In Situ Real-Time Monitoring of interfacial Chemical-Electrical-Optical Phenomena in CVD-Graphene/Metal Hybrids

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As engineering applications of graphene attract increasing interest, we need *in situ* methods enabling *real-time* control of graphene growth in order to control its thickness and to tailor properties, as well as enhancing understanding interfacial phenomena involving graphene interactions with metals in hybrid devices. Among various synthesis approaches, chemical vapor deposition (CVD) has emerged as a reliable technological process for fabricating large area graphene.
The scope of this contribution is to highlight experimental achievements obtained using real-time optical metrology with spectroscopic ellipsometry on the CVD growth of graphene, and its interactions with metals. Specifically, we show

- Improvements in the properties of graphene achieved by optimizing CVD growth and establishing correlations between process kinetics and thickness. We have (i) demonstrated a *real-time* optical probing method to monitor and relate all steps involved in graphene growth by CVD (using CH_4-H_2) with its final thickness and quality; (ii) demonstrated a novel improved low-temperature H_2 plasma process for the cleaning and crystallization of the metal catalysts Ni and Cu, to improve substrate quality and reduce the impact of grain boundaries effects on graphene properties; (iii) characterized carbon diffusion kinetics when CH_4 in injected into the CVD system and demonstrated control of graphene thickness [Figure 1]; (iv) measured and articulated the impact of the H_2/CH_4 ratio on CVD growth kinetics, graphene thickness and structural and optical properties [Figure 2]. The quality of the synthesized graphene is revealed by the perfect Lorentzian fit of the 2D peak at 2702 cm^{-1} with FWHM of approximately 33 $cm^{-1.}$ The absence of the Raman D peak at 1350 cm^{-1} indicates the absence of defects. Furthermore, microscopy indicates a good uniform thickness coverage, which from the I_{2D}/I_G Raman ratio, can be estimated to be from a monolayer to a 3-layers depending on growth conditions.
- New opportunities for the facile design of plasmonic graphene/metal systems based on charge transfer. Charge transfer is crucial for characterizing metal/graphene interfaces and understanding a wide range of light-matter interactions and devices, such as plasmon-coupling across the materials components and plasmon-electron coupling in plasmaron-based devices.. In addition, metals on graphene allow the controlled modification of the Fermi energy across the system, enabling effective graphene doping. Here, we provide for the first time the direct evidence of the tunability of the plasmon resonance of graphene coupled to plasmonic metal nanoparticles (NPs) [Figure 3]. The novel Ga NP/graphene system is an excellent model of a weakly-bound metal-graphene interface thus preserving graphene electronic structure. Unlike transition metals, Ga (gallium) is a *sp* metal yielding a predominantly ionic interaction with graphene, i.e. without strong hybridization between the p_z orbitals of graphene and the valence electrons of Ga, and with a weak bonding charge yielding minimal distortion of the graphene lattice. Furthermore, graphene/Ga NPs offer a plasmonic system with broad surface resonance tunability, from the UV to the near-IR range, enabling coupling of the plasmon resonance with graphene UV absorption at 4.6 eV and its intrinsic π plasmon. The role of graphene in the charge transfer, between the metal NPs and the substrate, on the plasmon resonance energy and amplitude is discussed also in comparison with other metals such as silver (Ag) that interacts electronically much more strongly with graphene
- Improvements in graphene/Ag system stability. The interface chemistry and electronic phenomena underpinning the coupling of graphene with silver gratings and fishnet structures enable novel realizations of hybrid functional materials, which are oxidation resistant and possess stable plasmon resonances in the visible range. A chemical model based on the electron transfer from graphene to silver is articulated to rationalize the oxidation resistance behavior of silver/graphene structures and the new chemical/optical properties of the hybrid [Figure 4].

These results on graphene/metals have significant impact on a variety of fields, including optical metrology, SERS-based sensors, renewable energy, plasmonics, metamaterials, specifically through the development of novel graphene/silver composites.

References

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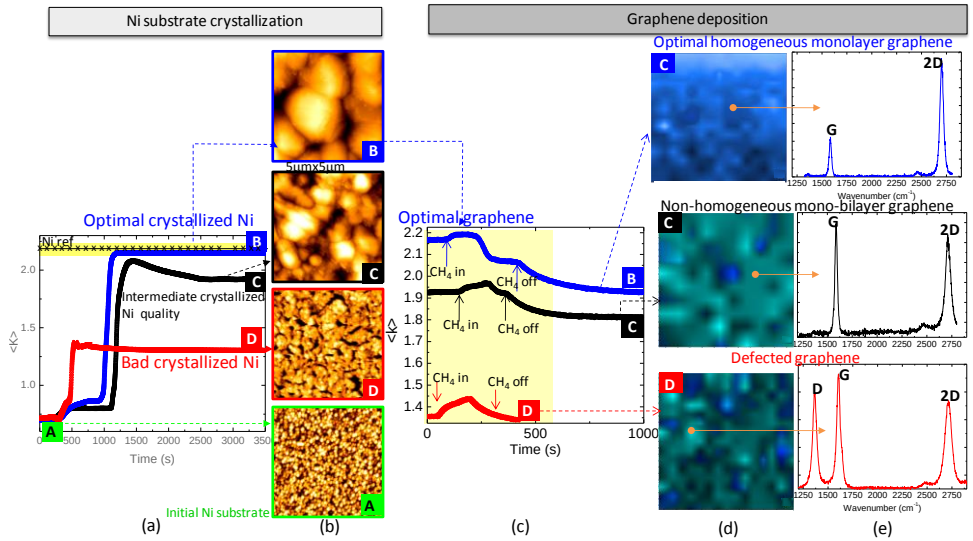

Figure 1. *Correlation between real time monitoring of graphene CVD growth and final graphene quality. (a) Real-time evolution of extinction coefficient, <k>, monitored during annealing of the 300 nm Ni/300 nm SiO_2/Si substrate in H_2. (b) Corresponding AFM images recorded for the three Ni substrates annealed at different temperature. (c) Real-time <k> evolution during graphene growth on the three characteristics Ni substrates. (d) Raman 100 μmx100 μm maps of the I_{2D}/I_G intensity ratio for FLG samples corresponding to the various kinetics and (e) Raman spectra acquired in characteristic points indicated by the yellow dot. Blue region corresponds to monolayer-graphene; green region to 2-3 layers graphene and light green to >3 layers graphene [1].*

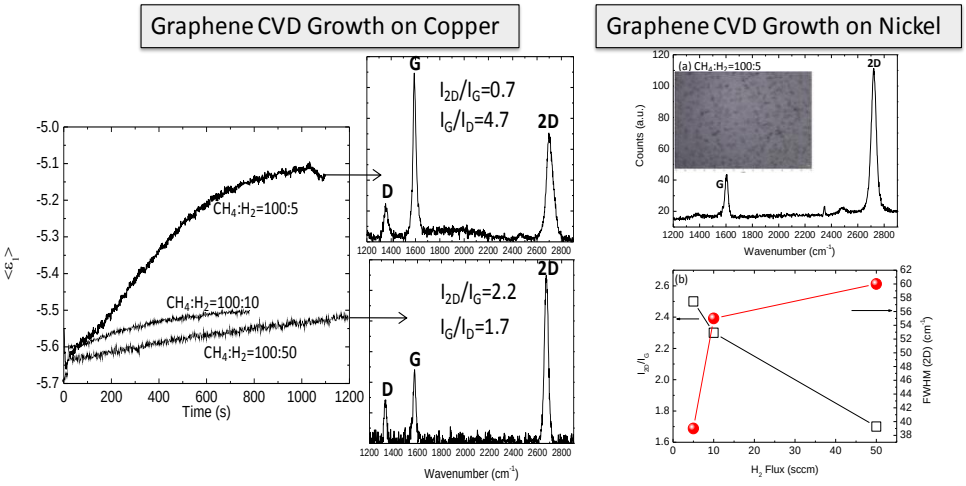

Figure 2: *Impact of CH_4-H_2 ratio on graphene growth on Ni and Cu. (a) Real-time evolution of $<\varepsilon_1>$ monitored during graphene growth on Cu at various CH_4/H_2 ratios. The Raman spectra for 2 samples are also shown with explicit I_{2D}/I_G ratio, indicative of the graphene thickness, and I_G/I_D ratio, indicative of defects. (b) Typical Raman spectrum for graphene grown on Ni at CH_4:H_2=100:10; no D-peak is observed; the dependence of the 2D peak intensity and FWHM, as a function of increasing H_2 for graphene on Ni is also shown [2].*

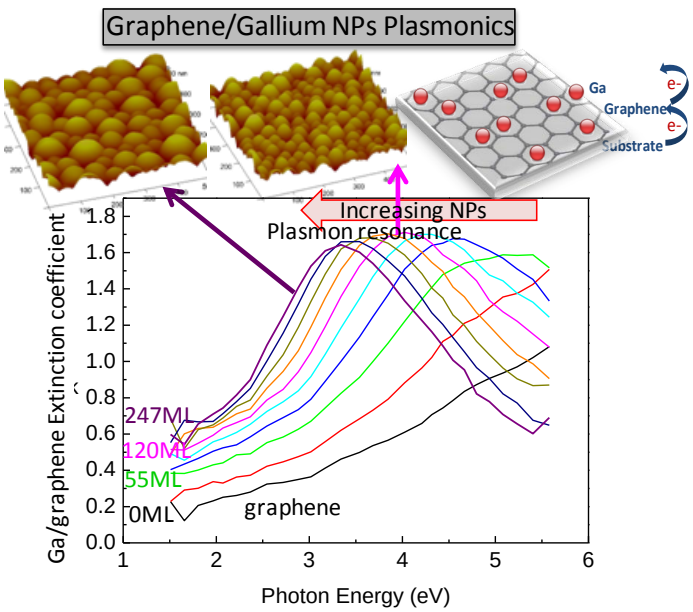

Figure 3: *Plasmon Resonance for Ga NPs/graphene plasmonic hybrids. Real-time evolution of the extinction coefficient spectra of the plasmon resonance for plasmonic Ga nanoparticles/graphene [3].*

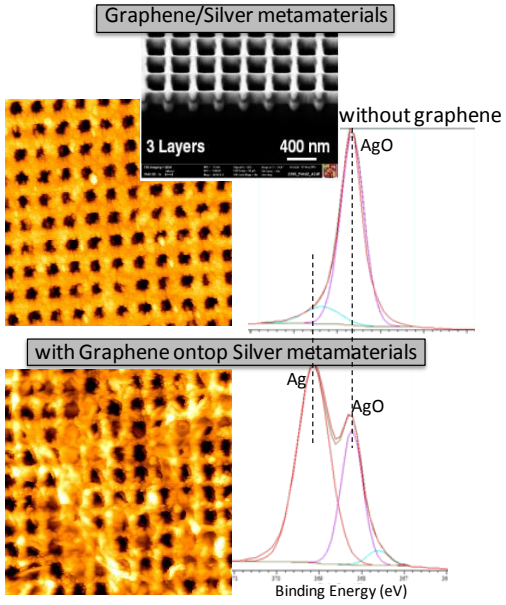

Figure 4: *Graphene-Silver Metamaterials. AFM and SEM views of a graphene-silver metamaterials in the visible. XPS shows that advantage of graphene is preserving the metal Ag structure after 1 month of air exposure.*