

Rapid graphene growth using ethanol-CVD

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Abstract. We studied fast growth of graphene on copper using ethanol precursor, by low pressure chemical vapor deposition. We have used three different types of copper foils to investigate the effects of copper purity and crystallographic orientation on the nucleation density of graphene for a fixed growth time of 10s. We have used X-ray diffraction (XRD) and Electron back-scattered diffraction (EBSD) to investigate the facets present in the copper foils. In this rapid growth process, the nucleation density of graphene islands is found to be independent of facets in all the three Cu foils but we observed a variation in nucleation density and island size on different copper foils keeping all the growth parameters same.

1. Introduction

Ethanol is a promising liquid precursor for the Chemical vapor deposition (CVD) of graphene on copper due to its low cost and easy handling. It offers different and faster growth kinetics, probably because of oxidizing environment [1] and one can get full graphene coverage on copper in a few seconds [2,3,4]. Therefore, further exploring this efficient growth method and understanding growth mechanism is important. Recently Lisi et. al. [2] reported fast growth of graphene and they could not identify individually separated graphene islands with duration of a few seconds growth. Faggio et. al. [3] studied the fast growth process using unpolished and electro-polished copper foils. Previously, we have reported [4] full coverage of graphene on copper in just 30 sec. In this fast growth process, we have attributed, individual graphene island shapes to an interplay between island growth rate and its relaxation rate.

Wrinkles, grain boundary, surface roughness, step-bunches, chemical impurity and facet orientation in copper foil affects the nucleation density of graphene islands. Liu et al. studied [5] effect of purity of copper substrate on graphene growth using methane and found that graphene growth on the low purity Cu foil was bilayer while on high purity Cu, graphene was single layer. Cu facets Cu(100) and Cu(111) have been reported to be more auspicious for monolayer graphene growth [6,7].

In this paper, we report on the nucleation density and growth of graphene islands on different Cu foils, assessing how the nucleation density depends on facets, chemical impurity and surface defects. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and Electron-backscattered diffraction (EBSD) mapping are presented to correlate the graphene nucleation density with slightly different purity copper foils containing different facets.

2. Experimental Details

We have used three types of commercial Cu foil: two from Alfa Aesar with 99.8% purity (CF-1) and 99.999% purity (CF-2) and 3rd from Sigma Aldrich with 99.98% (CF-3) purity. As received Cu foils



were cut into pieces of 0.5×0.5 cm² size and immersed in acetic acid, acetone and 2-propanol sequentially, for 5 min in each liquid. These Cu foils are first put in 8-cm-long quartz boat, which is placed inside a long quartz tube kept inside a tubular furnace. The detailed description of our CVD system can be found elsewhere [4]. It consists of a hot-wall tube furnace where the samples can be rapidly inserted and extracted from the hot zone by sliding Quartz tube. Ethanol vapor was flown inside the quartz tube with Ar/H₂ (5% H₂ in Argon) as carrier gas and CVD was performed at 980°C for 10s.

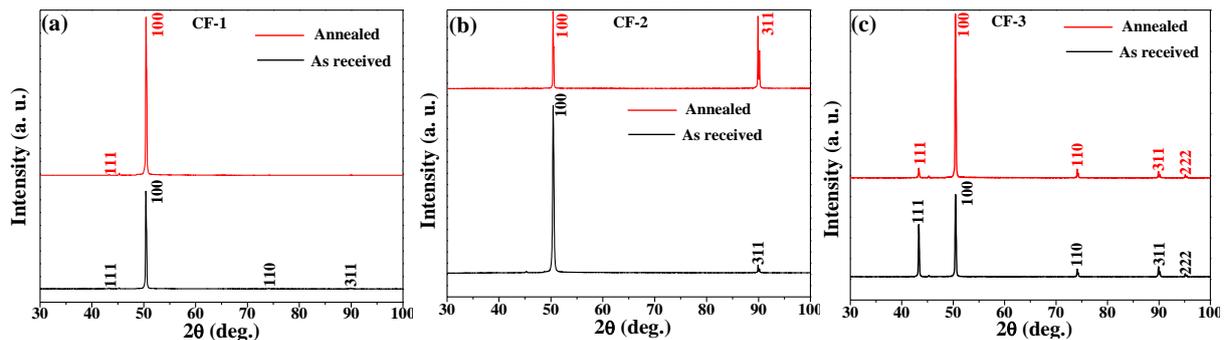


Figure 1. XRD pattern of all three copper foils as received and 20 min Ar/H₂ annealed state (CVD was stopped just before the deposition): (a) Copper foil-1, (b) copper foil-2 and (c) copper foil-3.

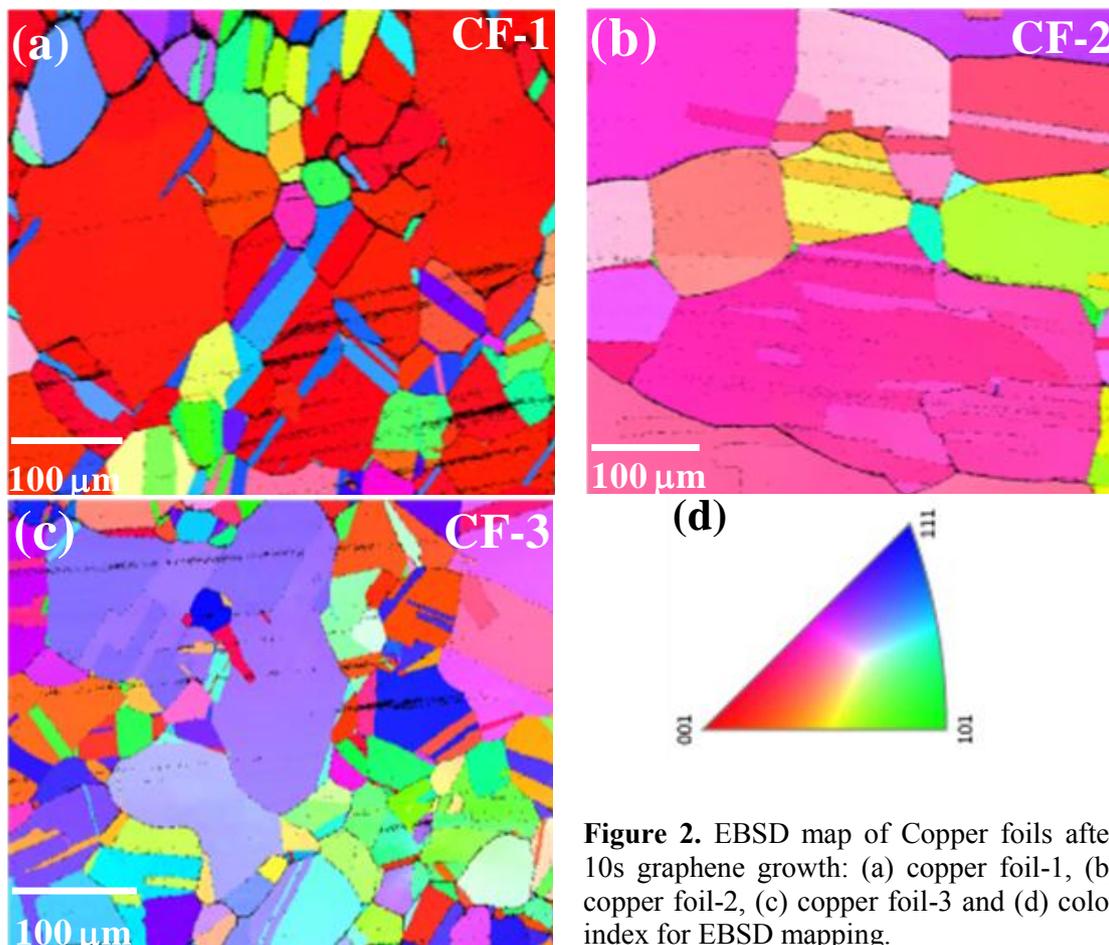


Figure 2. EBSD map of Copper foils after 10s graphene growth: (a) copper foil-1, (b) copper foil-2, (c) copper foil-3 and (d) color index for EBSD mapping.

We used a EVO-18 Zeiss SEM with low beam voltage in secondary electron detection mode to study the graphene nucleation density on Cu foils. To determine the facets present in the Cu foil, we performed XRD and EBSD orientation mapping on a different SEM (Zeiss, EVO-50) using EBSD detector.

3. Results and Discussion

The crystallographic orientation of the Cu foil affects carbon adsorption. It means facets can affect nucleation density of graphene islands. In order to explore the role of Cu facets on graphene nucleation density, XRD and EBSD mapping of all the three Cu foils were performed. Figure 1 (a), (b) and (c) show the XRD patterns of the CF-1, CF-2 and CF-3 in as received as well of Ar/H₂ annealed foils, respectively. Different facets detected from XRD are marked in the figure. Figure 2 (a), (b) and (c) show the EBSD map of the CF-1, CF-2 and CF-3 after graphene deposition. Figure 2 (d) shows inverse pole color index for EBSD map. EBSD measurement gives the crystallographic orientation in x, y and z direction, but here we will only consider z plane of copper surface.

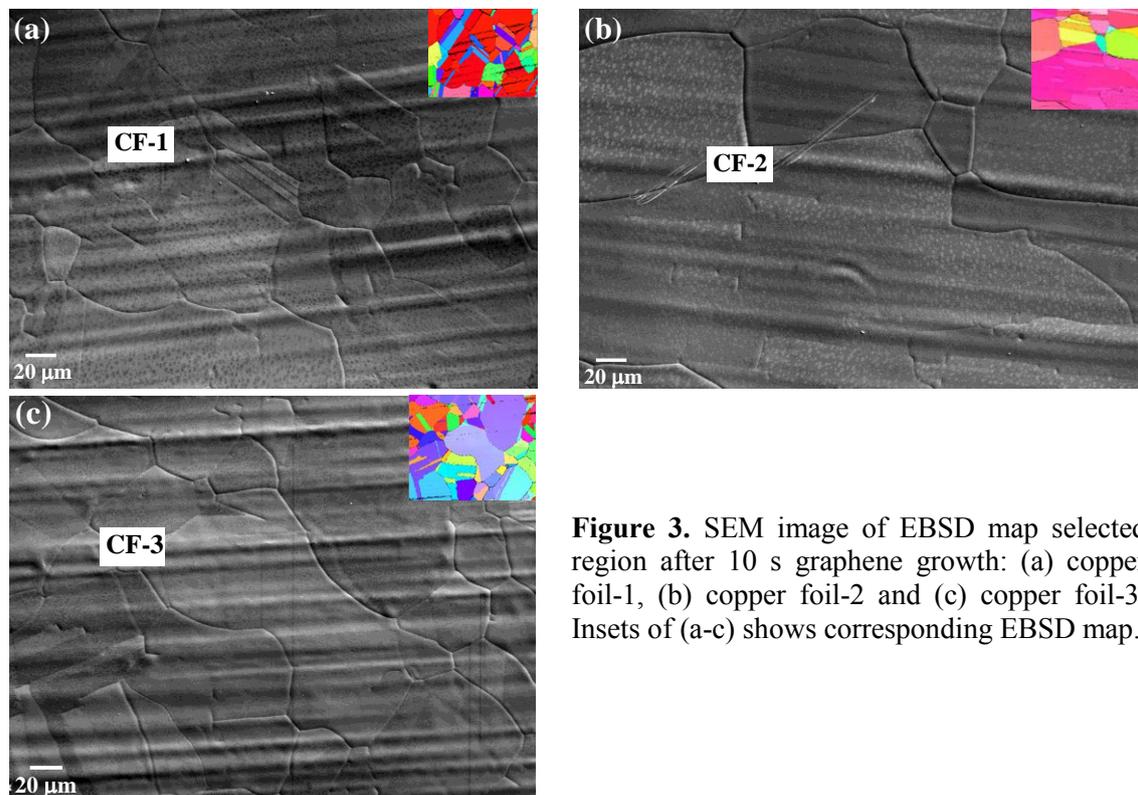


Figure 3. SEM image of EBSD map selected region after 10 s graphene growth: (a) copper foil-1, (b) copper foil-2 and (c) copper foil-3. Insets of (a-c) shows corresponding EBSD map.

Figure 1 (a) shows the XRD with various copper planes as in CF-1. After annealing, the copper foils become more textured along $\langle 100 \rangle$ direction as confirmed from the EBSD map [Figure 2 (a)]. CF-2 has (100) and (311) facets as received as well as after annealing [Figure 1 (b)]. After annealing, the height of (100) peak decreases but the height of (311) peak increases indicating the increase in higher index facets in CF-2 with annealing. XRD pattern in Figure 1 (c) shows the facets present in CF-3 before and after annealing indicating its polycrystalline nature. After annealing the intensity of (100) plane increases and other plane, namely (111), (110), (311), and (222), intensity decreases. CF-3 has (100) and (111) facets in higher volume fraction as confirmed from EBSD map [Figure 2 (c)]. If we compare low index facets in the three copper foils – all the foils are polycrystalline and preferred orientation of grains in CF-1 is (100), in CF-2 is (100) and (311) and in CF-3 it is (100), (111) and (110).

Figure 3 (a), (b) and (c) show the SEM images of selected regions of Figure 2 (a), (b) and (c), respectively, after 10s graphene growth. By correlating these SEM images with corresponding EBSD maps (see inset of figure), it is clear that graphene nucleation density is independent of underlying facets for all the three copper foils. To investigate whether the impurity present in Cu foil affects the nucleation density, we analyzed nucleation density present in all three copper foils. We find nucleation density on CF-3 to be 5 times higher than CF-2 and that on CF-1 to be two times higher than CF-2. The impurities present in CF-1, CF-2 and CF-3 are 0.2%, 0.001% and 0.02%, respectively indicating the nucleation density is not influenced by small change in copper foil purity. We have also altered the position of the copper foil inside the quartz boat, but the nucleation density remains independent of this position. Nucleation density, copper foils' purity and the dominant texture of the foils are summarized in Table 1.

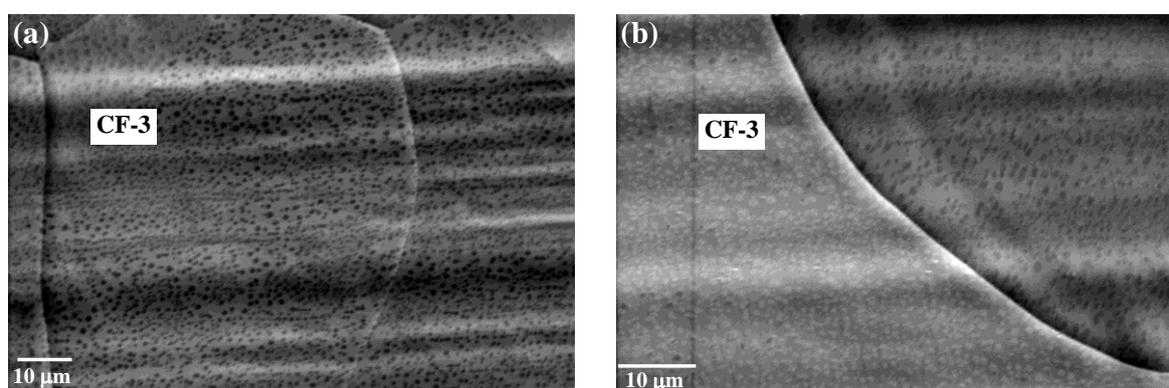


Figure 4. SEM images of copper foil-3 to see the effect of surface defects density on nucleation density: (a) effect of polish line on nucleation density and (b) effect of surface contamination on nucleation density.

From the SEM images of copper foils (Figure 3), it is clear that the density of surface defects, such as polish lines [5] and grain boundaries, in CF-2 is the lowest while in CF-3, it is the highest. This indicates a correlation between nucleation density and surface defects density. Figure 4 further illustrates this point on the same Cu foil but having different defect density in different regions. Nucleation density of graphene islands along the direction of the polish lines is much higher as seen in Figure 4 (a). Surface contaminants present in copper foils also affect the nucleation density [Figure 4 (b)].

Table 1. Summary of nucleation density, copper foils' purity and the dominant texture present in copper foils.

Sample Name	Thickness (μm)	Vendor/Product Number	Purity (%)	Facets	Nucleation density in $500 \mu\text{m}^2$
CF-1	25	Alfa Aesar/ #13382	99.8	(100)	82-112
CF-2	25	Alfa Aesar/ #10950	99.999	(100), (311)	46-65
CF-3	25	Sigma Aldrich/ #349208	99.98	(100), (111)	190-280

Graphene island's size is found to depend on copper foils: CF-2 has largest island size while CF-3 has smallest island size among the three copper foils. This anticorrelates with the nucleation density. From this we surmise that the carbon containing species present inside the tube above the copper foils have uniform density but the adsorption of these species depends on the surface defect density. The

later does not directly depend on the purity of copper foil and facets. Our previous report showed that the shape of islands is influenced by underlying facets present in the copper foil [4]. We believe that in our experimental conditions the diffusion of carbon containing species depends on the facets but not their adsorption.

4. Conclusion

In summary, we have analyzed graphene nucleation density on three different copper foils for 10 s growth time using ethanol precursor. By correlating electron microscopy images with the EBSD maps we find nucleation density does not depend on underlying facets for all the three copper foils. Further, the nucleation density is not influenced by small change in copper foil purity; it depends strongly on density of surface defects such as like scratch due to polishing.

Acknowledgments

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