EBSD study of substrate-mediated growth of hexagonal boron nitride

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Abstract. Hexagonal Boron Nitride (h-BN) is a promising insulating material to complement and enable graphene electronics. Given the good lattice match to graphite, graphene/h-BN heterostructures may be grown with negligible amounts of strain and defect states, resulting in high carrier mobilities approaching values for suspended graphene. Chemical vapour deposition (CVD) has emerged as one of the preferred routes for the synthesis of 2D materials for electronic applications. Here we report on the growth of h-BN by low pressure CVD, using borazine as a precursor. Electron backscattered diffraction (EBSD) in conjunction with topographic imaging in the scanning electron microscope are used to investigate the change in crystal structure and orientation of three metallic catalyst substrates: Co, Ni and Cu, by high temperature processing and the growth of nanoscale h-BN domains. The behaviour of the metal foils is interpreted in light of the prevalent growth models. EBSD and imaging conditions are optimized to allow efficient acquisitions for these composite and nanostructured specimens.

1. Introduction
Hexagonal boron nitride (h-BN) is a promising insulating material to complement graphene in two dimensional electronics. The ultra-flat morphology and insulating properties of h-BN allow carrier mobilities to approach values reported for suspended graphene [1]. Growth of h-BN was demonstrated using chemical vapour deposition (CVD) on metallic substrates, with recipes conceptually analogous to those employed for the synthesis of graphene. In particular, here we adopted borazine (HBNH3) as B-N precursor in a low pressure CVD (LPCVD) approach, because the gas already carries a stochiometric balance of the constituent elements, with a low pressure of H2. In the literature, a range of macroscopic characterization techniques is employed to analyse the initial stages of BN growth, including Raman spectroscopy and electron backscattered diffraction (EBSD) in the scanning electron microscope (SEM). To gain control over the deposition in view of applications, it is important to understand how the specific CVD conditions (p, T, precursor dilution) affect the re-structuring of the metallic substrate, which in turns affects the growth in term of nucleation and the quality of the formed layers.

Here we present a survey of the effect LPCVD processing has on grain size and crystal orientation of three common metallic foils used as substrates for the growth of h-BN. Topographic secondary electron imaging (topo-SEI) complemented by electron backscattered diffraction (EBSD) are used for
characterising the morphology of the h-BN phase and the orientation of the metallic substrate, grain by grain.

2. Experimental methods

LPCVD growth of boron nitride was performed using a borazine (HBNH)_3 precursor at 800-1000°C for 30 minutes to produce h-BN nuclei on Co (μm Alfa Aesar purity > 99.9%), Ni (μm Alfa Aesar purity > 99.999%), and Cu (25 μm Alfa Aesar purity > 99.999%) foils. The crystallographic phase of BN was confirmed by various characterization techniques including Raman spectroscopy post transfer from the metallic substrate.

Topo-SEI and EBSD were performed using a FEI Helios FEG SEM/FIB microscope. The Channel 5 software suite distributed by Oxford Instruments with the EBSD Nordlys II detector was used for data acquisition and processing. The metallic foils were mounted on SEM stubs and loaded in the SEM chamber and imaged at a working distance of about 4 mm. This was found to be a good compromise because it allowed sufficient spatial resolution for topo-SEI of the boron nitride islands, as well as efficient detection of the EBSD signal for a specimen tilt angle of 60°. The acceleration voltage was set to 2 kV for topo-SEI to improve the visibility of the overlayers, to 20 kV for low mag topo-SEI, and to 20 kV for EBSD analysis. The optimum beam current for these acquisitions was found to be 0.69-1.4 nA. MonteCarlo simulations were used to calculate the maximum escape depth of the backscattered electrons for the three metals (Z = 27, 28 and 29 for Co, Ni, and Cu, respectively) using the software CASINO v. 3.2.0.1. This was found to be of the order of 200 nm and therefore much smaller than the average size of the metallic grains within the foils.

For each location we acquired a low magnification topo-SEI micrograph and corresponding EBSD map, followed by a set of high magnification, low kV, micrographs of the metallic grains in the map to identify h-BN growth habit as a function of crystal orientation. The main factors limiting mapping efficiency were found to be surface coverage and macroscopic surface roughness, the latter causing contrast inversion that prevents automatic indexing during mapping.

3. Results and discussion

3.1 Cobalt

The grains in the Co foil have an average grain diameter of about 20 μm, and a wide range of crystallographic orientations. A unique feature observed on Co is the presence of heavily stepped grains along-side smooth ones. By correlating topo-SEI and EBSD phase maps, e.g. in figure 1(a-b), it appears that stepped surfaces correspond to the hexagonal phase, while smooth surfaces, decorated with BN dendrites, correspond to the cubic phase. We note that the indexing rate on stepped surfaces is lower than on smooth surfaces, and seems to be influenced by the relative orientation of the steps, possibly due to differences in the take-off angle of the backscattered electrons. Beyond this observation, statistically significant correlations between Co grain orientation and h-BN growth were hard to find. This is evident from Figure 1(a) and 1(c) [2].

3.2 Nickel

Ni foils have an average grain diameter of 50 μm, and display a strong preponderance of grains for which the [100] is perpendicular to the foil surface, with a few that are [111]-oriented. Figure 2(a) shows an example of BN nuclei on a [111] Ni grain, from which it is clear that the growth is partly 3D and is attributed to conditions specific to the LPCVD recipe in this case. Figure 2(b) shows a low mag image of the Ni foil from which the EBSD map in (c) was acquired.
Epitaxial growth of h-BN on Ni(111) was first demonstrated by Nagashima and co-workers [3], and arises from a good lattice match between the two materials. The 0.5% mismatch gives rise to corrugations of the h-BN according to Auwarter et al. [4], and indeed figure 2(a) shows a strong interplay of the two phases, much more than observed in Co. Dendritic h-BN growth can also be observed on a (101)-like facets. Two growth mechanism on reconstructed (101) surfaces are suggested [5], 1x6 being energetically favourable because corrugation of the film can compensate mismatch. 7x5 structure produces negative mismatch that introduces strain in film.

![Figure 1](a) Secondary electron SEM image of Co foil after processing, the scale bar corresponds to 20 μm (20 kV acceleration voltage). The dashed rectangle corresponds to the area of the EBSD maps shown in (b) and (c). The EBSD phase map in (b) displays the hexagonal (green) and cubic (blue) grains in the foil. The map in (c) shows the relative orientation of the cubic grains, colour coded according to the legend shown on the right.

![Figure 2](a) Secondary electron SEM image of the Ni foil after processing. Boron nitride islands are visible in the topographic image acquired at 20 kV acceleration voltage. The scale bar corresponds to 2 μm. (b) Low mag SE image of the Ni foil. The scale bar corresponds to 10 μm. The dashed rectangle corresponds to the area of the EBSD maps shown in (c), which shows the relative orientation of the cubic grains, colour coded according to the legend shown on the right.

### 3.3 Copper
Copper foil responds to the processing by forming the largest grains, up to 200 μm, but with a large size distribution, visible in figure 3(b). A large fraction of the grains is oriented such that the [100] axis is parallel to the surface normal. The EBSD map of figure 3(c) shows that only a small fraction of the foil surface is (111), but the morphology of these regions is peculiar, i.e. the domains form long, thin strips. In the literature h-BN growth was only reported on (100) and (111)-like facets, but in this study we observed nuclei on (110) too, as shown in the image in figure 3(a).
Growth of h-BN (001) on Cu (111) surfaces is likely to be epitaxial, as reported by Preobrajenski [6] and Kim [7]. This is due to the fact that the two have the same symmetry and lattice spacings, where residual misfit is possibly accommodated by the h-BN. Growth on Cu (100) was only reported by Guo [8], no clear mechanism was reported for it. It is interesting to note that h-BN nuclei stretch across grain boundaries.

4. Conclusions

The synthesis of 2D h-BN by CVD methods requires a detailed understanding of the role of transition metal foils both as catalysts and as substrates. In this study, our aim was to observe to what extent a specific high temperature LPCVD process affected the grain size and crystallographic orientation of cobalt, nickel, and copper foils. EBSD mapping revealed that for Ni and Cu foils the [100] is predominantly parallel to the surface normal. Low voltage topographic secondary electron imaging of the foils showed boron nitride nuclei on all surfaces, some with a marked dendritic character, e.g. on cubic Co grains, and some with a more irregular shapes, e.g. with Cu (101) surfaces.

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