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 sidewall species, methylgermane, in an attempt to overcome this.

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$_4$CH$_3$ 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$_4$CH$_3$ [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 1: (a) Schematic of the VLS growth method and schematic of wire growth (b) with and (c) without GeH$_4$CH$_3$.
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$_3$CH$_3$ increased, the Ge concentration in the nanowires also increased, as seen in Figure 3. By comparing SEM images of nanowires grown with and without GeH$_3$CH$_3$ (Figure 4), it can be seen that GeH$_3$CH$_3$ 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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**References:**