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Growth of Bilayer Graphene with AB-Stacking Ratios Exceeding 99% by CVD on Cu-Ni Thin Films

The research on bilayer graphene (BLG) has gained significant attention since the last year, owing to recent discoveries of interesting behaviors for low-angle twist stacking BLG [1]. These discoveries have revealed that BLG is a rich material, for which the electronic properties are intimately linked to the stacking order of the individual layers. The most stable crystallographic configuration of BLG, known as AB (or Bernal) stacking, is also of a great technological importance. This is due to the possibility to open a tunable band gap in AB-BLG by applying an out-of-plane electric field [2]. However, this requires an almost perfect AB-stacking of the layers, with misalignments over 0.1° being known to modify the band structure enough to prevent the opening of the gap [3]. Owing to the higher energy stability of the AB stacking, artificial stacks of twisted BLG can be relaxed to AB by annealing at moderate temperatures [4]. However, this approach only works for low BLG coverages and relatively small misorientation angles. Thus, development of efficient methods for the direct synthesis of AB-BLG with such high degree of alignment is mandatory for the large-scale production required on practical applications.

Chemical vapor deposition (CVD) on metal catalyst is one of the most promising techniques for the growth of graphene and other 2D materials with high quality and at large scales. By controlling the C solubility of the metal catalyst, CVD growth of graphene with a selected number of layers is possible, and in particular of BLG. This can be done by alloying metals with low and high C solubilities, such as Cu and Ni, respectively. By adjusting the ratio of Cu and Ni, and carefully controlling the CVD growth conditions, it is possible to obtain homogeneous BLG with a high-coverage and on relatively large areas [5]. However, the BLG obtained usually consists of a mixture of AB and twist stacking regions, with only ~ 70 % of AB stacking. The presence of these twist regions render the BLG unsuitable for certain electronics applications. Therefore, new CVD growth approaches are required that allow to optimize the ratio of AB-stacking without affecting the coverage of BLG.

Here, we present our latest findings on the CVD synthesis of large-area AB-stacked BLG on Cu-Ni alloy thin-films [6]. The catalyst films were prepared by the successive sputtering of Ni and Cu thin films on a c-plane sapphire substrate. After the sputtering, the film was alloyed by annealing in an H_2 enriched environment at ~1000 °C. Electron backscatter diffraction (EBSD) measurements show that the alloyed film has an fcc structure with the (111) surface on the top (Fig. 1a). Immediately after the annealing, the graphene growth was started by flowing CH_4. Scanning tunnel microscope (STM) images taken from as-grown CVD on Cu-Ni confirmed the growth of high quality BLG (Fig. 1b). By a combination of optical microscopy and Raman spectroscopy, it is possible to determine the number of graphene layers after transferring the sample to SiO_2. Moreover, Raman is an essential tool that allows distinguishing between AB and twisted BLG (Fig. 2a). This is mainly due to the large differences existing in the 2D band, which for the case of AB stacking is broader and can be decomposed in four components (inset of Fig. 2a). This allowed us to control the CVD growth parameters in order to increase the ratio of AB-stacked BLG from ~ 70 % [5] to a value over ~ 99 %, with virtually no presence of twisted areas (Fig. 2b, c). In contrast to our previous work, for which the BLG growth occurs during the cooling down step of the CVD [5], we now succeeded in promoting the growth during the high temperature step. This allows for a better control on the stacking orientation, which is not possible for the segregation processes occurring during the cooling down. Thus, owing to a continuous selective etching and regrowth during the CVD, the AB ratio increased with the CVD time [6]. Interestingly, the BLG coverage remained essentially constant, at values exceeding 90% of the surface by further optimization of the alloy catalyst. This new growth mechanism is expected to contribute to the realization of large-area semiconductor device arrays based on AB-stacked BLG.

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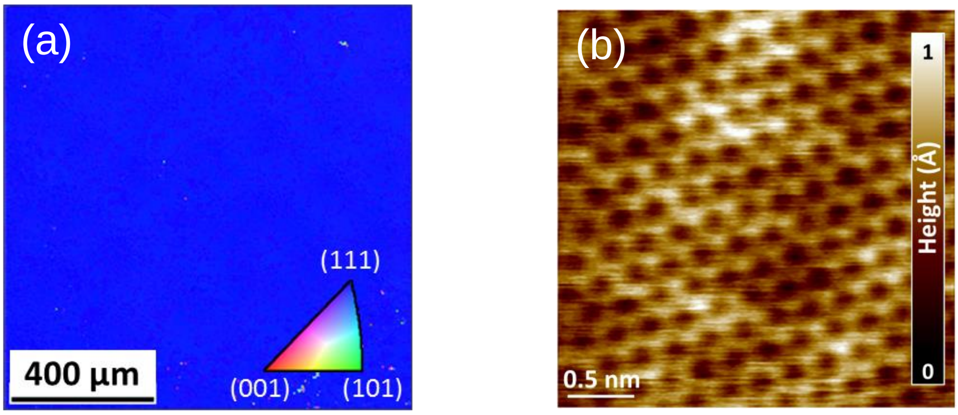

Figure 1: (a) EBSD mapping of the alloyed Cu-Ni thin film. (b) STM image of the as-grown BLG on Cu-Ni.

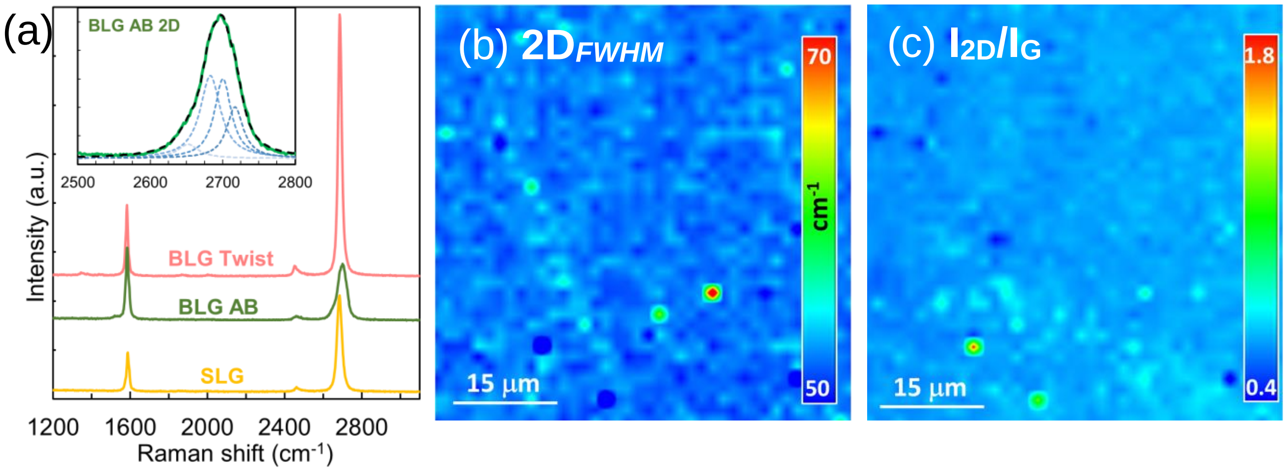

Figure 2: (a) Raman spectra of SLG and of AB and twist BLG. Inset shows an enlargement of the 2D band of AB-BLG. (b, c) Raman mapping of the 2D band width (b), and of the intensity ratio of the 2D and G bands (c).