III-V/Si Wafer Bonding Using Transparent, Conductive Oxide Interlayers

Adele C. Tamboli1, Maikel F.A.M. van Hest1, Myles A. Steiner1, Stephanie Essig1, Emmett E. Perl2, Andrew G. Norman1, Nick Bosco1, and Paul Stradins1
1National Center for Photovoltaics, National Renewable Energy Laboratory, 15013 Denver West Pkwy, Golden, CO 80401 and 2Department of Electrical and Computer Engineering, University of California, Santa Barbara, CA 93106-9560
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We present a method for low temperature plasma-activated direct wafer bonding of III-V materials to Si using a transparent, conductive indium zinc oxide interlayer. The transparent, conductive oxide (TCO) layer provides excellent optical transmission as well as electrical conduction, suggesting suitability for Si/III-V hybrid devices including Si-based tandem solar cells. For bonding temperatures ranging from 100°C to 350°C, Ohmic behavior is observed in the sample stacks, with specific contact resistivity below $1 \, \Omega \, \text{cm}^2$ for samples bonded at 200°C. Optical absorption measurements show minimal parasitic light absorption, which is limited by the III-V interlayers necessary for Ohmic contact formation to TCOs. These results are promising for Ga0.5In0.5P/Si tandem solar cells operating at one sun or low concentration conditions.

Integration of III-V materials with silicon has been a persistent scientific challenge. For optoelectronic applications, it is desirable to combine the excellent optoelectronic properties of direct band gap III-V materials with technologically mature Si on which CMOS technology is based. For photovoltaic applications, III-V/Si tandem devices are desirable because silicon solar cells are currently the most commercially available technology, but the highest conversion efficiencies have been achieved using III-V semiconductors. Combining these two technologies offers a promising approach to scalable, efficient photovoltaic devices. Adding a wider band gap III-V top cell to a Si bottom cell (e.g., a 1.8 eV Ga0.5In0.5P top cell) reduces the thermalization losses, boosting the cell efficiency, with a practically achievable efficiency of ~31-32% using known Si and Ga0.5In0.5P device parameters. The detailed-balance efficiency limit for a two-junction tandem cell with Si as the bottom cell is even higher, at 45%. To date, the primary method used to combine Si and III-V materials has been direct growth of III-V epilayers on Si substrates. This method is challenging due to mismatch in lattice constant and thermal expansion coefficient between Si and relevant III-V alloys as well as antiphase disorder due to polar on non-polar epitaxy. Additionally, recent explorations have shown that exposing Si to III-V growth conditions can result in degradation of the Si bulk lifetime, compromising the efficiency potential of the Si bottom cell.

Direct wafer bonding offers a route to integration of high quality Si and III-V cells that have been separately grown and optimized. However, the realization of a two-terminal tandem device requires a bonded interface that is mechanically stable, optically transparent, and electrically conductive. Achieving all of these properties simultaneously has presented a challenge. Typical direct wafer bonding methods include either a high temperature treatment, where thermal expansion mismatch can be problematic, or a plasma activation step, which can result in oxidation of the semiconductors and surface damage. Recently, equipment has been developed to enable surface activation in situ using a fast atom beam treatment, which prevents oxidation, a method that has resulted in 30% efficiency triple junction Ga0.5In0.5P/GaAs//Si solar cells under concentrated sunlight. However, this specialized tool requires a UHV chamber equipped with fast atom or ion beam sources. There have been several reports of using transparent, conducting oxides (TCOs) as interlayers for bonding. Eichler, et al., measured bond strength for Si/ITO//ITO/Si bonds as a function of annealing temperature and time, using a plasma activated process. ITO has also been used as an interlayer for anodic bonding of Si to glass. High temperature (>500°C) bonding of III-V light-emitting diodes to III-V substrates has been reported, but such temperatures are too high for III-V/Si integration. III-V/Si integration has been reported using ZnO-mediated bonding, with a highly transparent bond interface, but the resistance of the interface was very high due to unoptimized ZnO doping.

We have developed an ex situ plasma-activated wafer bonding process that utilizes an amorphous indium tin oxide (IZO) film on each semiconductor surface. This IZO film acts as a transparent contact, ensuring optical and electrical transmission between the subcells. An oxygen plasma treatment enables bonding between the IZO layers at low temperature without introducing damage in the semiconductor layers. While we have also used more conventional TCO materials, such as crystalline indium tin oxide, for this bonding process, we focus here on samples bonded using IZO interlayers. IZO was chosen for its excellent optical and electrical properties, as well as its smoothness. This TCO material forms as an amorphous film when deposited at room temperature and with compositions ranging from 55-84% In. In this experiment, we present a method for low temperature plasma-activated direct wafer bonding of III-V materials to Si using a transparent, conductive indium zinc oxide interlayer. The transparent, conductive oxide (TCO) layer provides excellent optical transmission as well as electrical conduction, suggesting suitability for Si/III-V hybrid devices including Si-based tandem solar cells. For bonding temperatures ranging from 100°C to 350°C, Ohmic behavior is observed in the sample stacks, with specific contact resistivity below $1 \, \Omega \, \text{cm}^2$ for samples bonded at 200°C. Optical absorption measurements show minimal parasitic light absorption, which is limited by the III-V interlayers necessary for Ohmic contact formation to TCOs. These results are promising for Ga0.5In0.5P/Si tandem solar cells operating at one sun or low concentration conditions.

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same range, the index of refraction is $\sim 2$, and the conductivity can be as high as $3000 \ \Omega^{-1} \ cm^{-1}$. For bonding, another key parameter is roughness; IZO films in the literature\cite{20} have reported root-mean-squared (RMS) values $< 0.4 \ \text{nm}$ for a wide range of stoichiometries, which is sufficient for bonding and lower than most crystalline TCO materials. Optical absorption within the visible spectral range is insignificant at the thicknesses we use here ($< 20 \ \text{nm}$). Importantly, this TCO does not change significantly upon annealing up to $\sim 600^\circ\text{C}$\cite{20}, and thus, bonding conditions (typically $100-400^\circ\text{C}$) can be optimized without considering the impact on the TCO interlayer. Here, we describe this wafer-bonding process, the resulting optical and electrical properties of the wafer-bonded interface, and its potential for tandem solar cell applications.

Two types of sample pairs, shown schematically in Fig. 1 were bonded: sapphire/IZO to GaAs/Ga$_{0.5}$In$_{0.5}$P/GaInNAs/IZO for testing optical properties, and Si/IZO to GaAs/Ga$_{0.5}$In$_{0.5}$P/GaInNAs/IZO for testing electrical properties. Sapphire substrates used for optical characterization (Fig. 1 left) were double side polished, 430 $\mu \text{m}$ thick c-plane sapphire. Silicon substrates used for electrical characterization (Fig. 1 right) were 500 $\mu \text{m}$ thick, (100), heavily doped, single side polished n-type Si wafers ($0.001-0.005 \ \Omega$-cm). III-V samples consisted of 650 $\mu \text{m}$ thick, (100), heavily doped n-GaAs substrates ($n=1-4 \times 10^{18} \ \text{cm}^{-3}$) with a nominally 25 $\mu \text{m}$ thick GaInNAs contact layer and nominally 500 $\mu \text{m}$ thick Ga$_{0.5}$In$_{0.5}$P etch stop layer. The n-type GaInNAs layer is a heavily selenium-doped contact layer needed to make Ohmic contact to TCO layers. The n-type Ga$_{0.5}$In$_{0.5}$P layer acts as both an etch stop for substrate removal, and as a stand-in for an eventual Ga$_{0.5}$In$_{0.5}$P top cell on Si. All samples were coated with an 8 nm thick film of amorphous IZO (70 at.% In/30 at.% Zn) by RF sputtering. The III-V semiconductor samples were cleaved into 1x1.2 cm$^2$ pieces. Samples were cleaned in acetone, isopropanol, and tergitol and then loaded into an EVG 810 plasma activation tool. Samples were then treated with a 100 W O$_2$ plasma for 30 s. Several samples were set aside after plasma activation for atomic force microscope (AFM) measurements. Samples to be bonded were immediately stacked face to face upon unloading from the plasma chamber and loaded into a Süss SB6e wafer bonder. Bonding was performed under vacuum, at temperatures ranging from 100-400$^\circ\text{C}$, for two hours. The applied pressure was 225 mbar for all samples.

The GaAs substrates of the bonded sapphire/IZO//IZO///GaAs/Sapphire samples were etched away chemically using a 1:1 mixture of H$_2$O$_2$ and NH$_4$OH, similar to the process described in ref.\cite{23}. A wax coating around the sample edges prevented parasitic etching of IZO and GaInNAs layers. The resulting sample structures consisted of 500 nm Ga$_{0.5}$In$_{0.5}$P, 25 nm Ga$_{0.5}$In$_{0.5}$P, 16 nm of IZO, and a 430 $\mu \text{m}$ substrate IZO (Fig. 1 left). MgF$_2$ (75 nm)/ZnS (40 nm) antireflection coatings (ARC) were then deposited on the Ga$_{0.5}$In$_{0.5}$P surface. Optical properties of these samples were measured using a Cary 5000 UV/Vis/NIR transmission/reflection measurement tool. For testing the electrical conductivity through the Si/IZO///GaAs/Sapphire samples, Ti/Ag/Pd metal stacks and Ga/In eutectic layers were deposited on the HF-etched Si and mechanically scribed GaAs back surfaces, respectively (Fig. 1 right). Strength testing was performed on the same III-V/IZO/Si samples after etching off the metals. These samples were attached to glass plates on the Si side and Al blocks on the GaAs side using epoxy, and then a pull test was performed until the samples separated.

Figure 2 shows a comparison of AFM images that were measured on 8 nm thick IZO films on Si before and after plasma activation. Both surfaces are very flat, and AFM measurements (Fig. 2) show low RMS roughness ($< 0.1 \ \text{nm}$), well within the constraints required for bonding. Spectroscopic ellipsometry measurements confirm that the IZO thickness, 8 nm, did not change after plasma activation. All samples bonded at 100-400$^\circ\text{C}$ adhered, but the Si/III-V samples bonded at high temperature cracked out of the sample plane upon cooling due to mismatched thermal expansion coefficients. At 400$^\circ\text{C}$, both the GaAs and Si cracked macroscopically through the bulk of the substrates, and some small pieces also delaminated. At 300-350$^\circ\text{C}$, small cracks formed in the 650 $\mu \text{m}$ thick GaAs substrates. III-V/Si samples bonded at $\sim 200^\circ\text{C}$ demonstrated larger bonded areas without cracking, and exhib-
absorption from the GaInNAs layer. Transmission, reflection, and absorption (A = 1 - T - R) data for the test structures are shown in Fig. 4. An ARC was used to reduce the reflection from the air/Ga0.5In0.5P interface at the front side of the structure. Consequently, the majority of the experimentally measured reflectance from the sample comes from either the III-V/IZO/sapphire interface (IZO and sapphire are nearly index matched) or the sapphire/air bottom interface. In a solar cell structure on Si rather than sapphire, these two mechanisms would not contribute significantly to reflective losses.

At wavelengths below 600 nm, the Ga0.5In0.5P layer absorbs most of the light. At wavelengths greater than 800 nm, the bonded structure is relatively transparent, proving its eligibility for transmitting long-wavelength light to a Si solar cell. A fit to the data using the transfer matrix method and known optical parameters for the III-V layers shows that most of the <10% parasitic absorption comes from the 25 nm thick GaInNAs contact layer, which has a 1 eV band gap. A heavily-doped contact layer is necessary to ensure Ohmic contact between the Ga0.5In0.5P layer and IZO contact, but could be thinned or replaced with a more optimized material. The fringes visible in the transmission and reflection data, which indicate light trapped in the Ga0.5In0.5P layer, suggest that further optimization of the AR coating is necessary, although this factor would be much less significant in a nearly index-matched III-V/Si structure.

Si/IZO/III-V stacks were used to investigate the elec-
FIG. 5. Electrical and strength properties of Ga$_{0.5}$In$_{0.5}$P/GaInNAs/IZO//IZO/Si stacks bonded at different temperatures. Linear IV curves are measured for all samples, but the contact resistance is minimized at ∼200°C. This correlates with a maximum adhesion strength measured at 200°C.

IV curves for samples bonded at 100-350°C. All samples exhibited Ohmic electrical behavior with varying resistance: at too low of a bond temperature, the bond was not sufficiently strong to yield excellent electrical properties, and at too high of a temperature, cracks inhibited current spreading. Thus, we found that the optimal condition is 200°C, where <0.5 Ω cm$^2$ was reliably achieved (5 samples measured). These results would contribute a voltage loss of < 10 mV in a tandem cell operating at one sun (∼20 mA/cm$^2$), sufficient for a high efficiency tandem cell.

We report on a low-temperature bonding process using a transparent, conductive intermediate layer, which enables a transparent and conductive connection between Si and III-V semiconductors. The process works at low temperature (∼200°C), which is beneficial for materials with mismatched thermal expansion coefficients. The process has been demonstrated here using optically-thin, amorphous indium oxide, but can also be applied to other TCOs, like indium tin oxide. This particular structure could be easily applied to tandem solar cells on silicon, and in particular, Ga$_{0.5}$In$_{0.5}$P top cells on HIT-type Si bottom cells, which already incorporate a TCO as the top surface. Such a device is promising for >30% efficiency one-sun or low concentration solar cells at reasonable costs.

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