

## Growth of Graphitic Carbon Layers on SiO<sub>2</sub> Surfaces of Silicon Nanowires

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### Abstract

A synthesis method is described for producing graphene sheets in three-dimensional architectures using silicon nanowires as a scaffolding substrate covered in a thin-film of SiO<sub>2</sub>. Experiments have shown that loose multi-layers of graphene or amorphous carbon have been produced in nanowire shapes over the entire nanowire substrate areas.

### 1. Introduction

Application of graphene related materials has generally had difficulty fitting to the constraints of its growth methods. Graphene layers for device applications are often produced on flat catalytic substrates, but device applications often involve complex architectures in limited areas on other substrate materials. So, graphene is typically exfoliated from a catalyst and transferred to the device. This procedure is time consuming, damages the graphene, and is limited to flat graphene configurations.

One solution to this issue is to form graphene with complex configurations on-site. Production of graphene on SiO<sub>2</sub> substrates has already been explored on two-dimensional surfaces[1][2][3]. Our group's research explores the possibility of using engineered substrate architectures to shape and preserve the graphene in potentially useful non-flat configurations. Nanowire configurations were selected as our group specializes in silicon nanowires.

### 2. Experimental

The process for achieving this solution was to use nickel or copper as the catalyst at an interface with a passivation layer such as SiO<sub>2</sub> on the surface of silicon nanowires. Carbon structures are formed from carbon precursors broken down on the catalyst surfaces during annealing and subsequent cooling. The metal catalyst can afterwards be removed by etching. This will leave the carbon film that remains on the passivation layer surface with the shape of the silicon architecture.

The substrates were nano-imprinted silicon nanowires oxygen-annealed to form at least 30nm thick SiO<sub>2</sub> thin films. The SiO<sub>2</sub> films are necessary to prevent destructive interactions between the silicon and nickel and may be replaced with other passivating layers. Here, the insulating SiO<sub>2</sub> surface aids with characterization of the resulting carbon structures. Nickel layers typically 200nm thick are deposited on the entire nanowires surfaces (Fig.1a)

Various growth conditions have been applied to the nanowires to find the conditions to produce graphene layers on the nanostructure surface. Research has focused on heating a methane or amorphous carbon precursor to ~900°C on the nickel catalyst surface before fast-cooling and using Marble's reagent to etch the nickel away while maintaining the carbon material (Fig.1b). Raman micro-spectroscopy supported by SEM and TEM observations have been used for the initial characterization of the resulting structures.

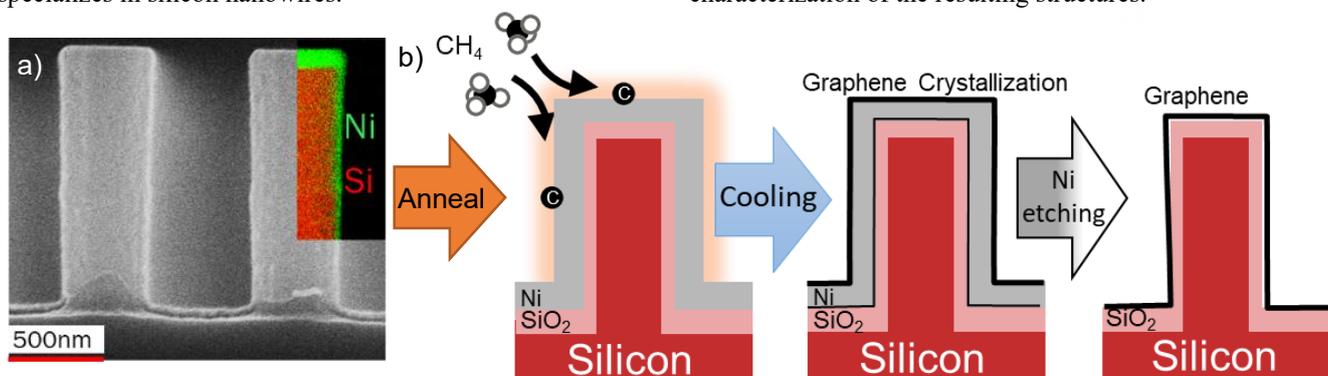


Fig. 1 Nanowire shaped graphene growth method. a) SEM image of nickel deposited on silicon nanowires with inset TEM-EDS image showing nickel and silicon layers. b) example process in which methane is decomposed on nickel during annealing to form graphene sheets that remain on the SiO<sub>2</sub> surface of Si nanowires after Ni etching.

### 3. Results

Graphitic carbon layers have been produced on the SiO<sub>2</sub> nanowires surfaces with complex shapes and coverage depending on the growth conditions. The carbon layers are able to conform to the surface to produce non-flat sheet configurations.

Nickel migration increases at high annealing temperatures and grain boundaries nucleate to form islands. The nanowire architecture facilitates orderly migration to the tops of the nanowires over a short but predictable time-frame. This behavior necessitates quick anneal times of around one minute, but can also be utilized to alter growth patterns. The nickel is cleanly removed during etching.

After quick annealing with methane and nickel etching, conductive carbon layers can be seen in SEM covering the entire nanowire surfaces and mimicking the nanowire shape (Fig.2). The layers are loose but do not wash away during etching due to the unique nanowire structure. Furthermore, these layers can cover the entire nanowire sample area which currently spans a few square millimeters.

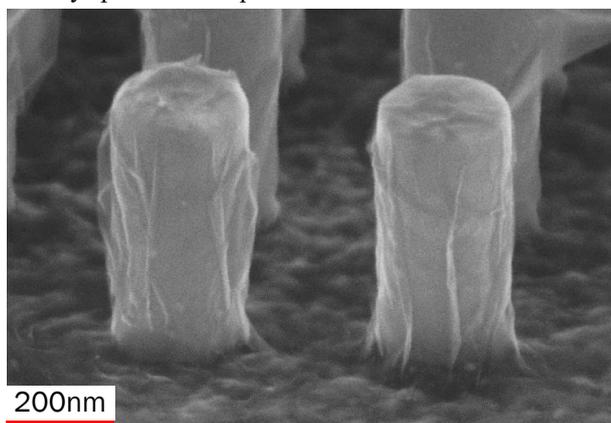


Fig. 2 SEM image of nanowire exhibiting a loose carbon sheet covering the entire wire and extending to the adjacent wires.

Raman micro-spectrography shows that the observed layers have a graphene structure as evident by strong carbon G and 2D peaks (Fig.3). The peak ratio suggests a multilayering of a few layers.

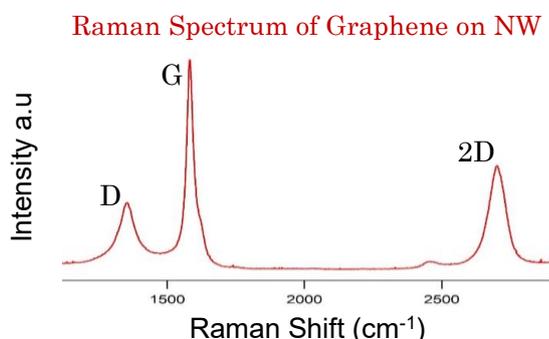


Fig. 3 Raman micro-spectrography results obtained from the sample in fig.2. The carbon G peak at ~1580cm<sup>-1</sup> and 2D peak at ~2700cm<sup>-1</sup> relate to the graphene structure. The carbon D peak at ~1350cm<sup>-1</sup> is related to defects in the graphene layer.

Nickel migration over longer anneal times favors exposing the curved nanowire walls and carbon layers form on the isolated nickel nanoparticles. Etching the nickel can produce small discontinuous caps on the tops of the nanowires showing graphene peaks in raman spectrography.

In alternative experiments involving amorphous carbon deposited at the interface in-between the SiO<sub>2</sub> nanowires and nickel layer, carbon layers remain that tightly cover the nanowires after nickel is etched. The carbon layers do not show as strong of a graphene structure like the methane trials.

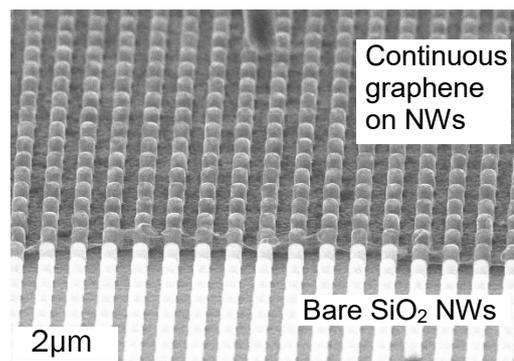


Fig. 4 SEM image of nanowire array covered in a large continuous carbon sheet. The sheet has been peeled off in the lower section of the image to show the contrast with the insulating SiO<sub>2</sub> wires.

### 4. Conclusions

The experiment has shown that the growth procedures are capable of being applied to complex surfaces such as nanowires. Carbon layers with graphene properties have been produced with nanowire shapes not previously seen. In addition, they have been produced on-site, over relatively large areas in limited regions.

The new configuration of graphene with regular bending structures is expected to have altered properties to be characterized in the future. The nanowire architecture may be favorable for future device configurations due to increased surface area and in combination with the optical properties of the silicon nanowires.

### Acknowledgements

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### References

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