

## Graphene Layer Control Enabled by Nickel-Copper Alloy Thin Film Catalyst

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Graphene is highly desirable for its wide-ranging material properties, however current synthesis requirements present challenges for many industrial applications. The focus of this study is to utilize metal alloy catalysts to produce graphene films with reduced catalyst thicknesses at lower temperatures. The increased catalytic ability of Ni, compared to Cu, has been shown to reduce synthesis temperature requirements, though graphene layer number control is difficult due to increased carbon solubility. Previously, 150 nm bimetallic catalysts (Cu/Ni and Au/Ni) were shown to enable mono-/few-layer graphene growth at 600 °C [1]. More recently, a theoretical study of graphene on Ni/Cu alloys concluded that improved layer number control may be achievable through adjusting the Cu content of the alloys [2]. Our experimental results suggest that thin film alloy catalysts can enable synthesis of continuous and primarily bi-/few-layer graphene films at 500 °C, while pure Ni catalysts produce multilayer films at the same temperature.

In this study, we compared graphene grown on two 50 nm thick catalysts: (1) pure Ni and (2) a Ni/Cu catalyst thin film (48 nm Ni with 2 nm Cu at the surface) which alloys upon heating. The metals were DC sputtered on Si/SiO<sub>2</sub> wafers and subjected to a single growth recipe in an inductively-coupled plasma enhanced CVD reactor at 500 °C.

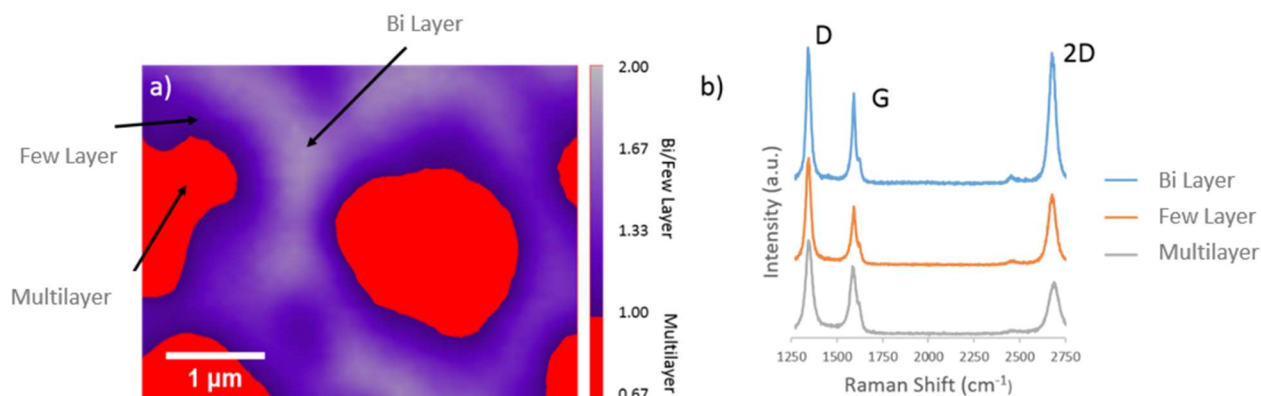
Raman spectroscopy was used to analyze the properties of graphene films synthesized on each catalyst. The intensity ratio of the 2D peak to the G peak,  $I_{2D/G}$ , is an indicator of layer number, where an  $I_{2D/G}$  of 1.00–2.00 represents bi-/few-layer graphene and <1.00 represents multilayer. Fig. 1 (a) displays an  $I_{2D/G}$  map of graphene synthesized on the Ni/Cu alloy with representative Raman spectra of bi-, few-, and multi-layer regions shown in Fig. 1 (b). It was observed that graphene synthesized on pure Ni produced 100% multilayer coverage while 73% of graphene synthesized on the Ni/Cu alloy was bi-/few-layer.

To characterize the effects of catalyst morphology on graphene quality, we acquired SEM images and EBSD data of as-grown graphene on each catalyst (Table 1). Fig. 2 (a) and (c) show SEM images of graphene on Ni and Ni/Cu respectively. The EBSD images of these two samples are shown in Fig. 2 (b) and (d), respectively with an inverse pole figure legend shown in Fig. 2 (e). The results indicate that grains on Ni/Cu and pure Ni catalyst are similar in size, with Ni/Cu catalyst grains slightly larger on average. Inverse Pole Figure Z maps suggest that the crystalline orientation of the catalyst grains is randomly distributed in both samples. To characterize the Ni/Cu elemental distribution within the catalyst, energy dispersive X-Ray spectroscopy (EDS) was performed in a TEM. Fig. 3 shows a line scan across grain morphology and boundaries of the samples. The spectra exhibit a consistent Ni to Cu ratio, indicating uniform alloying throughout the catalyst.

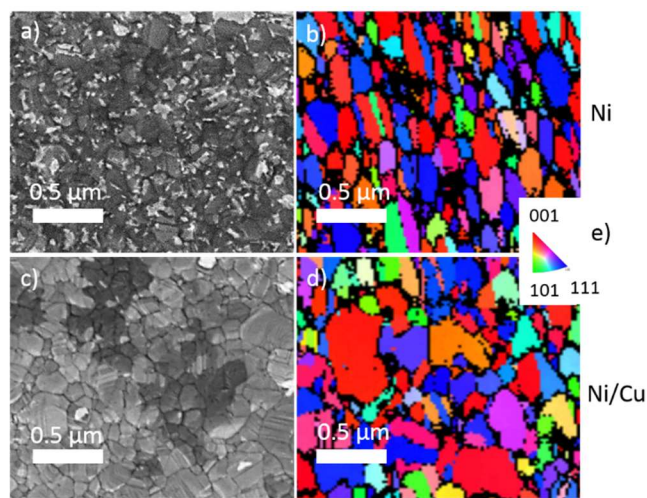
Our results indicate that Ni/Cu alloying occurs evenly in the catalyst, and that both grain size and orientation are not significantly altered during and after the graphene growth compared to pure Ni. This suggests that the Ni/Cu alloy enables graphene layer suppression primarily through reduction in carbon solubility, rather than through change in physical morphology [3].

References:

- [1] Yun Sung Woo et al., Carbon **64** (2013), p. 315.  
 [2] Xin Bian *et al*, RCS Advances **6** (2017), p. 74937.  
 [3] The authors acknowledge support from the National Science Foundation (No. 1560383), Oregon Metals Initiative (No. 1711994), Intel Corporation, and PSU Undergraduate Research and Mentorship Program.



**Figure 1.** a)  $I_{2D/G}$  Raman map of graphene grown on Ni/Cu, with bi/few layer gradient and multilayer in red. Example spectra location indicated. b) Representative Raman spectra.



**Figure 2.** a) and c) SEM images of as-grown graphene on Ni and Ni/Cu catalysts, respectively. b) and d) EBSD Inverse Pole Figure Z map of Ni and Ni/Cu catalyst, respectively. e) EBSD Inverse Pole figure legend

Catalyst Type	Ni	Ni Cu	Difference
Primary Crystal Orientation	Area		
(001)	24.16%	32.38%	8.22%
(101)	3.21%	5.01%	1.80%
(111)	17.93%	23.94%	6.01%
Other	54.70%	38.67%	16.03%
Grain Size	Area		
> 0.060 $\mu\text{m}^2$	25.17%	38.59%	13.42%
< 0.060 $\mu\text{m}^2$	74.83%	61.41%	13.42%
Average Area $\mu\text{m}^2$	0.0220	0.0249	0.0049

**Table 1.** Comparison of as-grown Ni and Ni/Cu catalyst composition, crystal orientation and grain size.

**Figure 3.** STEM image of as-grown Ni/Cu catalyst with EDS line scan location (in black) and overlaid X-ray counts of Ni, Cu, and normalized Cu

