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# Smooth epitaxial copper film on sapphire surface suitable for high quality graphene growth

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A B S T R A C T

Graphene, a two-dimensional material, can be grown on a metal substrate using chemical vapor deposition — this growth process is notably influenced by the crystal orientation and the roughness of the substrate surface. We prepared epitaxial Cu(111) films on sapphire substrates using thermal evaporation at various substrate temperatures and studied their crystal orientation and roughness. The well crystallized Cu(111) film with a smooth surface was obtained when the substrate was maintained at 473 K during the deposition. High quality graphene with few intrinsic defects was grown on this Cu film.

## 1. Introduction

Graphene, a two-dimensional carbon material composed of a single graphite layer, shows extraordinary electronic, thermal and mechanical properties [1–3]. In our group, we are developing an environment-controlled cell with a graphene window for *in-situ* electron microscopy and spectroscopy. The graphene window with clean and defectless area in the sub-millimeter scale is desired to ensure optimal signal collection. In our previous work, we have conquered the first step to transfer chemical vapor deposition (CVD) graphene without bringing considerable contamination to the film [4].

Graphene prepared by CVD withcommercial copper foils is usually polycrystalline, with the domain size within the micrometer scale [5–7]. It was reported that the domain size of the CVD graphene could be notably influenced by the domain size and the roughness of employed metal substrates [8,9]. Surface defects such as grain boundaries in the commercial polycrystalline copper can be the nucleation sites for multiple graphene domains [9,10], leading to polycrystalline graphene with small domains. Single-crystalline metal substrates, in which the grain boundaries are absent, can significantly reduce the nucleation sites and hence produce single-crystalline graphene with relatively large area [11–13]. However, the single-crystalline metals are expensive and impractical for the substrate-sacrifice transfer method, in which the substrate is dissolved with a chemical solution. On the other hand, large-scale graphene with reduced defects could be prepared on metal thin films with smooth surface [14,15]. Procházka et al. demonstrated that the graphene layer grown on an ultrasmooth copper film, which was deposited on a $SiO_2$/Si substrate, had a very low amount of defects, evident by the absence of D-band in the Raman spectra [14].

Recently, an easy way to prepare smoothly and uniformly oriented copper films on single-crystalline sapphire has been reported [16–19]. Because the crystal orientations of copper substrates can remarkably alter the growth dynamics of graphene [18], copper films with a uniform crystal orientation eliminate the diverse growth behavior of the graphene domains, providing chances to grow large-scale single-crystalline graphene. It has already been confirmed that graphene prepared on the Cu(111)/sapphire substrate was almost free of defects [16], and had a single domain with an area over 1 $mm^2$ [17]. However, these works are focused on either the growth or the characterization of the graphene films, whereas the methodology of the preparation of the epitaxial substrates were hardly studied.

In order to optimize the preparation of epitaxial copper films on sapphire, we investigated the crystal orientation and the roughness of copper films prepared at various substrate temperatures. The optimized sample was selected for graphene growth via CVD, with the results compared with that grown on a commercial copper foil. Our results showed that the Cu/sapphire substrate has a potential to prepare high quality graphene.

## 2. Experimental procedures

Copper films were deposited on the *c*-plane of sapphire, $\alpha$-$Al_2O_3$(0001) (10 mm × 10 mm × 0.5 mm, Shinkosha Co., Ltd.), using thermal evaporation. Copper beads 2–8 mm, 99.99%, Sigma-Aldrich) were put on a tantalum boat that was resistively heated inside the

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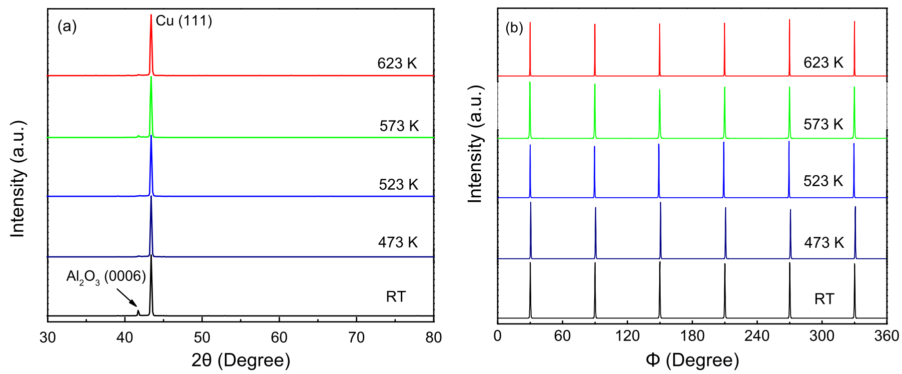


**Fig. 1.** XRD profiles of the Cu(111) films on $Al_2O_3$(001) deposited under varied substrate temperatures. The $\theta$–$2\theta$ scans (a) show only (111) reflections from the copper films; The $\phi$-scans (b) show Cu{111} diffractions appeared with an interval of 60°.

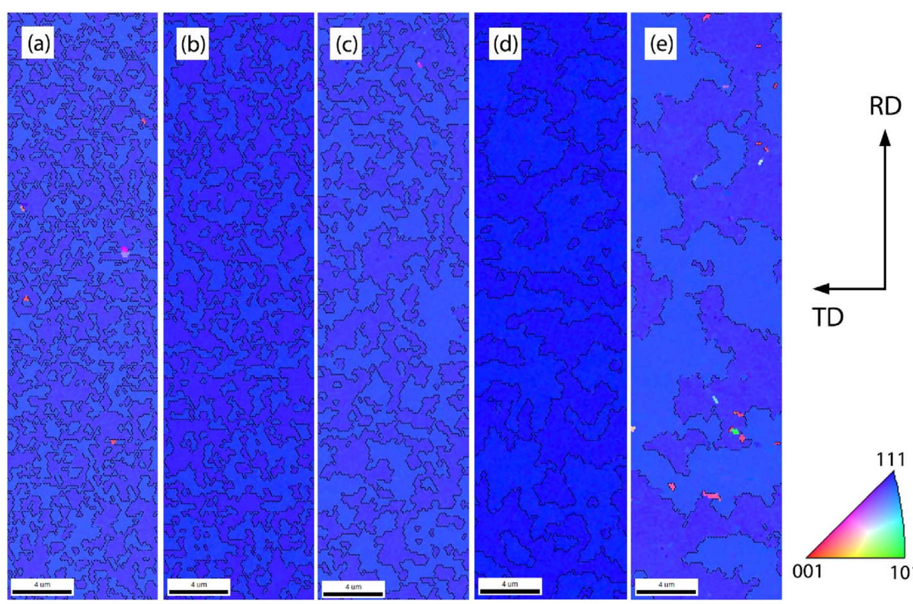


**Fig. 2.** EBSD images of the Cu(111) films evaporated epitaxially on $Al_2O_3$(0001) when the substrate was initially maintained at RT (a), 473 K (b), 523 K (c), 573 K (d), and 623 K (e). The scale bar is 4 μm. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

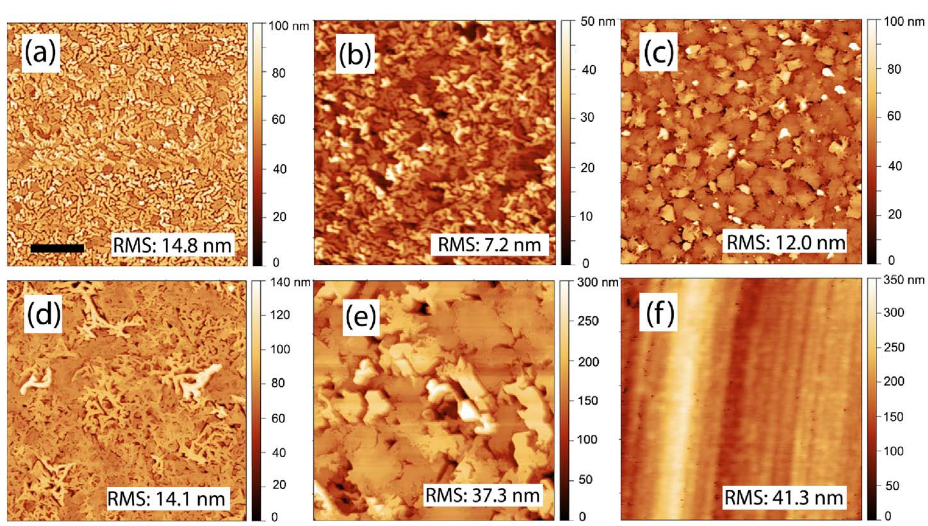


**Fig. 3.** AFM images of the Cu(111) films deposited epitaxially on $Al_2O_3$(0001) when the substrate was initially maintained at RT (a), 473 K (b), 523 K (c), 573 K (d), and 623 K (e). A commercial copper foil (f) was also scanned for comparison. The scale bar is 2 μm. The roughness of the samples was estimated by the RMS values shown in the figures.

evaporator. During the evaporation, the sapphire substrate was heated at varied temperatures from 473 K to 623 K using a platinum wire that was mounted close to the substrate. The substrate temperature was monitored by a thermocouple that was attached to the back side of the sapphire substrate. The evaporation rate, monitored by a quartz crystal unit, was kept to 0.2 nm/min until the thickness of the deposited film reached ~750 nm. We also evaporated the copper film without heating the substrate externally, which was denoted as the room-temperature (RT) sample; but note that the substrate was warmed radiatively by the evaporating source and its temperature was gradually raised to ~473 K when the deposition finished. The crystallography of the copper films was studied by X-ray diffraction (XRD; Bruker D8 Discover) with Cu $K_\alpha$ radiation: $\theta$–$2\theta$ scans were recorded in a range of $2\theta = 30°$–$80°$, which covers the main peaks of a face-centered cubic structure. The [111]-