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CVD Growth of Single-Layer Hexagonal Boron Nitride Sheet on Heteroepitaxial Cu Films

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Abstract

Hexagonal boron nitride (h-BN), consisting of a honeycomb lattice of boron and nitrogen atoms, is an atomically thin insulating material with a large band gap (6.0 eV). Mechanical flexibility and optical transparency of h-BN make it a promising material as a gate insulator of flexible devices. Here, we have studied chemical vapor deposition (CVD) growth of a h-BN sheet using an epitaxial Cu(111) catalyst by using ammonia borane (BH_3NH_3) as a precursor. From our scanning electron microscopy (SEM), well aligned triangular grains was observed and by low energy electron diffraction (LEED) measurements, six clear spots was obtained from grown continuous sheet on Cu(111) film which means that the orientation of the h-BN sheet is well controlled by the underlying Cu(111) lattice at large area.

1. Introduction

Hexagonal boron nitride (h-BN), a honeycomb lattice of boron and nitrogen atoms with a layered structure, is an excellent electrical insulator with large band gap (5.9 eV). Thus, it is a promising material for future heterostructure devices.[1] To develop various electronic and photonic applications, the controlled synthesis of large-area h-BN is essential, and recently CVD method has been widely employed using polycrystalline Cu foil as catalyst.[2-4] In the present study, we focused on the CVD growth of the single-layer h-BN on single-crystal Cu(111) substrates as a catalyst. The substrate was prepared by depositing the metal catalyst by sputtering on a c-plane sapphire, which allows to obtain catalyst thin films with a high quality.[5-7] By using epitaxial Cu thin films with controlled crystalline faces, the growth of triangular h-BN domains which are oriented in two directions was observed. In addition, controlled h-BN grains on the Cu(111) substrate at a large area was confirmed by low-energy electron diffraction (LEED).

2. Materials and Methods

Figure 1. is a schematic illustration of the CVD setup. Cu(111) obtained by sputtering was introduced into the tube furnace, and annealed in a flow of H_2/Ar gases at 1000 °C in the zone 2 for 1 hour, to increase the crystallinity of the Cu. After the annealing, the temperature was increased up to 1050 °C and the precursor gas was introduced. The precursor gas, which will be the source of nitrogen and boron, is supplied by the sublimation of ammonia borane (BH_3NH_3). After the reaction was completed, the sample was moved away from the hot area of the furnace, for a fast cooling down. To investigate morphologies of grown h-BN and surface conditions surface SEM and AFM measurements were carried out. To observe a diffraction pattern from h-BN/Cu(111) film, LEED measurement was conducted.

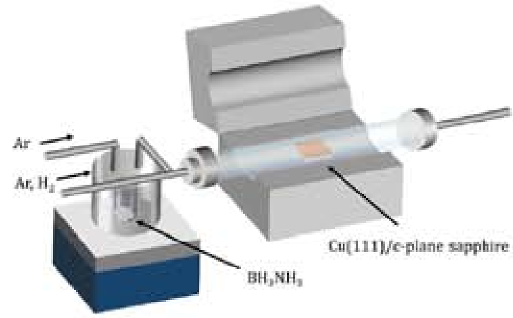

Figure 1. Schematic illustration of CVD setup for h-BN growth

3. Result and Discussion

Figure 2. shows a SEM images of h-BN grains grown on Cu(111) by CVD. After a short CVD process with 5 min reaction, triangular h-BN grains were observed on the Cu(111) surface. It is considered that the edge of triangular h-BN grains have zigzag edges and a previous theoretical study suggested that edge structures of h-BN with terminating nitrogen atoms are more stable in triangular grains.[8] Therefore, it is likely that obtained h-BN grains

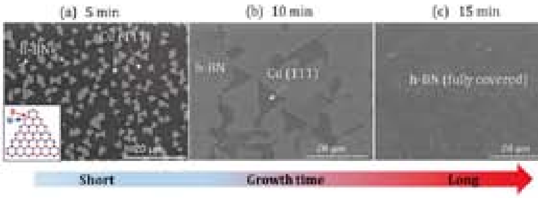

Figure 2. SEM image of CVD grown h-BN grains on heteroepitaxial Cu(111) film at reaction time of 5 min (a), 10 min (b) and 15 min (c). Inset of a is atomic model for triangular h-BN grain with zigzag edges terminated by nitrogen atoms.

have zigzag edges with terminating nitrogen atoms (Inset of Figure 3(a)). As can be seen in Figure 2(a), most of the h-BN grains are oriented in two specific directions. The existence of these two preferred orientations indicates an epitaxial growth of the h-BN on the Cu(111) surface. By extending the CVD growing time, the lateral size of h-BN grains increase, after long enough growing periods grains completely coalesce, and a uniform h-BN sheet covering the entire Cu surface can be obtained. This result suggests that h-BN grows preferentially on a Cu catalyst compare with the surface of h-BN.

An orientation of as-grown h-BN on a Cu(111) film was measured by LEED. Because a beam size of LEED we used is about 1mm, it is possible to investigate a macroscopic orientation of h-BN on Cu(111). Figure 3(a) shows LEED pattern measured with 100 eV and the six clear spots which are derived from both h-BN and Cu(111) lattices were measured. Therefore, the diffraction pattern obtained by LEED measurement support a epitaxial growth of h-BN on the Cu(111) suggested by SEM observation.

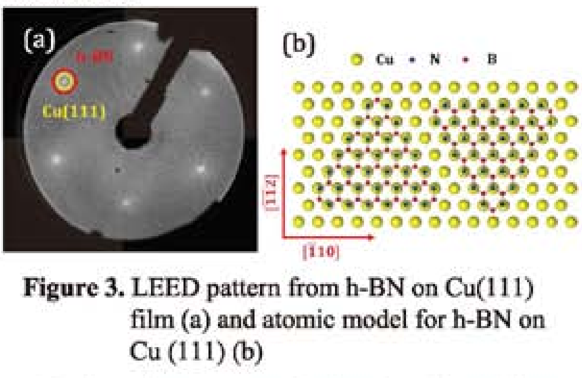

Figure 3. LEED pattern from h-BN on Cu(111) film (a) and atomic model for h-BN on Cu (111) (b)

To investigate growth behavior of multi-layer grains on Cu(111) film, CVD reaction was carried out by increasing concentration of sublimated gaseous intermediates which is 5 times higher than the concentration for growth of fully covered single layer h-BN film. After growth was finished and grown film was transferred onto SiO_2, points of optical contrast which can be distinguished from SiO_2 surface was observed as shown in Figure 4(a) and E_{2g} peak which corresponds with in-plane vibration of h-BN layer was measured in relatively strong parts of the optical contrast by Rama spectroscopy while this peak was not observed in parts of no contrast (Figure 4(b)). To investigate surface conditions and morphologies of multi-layer grains, AFM measurement was carried out and it was found that each of multi-layer grains is oriented in two specific directions (Figure 4(c)). This results suggested that multi-layer grains of h-BN is

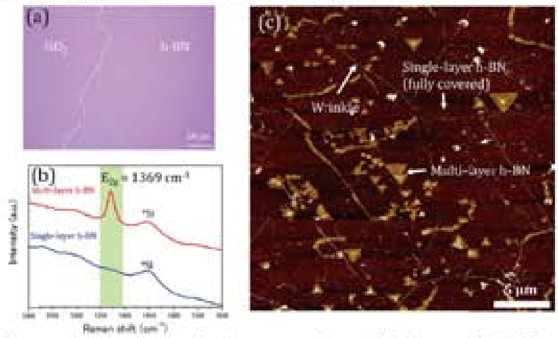

Figure 4. Optical image of multi-layer h-BN transferred onto SiO_2 substrate (a), Raman spectra measured on multi-layer and single-layer spots and AFM image of multi-layer h-BN transferred onto SiO_2 substrate (c)

epitaxially grown on single layer h-BN and orientations of multi-layer grains can be controlled by using single-layer h-BN films having well aligned grains.

4. Conclusion

Single-layer h-BN was grown by CVD on epitaxial Cu(111) thin film. The h-BN sheet was characterized by SEM, LEED and XPS. The epitaxial Cu(111) film enabled the orientation-controlled growth of single-layer h-BN, giving triangular h-BN crystals aligned in certain direction. Furthermore, we obtained well aligned single-layer h-BN sheet by extending reaction time. Furthermore, we succeeded to obtain well aligned multi-layer grains by growing on single-layer h-BN film on epitaxial Cu(111) thin film.

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