Controlling the Composition and Morphology of $Si_{1-x}Ge_x$ Nanowires

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Abstract:

Silicon (Si) and germanium (Ge) semiconductor nanowires can be utilized in next generation electronic, photonic, and energy conversion devices. Si, Ge, and $Si_{1-x}Ge_x$ materials are also well studied and currently used in industry. Optoelectronic properties, such as the band gap, can be tuned by modulating the alloy composition, thus allowing for a wider range of uses. The focus of this project was to create arrays of $Si_{1-x}Ge_x$alloy nanowires with varying, but simultaneously uniform, compositions. This goal has been difficult to achieve to date. Nanowires were grown with the gold catalyzed, bottom-up, vapor-liquid-solid mechanism throughout the compositional range. Using scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDX), and Raman spectroscopy, we demonstrated control of $Si_{1-x}Ge_x$ alloy composition, but struggled to achieve highly aligned arrays. Nanowires frequently kinked to the <112> directions and underwent conformal deposition, which resulted in tapered structures. Therefore, we employed a side-wall species, methylgermane, in an attempt to overcome this.

Introduction:

Semiconductor nanowires have many promising applications in next generation electronic, photonic, and energy conversion devices. Silicon (Si) and germanium (Ge) are superb choices for these semiconductor devices because there is already an extensive knowledge base of Si and Ge materials. By growing different concentrations of $Si_{1-x}Ge_x$ nanowires, it was possible to tune optoelectronic properties such as the band gap [1]. While alloy nanowire growth has been achieved, growing highly uniform arrays of $Si_{1-x}Ge_x$ nanowires with varying, but simultaneously uniform compositions has been difficult to date [2, 3].

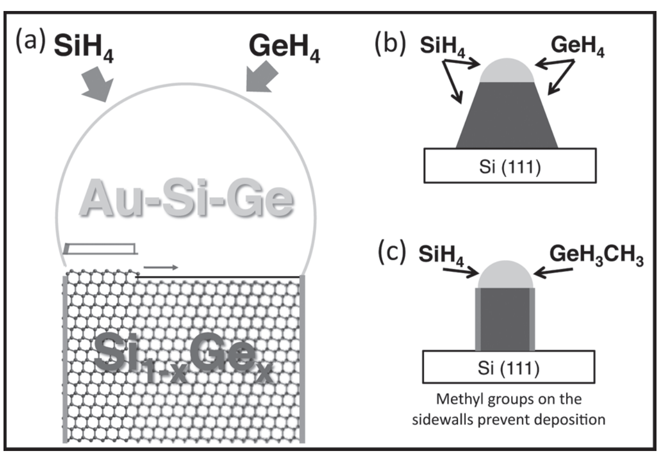

Figure 1: (a) Schematic of the VLS growth method and schematic of wire growth (b) with and (c) without GeH_3CH_3.

Experimental Procedure:

$Si_{1-x}Ge_x$ nanowires were grown using the gold catalyzed, bottom-up, vapor-liquid-solid growth method as seen in Figure 1. Fifty nanometer (nm) gold nanoparticles were deposited on a Si <111> wafer. The sample was heated in a cold-wall vapor deposition furnace to 375°C and GeH_4 partial pressure was raised to 0.44 Torr to grow short Ge stubs. Finally, GeH_4 partial pressure was dropped to 0.025 Torr and SiH_4 partial pressure was raised to 0.050-1.000 Torr. By varying the partial pressure of SiH_4, the concentration of the wires could be varied.

To determine the growth conditions, we used the Arrhenius equation, which allowed us to calculate the theoretical Ge concentration of the nanowires from the ratio of GeH_4 partial pressure to SiH_4 [4]. The nanowires were characterized using an SEM, leading to discovery of issues in the nanowire arrays such as kinking or tapering of wires.

Uncontrollably kinking and compositional gradients caused by tapering limits the usability of nanowire arrays in device applications. In order to increase the uniformity of the arrays, GeH_3CH_3 was used in place of GeH_4 during the growth step in order to introduce a methyl group as a sidewall species. As a result, the temperature of the growth step had to be raised to 475°C to prevent kinking caused by GeH_3CH_3 [5]. The concentrations of the wires were measured using EDX. Because the Si substrate would affect the EDX measurement, the nanowires were transferred to carbon tape.

Results and Conclusions:

Raman spectroscopy was used to confirm the nanowires were alloys and not another type of superstructure. As seen in Figure 2, the Raman spectrum of the nanowires showed a

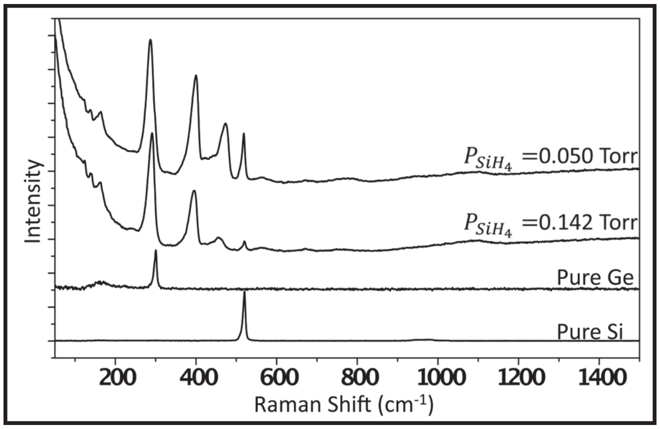

Figure 2: Raman spectrum of $Si_{1-x}Ge_x$ nanowires and pure Ge and Si wafers. Intensity scale is adjusted.

distinct shift in the Si-Si peak and the Ge-Ge peak as well as a strong intensity Si-Ge peak, which confirmed the existence of $Si_{1-x}Ge_x$ alloys [6]. EDX was used to determine the concentration of the nanowires. As the fraction of GeH_3CH_3 increased, the Ge concentration in the nanowires also increased, as seen in Figure3. By comparing SEM images of nanowires grown with and without GeH_3CH_3 (Figure 4), it can be seen that GeH_3CH_3 eliminated tapering at high Ge concentrations; however, kinking remains an issue at lower Ge, higher Si concentrations.

Future Work:

By tuning process conditions, it will be possible to grow nanowires over a wider range of Ge concentrations. Further research into surface chemistry will result in better control of nanowire sidewalls and increase the uniformity of nanowire arrays. Finally, once uniform arrays of $Si_{1-x}Ge_x$ nanowires are perfected, they can be used in many next generation electronic, photonic, and energy conversion devices.

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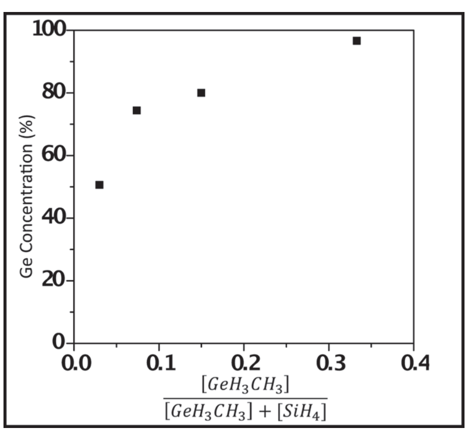

Figure 3: Percent Ge concentration as determined by EDX vs. the fraction of the GeH_3CH_3 partial pressure.

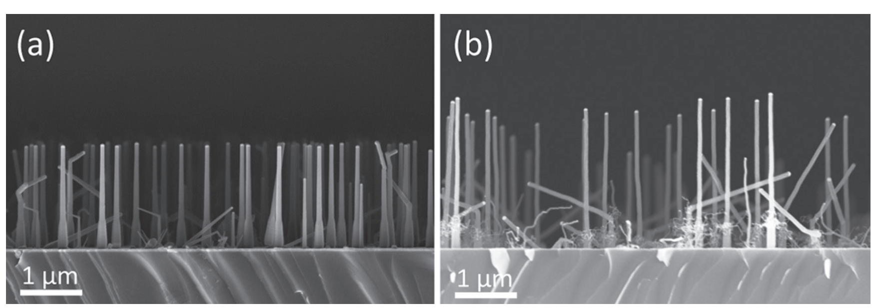

Figure 4: SEM images of $Si_{1-x}Ge_x$ nanowires.
(a) Wires grown with GeH_4 (375°C, P_{SiH_4} = 0.214 Torr, P_{GeH_4} = 0.105 Torr).
(b) Wires grown with GeH_3CH_3 (475°C, P_{SiH_4} = 0.025 Torr, $P_{GeH_3CH_3}$ = 0.050 Torr).