Si-Ge-Sn Based Compound Semiconductors for Photonic Applications

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Keywords: Si-Ge-Sn alloys, solar cell, III-V integration

Abstract

Si-Ge-Sn alloys can achieve bandgaps in the 1eV range and can facilitate the integration of III-V materials with both Ge and Si substrates. The development and current status of Si-Ge-Sn epilayer growth at Translucent is presented. The main aims of this work are the development of infrared absorbers with bandgaps below that of Ge for infrared detectors, 1 eV semiconductor materials for photovoltaic applications and group IV alloy integration with existing III-V MOCVD technology.

INTRODUCTION

III-V compound semiconductors, with their high mobilities and direct bandgaps, have driven the development of many different device architectures for photonic and electronic devices. Their integration with silicon is now a major focus for the industry, with a variety of approaches being developed, ranging from buffered epitaxial growth to wafer bonding [1,2]. With each method there are technical challenges and cost issues to overcome. The work at Translucent focuses on the development of group IV compound semiconductor alloys based on Si, Ge and Sn, which can offer an alternative to existing III-V materials in both optical and electrical performance. The Si-Ge-Sn materials system provides additional functionality via independent band gap and lattice parameter engineering [3]. These alloys offer a route to IR light emitting and detecting solutions, and also to the highly desired 1.0 eV cell in multijunction photovoltaic devices. Moreover, layers of group IV alloys can also serve as templates for integration of III-V compound materials with readily available silicon substrates.

The group IV growth process at Translucent is based on UHV-CVD deposition utilizing deuterated stannane SnD_4 and digermane Ge_2H_6 at low temperatures (300-450°C) [4]. This particular process is preferred since it allows compositional control of the Sn content in Ge, and with the addition of trisilane Si_3H_8, ternary Si-Ge-Sn alloys can also be obtained. These ternaries are of high interest for their ability to vary the bandgap while keeping the lattice constant fixed. All the precursors used in this work are commercially available, and their implementation in an industrial process is straightforward. For the SnD_4 a proprietary storage and supply system was developed, which permitted the achievement of several months of precursor lifetime and reproducible and precise control of precursor concentration.

Binary Ge-Sn alloys

The initial growth experiments consisted of alloys containing no Si. Binary Ge-Sn layers with Sn content up to 4% (determined by RBS) were first synthesized directly on bulk Si substrates. The grown layers exhibited good crystallinity and high temperature stability up to 700°C upon rapid thermal annealing. The Ge-Sn material grown on Si substrates is relaxed for all compositions (based on X-ray reciprocal space maps).

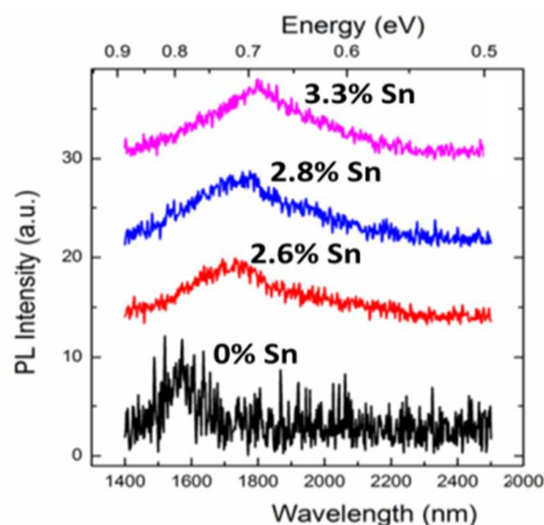

Figure 1: Photoluminescence spectra from Ge-Sn films grown on Si substrates with increasing Sn content up to 3.3%.

To demonstrate the variable bandgap in these alloys, the photoluminescence (PL) signal from several layers with increasing Sn content was collected. The PL data is shown in the Figure 1. The main peak of the emission spectra shifts to higher wavelengths - lower bandgap (Eg) - with increasing Sn content. At 3.3 % Sn the emission peak maximum is in

the range of 1850 nm (0.72 eV) – far beyond the emission spectra of Ge (0% Sn, bottom curve). This range of emission wavelengths overlaps with the bandgaps of high In containing InGaAs alloys. Hence these Ge-Sn materials show promising potential for future applications in mid and far infrared light LEDs, lasers and detectors.

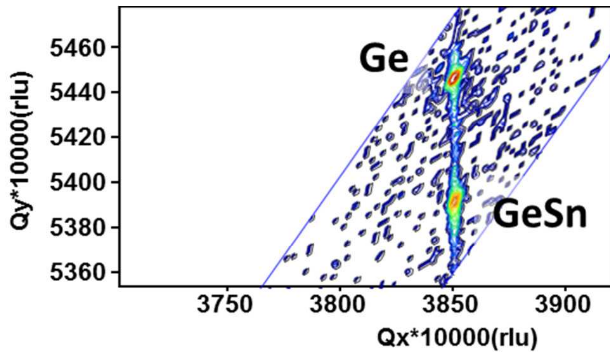

Figure 2: XRD reciprocal space map around the (224) peak of a Ge substrate, showing a fully strained 300 nm thick GeSn epilayer with 5% Sn.

Ge-Sn was also grown directly on bulk Ge substrates. In this case, the Ge-Sn growth results in fully strained layers. Figure 2 shows an X Ray Diffraction (XRD) reciprocal space map of a 300 nm thick GeSn layer with 5 % Sn grown on bulk Ge. The map was collected around the (224) diffraction peak of Ge and it is clearly seen that the Ge-Sn alloy is fully strained to the underlying Ge since it has the same in-plane lattice parameter. Upon annealing at 650 °C the layer partially relaxes, however the relaxation is not complete.

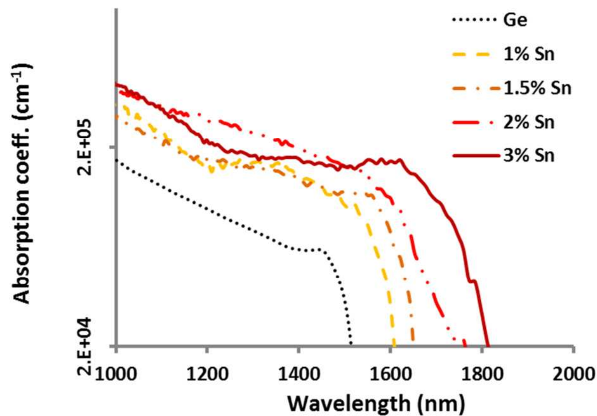

Figure 3: Measured absorption coefficient of Ge-Sn alloys with increasing Sn concentration.

The absorption properties of Ge-Sn alloys grown on bulk Ge with Sn contents up to 3% are demonstrated in Figure 3. With increasing Sn content, the absorption coefficient obtained from spectroscopic ellipsometry measurements is increasing in absolute value above that of bulk Ge (lowest dotted trace for reference), and the position of the absorption edge is shifting beyond 1600 nm to larger wavelengths. The sample with 3% Sn starts absorbing light at 1820 nm (solid trace with longest cutoff wavelength). For Sn concentrations in the range of 4-5% the Ge-Sn alloys can reach the highly desired 1900 nm wavelength response region. Hence these materials may offer material alternatives for the fabrication of infrared detectors based on extended InGaAs alloys.

Ternary Si-Ge-Sn alloys

The addition of Si to the Ge-Sn permits the alloy bandgap to be varied while the lattice parameter is held constant. The ternary bandgap range is also expanded to values higher than that of bulk Ge (0.6 - 1.4 eV). Such a range potentially covers alloys with a 1.0 eV gap, which is highly desirable for application in multijunction solar cell devices. Multijunction solar cells combine several different bandgap junctions, and are typically made of lattice-matched III-V compound semiconductors. The typical multijunction solar cell stack is comprised of Ge, InGaAs and InGaP, which are all lattice matched to the Ge substrate. However the energy gap between the Ge and InGaAs is so large that a fourth junction with a gap between the two (at ~ 1.0 eV) would significantly increase the device efficiency while satisfying the lattice matching and current matching conditions.

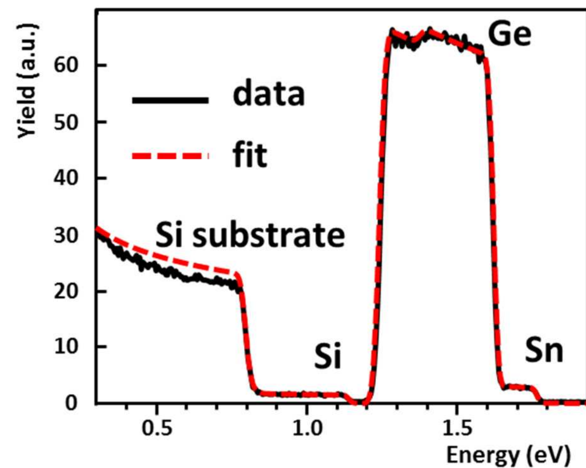

Figure 4: RBS spectrum and model fit of a 600 nm thick Si-Ge-Sn epilayer containing 2% Sn, 11% Si and 87% Ge with 600 nm thickness grown on Si substrate.

Figure 4 shows an RBS spectrum collected from a 600 nm thick Si-Ge-Sn epilayer grown on a Si substrate. The positions of the edges in the spectrum correspond to the different elements (Si, Ge, Sn) and their height is related to their atomic concentration. This particular sample contains 2% Sn, 11%Si and 87% Ge. The DCXRD spectrum in Figure 5 is taken from the same sample. For illustration, the DCXRD spectrum is overlaid with the spectrum obtained from pure Ge epilayer grown on a Si substrate. The overlapping positions of the two epilayers demonstrates that the SiGeSn alloy is lattice matched to Ge.

To examine material development for photovoltaic applications, we have grown Ge-Sn and Si-Ge-Sn alloys on both bulk Ge and GaAs substrates - the most common substrates used for solar cells. On both types of substrates the epitaxial layers exhibit high crystalline quality, as measured by the FWHM of the (004) XRD peak maxima. Figure 6 shows a DCXRD spectrum collected from a SiGeSn epilayer closely lattice matched to a GaAs substrate. Since the XRD maxima are split (472 arcsec), the FWHM of the substrate and the epilayer can be easily compared. The measured FWHM was 54 arcsec for Si-Ge-Sn grown on GaAs compared to 38 arcsec for bulk Ge or GaAs substrates. These FWHM values represent material with a density of threading dislocation defects well below the 10^6 /cm^2 limits typically required for solar cell applications.

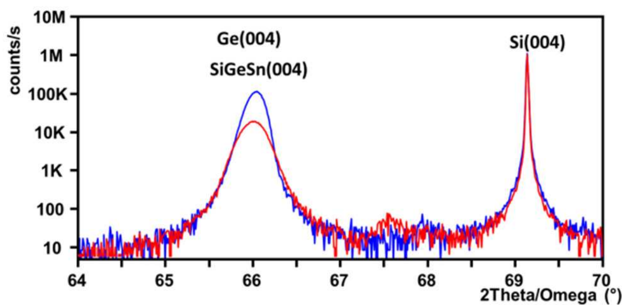

Figure 5:DCXRD (004) scan of a SiGeSn epilayer demonstrating alloy lattice matching to Ge (bottom curve).

The surface morphologies of the SiGeSn epilayers lattice matched to the Ge substrate are very smooth. The typical AFM rms roughness was in the range of 0.2 nm, which is comparable to roughness of the bulk Ge substrate surface. The morphology resembles a terraced surface, with the step direction matching the <111> substrate miscut direction.

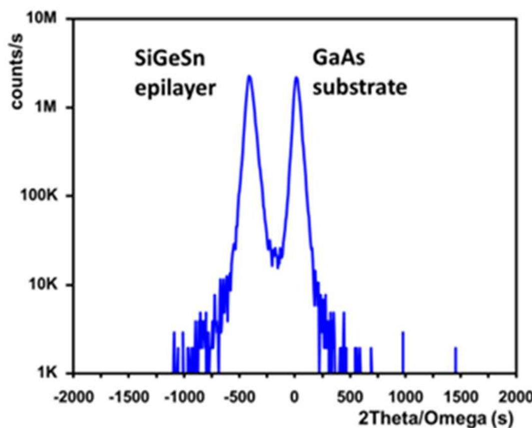

Figure 6:XRD spectrum of a SiGeSn epilayer grown on a GaAs substrate.

The SiGeSn epilayers grown on Ge substrates showed photoluminescence using 780 nm laser light excitation (Figure 7). This particular 300K PL spectrum was obtained from a $Si_{0.10}Ge_{0.87}Sn_{0.03}$ epilayer, and shows a main peak located at 1210 nm corresponding to a bandgap of 0.95 eV. At these Si and Sn compositions the bandgap character is still indirect. However, the direct gap transition is observed as a shoulder at lower wavelengths (1000 nm).

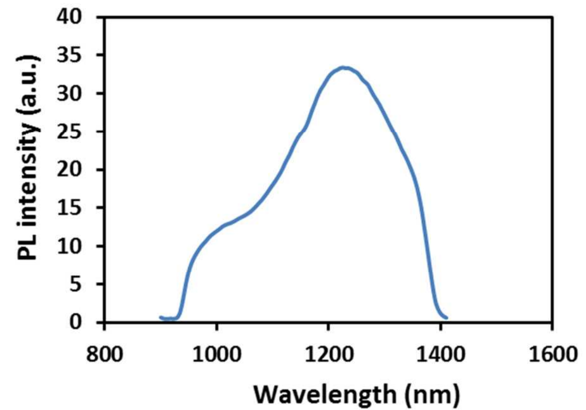

Figure 7: PL spectra obtained from a SiGeSn epilayer grown on a Ge substrate showing a nominal 0.95 eV bandgap.

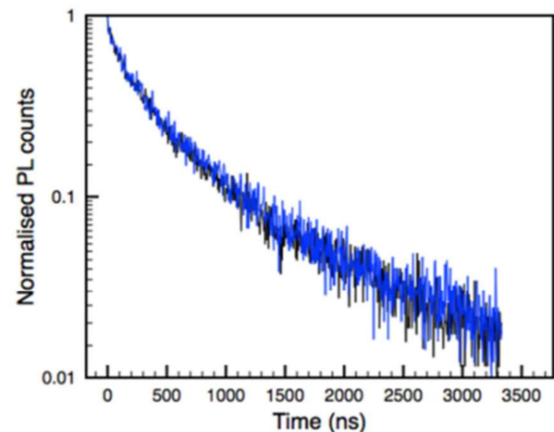

Figure 8: Photoluminescence decay curve measured on a SiGeSn epilayer with nominal 0.95 eV bandgap.

Time resolved PL can be used to characterize the photo-generated carrier lifetime in the epilayer alloy. The decay of PL peak intensity (Figure 8) at the maximum wavelength was used to estimate the photogenerated carrier lifetime. In this particular film, the epilayer thickness was 0.5 microns and the layer surfaces were not passivated. The measured lifetimes reached 1 microsecond. This result was independently confirmed using a microwave decay method yielding similar values for minority carrier lifetimes.

MOCVD of III-V compounds on group IV alloys

Translucent's main focus for group IV alloy applications is a multijunction solar cell device. We have tested the GeSn and SiGeSn epilayers grown on Ge and Si substrates (herein called templates) for compatibility with existing standard III-

V MOCVD processes in a production growth III-V reactor. Initial experiments were aimed at determining the thermal stability and nucleation properties of III-V layers on Si-Ge-Sn templates grown on Ge substrates. As noted above, the roughness and miscut of the group IV layer surface was preserved from the underlying Ge substrate. Pure Ge substrates were used to benchmark the III-V process comparisons.

Ge-Sn alloys with Sn content up to 3% and Si-Ge-Sn compounds with Si up to 10% and Sn up to 3% can both withstand the entire MOCVD growth cycle required to deposit a 6 micron thick InGaAs layer at typical growth conditions. The SiGeSn surfaces did not deteriorate and the layer crystalline quality was preserved for all template compositions and thicknesses (0.5-3 microns).

Adjustment of III-V nucleation conditions may be required to obtain good morphological and crystalline properties of III-V epilayers grown on these ternary Si-Ge-Sn templates. Test growths were performed using a typical nucleation protocol for growth of 0.2 microns InGaAs on a Ge substrate as a baseline. In these growth experiments only $Si_{0.10}Ge_{0.87}Sn_{0.03}$ templates on Ge were used in order to meet the ultimate goal of a multijunction solar cell stack. The initial growth using the exact baseline III-V process produced an InGaAs layer with a hazy surface (> 12000 ppm). The haze values were measured using a Surfscan tool (KLA Tencor 6420). The surface haze significantly improved via alteration of the nucleation temperature and the III-V ratio. After optimization InGaAs films with haze of 230 ppm were obtained. For comparison, the typical haze for the baseline InGaAs growth on a pure Ge substrate was <= 25 ppm.

The optimized III-V growth process will next be used to grow multijunction solar cell structures on these SiGeSn templates.

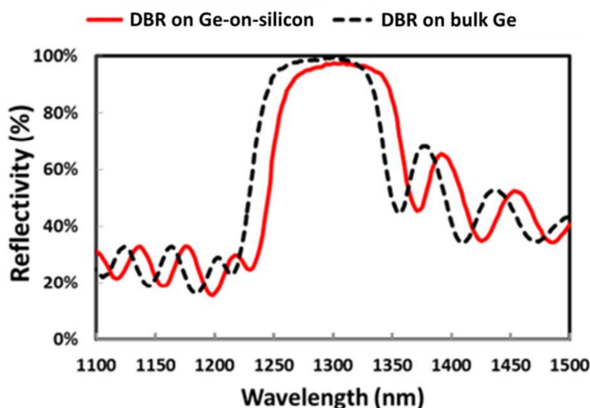

Figure 9: Reflectivity curve of 1300 nm DBR structure grown on bulk Ge and Ge-Sn/Si template. Silicon spelled incorrectly in figure; should it be DBR on Ge-Sn on Si?

As a part of a photonic integration applications effort, a III-V Distributed Bragg Reflector (DBR) was grown on a Ge-Sn epilayer grown on a Si substrate. This is a simple demonstration of a functional block used in a typical III-V vertical cavity surface emitting laser. Figure 9 shows the reflectivity spectrum of a test GaAs/AlAs DBR structure, which was designed to have a 1300 nm passband center. The figure overlays the reflectance spectra for the DBR grown on both a pure Ge substrate (dashed trace) and on the Ge-Sn on Si template (solid trace). The reflectivity spectra are comparable, with a slight shift to higher wavelength for the DBR grown on the Ge-Sn on Si template. The reflectance fringing is preserved for both samples.

CONCLUSIONS

Ge-Sn and Si-Ge-Sn compound semiconductors can be produced in a semiconductor industrial environment using commercial precursors and growth processes. These alloys provide potential new routes for light emitters and detectors working in the far infrared (below 0.8 eV) range, and also offer a new solution for achieving 1.0 eV gap solar cells. These materials are compatible with and viable for integration with standard III-V compounds.

ACKNOWLEDGEMENTS

The authors would like to thank prof. Shui-Qing Yu from University of Arkansas for PL measurements of Ge-Sn alloy layers and prof. N. J. Ekins-Daukes at Imperial College for PL of Si-Ge-Sn ternary alloys.

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ACRONYMS

PL: Photoluminescence
CVD: chemical vapor deposition
XRD: X-ray diffraction
DCXRD: Double crystal X-ray diffraction
RBS: Rutherford backscattering spectroscopy
FWHM: Full width at half maximum
MOCVD: Metal Organic Chemical Vapor Deposition
DBR: Distributed Bragg reflector
AFM: Atomic Force Microscopy
UHV: Ultra High Vacuum
LED: light emitting diode