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To cite this article: Mitchell Robson et al 2017 Nano Futures 1 035001

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Multispectral absorptance from large-diameter InAsSb nanowire arrays in a single epitaxial growth on silicon

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Keywords: InAsSb, nanowire, molecular beam epitaxy, absorptance, selective-area epitaxy, photodetector, multispectral

Abstract

Vertical III-V nanowires are capable of resonant absorption at specific wavelengths by tuning the nanowire diameter, thereby exceeding the absorption of equivalent thin films. These properties may be exploited to fabricate multispectral infrared (IR) photodetectors, directly integrated with Si, without the need for spectral filters or vertical stacking of heterostructures as required in thin film devices. In this study, multiple InAsSb nanowire arrays were grown simultaneously on Si by molecular beam epitaxy with nanowire diameter controlled by the nanowire period (spacing between nanowires). This is the first such study of patterned InAsSb nanowires where control of nanowire diameter and multispectral absorption are demonstrated. The antimony flux was used to control axial and radial growth rates using a selective-area catalyst-free growth method, achieving large diameters, spanning 440–520 nm, which are necessary for optimum IR absorption. Fourier transform IR spectroscopy revealed IR absorptance peaks due to the HE11 resonance of the nanowire arrays in agreement with optical simulations. Due to the dependence of the HE11 resonance absorption on nanowire diameter, multispectral absorption was demonstrated in a single material system and a single epitaxial growth step without the need for bandgap tuning. This work demonstrates the potential of InAsSb nanowires for multispectral photodetectors and sensor arrays in the short-wavelength IR region.

Introduction

At present, the most widely used material system for high performance infrared (IR) photodetection is Hg1−xCdxTe (MCT) [1–3]. MCT has a composition-dependent, tunable and direct energy bandgap that spans the IR spectrum from short-wavelength IR (SWIR) to very long-wavelength IR [1]. The change in lattice constant with composition is also negligible, allowing for the fabrication of high quality graded and layered MCT thin film heterostructures with negligible lattice-mismatch defects [3]. However, MCT suffers from bulk, surface, and interface instabilities due to weak Hg–Te bonds [1]. The commonly used CdZnTe substrate, while lattice-matched to MCT, is expensive, and suffers from integration issues with Si readout integrated circuits (ROICs) [3, 4]. Si substrates were investigated as an alternative, using a CdTe/ZnTe buffer layer; however, the resulting MCT thin film quality is poor compared to MCT thin films grown on CdZnTe substrate [4]. The above drawbacks have stimulated the investigation of alternative material systems for IR photodetection [1, 3].

III-V nanowires are a potential alternative to MCT or other material systems for IR photodetection. III-V nanowires can accommodate lattice-mismatch strain by elastic relaxation at the nanowire sidewalls, allowing for epitaxial growth on lattice-mismatched substrates and therefore monolithic integration with Si ROICs [5]. III-V nanowires can incorporate radial and axial homo- and hetero-junctions for efficient collection of photogenerated carriers. Due to the presence of radial resonant waveguide modes, nanowires also have the
capability of producing absorption bands with narrow spectral ranges by tuning the nanowire geometrical parameters [6–8]. Peaks in the resonant absorption bands can exceed absorption from a thin film of the same material and thickness. These advantages eliminate the need for additional spectral filters above the photodetector, or vertical stacking of heterostructures of different bandgaps, for a multispectral detector [8].

Recently, absorption in vertical nanowire arrays were simulated for GaAs, InP, InAs [6], and InSb [7] and found to be dominated by guided mode resonances. Guided modes arise in the nanowire because of its radially symmetric boundary conditions imposed on the electromagnetic wave solutions. Incident light near a resonant wavelength couples efficiently to an HE_{1n} mode in the nanowire, significantly increasing the absorption in the material [9]. This unique phenomenon results in a high absorptance peak with a narrow full-width at half-maximum (FWHM) and a spectral position controlled primarily by the nanowire diameter [6–8]. The study of optimized InSb nanowire geometrical properties indicated the need for nanowire diameters from 200–550 nm to achieve sharp resonance absorptance spectra in the SWIR region [7]. Svensson et al [10] demonstrated the diameter-dependence of photocurrent from InAsSb nanowires grown on InAs substrates by metal-organic vapor phase epitaxy. They found a red-shift in photocurrent measurements corresponding to an increase in average nanowire diameters for randomly dispersed arrays. Compositional changes were found to affect only the magnitude of the absorptance, while it had negligible influence on the peak position.

In this study, we present large diameter catalyst-free InAsSb nanowires grown on a Si substrate by selective-area molecular beam epitaxy (MBE). This is the first study of patterned InAsSb nanowires where control of nanowire diameter and multispectral absorption are demonstrated. Nanowires were grown simultaneously in four separate arrays on the same Si substrate, each with a different diameter (440, 475, 505 or 520 nm) and period (1000, 1500, 2000 or 3000 nm). Nanowires are shown to have consistent core–shell compositions, and diameters that are controlled by the nanowire array period. Spectroscopy measurements reveal absorptance peaks in the SWIR region due to HE_{1n} guided mode resonances and are confirmed by theoretical simulations. Fabrication of the four arrays occurred in a single epitaxial growth; thus, we have achieved multispectral absorptance without the need for bandgap tuning, paving the way towards nanowire-based multispectral IR photodetectors and sensors.

**Experimental details**

InAsSb core–shell nanowires were fabricated in a gas source MBE system in which Sb_{2} was supplied by a 3-stage effusion cell operating at 565 °C, 800 °C and 930 °C for the crucible, valve and cracker, respectively. Indium was supplied by a standard effusion cell and As_{2} was supplied from a hydride (AsH_{3}) gas cracker operating at 950 °C. Growth was performed in three stages; a short (50 nm) InAs stem for optimized yield and epitaxy [11], an InAsSb core with a Sb beam equivalent pressure (BEP) of 1 × 10^{-7} Torr, and an InAsSb shell with an Sb BEP of 2.84 × 10^{-7} Torr to achieve 5% and 14% fractional flux (flux of Sb relative to the total group V flux), respectively. In a fractional flux study (see supporting information available online at stacks.iop.org/NANOFT/1/035001/mmedia) 5% fractional flux produced InAsSb nanowires with 23% Sb, and a 14% fractional flux resulted in 33% Sb. The lower Sb composition core, which was in an axial growth regime, achieved a nanowire length more than 1 μm. The higher Sb composition shell was in a radial growth regime to enlarge the diameter of the nanowires to the desired value (440–520 nm, depending on the nanowire period) for strong IR absorptance. InAs stems were grown for 5 min at a V/III flux ratio of 4 while the InAsSb core and shell were each grown for 2 h at a V/III flux ratio of 10. All growth stages had an In impingement rate of 0.125 μm h^{-1} and a substrate temperature of 440 °C. Nanowires were grown on a low boron-doped (<1.33 × 10^{14} cm^{-3}) Si (111) substrate following the catalyst-free selective-area epitaxy growth method [11]. Electron beam lithography (EBL) and etching precisely defined the position of holes in a 20 nm SiO_{2} layer deposited by chemical vapor deposition. The EBL pattern was comprised of four 100 μm × 100 μm arrays each with a different triangular lattice period (1000, 1500, 2000 and 3000 nm; figure 1(a)) but the same oxide hole diameter (90 nm; figure 1(b)).

Lamellas were prepared on a Zeiss NVision40 focussed ion beam (FIB) instrument. The FIB uses a focused beam of gallium atoms to extract a lamella and thin it to ~100 nm for transmission electron microscopy (TEM) analysis. Ultramicrotome was performed using a diamond blade to cut ~100 nm slices. Nanowire morphology was characterized using a JEOL 7000F scanning electron microscope (SEM). Nanowire structure and composition were characterized by a JEOL 2010F scanning TEM with energy-dispersive x-ray spectroscopy (EDX). Optical characterization was performed by Fourier transform IR spectroscopy (FTIR) using a BRUKER Hyperion 3000 system with a halogen source and an MCT detector with an operating wavelength range of 1.25–16 μm. IR light was incident and collected through a 15x objective lens with a numerical aperture of 0.4. A knife-edge aperture was set to an area just less than 100 μm × 100 μm to ensure that absorbance data only included the nanowire array. The same aperture setting was used for all background measurements. All FTIR measurements were performed with the source normally incident on the nanowire array (front-side
illuminated) and at room temperature. The FTIR spectra were smoothed using a Savitzky–Golay filter to remove high frequency noise.

Optical simulations of the nanowire absorptance were performed using the finite element method in COMSOL 3.5a RF Module. Periodic 2D triangular lattice nanowire arrays on a Si substrate were simulated using the measured average diameter, average length, and period of the nanowires within a given array. The nanowire cross-section was hexagonal, representative of the grown nanowires. A schematic of this array is presented in figure 1(a). The real part ($n(\lambda)$) of the complex refractive index of the InAs$_{1-x}$Sb$_x$ nanowires was acquired from Paskov [12]. The imaginary part ($k(\lambda)$) of the complex refractive index of the InAs$_{1-x}$Sb$_x$ nanowires was acquired from Stringfellow and Greene [13] and is like that of InAs and InSb below $\lambda = 3 \text{ nm}$ as acquired from Palik [14]. The complex refractive index for Si was acquired from Palik [14]. The medium surrounding the nanowires was air with $n = 1$. A perfectly matched layer subdomain was used above the nanowire geometry and below the substrate to simulate an infinitely extending air medium above the nanowire array and an infinitely extending Si substrate below the nanowire array. A port was set on an ‘assembly pair’ constructed above the nanowire array to generate $Y$-polarized incident waves at normal incidence to the nanowires (parallel to the nanowire axis). The absorptance spectra of the nanowire array was found to be polarization independent. Wavelength-dependent absorptance was calculated by taking the difference between transmittance at the nanowire array top and bottom.

Figure 1. Morphological aspects of nanowire arrays. (a) Schematic of nanowires in a triangular lattice with hexagonal cross-sections and the diameter ($D$), period ($P$), and length ($L$) indicated, (b) plan view SEM of 1000 nm period array of holes in the Si oxide, (c) droplets and crystallites on the oxide away from the nanowire arrays, (d) 30° tilted SEM of a nanowire from 1000 nm period array, and (e) trends of diameter and length versus array period. Error bars represent standard deviations.
Results and discussion

SEM images, such as that shown in figure 1(d), confirmed that the nanowires were droplet-free with a flat top facet, smooth sidewall facets, negligible tapering, and a hexagonal cross-section. Figure 1(b) shows the EBL patterned oxide holes in SEM with a consistent diameter of 90 nm and a period written with a positioning accuracy of 0.6 nm and a field stitching accuracy of 20 nm. For periods of 1000, 1500, 2000 and 3000 nm, nanowires had average diameters of 440, 475, 505 and 520 nm and average lengths of 1180, 1190, 1280 and 1400 nm, respectively. Both diameter and length increased with period (figure 1(e)), although an inverse relationship between diameter and length has been observed in other studies of InAsSb nanowires [15–18]. Often this trend is attributed to declining In adatom competition, occurring when nanowire spacing is less than twice the In diffusion length [19]. However, the In diffusion length is believed to be ~750 nm for nominal InAs on Si growth conditions [19], and reduced under Sb flux in the MBE [20]. Since the smallest period of 1000 nm in our study is likely beyond this competitive growth regime, which is evidenced by the In/Sb droplets between the nanowires, it cannot explain our diameter trend with period. Instead, vapor–solid growth can show a proportional relationship, as in our study, since it does not rely on the supersaturation of a catalyst particle for axial growth [11]. In this case, the diameter difference between the arrays can be attributed to an increased adatom re-emission flux from the oxide surface between neighboring nanowires [21, 22]. Saturation at 3000 nm period occurs as the maximum capture of the re-emission flux is approached. The saturation limits the ability to control the diameter with the period for larger diameter nanowires. However, larger nanowire diameters can be achieved by increasing the growth duration, which is beyond the scope of the present study. Nanowires within the 3000 nm period had a higher radial growth rate than those in the 1000 nm period. It follows that longer growth times will further spread the diameters among the arrays under the same growth conditions, while increasing the diameters of all arrays.

FIB-cut vertical cross-sections along the nanowire length, and ultramicrotome horizontal cross-sections, were performed on each of the four nanowire arrays. The resulting FIB lamellas were approximately 100 nm thick, less than one quarter of the smallest nanowire diameters, and cut through the center of a row of nanowires. Figures 2(c)–(f) show the bright field TEM images for FIB-prepared nanowires cut in the growth direction. SAD patterns (figure 2(a)) revealed a twinned zincblende (ZB) crystal structure, as observed previously for similar nanowires [12, 23, 24]. These twins, identified as contrast stripes in the TEM images, propagate across the whole nanowire diameter suggesting epitaxial growth of the shell on the core. A separate growth of the core without a shell found a similar twinned ZB crystal structure (see supporting information). High resolution TEM identified epitaxial contact between the nanowires and the silicon substrate across the entire ~90 nm hole (figure 2(b)).

Horizontal ultramicrotome cuts were also created to further investigate the composition of the core and shell. The high-angle annular dark field scanning TEM (HAADF-STEM) image of a nanowire from the 1000 nm...
period array is shown in figure 2. A separately grown core without a shell revealed that the core diameter was 200 nm for the 1000 nm period (see supporting information). Accompanying EDX area, line, and point measurements are indicated in figures 2–(j). The EDX area maps reveal segregation of As and Sb atoms at the corners of each 〈110〉 side facet. The segregation forms a high As content along 〈112〉 directions extending from the core to the corners of the shell. Previous reports of segregation in ternary shells (GaAs-AlInP [25] and GaAs-AlGaAs [26, 27]) found this was a result of differences in diffusion lengths at the corners of the shell. In the AlGaAs shells, Ga diffused away from the corners more readily than Al leading to higher Al concentrations along the 〈112〉 directions. Presumably, segregation of As and Sb in our nanowires is a result of a similar effect. Due to the growth temperatures used in our study, it is more likely that Sb more readily diffuses from the 〈112〉 facets, while As is governed by a desorption process [28]. The line scan for As content in figure 2(i) shows a gradient decreasing radially out from the core along one of the As-rich ridges. Other reports [29] indicate a constant composition along the ridges and sharp heterojunctions at the core and shell interfaces. The radial gradient in our study may be a result of an Sb surfactant effect [30]. A line scan for Sb content through the Sb-rich shell is shown in figure 2(j). Point scans in figure 2(g) quantify the Sb content of three major regions: core (29%), Sb-enriched shell (40%), and As-enriched corners (32%). All four nanowire arrays were compositionally consistent, within 2%, for each of the point scans.

FTIR measurements were used to obtain the diameter-dependent IR absorptance from each of our four nanowire arrays. A background absorptance measurement was performed on a clean Si substrate without any oxide mask or III–V growth. The resulting absorptance from the Si (gray curves in figure 3) was negligible, as expected for low doped silicon in the IR region. Another background measurement was taken for an area just outside each of the four arrays (dashed–dotted lines in figure 3), which included some droplets and crystallites on the oxide but did not include any nanowires (figure 1(c)). This measurement was included as a reference for the nanowire absorptance. It represents the absorptance of several droplets and crystallites on the substrate surface near the nanowire array but does not quantitatively match the droplet or crystallite density inside the array and cannot be used to normalize the experimental nanowire data. However, the background measurement confirms that the peak in the nanowire absorptance spectra are indeed due to the nanowire array, and the background absorptance surrounding the peaks is due to the crystallites and droplets on the oxide between the nanowires. Experimental nanowire absorptance peaks in figure 3 red-shift with nanowire diameter with peaks...
appearing at approximately 2100, 2400, 2500 and 2700 nm for the period of 1000, 1500, 2000 and 3000 nm, respectively.

Optical simulations in COMSOL Multiphysics were performed to further investigate the characteristics of the experimental absorptance peaks and their dependence on nanowire diameter. Simulations used the same average geometric parameters as the experimental nanowire arrays while excluding the stacking faults and the composition segregation in the shell. They revealed absorptance peaks in the SWIR (dashed lines in figure 3), closely matched in magnitude and wavelength to the experimentally observed peaks. Furthermore, E- and H-field component profiles (see supporting information) for the 1000 nm period and 440 nm diameter array at $\lambda = 2050$ nm incident wavelength identified that the peak absorptance is due to the HE$_{11}$ guided mode resonance [6–8]. Previous reports [6–9] found that the dominant effect on HE$_{11}$ peak position is the nanowire diameter. Additionally, period and length were shown to have a negligible effect on peak position, although nanowire length increases the magnitude of the absorptance. Changes in nanowire composition are also not expected to affect the peak position [6–8]. For example, simulations have shown that the red-shift of the HE$_{11}$ absorptance peak wavelength with unit change in nanowire diameter (nm of red-shift per nm increase in diameter) is similar for different materials (GaAs, InP, InAs, InSb) and is not strongly dependent on composition or period [6–8]. Furthermore, compositional changes between nanowire arrays are small (<2%) and cannot account for changes in the absorptance peaks [10]. Instead, the red-shift in absorptance peaks is primarily due to an increasing nanowire diameter, associated with the HE$_{11}$ guided mode resonance.

The absorptance magnitude for both simulated and experimental peaks decline with increasing period due to a decreasing fill factor (or diameter/period ratio) of the nanowire array. The nanowire arrays have an optimal fill factor at which maximum absorptance is achieved [7]. For sparse nanowire arrays, when nanowire diameter is less than 1/3 of the period ($D/P < 1/3$), a large fraction of the incident light passes through the array to the substrate instead of being absorbed in the nanowires. Absorptance increases to a maximum between $1/3 < D/P < 1/2$ and then begins to decrease as the reflectance from the top of the nanowires approaches thin film conditions ($D/P > 1/2$) and the near field coupling between nanowires increases [31]. Fill factors for our 1000, 1500, 2000, and 3000 nm period arrays are $D/P = 0.44, 0.32, 0.25$ and 0.17, respectively. Optimal fill factor conditions are met with the 1000 nm array while the larger period arrays move into the sparse regime and a corresponding magnitude decrease for the absorptance peak is observed. Thus, increasing the nanowire diameter via increasing period is not viable indefinitely without a significant loss in absorptance. However, future growths may simultaneously employ other techniques, such as longer growth duration, to increase nanowire diameter and help maintain an optimal fill factor.

The distribution in the diameter of the fabricated nanowires, which was in the range of ±16 to 36 nm, leads to a range of spectrally unresolved HE$_{11}$ resonance peaks, closely spaced in wavelength, which broadens the FWHM of the HE$_{11}$ peak. The red-shift of the HE$_{11}$ absorptance peak wavelength (in nm) per unit change in nanowire diameter (in nm) can be extracted from simulations [6–8, 10, 32]. For example, in [7] the red-shift for the 1000 nm period array near a nanowire diameter of 440 nm ($P = 1000$ nm, $D = 440$ nm) is 4.13 nm nm$^{-1}$. The measured nanowire diameter for this nanowire array varied by ±20 nm. Hence, the contribution of the nanowire diameter variation to the broadening of the absorptance peak can be estimated as $2 \times 20$ nm $\times 4.14$ nm nm$^{-1} = 165$ nm.

Conclusions

In summary, patterned arrays of large diameter (440–520 nm) InAsSb nanowires were grown on Si, demonstrating the potential for future integration with Si ROICs. Four distinct absorptance peaks were produced in the SWIR region by fabricating arrays of different diameters in a single epitaxial growth controlled by the array period. In future work, we will be able to create absorptance peaks at longer wavelengths (e.g., in the MWIR region) by changing growth conditions, increasing growth time, and increasing hole diameters.

Acknowledgments

The authors gratefully acknowledge funding from the Natural Sciences and Engineering Research Council of Canada, Ontario Centres of Excellence, Lockheed Martin Canada, Teledyne DALSA Inc. as well as scientific collaborations with the Centre for Emerging Device Technologies, the Canadian Centre for Electron Microscopy, the Toronto Nanofabrication Centre, and the Electron Microscopy Facility in the Faculty of Health Sciences at McMaster University.
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