns for Sample 2, indicating comparable minority carrier life-

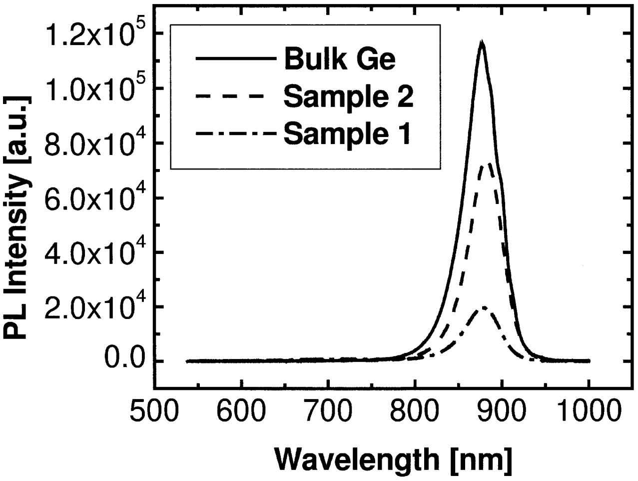

Fig. 3. GaAs band-edge emission photoluminescence of MOCVD grown triple-junction tandem solar cells on Ge/Si heterostructures and on a bulk Ge wafer.

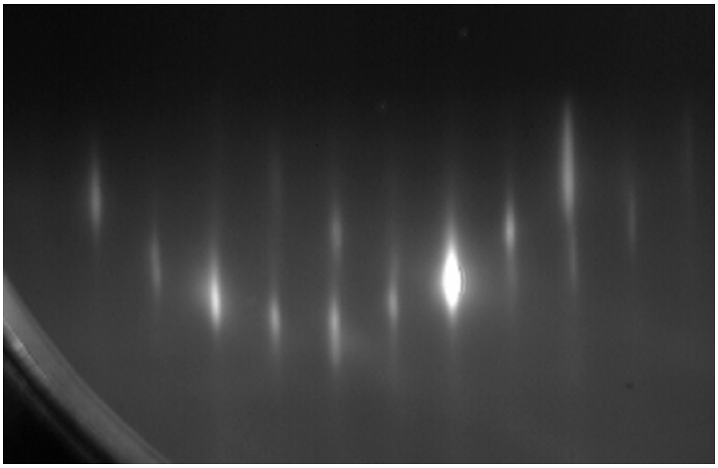

Fig. 4. Post-growth RHEED image of the surface showing Bragg rods and a reconstructed surface indicating a smooth top plateau.

times in the two structures, if similar surface recombination velocities are assumed. The GaAs contact is not passivated by an AlGaAs heterostructure, thus shortening the minority carrier lifetime of the GaAs contact layer, due to a high recombination velocity at the exposed surface. Additionally, the heavy doping in the GaAs contact layer also limits the minority carrier lifetime in this layer.

3.4. Ge surface smoothing with epitaxial Ge buffer layer

The triple-junction solar cell optical performance results indicate that without any surface preparation following the H-induced cleavage of the Ge layer, high quality III–V photovoltaic materials can be grown with good PL intensity and minority carrier lifetime properties relative to a cell grown on a bulk Ge substrate. However, to further improve the optical and electrical properties, it is desirable to reduce the exfoliated surface roughness. To smooth the exfoliated Ge surface a 250-nm-thick Ge buffer layer was grown on the surface of the Ge/Si heterostructure by molecular beam epitaxy at 450°C at a rate of 0.1 nm s^{-1}. The surface evolution was monitored in situ with reflection high electron-energy diffraction. The RHEED pattern following the growth also indicated a smooth (2×1) reconstructed Ge (100) surface, as shown in Fig. 4. Epitaxial Ge growth reduced the surface rms roughness of the transferred Ge layer from ~11 to ~2.2 nm. In addition, the morphology of the surface drastically changed to a mesa-like form, with a large relatively smooth layer of less than 1 nm surface roughness, as illustrated in Fig. 5.

4. Conclusions

Fabrication of high quality, ~1 cm^2 area Ge (100)/Si (100) heterostructures by hydrophobic wafer bonding and H-induced layer splitting has been demonstrated. Bonded Ge/Si heterostructures exhibit ohmic interfaces and are suitable as templates for MOCVD growth of InGaP/GaAs/Ge triple-junction solar cell structures with photoluminescence intensity and decay lifetimes comparable to those found in solar cell structures grown on bulk Ge (100) substrates. Epitaxial growth of Ge buffer layers on transferred Ge/Si layers shows promise as a means of reducing the Ge surface roughness and improving the optical quality of epitaxial GaInP/GaAs/Ge layers.

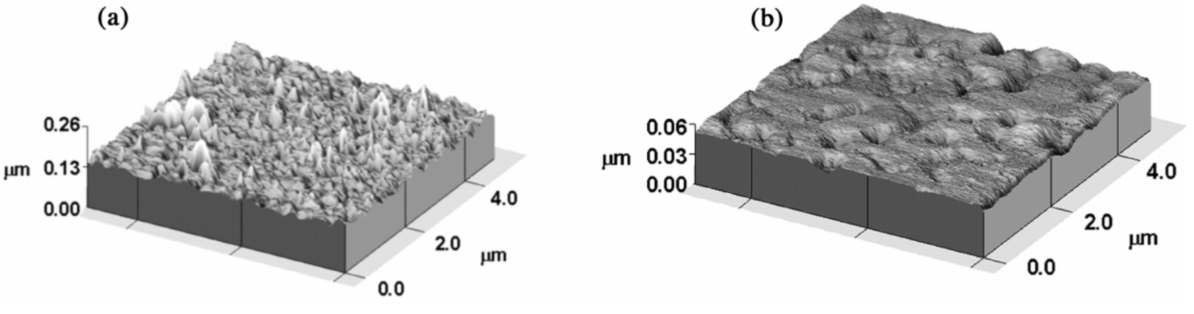

Fig. 5. (a) Exfoliated Ge surface prior to MBE Ge buffer layer growth with 110 Å rms roughness; (b) smoothed to just 22.6 Å rms roughness with a mesa geometry.

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