CITY UNIVERSITY OF HONG KONG

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Studying the Effect of Carbon Substrates on Cubic Boron Nitride Film Growth

立方氮化硼膜生長於碳基底的研究

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Abstract

Cubic BN (cBN) is the material with the second highest hardness, elastic modulus and thermal conductivity next to diamond. It is, however, superior to diamond in higher graphitization and oxidation temperatures and chemical inertness to molten ferrous materials. These properties make cBN the best material for mechanical applications involving steels and all ferrous materials. Cubic BN is also a potential candidate for construction of high-power and high-speed electronic devices owing to its high thermal conductivity and electronic properties. It has a wide bandgap (~6.2 eV), high carrier mobility and doping capacity for both n- and p-type conductivity, while n-type doping of competitive diamond is still questionable. The wide bandgap characteristic makes cBN suitable for ultraviolet (UV) detectors and UV light emitting diodes (LEDs). The extreme properties also make cBN films very attractive for space and nuclear fusion applications.

Many types of substrates have been used at cBN synthesis, but because of the mismatch of physical and chemical parameters of the substrate and cBN as well as their compatibility, many cBN syntheses have had very poor outputs. Cubic BN films often grow via an intermediate amorphous/turbostratic (aBN/tBN) layer on many substrates. The energetic ion bombardment essential for cBN formation and the existence of soft and humidity sensitive aBN/tBN precursor layers lead to high compressive stress, poor film adhesion and stability as well as limited film thickness (<200 nm) and thus hamper practical applications.

This research work studies the effect of carbon substrates on cBN film growth and provides evidences that carbon substrates are generally suitable for cBN growth particularly because of carbon chemical nature. Carbon systems are compatible with BN systems and can be used in many cases of cBN deposition as interlayer to enhance adhesion and functionality of the films. The carbon substrates employed in this study

are amorphous tetrahedral carbon (ta-C) and nanocrystalline diamond (nanodiamond) films deposited on silicon substrates.

Introducing ta-C as interlayers enables deposition of more adherent cBN films with higher cubic phase content and better crystalline quality than those prepared on bare Si substrates. The partial transformation of ta-C interlayers at high deposition temperature (~900 °C) with the effect of ion bombardment results in some graphitic carbon structures with basal planes preferentially oriented perpendicular to the substrates. High-resolution transmission electron microscopy (HRTEM) combining with elemental mappings using electron energy loss spectroscopy (EELS) show that oriented tBN grows directly on the restructured carbon interlayer without intermediate amorphous BN layer. The cBN films grown on these interlayers are stable in ambient environment. The film stability is provided by carbon atoms in the interfacial zones. Carbon atoms diffuse and passivate the reactive boron-dangling bonds at BN/C interface. The thermally driven carbon diffusion is enhanced by unceasing ion bombardment. The dense sp^3-bonded carbon structure at the interface in addition confines the residual reactive boron sites and acts as a barrier obstructing water and oxygen diffusion into these sites. Thus, it precludes oxidation reaction and formation of unstable boron oxide and oxyhydrides that otherwise would lead to film delamination. The restructured carbon interlayer also improves the crystallinity of the oriented tBN layer because of their similar structure which consequently results in reducing the nitrogen-void defects and enhancing the film stability.

The effect of nanodiamond buffer layer on the nucleation and growth of cBN film is studied based on detailed HRTEM analyses. The direct growth of cBN on nanodiamond crystals without aBN/tBN interfacial layers is found owing to the similarity in lattice parameters and physical properties of cBN and diamond as well as nanocrystalline nature of both materials. Some cBN crystals grow on diamond nanocrystals with twinning orientation. Epitaxial relation of $(111)_{cBN}$ parallel to $(111)_{Diamond}$ planes is observed as well as small-angle cBN/diamond grain boundaries

of about 5-6 degrees because of the slight lattice mismatch. It is also found in some local areas that oriented tBN nucleates on amorphous carbon region serving as cBN nucleation sites. The cBN and surface layers are well crystallized without notable hBN/tBN inclusions. Cubic BN nanocrystals seem to extend directly to the film surface while tBN/aBN structures covering the cBN crystals are hardly observed. The reason is attributed to the considerable reduction of ion kinetic energy during film growth.

The phase composition and crystallinity of cBN films were also been are usually investigated by spectroscopic methods, such as visible Raman and Fourier transform infrared (FTIR) spectroscopy. However, cBN signal in visible Raman analysis does not usually emerge when the structure is nanocrystalline and highly defective, especially for films prepared by physical vapor deposition (PVD). In this research work, cBN films grown on nanodiamond by radio-frequency magnetron sputtering (RF-MS) at record low bias voltage (-35 V) among PVD methods are investigated by ultraviolet (UV) Raman spectroscopy. The UV Raman spectroscopy is obviously more powerful for hBN identification in contrast to FTIR analysis owing to a very large scattering cross-section of hBN structure at UV light excitation. In comparison to FTIR spectroscopy, UV Raman scattering is demonstrated herein to identify the crystalline quality of thick cBN films. It also enables the quantitative estimation of cBN content of thick cBN films contrasting the FTIR analysis which is influenced by the interfacial structure and film thickness.

The mechanical properties of cBN/nanodiamond multilayer coatings are investigated by nanoindentation measurements and compared with those of individual cBN and nanodiamond layers. The residual stresses are estimated using an optical interference method. The deposition time of each layer was well controlled in order to obtain equivalent thicknesses (~100 nm) of all consecutive layers. Engineering the cBN/nanodiamond multilayer enhances the properties of individual materials and introduces novel properties of the multilayer coating. The much lower stress confined

in multilayer film as compared with single-layered cBN film extends the interest for using cBN/nanodiamond multilayer films in cutting tools and tribological applications.

Briefly the major and pioneering contributions of this work to the presented field are:

i)   Synthesis of thick films (>1 µm) on carbon substrates. Limitation is particularly in deposition rate which can significantly be increased by scaling up the system and deposition power used.

ii)   Record low bias voltage (–35 V) ever applied for PVD growth yielding cBN films.

iii)   Considerably improved crystallinity of cBN films prepared by PVD method.

iv)   Original study of the role of carbon at passivation of boron-dangling bonds for preparation of thick and stable cBN films.

v)   First study and detection of traces of hBN in cBN films, which are below the detection limit of conventional FTIR technique, using UV Raman spectroscopy.

vi)   Design and fabrication of the first cBN/nanodiamond super-lattices with extreme mechanical properties (hardness of 82 GPa) and exceptional smooth surface morphologies (roughness of 9.8 nm).

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