Final Report

Project Title: Advanced Semiconductor Materials for Breakthrough Photovoltaic Applications

Covering Period: July 1, 2008 to January 31, 2012

Date of Report: January 7, 2013

Recipient: Arizona State University

Award Number: DE-FG36-08GO18003

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1 Executive Summary

The project addressed the need for improved multijunction solar cells as identified within the Solar America Initiative program. The basic Ge/InGaAs/InGaP triple-junction structure that has led to record commercial efficiencies remains unoptimized due to excess current in the germanium component. Furthermore, its deployment cannot be scaled up to terawatt-level applications due to bottlenecks related to germanium's cost and abundance. The purpose of the program was to explore new strategies developed at Arizona State University to deposit germanium films on much cheaper silicon substrates, largely eliminating the germanium bottleneck, and at the same time to develop new materials that should lead to an improvement in multijunction efficiencies. This included the ternary alloy SiGeSn, which can be inserted as a fourth junction in a Ge/SiGeSn/InGaAs/InGaP structure to compensate for the excess current in the bottom cell. Moreover, the possibility of depositing materials containing Sn on Si substrates created an opportunity for replacing the bottom Ge cell with a GeSn alloy, which, combined with new III-V alloys for the top cells, should enable 4-junction structures with perfectly optimized band gaps.

The successes of the program, to be described below, has led to the developments of new strategies for the growth of high-quality germanium films on Si substrates and to a widespread recognition that SiGeSn is likely to play a significant role in future generations of high-efficiency devices, as demonstrated by new research and intellectual property efforts by major US industrial players.

2 Comparison of Accomplishments with goals and objectives

The primary goal of developing Ge-buffered Si substrates as a replacement for costly Ge wafers was accomplished in multiple ways. While at the start of the program we had a single method to grow Ge films on Si—using organometallic additives—during the course of the DOE-sponsored research we developed three additional approaches: extremely diluted GeSn alloys in which trace amounts of Sn do not change the electronic properties in any measurable way but promote smooth epitaxial growth, and film grown via trigermane (Ge_3H_8) and tetragermamane (Ge_4H_{10}) precursors. The goal of scaling this growth to large area wafers was fully accomplished, as well as the goal of developing doping protocols for these Ge layers.

The goal of developing Ge-compatible SiGeSn layers was also achieved in a novel way that relied only on commercially available precursors, making the ternary alloy much more attractive from an industrial perspective. The goal of developing doping protocols for these alloys was also fully achieved.

The goal of developing III-V materials on Ge-buffered Si substrates was vigorously pursued, leading to high-quality GaAs and InGaAs layers on Si.

At the start of the program the field of devices based on GeSn, or SiGeSn was in its infancy and no results had been reported. The program led to dramatic advances in this area. Ge, GeSn, and SiGeSn *pin* diode structures can now be routinely fabricated and their optoelectronic properties characterized in detail. The expected redshift in responsivity in GeSn devices relative to Si was fully confirmed, and detailed simulations of the diode responses were developed to extract basic electronic structure parameters. Ge solar cells as well as GaAs solar cells on Ge-buffered Si were fabricated and tested.

Integrated III-V/group-IV structures for multijunction solar cells were grown and characterized, but lack of time prevented the fabrication of working III-V/group-IV solar cell structures including tunnel junctions. The major obstacle faced by the program was the development of SiGeSn *pn* structuctures. For a long time it was not clear whether the difficulties stemmed from the specific growth/fabrication approach or represented an intrinsic property of the SiGeSn alloy, in which the large size mismatch between Si and Sn might promote defect formation. The recent demonstration of high-quality SiGeSn *pin* diodes on Si and Ge wafers provided a resolution of the problem, demonstrating that SiGeSn is compatible with PV applications and fueling the current great industrial interest in this material.

3 Project activities

The project activities can be conceptually divided into three main areas. The first area focused on lowering device costs by developing virtual Ge substrates on cheap Si substrates. The second group of activities targeted the development of ternary SiGeSn alloys as the 1-eV gap material that could be inserted as a junction to increase the efficiency of Ge/InGaAs/InGaP solar cells. Finally, the third group of activities was devoted to the integration of III-V materials with Ge/SiGeSn group-IV structures as needed for future 4/5 junction devices.

3.1 Lower cost: Si(100)/Ge platforms for low cost InGaAs/InGaP solar cells

An initial objective of the program was to replace the expensive Ge substrate in the conventional Ge/InGaAs/InGaP triple-junction structure with a new class of Ge buffers possessing the necessary structural, morphological electrical and optical properties for this photovoltaic integration.

Objectives

- Development of large scale Ge/Si(100) hybrid platforms for a dramatic reduction in the cost of Ge/InGaAs/InGaP multijunction solar cells, circumventing the need for bulk Ge.

Objectives achieved:

- Scaled-up growth of the ASU Ge on Si process to large area wafers.
- Development of three additional processes for the deposition of Ge on Si.
- Growth of thick Ge in the range needed for (a) absorption of 85% of the GaAs-filtered light relative to Ge wafers and (b) sufficient to generate matching current.
- Fabrication of high performance Ge on Si *p-i-n* diodes with superior electrical response than state of the art en route to solar cell junctions.

3.1.1 Phase I work

Growth: Virtual Ge/Si(100) wafers were produced using novel CVD methods potentially leading to dramatic cost reduction in multijunction solar cells. The specially designed Ge layers were fabricated on large scale Si platforms with 4” diameters. Previously these materials were grown on small area (1x1 cm^2) substrates and exhibited superior morphology and microstructure.

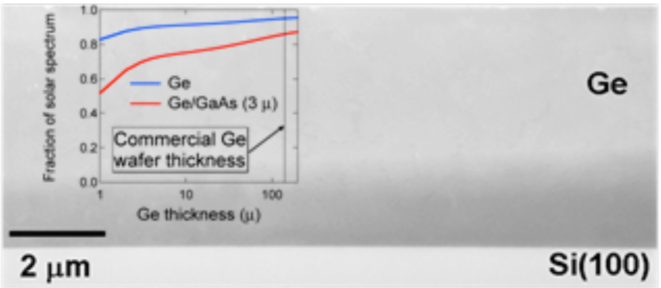


Figure 1 Electron micrograph of a Ge-buffer layer grown on Si (001).

In this project the growth was conducted on a newly fabricated single-wafer low pressure CVD reactor which was specifically designed and constructed for this application. The deposition reactions were based on optimized molecular mixtures of Ge_2H_6 and $(GeH_3)_2CH_2$ at 350 ^{o}C. The layers produced via this method (see Fig. 1) were found to exhibit strain relaxed microstructures, extremely low defect densities of ~ 10^5/cm^2 and atomically flat surfaces, thus providing an ideal platform for the subsequent formation lattice matched InGaAs/InGaP overlayers as required for the target PV application. Ge layers approaching 1-4 microns in thickness were manufactured for the first time.

Doping: Doped films were obtained using B_2H_6 and $P(GeH_3)_3$ as *in situ* molecular precursors. The $P(GeH_3)_3$ compound was developed specially for this program and had not been previously utilized for semiconductor doping. Nominal carrier concentration levels in the range of 10^{16} to 10^{19} cm^{-3} in B-doped (*p*-type) and 10^{17} to 10^{20} cm^{-3} in P-doped (*n*-type) layers were achieved, as determined by infrared spectroscopic ellipsometry and Hall measurements.

Devices: Ge *p-i-n* photodiodes were grown on silicon with variable active layer thickness, using the novel low-temperature chemical vapor deposition process developed at ASU, and their device properties were measured. The external quantum efficiencies of the devices with active layers as thin as 350 nm were found to be 0.09 and 0.04, at 1.3 and 1.55 μm, respectively. Current-Voltage measurements showed dark currents at the level of 10^{-6} A and a diode ideality factor of 1.2, indicating superior crystallinity and electrical-optical behavior as required for the subsequent development of photovoltaic junctions directly on Si wafers. Improved electrical properties and higher photoresponse was demonstrated in devices incorporating thicker (1 micron) active layers, as expected.

3.1.2 Phase II work

Materials: The Phase I approach to Ge-on-Si yielded thick, device quality films with extremely low dislocation densities (<10^5/cm^2) and atomically flat surfaces. The single-wafer nature of this method, however, casted doubts regarding its industrial viability. Accordingly, we explored a CVD approach to the epitaxial growth of Ge on Si substrates that enables the fabrication of a high quality material on multiple substrates during a single run, at industrial scale growth rates approaching 30 nm/minute. The method is an extrapolation of the approach we had previously used to grow $Ge_{1-y}Sn_y$ alloys. When the Sn concentration is reduced to doping levels around 10^{19} cm^{-3}, no measurable difference is seen between the optical properties of the Sn-doped material and that of pure Ge, but the

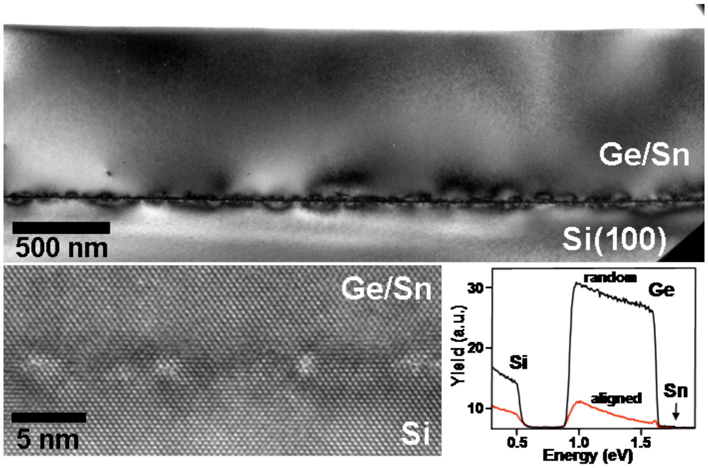


Figure 2. (a) XTEM image of “quasi Ge”-on-Si film doped with 0.06 % (~10^{19}/cm^3) level of substitutional Sn. (b) High resolution image show a quasi periodic array of edge dislocations confined at the interface plane. (c) Random and channeled RBS spectra of the same material. A weak Sn signal is observed confirming the presence of about 0.1 % Sn% atoms. The high degree of channeling (red trace) indicates near perfect alignment between the film and the underlying Si(100).

interaction of SnD_4 with the Ge_2H_6 Ge source suppresses the Stranski-Krastanov (SK) growth mode and promotes Frank-van der Merwe (FM), *i.e.* layer-by-layer growth. These extremely diluted alloys were dubbed “quasi-Ge”. Figure 2(a) shows a representative film with a thickness of 1.2 μm. The structural characterization data collectively indicate that the layer morphology and crystallinity are improved compared to those of pure Ge films grown via the previously developed gas-source MBE approach used in Phase I.

More recently, we introduced two alternative growth methods based on the higher-order germanes Ge_3H_8 (trigermane) and Ge_4H_{10} (tetragermane). These hydride products are found to exhibit a remarkable stability and an “ease of use” comparable to conventional group IV chemical sources, making them compatible with current industry standards. Figure 3 reveals the near absence of threading defects in a sample grown via the trigermane route, corroborating the high degree of crystalline perfection in the samples The sample in Fig. 3 was grown at a rate of 25 nm/min, which is unprecedented under these pressure/temperature conditions of $1x10^4/330^oC$. As a comparison, the corresponding growth rate for a film of comparable quality, using Ge_2H_6 mixed with metal organic additives (the method favored in Phase I) is negligible at <0.5 nm/min under the same conditions. The above outcomes indicate that our growth involving high reactivity Ge_3H_8 provides a unique low temperature route enabling growth directly on Si. This in itself should represent a major advantage and advance in crystal growth of thick and fully relaxed films in which a majority of the volume fraction exhibits bulk-like crystal behavior.

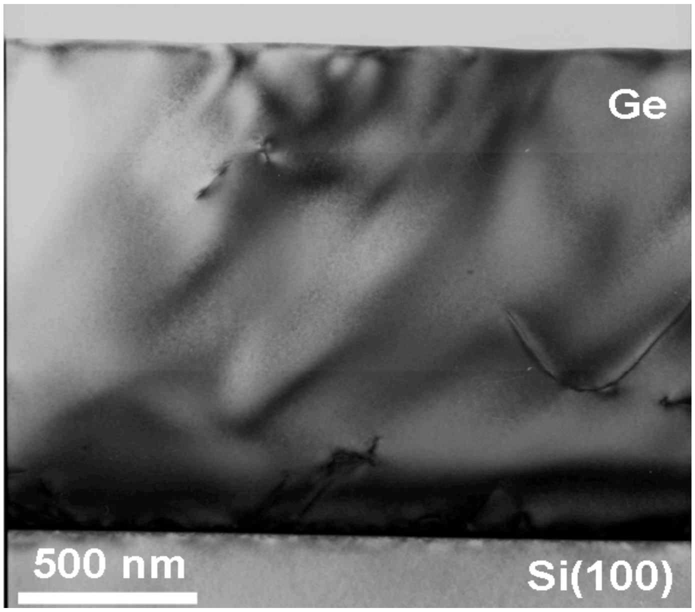


Figure 3: Electron micrograph showing the entire 1.5 μm Ge layer thickness of a monocrystalline film with a flat surface grown at 330 ^oC using trigermane.

Devices: *n-i-p* diodes based on quasi-Ge were fabricated. Circular mesas with diameters ranging from 50-3000 μm were defined by photolithography and etched using reactive ion plasmas generated by BCl_3. The mesas were passivated by a 270 nm thick SiO_2 layer which also served as antireflection coating. The Cr/Au metal contacts were deposited by e-beam and defined by lithography. Typical dark current density for the Sn doped Ge device at -1 V bias is ~ 0.02 A/cm^2, which is comparable to the 0.027 cm^2 value found in corresponding pure Ge devices grown on Si. These current density levels are consistent with high quality material possessing threading defect densities below 10^5 $/cm^2$.

The spectral responsivity of the photodiodes, measured at zero bias, is plotted in Fig. 4 and compared with corresponding data for a pure Ge reference device in *p-i-n* geometry. Both curves show a sharp drop in the vicinity of ~ 1600 and 1640 nm, respectively, corresponding to the direct gap absorption edge. The 1600 nm value is nearly identical to that measured in various *pin* and *nip* Ge photodiodes reported in the literature. A theoretical calculation of the EQE revealed that the collection efficiency at zero bias is about η = 80% in the quasi-Ge diode, whereas the pure Ge diode had a collection efficiency of η = 34%. The superior collection efficiency of the quasi-Ge diode probably indicates a lower level of residual doping in the nominally intrinsic layer.

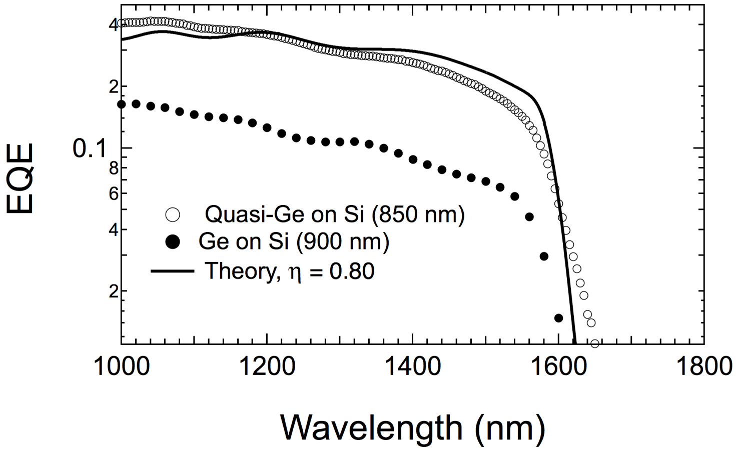


Figure 4: External quantum efficiency (EQE) for a quasi-Ge heterostructure *pin* diode measured at zero bias (empty circles), compared with a similar device based on pure Ge layers (full circles). The solid line is a theoretical curve that assumes a collection efficiency η = 0.80 for the optically generated carriers.

Ge solar cells on Si based on the Phase I metalorganic additive method were fabricated and tested. A Ge thickness of 3 microns was deemed to be sufficient to capture a significant fraction of the solar spectrum filtered by a GaAs overlayer, as typically employed in a multijunction format of high efficiency designs integrated upon bulk Ge platforms. The as-grown material is normally found to be *n*-type with background levels in the range of ~ 5×10^{15} and ~4×10^{16} cm^{-3}. In the present study the active component of the cell was therefore intentionally counterdoped with acceptor atoms using diborane to both compensate the intrinsic *n*-type impurities and simultaneously generate a lightly doped *p*-type base as required for the fabrication of semiconductor-based solar devices. Using this approach we obtained active density of boron at 3×10^{16} atoms/cm^3 as measured by the Hall method. This *p*-layer was capped with a thin n-type Ge overlayer (150 nm) doped with P and serves as the emitter component of the device. SIMS profiles of the *pn* heterostructure revealed an abrupt and well defined step between the n and p regions of the film and indicated that the donor levels are in the vicinity of ~ 3×10^{19} cm^{-3}, which is consistent with complementary ellipsometric determinations of the transport properties. The SIMS data also corroborated the acceptor densities of 3×10^{16} measured by Hall in the base layer of the device.

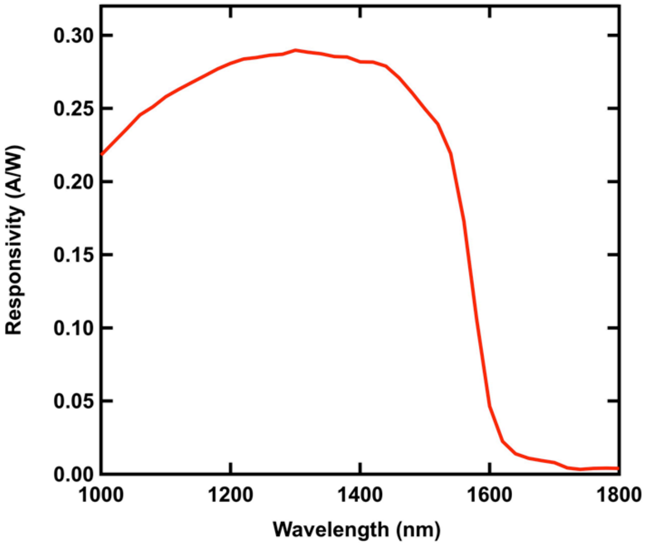


Figure 5 Spectral dependence of the responsivity measured on a 300 square micron Ge device with thickness of 3 microns and p-n geometry. The shape of the plot is similar to that measured on bulk Ge detectors

The samples were subsequently processesed into solar cell patterns with square mesas of 2.5 mm^2 perfectly suited for evaluation of the inherent photovoltaic performance of our material at AM1.5 G for the first time. In addition we also patterned on the same wafer photodiode- detectors as square mesas with smaller sizes ranging from 0.1 to 1.0 mm^2.

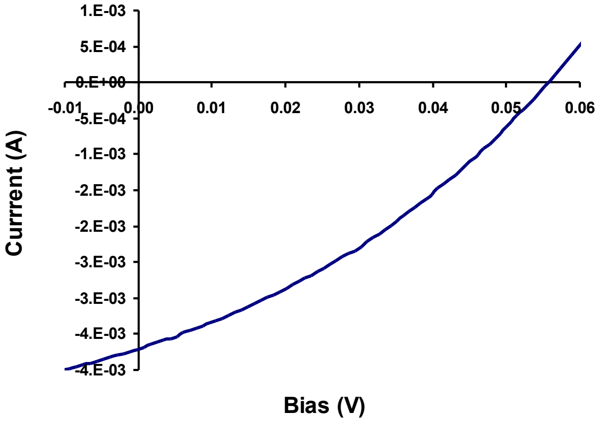


Figure 6 Current-Voltage curve of the 3 micron thick p-n Ge junction grown on Si(100). The measurement was conducted using AM1.5G spectra.

These were used as test structures to determine the lateral dependence of the dark current densities and associated quantum efficiencies of the material. Figure 5 shows the device responsivity. Measurements of the I-V characteristics for a representative device with lateral dimensions of 2.5 mm^2 under solar irradiance (2350 Watts/m^2) were conducted using a conventional solar simulator apparatus with AM1.5 G filter. The data are plotted in Figure 6 and show the following values for the typical device parameter quoted in these technologies: Voc = 5.6 x10^{-2} Volts, Isc = 3.7x10^{-3} A and maximum power of 6.9x10^{-5} Watts, Fill factor = 0.332. We note that the cell measurements in this case were performed without antireflective coating and surface passivation layers that are typically needed to optimize performance.

3.2 High efficiency: solar cell designs via SiGeSn alloys with 1 eV optical gaps

A second objective of the project was to develop a new candidate material that can be potentially incorporated as the long sought "missing" fourth junction in the Ge/InGaAs/InGaP multijunction design for a boost in efficiency. The idea is schematically depicted in Fig. 7. This material is based on SiGeSn alloys with tunable direct gaps in the range of 0.87-1.2 eV at a fixed lattice constant identical to Ge, as required for the proposed integration.

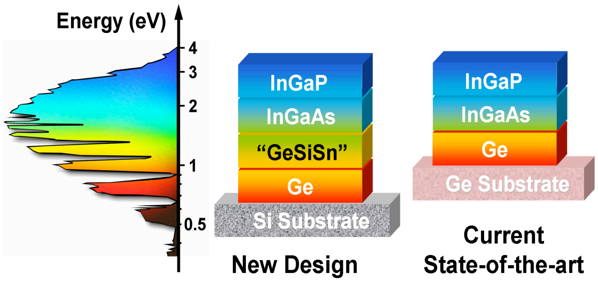


Figure **7** Schematic showing existing (right) and proposed (center) multi-junction cell structures based on group IV and III-V hybrid designs. The solar spectrum is shown on the left.

Objectives:

- Develop SiGeSn ternaries with 1 eV gaps lattice matched to Ge as the "missing" fourth junction for a boost in efficiency in Ge/InGaAs/InGaP solar cells.
- Optimal efficiency provided via higher absorption at lower energies by inserting a fourth GeSn junction with optimal bandgap in Si(100)/GeSn/SiGeSn/InGaAs/InGaP
- New simplified designs with improved efficiency via a new design incorporating GeSn layers on Si for two-junction solar cells using GeSn as the lower gap junction.

Objectives achieved:

- Produced SiGeSn lattice matched to Ge on Si and optical electrical and thermodynamic properties were evaluated. Materials with the desired 1 eV band gaps were grown.
- Developed doping protocols of SiGeSn using designer chemistry approaches suitable for in situ low temperature processing en route to photodiode junctions.
- Extended IR performance in GeSn diodes to include all IR telecom windows was obtained for the first time using entirely group IV materials.
- The optical response of GeSn devices was found to be at least 5 x higher than pure Ge representing a major performance gain.
- A significant degree of overlap with the solar spectrum not currently captured by Ge was obtained making the material an enabling candidate for solar applications in the IR.
- Ge(100)/$Ge_{1-x-y}Si_xSn_y$ solar cells structures and Si(100)/$Ge_{1-x-y}Si_xSn_y$ analogs were fabricated and the diode behavior in both cases was measured

3.2.1 Phase I work

Growth: The SiGeSn materials were synthesized for the first time directly on 4-inch Ge buffered Si(100) via low temperature reactions of Si/Ge/Sn hydrides including SnD_4, SiH_3GeH_3 $SiH_2(SiH_3)_2$, and Ge_2H_6 as stated in the scope of work. These compounds enable facile adjustment of the elemental content in the alloy leading to a wide range of materials that possess a fixed lattice constant identical to that of Ge by maintaining the Si:Sn ratio close to 4:1 in the ternary. For low Sn concentrations (y ~0.02), the films can be grown at 350 °C using only SnD_4, Ge_2H_6 and Si_3H_6. To obtain higher Sn concentrations y ≥ 0.05, the growth temperature must be lowered to 300°C-330 °C. Under these conditions the reactivity of trisilane is considerably reduced, and growth of the ternary is achieved using SiH_3GeH_3 as the main source of Si and Ge, with trisilane included as an additive to fine-tune the composition.

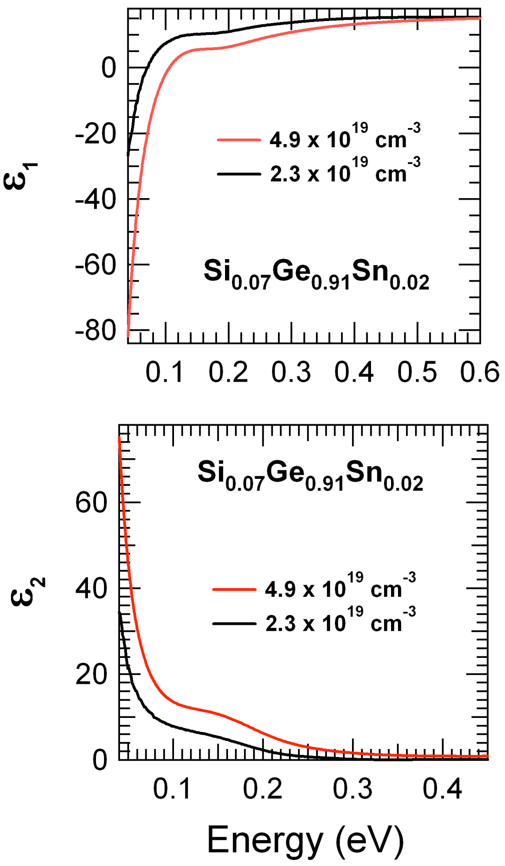


Figure 8 Real (ε_1) and imaginary (ε_2) parts of the infrared dielectric function of *p*-type SiGeSn, displaying the Drude-type behavior characteristic of free carriers.

Materials characterization: As indicated in the scope of work the compositional dependence of the direct band gap in SiGeSn alloys was initially determined. These materials can be described with the general formula $Ge_{1-x}(Sn_{0.20}Si_{0.80})_x$ and incorporated Si and Sn contents up to 45% and 12 %, respectively. The E_0 transition was measured for a series Ge/SiGeSn samples with 2-11% Sn using spectroscopic ellipsometry and photoreflectance yielding tunable absorption coefficients and band gap energies in the range of 0.9 - 1.4 eV at fixed lattice constant. This observed “decoupling” of bandgap and lattice constant is a behavior typical for III-V quaternary compounds that has led to widespread

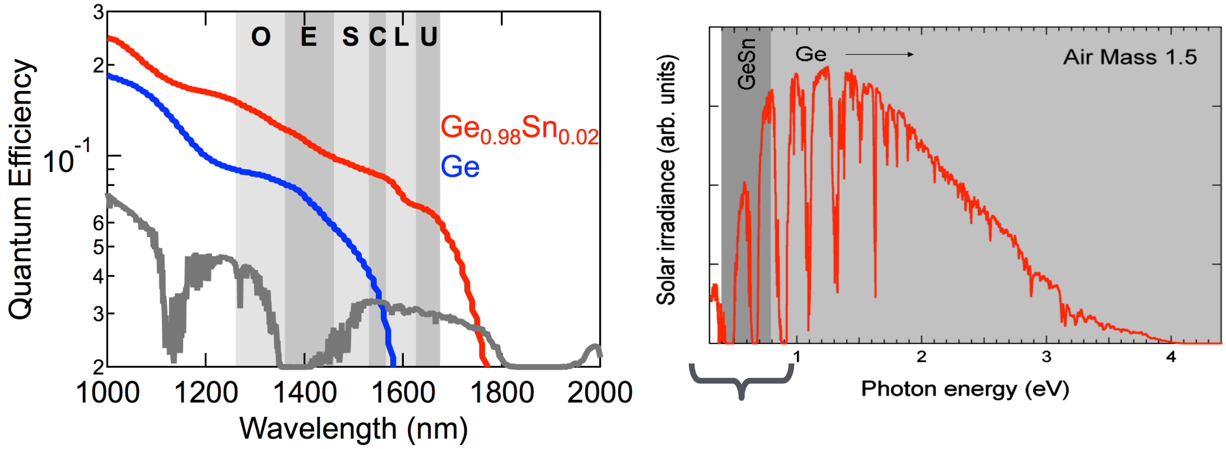


Figure 9 (left) Optical response of a 350 nm thick GeSn photodiode. The spectra indicate a significantly higher external quantum efficiency relative to pure Ge and an extended IR detection range down to 1800 nm. The incorporation of 2% Sn allows a significant degree of overlap with the solar spectrum. The bracket at right panel indicates the range of additional solar irradiation absorbed relative to pure Ge.

applications in commodity device fabrication using these materials. However, this is the first time it is observed for group-IV elements, because the dominant group-IV alloy, SiGe, possesses a single degree of compositional freedom.

The measured optical band gaps observed in the SiGeSn alloys are higher than that of Ge (0.80 eV), making these materials promising candidates for high efficiency photovoltaic applications.

Doping: Crucial for the fabrication of solar cells was the development of doping protocols for all proposed Si-Ge-Sn active layers. In these experiments B_2H_6 and $P(GeH_3)_3$ were used as molecular precursors for in-situ low-temperature doping and activation. Nominal carrier concentration levels in the range of 10^{16} to 10^{19} cm^{-3} in B-doped (*p*-type) and 10^{17} to 10^{20} in P-doped (*n*-type) layers were achieved, as determined by infrared spectroscopic ellipsometry and Hall measurements. Figure 8 shows the infrared dielectric response of doped films. Boron and Phosphorus doped ternaries, lattice-matched to Ge, with compositions adjusted to independently tune the band gap have been developed. Device-level carrier concentrations were produced yielding film resistivities and carrier mobilities comparable to those of Ge, indicating negligible alloy scattering. Similarly doped SiGeSn alloys were grown directly on Si substrates. These alloys are specifically designed to possess band gaps in the range required for the fabrication of the proposed multijunction solar cells.

Devices: A final PV concept that was investigated in this study proposed the replacement of the Ge layer in Ge/InGaAs/InGaP stack by a tandem GeSn/SiGeSn alloy structure, in which the compositions can be adjusted to approach the theoretical efficiency limit as proposed in the objectives. The initial stages of the work as described in the scope of work involved growth, fabrication and measurement of GeSn photodiodes for the first time in this class of materials. Processing and testing of the first generation of PIN devices with Sn composition in the range of 0.1-3 % was completed and demonstrated that photodiodes based on $Ge_{0.98}Sn_{0.02}$ active layers yield significantly higher photoresponse than elemental Ge over a broader spectral range as shown by left panel of Fig. 9. This finding supports the claim that GeSn alloys are suitable materials for application in high efficiency photovoltaics. In particular, our GeSn diodes are able to capture a significant fraction of the infrared solar spectrum beyond the spectral range of current Ge-based multijunction solar cells as shown by right panel of Fig. 9.

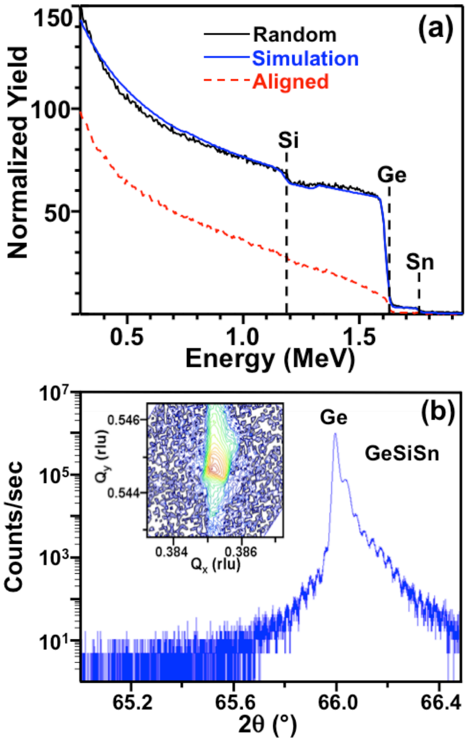


Figure 10 (a) RBS spectra of a 1 µm-thick Ge$_{0.886}$Si$_{0.094}$Sn$_{0.02}$ film showing a high degree of crystallographic alignment with the Ge substrate; (b) XRD 2θ/ω plot and 224 reciprocal space map (inset) indicating very close lattice-matching between the film and the substrate.

3.2.2 Phase II work

Growth: An important byproduct of our trigermane /tetragermane approach to Ge films on Si was the development of an entirely new strategy to SiGeSn films on Ge and Si substrates based on reactions of of tetrasilane (Si_4H_{10}), tetragermane (Ge_4H_{10}), and deuterated stannane (SnD_4). The Si_4H_{10} was procured from Voltaix Corporation and used as provided, while the Ge_4H_{10} was prepared in our labs The substrates were 150-µm-thick, 100-mm-diameter Ge(100) wafers off-cut by 6 ° toward (111) and doped with Ga (p=6×10^{17} cm^{-3}). The off-cut geometry is standard for photovoltaic applications because it prevents the development of anti-phase domains when III-V compounds are grown on group-IV substrates. Each "epi-ready" wafer was loaded as received into the chamber and then heated to 550 °C for 5 minutes under high vacuum to remove the surface oxide. Gaseous stock mixtures were prepared by diluting the Si_4H_{10}, Ge_4H_{10}, and SnD_4 with research-grade H_2, and the molecular flux was then introduced into the chamber at a steady flow, controlled by a leak valve. The growth pressure was maintained constant at 1×10^{-4} Torr and the temperature was adjusted in the range of 320-285 °C depending on the desired composition. The growth rates were estimated to be 9-10 nm/min for ~310-315 °C, respectively. The atomic fraction in the films was consistently controlled by the relative amounts of the molecules in the gaseous mixtures. We targeted Si/Sn ratios as close as possible to 3.7 to maintain perfect lattice match with the Ge substrates.

The as-grown materials were found to be optically featureless by Nomarski microscopy. Rutherford backscattering spectrometry (RBS), high-resolution x-ray diffraction (HR-XRD), atomic force microscopy (AFM), and cross-sectional transmission electron microscopy (XTEM) studies were subsequently carried out on most samples to determine their structural properties. Figure 10 shows representative RBS/XRD data from a film grown at 315 °C. Modeling of the random RBS using the program RUMP reveals uniform Si/Sn content throughout the films with a margin of error of 0.1 % Sn and 1% Si, while the channeling analog indicates single-phase crystalline material grown with epitaxial alignment to the underlying wafer. XRD measurements were employed to refine the Si content determination using the measured lattice constant of the epilayer in conjunction with Vegard's Law. The 2θ/ω plots and 224 reciprocal space maps typically contain a single Bragg reflection in each case, corresponding to overlapping contributions from the intrinsic and n-type over-layers. The 004 reflection of the SiGeSn epilayer appears as a shoulder on the Ge wafer peak. The width of the peak is similar to that of bulk Ge, indicating minimal mosaic spread and flawless hetero-epitaxial alignment, which is further corroborated by the presence of thickness fringe patterns on both sides of the peak.

Devices: SiGeSn alloys grown via the above procedure were used to fabricate the first working SiGeSn-based *pn* structures, finally overcoming what turned out to be the major challenge to the success of the overall program. While Ge- and GeSn-based diodes were relatively straightforward to fabricate, SiGeSn counterparts could only be demonstrated toward the end of phase II using our new growth strategies. Photodiodes were fabricated with stacks of several compositions using procedures previously developed for near-infrared GeSn devices. The materials were processed in pristine as-grown condition with no further thermal treatment. Devices in circular mesa geometry were produced with diameters between 100 μm and 1000 μm. In all cases, the dark current densities are in the 10^{-3} A/cm^2 range, much lower than those measured in similar devices based on Ge-on-Si and $Ge_{1-y}Sn_y$ alloys. The lower dark current in SiGeSn suggests that the electrical properties of the ternary are not dominated by defects associated to the likely presence of Si-Sn bonds. The diluted ternary alloy devices (1-2% Sn) exhibit ideality factors close to unity at n = 1.1-1.2, while the more concentrated analogs (3-5%) show slightly higher values in the n = 1.3-1.4 range.

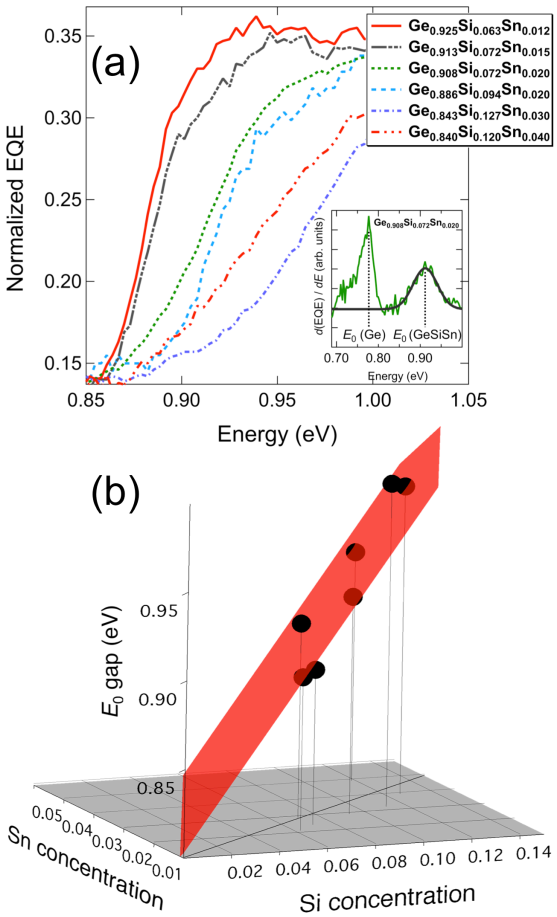


Figure 11 (a) Normalized EQE plots of diodes with 1-4% Sn content. The inset shows the numerical derivative of EQE for one of the diodes. The solid black line is a Gaussian fit from which the E_0 gap is determined. (b) The solid spheres show the measured E_0 gap energies as a function of the Si- and Sn-concentrations. The colored plane is a bilinear fit of these energies, whose linear coefficients are given in Eq. (1). The solid line in the concentration plane indicates the Si/Sn concentrations that give a perfect lattice match between $Ge_{1-x-y}Si_xSn_y$ and the Ge substrate.

The external quantum efficiency was measured at zero bias in a selected subset of devices, as indicated in Figure 11(a), which compares in detail the GeSiSn absorption edge for photodiodes containing ~ 1-4 % Sn. The maxima were normalized to facilitate comparisons of the EQE across devices. In general the plots show that the simultaneous increase of Sn (1-3%) and Si (6-13%), while keeping the Si/Sn ratio at 4±1, produces a systematic and significant shift of the absorption wavelength (nearly 150 nm within this range). We obtained the direct gap E_0 by computing numerically the energy derivative of the EQE, and fitting the resulting lineshape with a Gaussian. The Gaussian maximum is identified as E_0. An example is shown in the inset in Figure 11(a). The energies extracted from our fits are corrected for strain effects using the measured strain from our x-ray data and literature deformation potentials. A bilinear fit to the band gap energies is shown as a colored plane in Fig 11(b).

3.3 Integration: III-V materials and devices on ASU virtual group-IV substrates

Objectives:

- Integration of III-V materials on group IV on Si platforms, ultimately yielding the components of future ultra-high efficiency 4-5 junction devices.
- Demonstrate the growth of III-V materials on the ASU Ge/Si virtual substrates.
- Produce and characterize III-V devices on Ge/Si layers.

Objectives achieved:

- Demonstrated growth of optical quality InGaAs on Ge buffered Si at the industrial scale by Epiworks and identified optimal nucleation conditions using MOCVD.
- Fabricated a single junction GaAs solar cell on engineered Ge substrates produced at ASU. The same devices were grown on ASM Ge/Si substrates to serve as reference materials. Prototypes were processed and measured at NREL to evaluate their optical response and determine their photovoltaic efficiencies.
- Conventional triple junction structures were grown on Ge(Sn)/Si(100) platforms by industrial partner IQE in the UK

3.3.1 Phase I work

Growth: InGaAs layers with thickness up to 3 microns were subsequently grown lattice matched to Ge via conventional MOCVD by our industrial partner Epiworks on large area Ge on Si wafers fabricated at ASU (see Figure 12). The purpose of the study was to develop growth recipes and deposition protocols for subsequent integration of III-V solar cell junctions on Ge-buffered Si.

The InGaAs films were doped with suitable levels of Zn donor atoms and were characterized for structure, morphology and optical response using low temperature PL, time resolved PL (Figure 13), Nomarski/AFM, XTEM, and high-resolution XRD. These samples represented the first attempt to grow InGaAs on ASU's Ge/Si artificial substrates, and allowed comparisons of their optical properties with a mature and commercially available technology such as InGaAs on Ge wafers. The results clearly indicated the need for misoriented wafers to successfully integrate photovoltaic quality III-V materials on large area Si substrates. In general the study demonstrated the viability of ASU's technology for large-scale low-cost production of enabling platforms and the material produced is found to be perfectly suitable for further solar cell device development. In fact, our initial assessment indicates that the films grown on our Ge buffers are of comparable quality to those grown on bulk Ge wafers of the type currently used to fabricate multijunction solar cells. Moving beyond III-V solar cell stacks were fabricated and measured during phase II of the performance period.

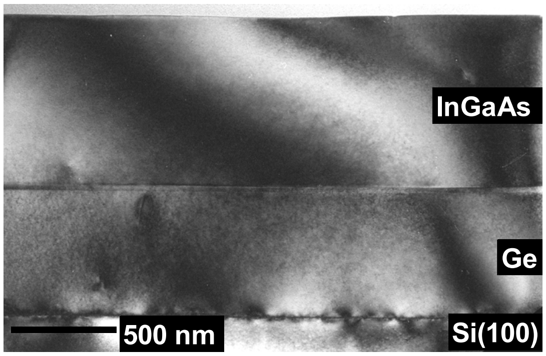


Figure 12 XTEM of defect free InGaAs grown on Ge buffered Si(100) miscut by 5^{o} towards <111> via an intermediate tunnel junction layer.

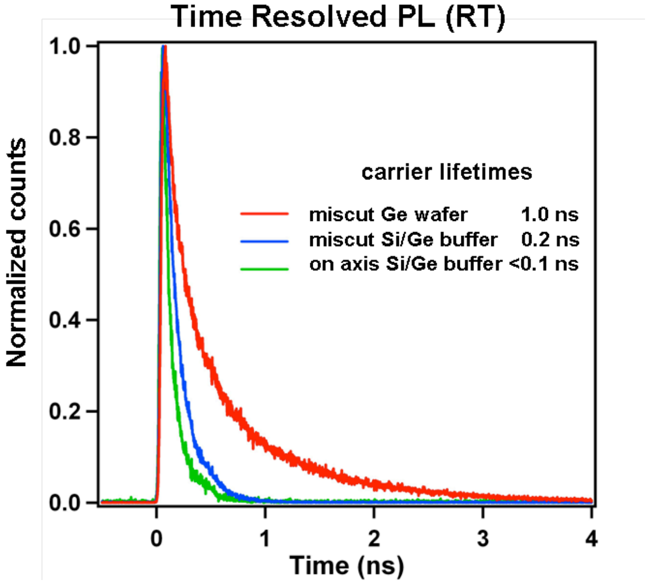
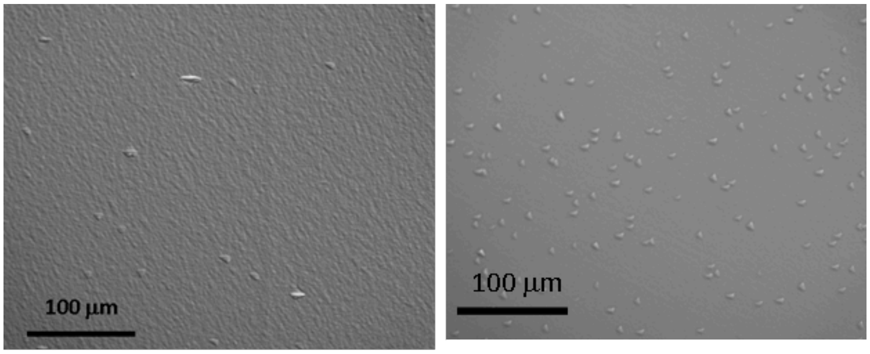


Figure 13. Time resolved PL indicates carrier lifetimes of 0.2 ns compared to 1 ns for photovoltaic quality InGaAs grown on Ge wafers under same conditions

3.3.2 Phase II work

Growth: GaAs layers were deposited on Ge-buffered Si substrates by our partner Epiworks, Inc. Figure 14 compares Nomarski images for GaAs was on ASU-provided material, on Ge-layers grown by our partner ASM, and on a control Ge-substrate. Proof-of-concept MOCVD of GaAs and InGaAs reference films was also conducted on Ge/SiGeSn templates to demonstrate the potential of the latter in the fabrication of group IV/III-V hybrid solar cell from a crystal growth perspective. Our characterization experiments showed that the resultant Si(100)/Ge/ SiGeSn/InGaAs hetero-structures exhibit high quality structural properties indicating that integration of InGaAs on these group IV platform appears feasible under conditions compatible with Si CMOS processing. Their use for the subsequent creation of complete four-junction photovoltaic device structures was proposed at a later time in a patent filed by Emcore Corp. underscoring significant interest in the PV potential of this system from an industrial perspective.

Devices: A complete GaAs solar cell structure was fabricated on a ASU Ge-buffered substrate. The device is shown schematically in Fig. 15. A single junction GaAs solar cell was grown by our industrial partner EpiWorks on engineered Ge substrates produced at ASU. The same device structure was grown on Ge/Si substrates produced by our industrial partner ASM International, using their own Ge wafers to serve as reference materials. Reference cells were also grown on Ge wafers. The three prototypes were processed and measured at NREL to



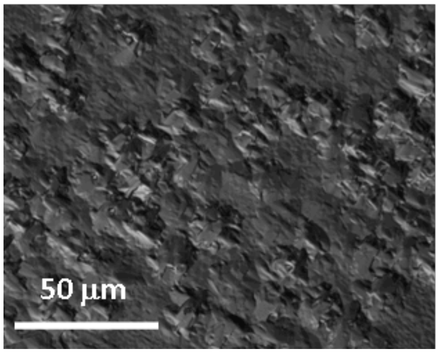


Figure 14. Nomarski images showing the surface structure/morphology of the GaAs solar cell structure grown on the ASU Ge/Si (top left), ASM Ge/Si (top right) and on EpiWorks Ge wafer (bottom). The quality of the ASU sample appears to be slightly better than that of the pure Ge substrate. The ASM material is rough and highly defective.

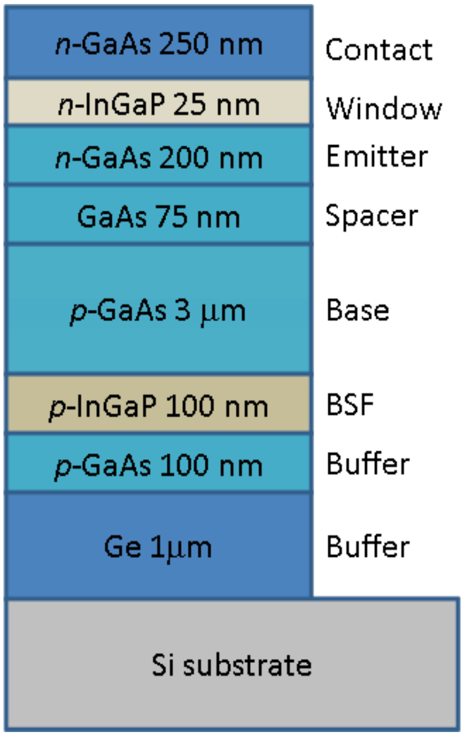


Figure 15 Single junction photovoltaic device grown on the ASU Ge buffered Si (100) substrate.

evaluate their optical response and determine their photovoltaic efficiencies. The IV characteristics of all devices were obtained under AM1.5G illumination and the data indicated that the GaAs/Ge(100) reference sample exhibited the best performance values, as expected. The typically reported parameters V_{OC} = 0.9434 V, J_{SC} = 18.42 mA/cm^2 and FF = 80.7 (%) were found to be near state of the art for the design employed. This behavior is consistent with XTEM examination of the photovoltaic stack which suggested relatively low densities of threading dislocations as expected for fully optimized lattice matched heteroepitaxy of GaAs on bulk Ge. The best devices grown on the ASM and ASU substrates indicated that the V_{OC}, J_{SC}, and FF values for the latter were substantially higher than the corresponding ASM counterparts. Nevertheless these results were inferior to those found in the reference Ge samples. Figure 16 shows typical IV curves obtained from three cells in each sample. The FF of the ASU material varied from 60-68 % while the ASM showed fairly a constant value at 58% compared to 80% for the industrial standard. These results can be explained by examining the dislocation densities in the processed samples using the EBIC method. The estimated dislocation densities for the ASU and ASM devices were found to be 10^7 and 10^6 /cm^2 respectively. The latter sample however showed numerous antiphase induced defects in the III-V materials while the ASU device was devoid of such defects. Both ASU and ASM samples displayed sporadic cracks spaced ~ 50-100 microns apart and running along the 110 direction of the wafer surface. We note that the densities of these appeared to be higher in the ASM sample while they were completely absent on the devices grown upon Ge(100). Cracks were observed in as grown materials prior to solar device processing and are likely formed during the cooling phase of the MOCVD of the III-V due to the thermal mismatch of the Si platform with the thick epilayers.

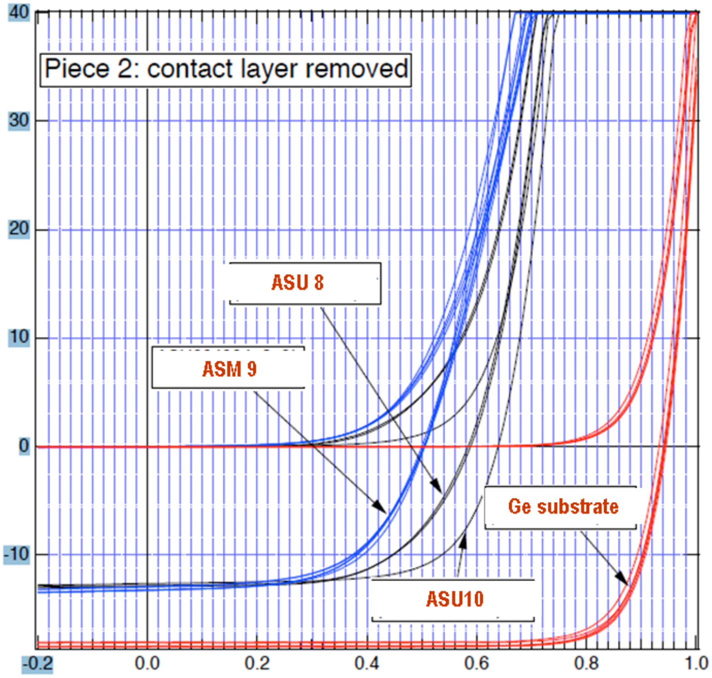


Figure 16 IV curves for representative solar cells fabricate on ASU ASM engineered substrates and on bulk Ge wafers, (black. blue and red traces, respectively)

Optimization of the growth condition should mitigate the formation of such imperfections which may contribute to the low Voc values measured in the device grown on Si wafers.

Finally, an industrial scale batch of Ge(Sn)/Si(100) 4” wafers were produced at ASU and used to grow full triple junction prototypes by industrial partner IQE in the UK. These proof-of-concept experiments provided promising initial results for the development of low-cost Si integration on the basis of structural, micro-structural and morphological characterizations performed at ASU and IQE.

3.4 Intellectual Property

Four international patent applications were published, as shown below. A licensing agreement was executed with Translucent Inc. to explore the PV application of the ASU GeSn/Si(100) engineered substrates and SiGeSn 1eV junctions developed under this program (1 and 4 below) Translucent is a materials technology company which has a focus on the electronic and solar markets. It is located in Palo Alto CA and it is a subsidiary of Silex Systems Ltd, an Australian energy company. A research program was initiated on 09/2010 with Emcore Inc to develop SiGeSn solar cells on Ge platforms. Additional collaborative work with IQE in the UK explored the use of GeSn platforms in the integration of 3-junction PV devices on Si. No intellectual property was generated with IQE. In the case of Emcore, the company submitted an application regarding the use of SiGeSn layers in inverted solar cell structures.

3.4.1 Patent list

1. **WO 2012068451** (International Patent Application Number) “Dilute Sn-doped Ge alloys” J. Kouvetakis, R. Roucka, R. Beeler, and J. Menendez (National and PCT applications filed November 18, 2011).
2. **WO 2010033638** (US2011/0316043)**:** “Thin group IV semiconductor structures” J. Kouvetakis **and** J. Menendez, PCT int. appl. published 2010.
3. **WO 2010033641** (US2009/057218) “GeSn infrared photodetectors”, J. Kouvetakis, J. Menendez, R. Roucka and J. Mathews, PCT int. appl. published (2010).
4. **WO/2010/044978** (US2011/0254052)**:** “Hybrid Group IV/III-V-semiconductor structures” J. Kouvetakis and J. Menendez (filed 09/2009). PCT international application Number 13/062,304.

3.5 Journal publications

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2. “High-performance near-IR photodetectors with independently tunable structural and optical properties based on Si-Ge-Sn”: Chi Xu, R.T. Beeler G. Grzybowski, A.V.G Chizmeshya J. Menendez and J. Kouvetakis *Journal of the American Chemical Society* **134(51),** 20756-20767 (2012).

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8. “Practical routes to P(SiH$_3$)$_3$”: Applications in group-IV semiconductor activation and in group-III-V molecular synthesis” J.B. Tice, A.V.G. Chizmeshya, J. Tolle, and J. Kouvetakis, *Dalton Transactions* 39, 4551 (2010).

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3.5.1 Extended conference papers

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