Low Temperature Surface-Mediated Growth of Graphene On Ultra-Thin Metal Catalysts

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Graphene, a single layer of sp^2-bonded carbon atoms arranged in a hexagonal lattice, has a myriad of potential applications in the semiconductor industry. It has excellent electron mobility, allowing for the creation of graphene-based field-effect transistors (FETs), and is also capable of acting as a highly effective diffusion barrier [1, 2]. In order to enable use of these properties in modern microelectronic fabrication processes, a low-temperature graphene synthesis process that is capable of directly forming graphene onto targeted materials is needed. Current chemical vapor deposition (CVD) processes use thick (200–2,000 nm) catalysts and require growth temperatures exceeding 700 °C to produce graphene. Here, a method for CVD-fabricating graphene films at a temperature of 450 °C is presented using a 1 nm Ni/Au catalyst, presenting an avenue toward low-temperature direct growth.

To achieve this growth, 1 nm of a Ni/Au alloy was deposited onto a Si/SiO_2 wafer via electron beam evaporation. The wafer was then heated to 450 °C in a CVD system under H_2. Upon reaching 450 °C, H_2 flow was halted and 0.1 sccm of the carbon precursor (C_2H_2) was introduced for varying durations. SEM inspection of the wafer post-growth showed that the metal catalyst conglomerated into circular islands (Fig. 1). Raman spectroscopy of the post-growth wafers showed a consistent 2D peak full-width half-maximum ($FWHM_{2D}$) with extended growth durations, wherein a thinner $FWHM_{2D}$ indicates fewer graphene layers [3]. Comparatively, SEM micrographs and Raman spectra of growths conducted on a 50 nm substrate for 0.5–3 minutes are shown in Fig. 2. The $FWHM_{2D}$ of these spectra become significantly broader with longer growth times, indicating increasing layer number. The SEM micrographs of the 50 nm catalysts show grains (Fig. 2) in lieu of the catalyst islands observed on the 1 nm samples (Fig. 1).

Raman spectra representative of growths conducted on a 1 nm catalyst and a more typical, thicker catalyst are compared in Fig. 3 (a). The spectrum of the 1 nm sample displays drastic peak shifting, which occurs when the crystal structure of the graphene experiences axial stress [4]. The Raman spectrum of the 1 nm catalyst also displays a splitting of the G peak, a feature found on graphene with broken planar symmetry [5]. The observation of both of these Raman features indicates that the graphene on the 1 nm catalyst is stressed and lacks planar symmetry. A proposed growth mechanism is elucidated in Fig 3 (b). Upon introduction of the carbon precursor, the ultra-thin catalyst immediately grows layers of graphene without precipitation of further layers over time due to the absence of a bulk volume. The catalyst under the graphene then aggregates into islands, inducing stress on the graphene sheets and breaking their planar symmetry as the sheets sag in the gaps between the catalyst islands.

The consistency of the Raman spectra with extended growth time on the 1 nm catalyst indicates that the growth mechanism is surface-mediated, as there is not an appreciable bulk volume of catalyst for large amounts of carbon to dissolve into and subsequently precipitate out of. In comparison, the 50 nm catalyst presents a bulk volume capable of dissolving more carbon. This increased amount of dissolved carbon leads to additional layers of graphene precipitating out of the catalyst. These results indicate that 450 °C growths on ultra-thin catalysts present an avenue toward direct growth of reduced layer-number graphene due to the absence of an appreciable carbon reservoir [6].

References:

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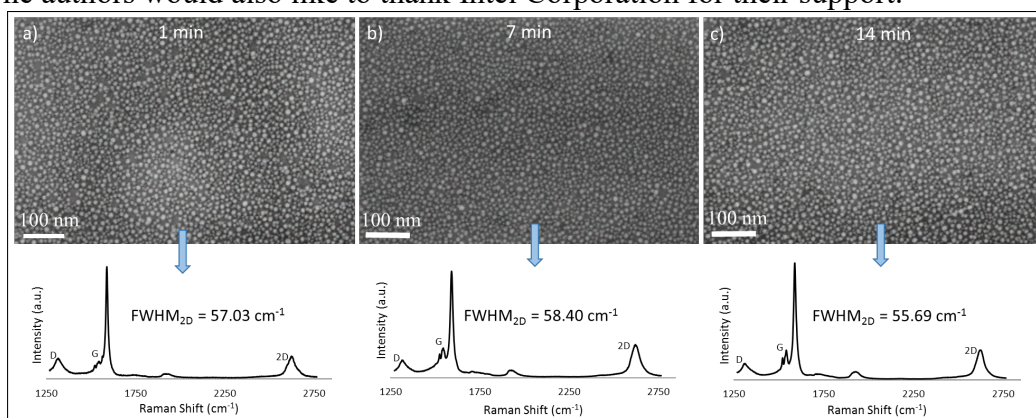

Figure 1: Comparison of SEM/Raman of growths conducted for (a) 1 minute, (b) 7 minutes, and (c) 14 minutes on 1 nm catalyst. Note the consistency of both the micrographs and the Raman spectra.
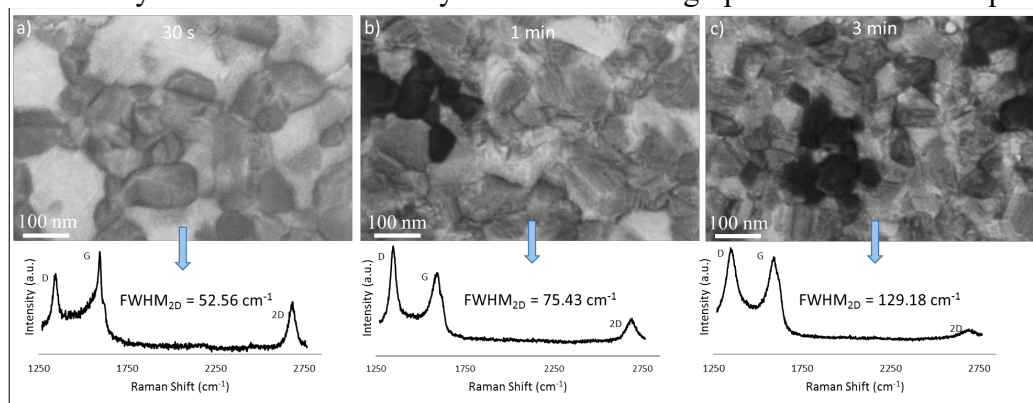

Figure 2: Comparison of SEM/Raman of growths conducted for (a) 30 seconds, (b) 1 minute, and (c) 3 minutes on 50 nm catalyst. Note the widening of the 2D peak in the Raman spectra and the absence of catalyst islands in the SEM. Darker areas in the SEM micrographs are areas with more graphene layers
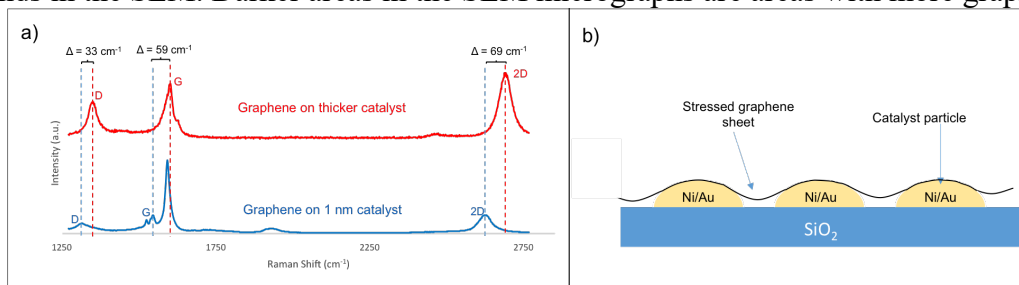

Figure 3: (a) Raman of graphene on 1 nm catalyst (blue) compared to Raman of graphene grown on a thicker catalyst (red). Note the peak shifting and G peak splitting that occurs on the 1 nm catalyst. (b) Proposed mechanism of graphene growth on ultra-thin catalyst.