Photothermal Structural and Optical Changes in GaAs Nanowires

Jaspreet Walia[*], Navneet Dhindsa[*], Jeremy Flannery[**], Jamie Forrest[**], and Simarjeet Saini[*]

[*]Department of Electrical and Computer Engineering, University of Waterloo, Canada,
j2walia@uwaterloo.ca
[**]Department of Physics and Astronomy, University of Waterloo, Canada

ABSTRACT

Structural and optical changes in vertically arranged GaAs nanowires are examined using Raman spectroscopy. In this contribution, it is shown that the dissociation of arsenic from the GaAs lattice happens at temperatures which are reduced by about 220 K relative to bulk. The salient changes in the optical properties are easily seen in a microscopy and show for the first time that a laser can be used to tune the color of GaAs nanowires.

Keywords: Gallium Arsenide, Nanowires, Raman Spectroscopy, Color Generation

1 INTRODUCTION

The recent progress in fabrication technologies has allowed for a wide variety of nano structures to be realized. This disorder and associated structural changes will cause changes in electrical, mechanical, and optical properties of the material. Raman spectroscopy has been used quite successfully in the study of arsenic (As) cluster formation in bulk GaAs. It has been generally well accepted that after annealing, the Raman spectra associated with ZB GaAs is not altered, and the newly formed peaks can be associated with crystalline As. In most cases it has been observed that the peaks associated with c-As are shifted relative to their bulk counterparts. Both tensile stress, and phonon confinement models have been put forth as explanations for the observed shifts. Even though the formation of c-As in GaAs and InAs nanowires has been observed, a detailed analysis of the physical nature of c-As, and the associated changes in optical properties has not been applied to these systems. Understanding the photothermal properties of nanowires is important for the efficient design of devices which create useful electrical current using heat generated from absorbed light. In this study, the structural and optical changes in vertically etched zincblende (ZB) gallium arsenide (GaAs) nanowires, annealed via photo-thermal conversion [1], are examined. The nanowires were fabricated using electron beam lithography, and exposed to 100 mW of incident laser power, to induce the onset of arsenic (As) formation. Four different nanowire diameters of 65 nm, 155 nm, 200 nm, and 245 nm, arranged in square lattices spaced 400 nm apart, were studied. Annealing temperatures were found be dependent on nanowire diameters, ranging from 480 K to 700 K, resulting from the different degrees of optical confinement in each sample [1]. The presence of As was confirmed using Raman spectroscopy. It was found that all diameters exhibited photothermal formation of crystalline arsenic (c-As), even for annealing temperatures as low 480 K, suggesting the temperature required for the onset of c-As formation in GaAs nanowires is reduced relative to the bulk by about ~ 220 K. Lastly and most importantly, the salient changes in structural color generation properties resulting from the annealing process are easily seen using an optical microscope, whereas no changes of any kind are seen with scanning electron microscopy. In this connection, it is shown for the first time that color generation properties of GaAs nanowire arrays can be locally tuned using a laser, and that the onset of these changes are initiated at lower temperatures than expected.

2 FABRICATION AND RAMAN MEASUREMENTS

The The nanowire sample was fabrication exactly as outlined in chapter 5. Once again, confocal micro-Raman spectra were measured using a Jobin-Yvon HR800 spectrometer in the backscattering configuration, with a spectral resolution of ~0.5 cm^{-1}. A 532 nm excitation laser was used, and focused down to a 100 μm^2 spot using a 0.35 N.A. 20x objective. Four different nanowire diameters of 245, 200, 155, and 65 nm were studied. Raman spectra were recorded before, and after the annealing process using an incident laser power level of 1 mW. Local heating was performed using the same laser and setup, with an incident power of 100 mW, and Raman spectra were also taken at this time. Each spectrum was acquired using an exposure time of 45 seconds and summed over 15 accumulations. The incident light field was polarized along one of the photonic lattice directions. The temperature that each sample experienced was calculated by using the following linear relationship relating the spectral shift of the GaAs phonon frequencies and local temperature [1],

$$d\upsilon/dT = 0.016 \text{ cm}^{-1} \text{ K}^{-1} \quad (1)$$

3 RESULTS AND DISCUSSION

Equations Raman spectra for the nanowire samples before and after thermal treatment are shown in Figure 1. Prior to annealing the spectra are dominated by transverse optical (TO) phonon scattering from GaAs at 267 cm^{-1}. The presence of weak longitudinal optical (LO) scattering is also

seen, especially for the 65 nm diameter sample. After photo-thermal annealing, new peaks centered at ~ 200 cm-1 and ~ 260 cm-1 appear in the spectrum and can be attributed to scattering from the TO and LO phonon modes of crystalline Arsenic (c-As)[2]. The frequencies of the TO and LO phonon modes related to GaAs remain unchanged after the annealing process for all diameters, suggesting that the annealing process is limited to the surface of the nanowires. The mechanism behind the formation of Arsenic is thought to arise from interfacial solid-solid reaction [3] $As_2O_3(s) + 2GaAs(s) \rightarrow Ga_2O_3(s) + 4As(s)$. This is a thermally activated process, and it has been found that elemental arsenic is generally formed at temperatures above 700 K, and amorphous arsenic (a-As) for lower temperatures down to about 450 K. The nanowire samples in this study were found to have temperatures which varied from 480 K to 700 K, and therefore one would expect very little Raman signatures associated with c-As. Temperatures were determined using the spectral shift of the TO phonon frequency of GaAs[1]. In contrast, all of the samples show c-As formation. Remarkably, c-As formation can be observed the 65 nm diameter sample, which was only exposed to a temperature of 480 K. Also, the crystalline peaks of GaAs and As in the Raman spectra of this sample ride on top a broad background that can readily be assigned to a-As. No clear evidence of a-As in the other samples exists. These results suggest that the input energy required in order to begin the onset of a-As and subsequently c-As is much lower for GaAs nanowires versus its bulk counterpart.

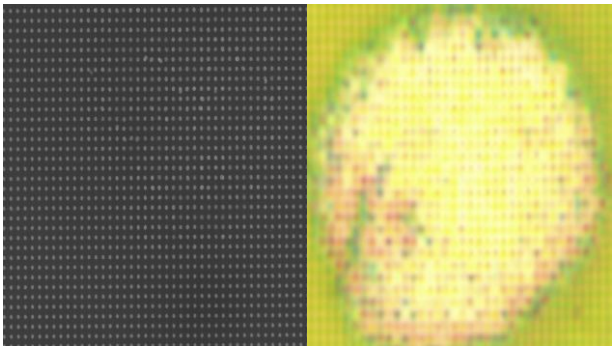

Figure 2. (Left) Representative Top-down SEM image showing a section of the annealed nanowire array containing 155 nm diameter GaAs nanowires. (Right) Microscope image taken at 100× magnification, showing the clear changes in structural color generation.

Scanning electron microscope (SEM) images after the annealing process are shown in Figure 2, and no clear evidence of any structural change, and confirming that the square lattice of nanowires remains intact. A bright field image of the 155 nm diameter sample imaged at 100 × magnification after annealing is shown as well. Clear color changes are perceptible within the area where the laser was incident on sample, with individual wires showing different colors. To our knowledge this is the first time where laser induced optical changes in nanowires are so clearly evidenced in a simple microscope image.

To conclude, Raman spectroscopy has shown that the temperatures required to initiate the onset of c-As formation from GaAs nanowires is reduced relative to the bulk by about 220 K. The associated changes in the optical properties of the nanowire arrays shows, for the first time, that structural colors generated by GaAs nanowire arrays can tuned using a laser.

4 CONCLUSIONS

To conclude, Raman spectroscopy has shown that the temperatures required to initiate the onset of c-As formation from GaAs nanowires is reduced relative to the bulk by about 220 K. The associated changes in the optical properties of the nanowire arrays shows, for the first time, that structural colors generated by GaAs nanowire arrays can tuned using a laser.

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