Effects of Polycrystalline Cu Substrate on Graphene Growth by Chemical Vapor Deposition

J. D. Wood, S. W. Schmucker, J. C. Koepke, A. S. Lyons, E. Pop, and J. W. Lyding

Beckman Institute, Micro and Nanotechnology Laboratory, and Dept. of Electrical and Computer Engineering, Univ. of Illinois at Urbana-Champaign, 405 N. Mathews Ave., Urbana, IL 61801, USA
jwood2@illinois.edu

Previous experiments have shown that graphene chemical vapor deposition (CVD) on copper can form large monolayer sheets that can be transferred to a target substrate [1]. Nevertheless, graphene's lack of epitaxy with the underlying Cu causes issues with the as-grown material quality. Typical CVD growths employ polycrystalline Cu substrates, whose surfaces possess multiple polycrystalline facets, grain boundaries, annealing twins, and rough nucleation sites. Understanding how these surface structures affect graphene is critical for high quality, reproducible graphene growth.

In this work, we determine that Cu surface structures interact strongly with graphene, contrary to previous study [2]. Non-primary Cu crystal facets promote the growth of dendritic graphene lobes, causing irregular grain boundaries with other patchwork grains. We also find that graphene growth is not favored on both Cu annealing twins and non-primary crystal facets.

We grow graphene by CVD using 99.9% pure Cu foils in all of our experiments in a low pressure CVD process (~0.5 torr growth pressure). Fig. 1(a) and 1(c) are SEM and AFM images, respectively, of partially nucleated graphene, showing multi-lobed graphene "flowers" similar to those seen previously [1,2]. Around ~1000ºC, the average Cu surface energy decreases, becoming comparable to the Cu(111) surface energy, the lowest energy Cu surface [3]. In this case, small changes in surface energy from polycrystalline Cu facets [e.g. Cu(311), Cu(221)] drastically alter the Cu growth front, leading to bizarre, anisotropic lobed shapes in the Wulff construction, shown in Fig. 1(d). Combining the Cu and graphene growth fronts gives the multiple lobes seen in fig. 1(a) and in graphene dendrites [4]. Fig. 1(c) shows some of these graphene grains coalescing, bringing about irregular armchair and zigzag grain boundaries. To address this problem, one must lower the growth temperature to suppress the surface energy and limit Cu atomic diffusion; doing so gives hexagonal graphene grains with regular edges and grain boundaries, given in fig. 1(b).

To further characterize the effects of polycrystalline Cu on graphene growth, we grow a full graphene monolayer on patterned Cu registration mesas, with optical images in Fig. 2(a) and (b). Further, in fig. 2(c), we gather electron-backscatter diffraction (EBSD) data on the Cu mesa, showing that mesa is predominantly Cu(110). However, the mesa has many annealing twins present and non-primary (362), (441) facets, displaying crystallographic diversity. We correlate the EBSD data with spatial Raman maps of the typical G', G, and D bands found in graphene in fig. 3. Fig. 3(c-e) denote sparse or nonexistent graphene growth on annealing twins and non-primary crystal facets like Cu(441) and Cu(362). From fig. 3(b), the graphene distorts along Cu grain boundaries, and it is mainly monolayer on the Cu(110) surface. The Cu(232) and Cu(100) twins do not grow graphene from full width at half-maximum (FWHM) analysis. Additionally, it is possible that the twinning regions or non-primary facets have higher roughness, affecting nucleation site density [5]. Therefore, we perform AFM measurements on the mesa's facets, but find no dependence for the G' FWHM, $I_{G'}/I_G$ (signifying monolayer coverage), or I_D/I_G (signifying defect coverage) on RMS roughness. Thus, the graphene growth mechanism appears to be crystallographically dominated, based on the surface energy and diffusion of the underlying Cu substrate's crystal structure.

Once one has high quality graphene on Cu, one needs an effective technique to transfer to it to a choice substrate. We developed a process using multiple layers of PMMA (polymethyl methacrylate) with differing molecular weights. From Raman analysis with the Tuinstra-Koenig relation [7], it appears this transfer procedure does not introduce significant defects, transfers several inch wide monolayer graphene sheets, and allows the creation of unique graphene superstructures.

Our study elucidates the high graphene-Cu substrate interaction. To grow monolayer graphene with large, hexagonal grains, one must grow at temperatures <900ºC and employ dominant Cu facets such as Cu(110), Cu(100), and Cu(111), consistent with other results [2,6]. Additionally, low growth gas flow rates should be used to lower pressure, force surface catalysis [1], and eliminate multilayer dendritic formation [4].

References

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Figures

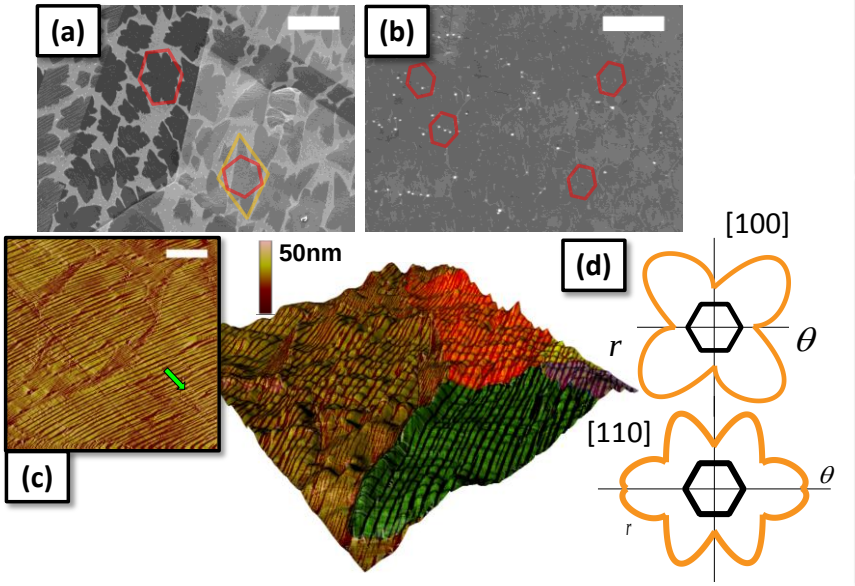

Figure 1. *(a) SEM of partial graphene coverage on 5 mil Cu (3 min, 1000ºC, 200 sccm CH_4). The graphene flowers possess more than four lobes due to underlying polycrystalline Cu facets. Yellow diamond indicates a primary Cu facet, giving four lobed graphene, and scale bar is 20 μm. (b) SEM of partial graphene on 5 mil Cu (5 min, 900ºC, 20 sccm C_2H_4). The lower temperature suppresses the Cu growth rate anisotropy. Perfect hexagons given in red, and scale bar is 5 μm. (c) False-color 3D rendering of an AFM image (inset) of coalescing graphene grains (green, purple, yellow, and red). (d) Wulff constructions for the [100] and [110] Cu zones (orange), showing asymmetric lobes for the Cu growth front (graphene growth front isotropic). For highly faceted surfaces, these lobes become more anisotropic, leading to dendritic graphene.*

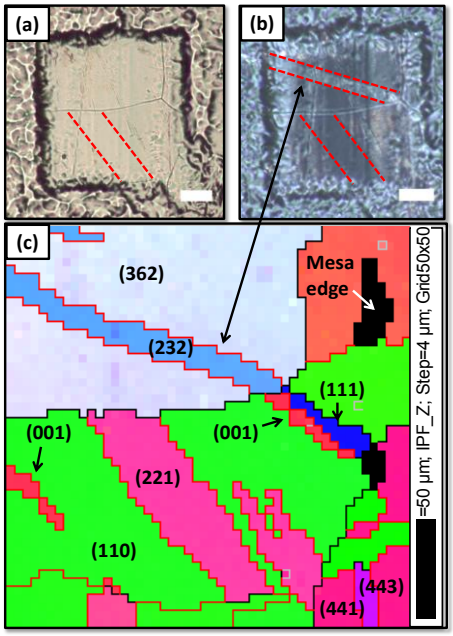

Figure 2. *Optical (a) and differential interference contrast (b) images of graphene on a Cu mesa, with Cu annealing twins in red. (c) Electron-backscatter diffraction (EBSD) data showing the different polycrystalline Cu facets, grain boundaries (black lines), and twins. Scale bar 50 μm.*

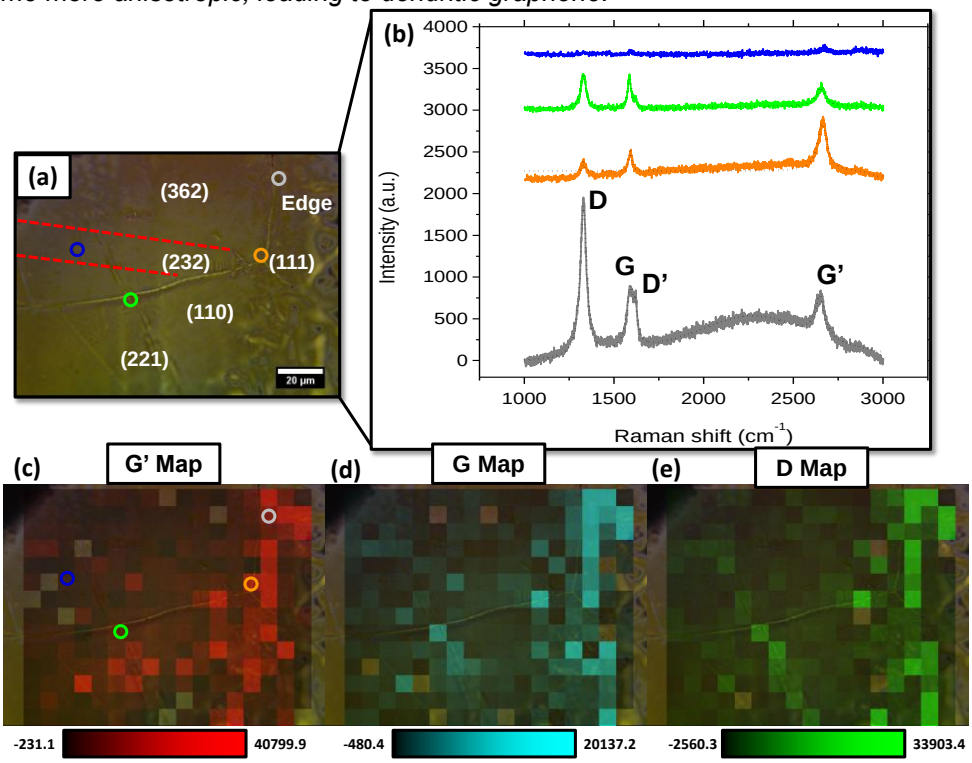

Figure 3. *(a) Mesa optical image, with Cu crystal facets identified. Raman spectra taken at the colored spots. (b) Raman spectroscopy of selected spots, with D, G, D', and G' bands present. The mesa edge shows defective graphene, and the Cu(232) twinning region has no graphene. Spatial maps for the G' band (c), G band (d), and D band (e), respectively. Highly faceted regions such as Cu(362) have lower G' and G intensities, indicating sparser graphene coverage. Raman pixel size is 7.5 μm.*