

Metal-catalyzed crystallization of amorphous carbon (a-C) to graphene

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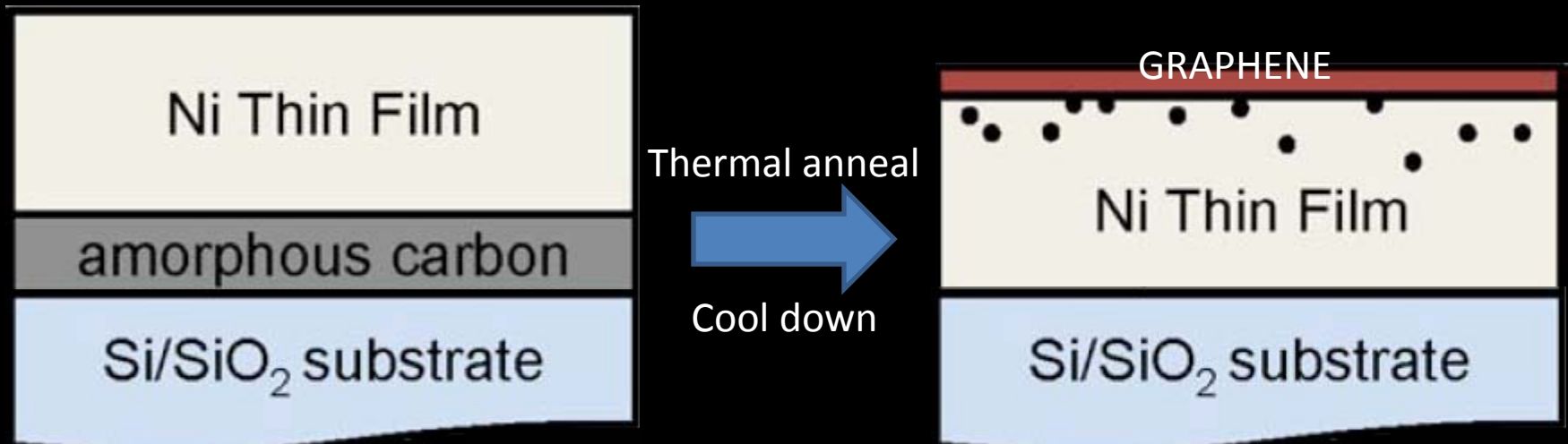
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Introduction

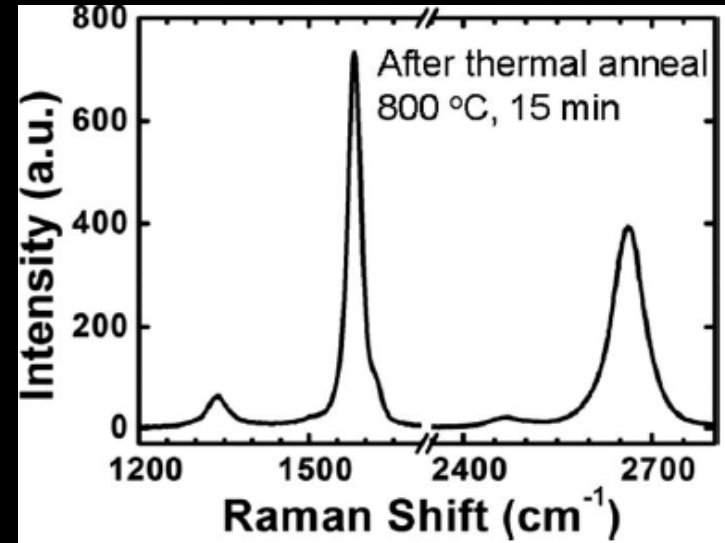
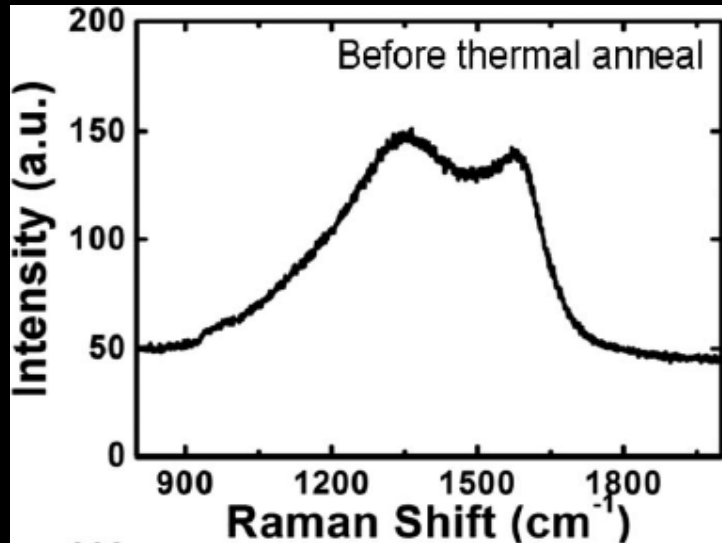
- Graphene: with exotic properties offers plethora of applications
- Major challenge is the controlled synthesis of large-area graphene sheets
- CVD has been an useful tool for graphene synthesis
- Due to its sensitivity to various parameters, precise control over the no. of graphene layers is difficult
- Simple and efficient method to synthesize graphene layers via metal-catalyzed crystallization of a-C by thermal annealing
- Highly controllable graphene synthesis, as the no. of graphene layers is primarily dependent on the initial thickness of the a-C layer

Process

- Deposition of a layer of a-C (2.5-40 nm thick) on Si/SiO₂ substrates, by electron-beam evaporation
- Deposition of nickel or cobalt metal thin film (100–300 nm)
- Thermal annealing (650–950°C), in a tube furnace under an argon flow and pressure of ~1.7 Torr
- Cooling at a rate of ~20°C/s results in a graphitic layer on the metal surface



Characterization with Raman



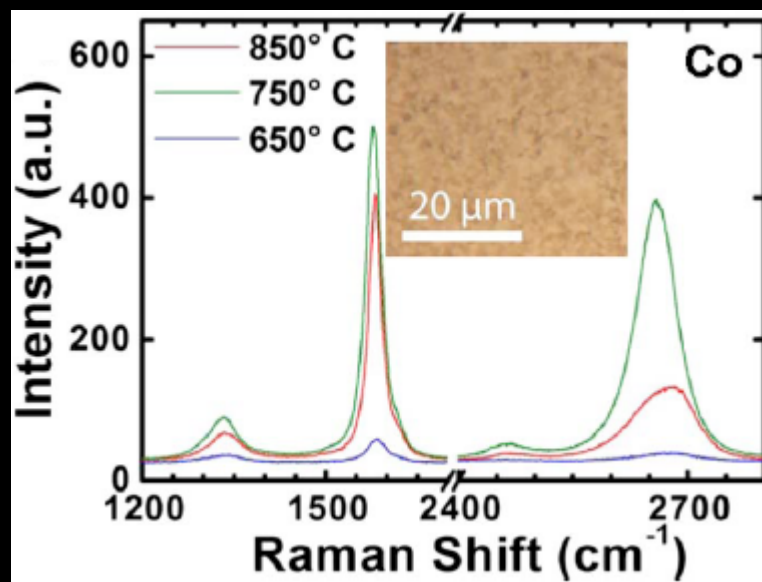
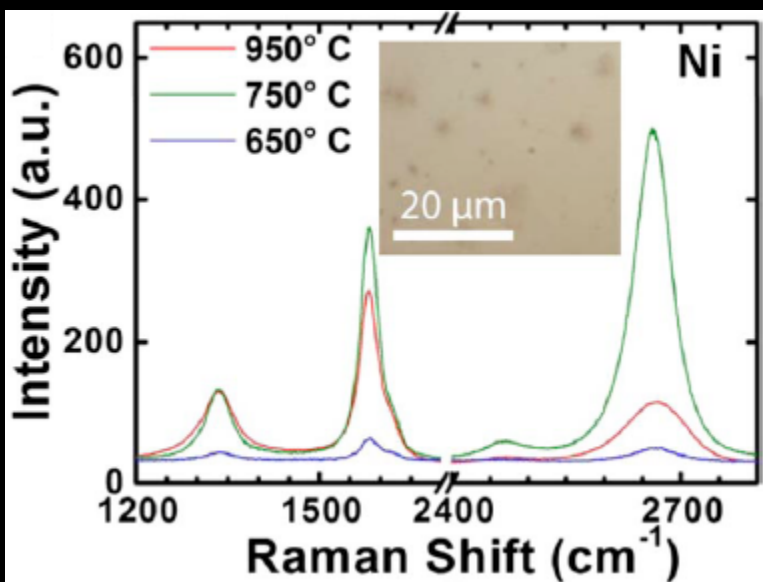
- Broad Raman peak over the 1000–1700 cm^{-1} range, indicative of a-C film
- After the Ni-catalyzed crystallization, Raman spectrum exhibits graphene characteristic fingerprints of D ($\sim 1395 \text{ cm}^{-1}$), G ($\sim 1580 \text{ cm}^{-1}$), 2D ($\sim 2690 \text{ cm}^{-1}$)
- Ratio of D to G peaks (I_D/I_G) ~ 0.09 with 2D FWHM of $\sim 51 \text{ cm}^{-1}$
- Indicates a multilayer graphene sheet with relatively low defect density, similar to the previously reported graphene sheets grown by CVD on Ni substrates

Process mechanism

- Similar to that of the metal-induced crystallization of inorganic semiconductors
- Carbon atoms diffuse into the metal layer at elevated temperatures, followed by precipitation as graphene on the free surface during the cooling, as the solid solubility limit is reached
- Given the annealing condition and cooling rate, no. of graphene layers is readily controlled by varying the thickness of the initially deposited a-C layer
- Important difference between this “limited source” process and the CVD processes: In CVD, carbon source is virtually unlimited and controlling the number of graphene layers depends on the tight control over a number of deposition parameters
- Ni and Co proved to be suitable catalysts, whereas no graphene was formed when Cu thin film was used as the catalytic layer, may be due to the low diffusivity and solid solubility limit of carbon in Cu

Effect of annealing temperature

- Important parameter that affects the metal-catalyzed crystallization process and the quality of the enabled graphene layer
- Graphene formation process is observed for annealing temperature in the range of 650–950°C for Ni and 650–850°C for Co
- Optimal temperatures for Ni and Co are ~800 and 750°C, respectively



Effect of annealing time

- Graphene is observed to form even when the samples (a-C thickness ~ 40 nm) were cooled immediately after reaching the annealing temperature
- Up to ~ 60 min, graphene formation and quality is relatively independent of the annealing time
- For longer annealing times, the areas with graphene are notably reduced
- For annealing time > 5 hrs, no carbon or graphene are detected by Raman spectroscopy
- Significant desorption of C atoms from the surface of the metal layer under the low pressure ambient

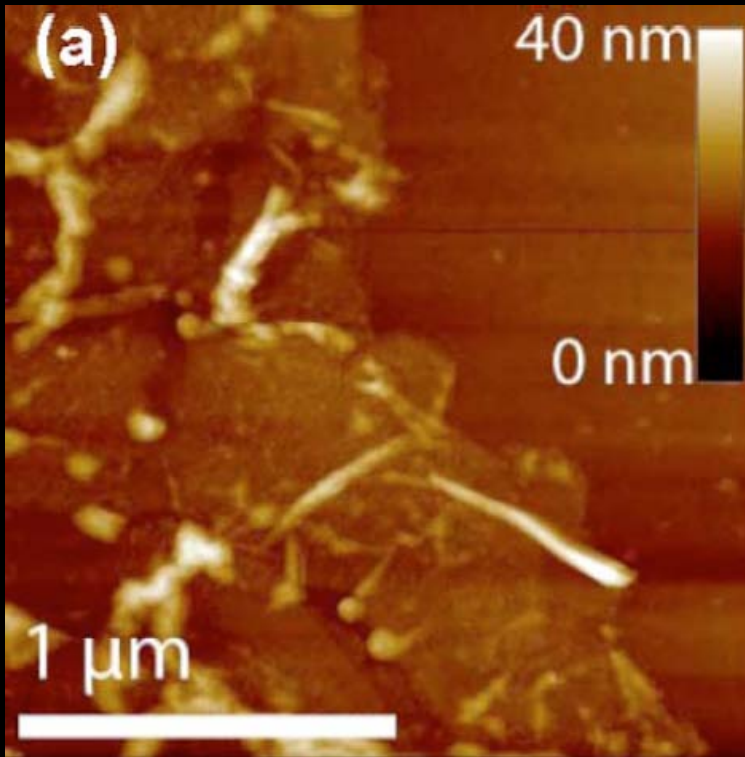
Transfer of graphene film

- Graphene layer formed on the metal film can be easily transferred to other substrates
- Sacrificial poly(methyl methacrylate) (PMMA) layer has been used to transfer the metal-crystallized graphene layer to Si/SiO₂ substrates
- After spin-coating a layer of PMMA onto the sample, the metal was etched away in 15% HCl solution and the detached film was placed in a water bath
- Then, the film was transferred to a Si/SiO₂ substrate, allowed to dry, and placed in an acetone bath to dissolve the PMMA support layer
- After a rinse with isopropyl alcohol, the samples were characterized
- Alternatively, the graphene could be transferred without the use of PMMA: by placing the samples directly in HCl, the graphene layer detaches and floats, enabling easy retrieval and transfer

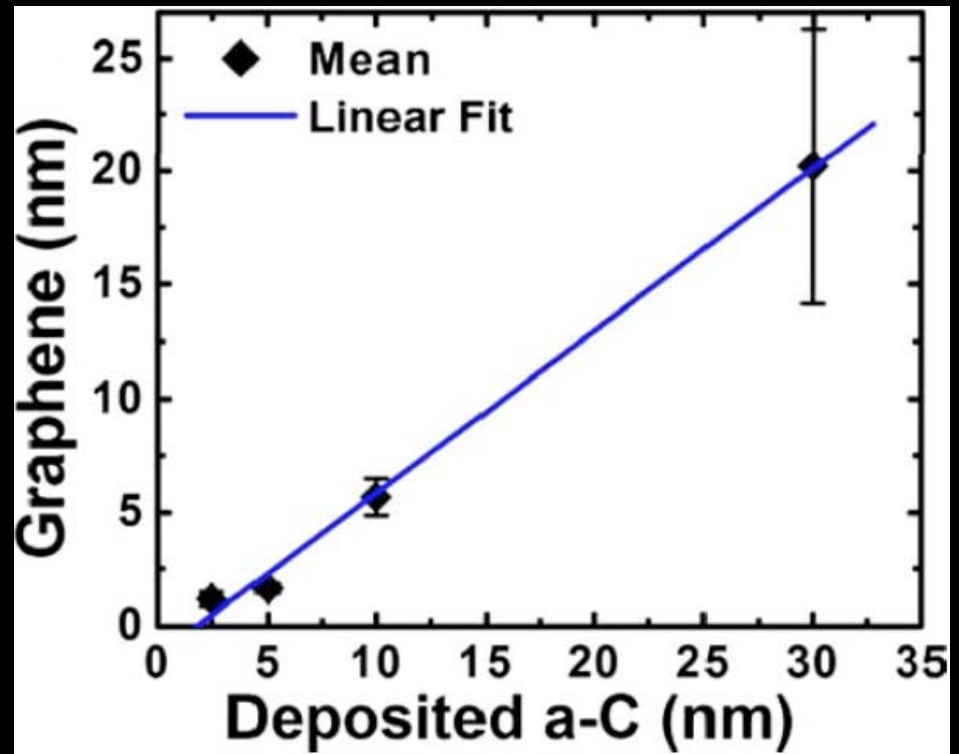
After transfer...

- Existence of graphene on transferred Si/SiO₂ substrates is confirmed by Raman spectroscopy
- No noticeable change in the spectrum after the transfer
- AFM is used to investigate, systematically, the thickness of precipitated graphene as a function of as-deposited a-C thin film by scanning the edges of transferred graphene sheets

AFM studies



AFM image of the transferred graphene layer, showing characteristic wrinkles and ripples



Thickness of the crystallized graphene layer as a function of the deposited a-C film

AFM studies

- Thickness of graphene shows a linear correlation with the thickness of the deposited carbon, with a slope of ~ 0.5 for an annealing temperature and time of 800°C and 15 min
- Assuming equal densities of the as deposited a-C and graphene, these results suggests that roughly half of the carbon source is crystallized into graphene with the rest either outgassing from the system or remaining in the Ni film
- Based on AFM and optical analyses, for samples with initial a-C thickness of 2.5–5 nm, $\sim 70\%$ of the surface is covered with monolayer, $\sim 15\%$ is bilayer, and the rest consists of thick dendritic islands, which can be ten times as thick as the surrounding graphene

AFM studies

- Exact mechanism for formation of these islands is unknown but these are possibly the grain boundaries or crystal faces with energetically favorable sites for multiple layers to form
- The ability to tune the no. of layers by the deposited a-C layer (i.e., limited source) presents a unique route toward controlled assembly and synthesis of graphene on large substrates, and presents an important advantage as compared to a CVD process where the carbon source is unlimited

Conclusion

- Metal-catalyzed crystallization of a-C to graphene by thermal annealing is demonstrated
- Thickness of the precipitated graphene is directly controlled by the thickness of the initial a-C layer
- In addition, based on the Raman analysis, the quality is comparable to other synthesis methods found in the literature, such as CVD
- By designing the metal-substrate interface properties, it may be possible to achieve the formation of graphene directly on the dielectric interface, which would further ease the fabrication complexity for device processing
- Process temperature can also be lowered by exploring various metal catalytic films, further enhancing the compatibility of this process with a wide range of substrates