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# Chemical vapour deposition growth of graphene layers on metal substrates

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**Abstract.** Graphene layers were grown by chemical vapour deposition (CVD) on Si wafers covered by a SiO<sub>2</sub> substrate layer and a Ni interlayer, and on copper and nickel foil. The obtained graphene layers were characterized by Raman spectroscopy. The films grown on SiO<sub>2</sub>/Ni substrate and Ni foil comprise mainly multilayer defect-rich graphene, while those on Cu foil exhibit the spectroscopic fingerprint of relatively defect-free single-layer graphene due to the low carbon solubility in copper and the suitably chosen substrate position in a quasi-closed volume. Optimal growth conditions and the nature of defects in the layers are discussed.

## 1. Introduction

Graphene is two-dimensional zero band-gap material with charge carriers behaving as Dirac fermions (zero effective mass) [1] with extraordinary mobilities and ballistic transport distances. These properties make it potentially useful for high-frequency electronic devices [2] while its exceptionally low absorbance bears potential for an ideal transparent conductor [3].

Application in integrated devices requires technology for wafer scale deposition with controllable number of graphene layers. On the other hand, implementation as transparent conductor requires reproducible deposition of single- or few-layer graphene. Especially, synthesis of bilayer graphene becomes increasingly desirable as it was reported to develop a tunable band gap upon mechanical stress and electrical gating [4].

Although pristine graphene available through mechanical exfoliation has very low concentration of structural defects, this method is not suitable for industrial application as the thickness, size and location of the obtained graphene are not reproducible. The most perspective, inexpensive and readily accessible approach for deposition of reasonably high-quality graphene turns out to be chemical vapor deposition (CVD) onto transition metal substrates such as Ni or Cu [5].

One fundamental limitation of utilizing Ni as deposition substrate is that single- and few-layered graphene is obtained only over few-micron regions and the film is not homogeneous over the entire

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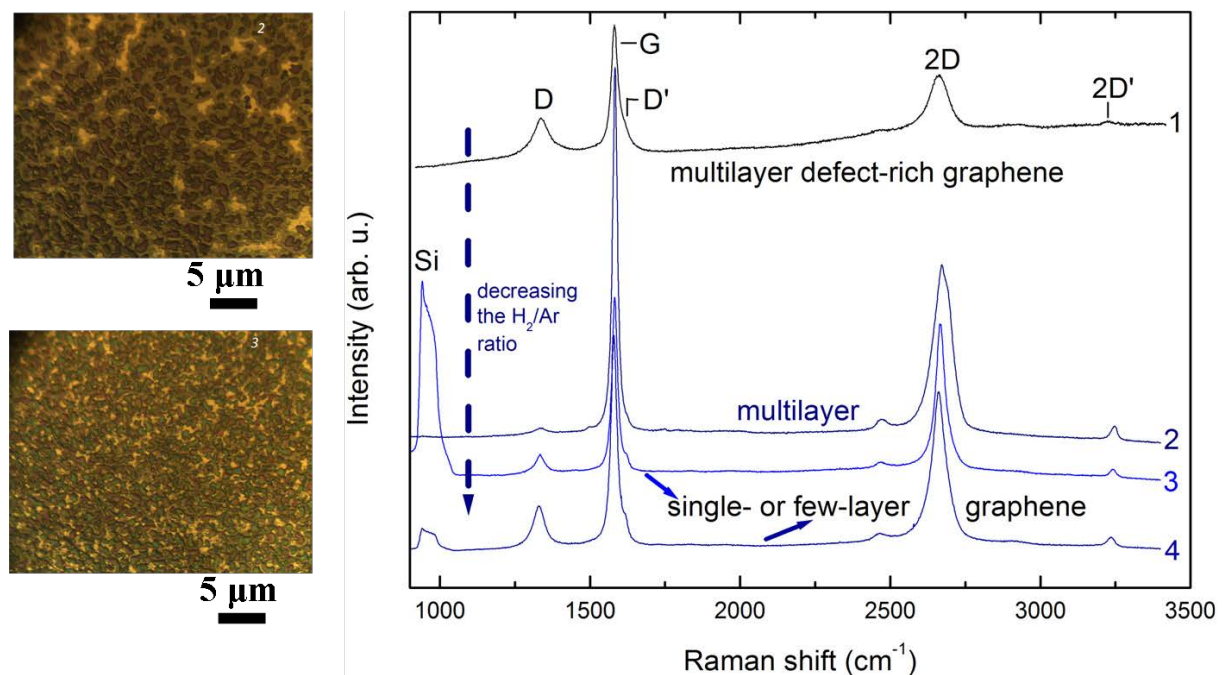


substrate. The impossibility to control the number of layers is partially due to the fact that the segregation of carbon from the metal carbide upon cooling occurs rapidly within the Ni grains and heterogeneously at the grain boundaries [6]. In addition, the degree of crystallinity and the surface quality of the metal substrate should also play a role. Initially, due to the substantial solubility of carbon in nickel at high temperature a solid solution forms. Subsequent lowering the temperature decreases the solubility, driving the carbon atoms to precipitate at the Ni surface and to arrange in hexagonal lattice for which the (111) orientation of the Ni layer serves as a template. In contrast, the peculiar combination of very low affinity between carbon and copper combined with the ability to form transient soft bonds facilitates formation of nucleation sites on the copper foil surface that form preferentially single-layer graphene through lateral growth. However, for a preferential growth of bilayer graphene, one may have to consider taking advantage of the precipitation process and Ni remains thus interesting for the graphene growth research.

In this paper we examine the CVD growth of graphene on different nickel-containing substrates with the purpose to establish favorable conditions for reproducible growth of single-layer and few-layer graphene. The obtained results are then compared to CVD graphene on copper foil.

## 2. Experimental

The CVD process was carried out in quartz tubes via thermal decomposition of high-purity methane in argon and hydrogen flow[4]. Initially, the Si wafers were cleaned in diluted HF (1:10) and subsequently their surface was oxygenated to obtain Si/SiO<sub>2</sub> structure. To improve the adhesion of the carbon atoms, the SiO<sub>2</sub> layer was coated with an interlayer of Ni. Besides the Si substrates, small pieces (ca. 1x1 inch<sup>2</sup>) of Ni and Cu foil 25 μm thickness were also used. X-ray diffraction measurements established that while the Ni interlayer sputtered on SiO<sub>2</sub> was mainly amorphous, the foils were polycrystalline with significant amount of (200)- and (111)-oriented grains. For the graphene growth on Si/SiO<sub>2</sub>/Ni and Ni foil substrates atmospheric pressure CVD was applied. The reaction times were between 3 and 10 min.



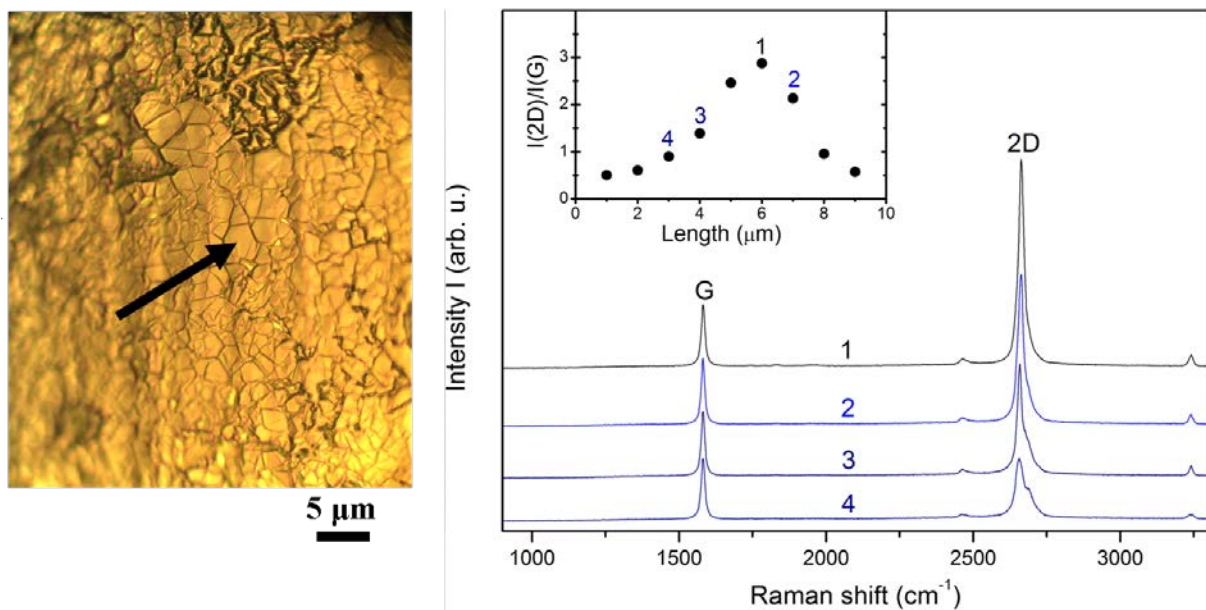
**Figure 1.** Raman spectra of graphene films on Si/SiO<sub>2</sub>/Ni with microscopic images of the corresponding sample regions.

Graphene growth on Cu foil samples was performed by low-pressure CVD. The samples were positioned in a one-zone 3-inch furnace equipped with a 2-inch quartz tube. The CVD was performed in 50 sccm high-purity hydrogen and 5 sccm methane. Prior to this process, the Cu foil was annealed at 1050 °C for 30 min. in hydrogen atmosphere. At a temperature of 1000 °C a methane flow was launched for 300 min. Afterwards, the sample was quenched at 60 °C/min. in hydrogen atmosphere to 300 °C. Cooling to room temperature was done in high-purity argon atmosphere.

The Raman spectra were measured on a Jobin Yvon Labram spectrometer with a CCD detector and entrance slits set to 1.5 cm<sup>-1</sup> spectral width. The 632.8 nm line of a He/Ne-laser was used for excitation, the absolute accuracy being about 1 cm<sup>-1</sup>. The laser beam with power of ≈ 1 mW was focused on a spot of about 1 - 2 μm in diameter on the sample surface using microscope optics.

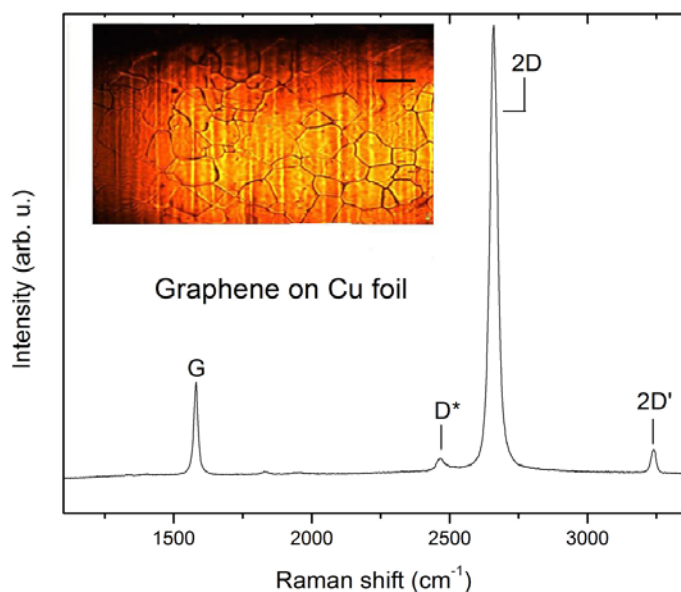
### 3. Results and Discussion

Figure 1 shows Raman spectra of graphene films grown on various Si/SiO<sub>2</sub>/Ni substrates. The first sample (corresponding to spectrum 1 in figure 1) was obtained at a flow ratio H<sub>2</sub>:Ar = 5:1. The large linewidth of the 2D band (ca. 65 cm<sup>-1</sup>) implies a higher number of graphene layers (> 5) [7] and the D band intensity reveals considerable defect density. The graphene quality is greatly improved and the layer number is presumably reduced to two upon decreasing the H<sub>2</sub>:Ar flow ratio and for reaction times of 5 – 6 min. judging from spectra 3 and 4 with 2D linewidth of ca. 35 cm<sup>-1</sup> in figure 1). The unstable 2D position (varying within 5 cm<sup>-1</sup>) shows non-intentional self-doping [8,9]. The grainy appearance of the films imply only small graphene areas of few μm. This is confirmed by the varying D band intensity and the broadened and upshifted 2D band [10] with frequency surpassing 2655 cm<sup>-1</sup>. Better quality graphene, though still confined on distinct Ni grains (see the line scan in Fig. 2) is achieved through CVD on Ni foil. This graphene film already contains single-layered grains of 1-2 μm which exhibit intensity ratio I(2D)/I(G) approaching 3 and no D band at all. This is presumably due to the better surface quality of the foil with larger single-crystalline grains, as can be appreciated from Fig. 2. On the other hand, larger areas of about 5 μm with high-quality single-layer graphene are obtained on copper foil positioned in a quasi-closed volume as inferred from the uniform Raman response over a wrinkle-limited grain (see inset) represented by the spectrum in Fig. 3. This spectrum displays an intensity ratio I(2D)/I(G) above 4, the 2D linewidth is about 30 cm<sup>-1</sup> and there is again no D band which emphasizes the low defect concentration.



**Figure 2.** Selected spectra (*right*) from a Raman line-scan in the arrow-marked region of graphene film grown on a Ni foil (*left*). Inset: intensity ratio of 2D and G mode I(2D)/I(G) along the scan line.

We find that depending on the growth conditions (low H<sub>2</sub>:Ar flow ratio and reaction times of 5 – 6 min.), films of preferentially double- or few-layer graphene can be grown by CVD on Si/SiO<sub>2</sub>/Ni and on Ni foil with occasional occurrence of even single-layered grains on the Ni foil. Raman characterization of the obtained graphene films reveal that their quality depends on the type and the degree of crystallinity of the metal substrate layer. Cu foil facilitates growth of high-quality single-layer graphene by coalescence of nucleation sites without precipitation.



**Figure 3.** Raman spectrum of graphene on Cu foil with optical microscope image of the corresponding sample spot. The scale bar represents 5  $\mu\text{m}$ .

#### 4. Conclusions

Our results demonstrate that CVD layers of graphene on Ni substrates are strongly non-uniform with single-layered graphene grains of up to 1-2 microns being obtained only occasionally, presumably due to the heterogeneous segregation of carbon atoms at the Ni grain boundaries. Depending on the growth conditions, films of preferentially double- or few-layer graphene can be grown by CVD on Si/SiO<sub>2</sub>/Ni and on Ni foil, while Cu foil facilitates growth of single-layer graphene by coalescence of nucleation sites without precipitation. Raman characterization of the graphene films on different Ni substrates reveal that their quality depends on the surface quality and the degree of crystallinity of the substrate layer.

#### Acknowledgments

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