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Direct nucleation of hexagonal boron nitride on diamond: Crystalline properties of hBN nanowalls

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ABSTRACT

Hexagonal boron nitride (hBN) nanowalls were deposited by unbalanced radio frequency sputtering on (100)-oriented silicon, nanocrystalline diamond films, and amorphous silicon nitride (Si_3N_4) membranes. The hBN nanowall structures were found to grow vertically with respect to the surface of all of the substrates. To provide further insight into the nucleation phase and possible lattice distortion of the deposited films, the structural properties of the different interfaces were characterized by transmission electron microscopy. For Si and Si_3N_4 substrates, turbostratic and amorphous BN phases form a clear transition zone between the substrate and the actual hBN phase of the bulk nanowalls. However, surprisingly, the presence of these phases was suppressed at the interface with a nanocrystalline diamond film, leading to a direct coupling of hBN with the diamond surface, independent of the vertical orientation of the diamond grain. To explain these observations, a growth mechanism is proposed in which the hydrogen terminated surface of the nanocrystalline diamond film leads to a rapid formation of the hBN phase during the initial stages of growth, contrary to the case of Si and Si_3N_4 substrates.

1. Introduction

Boron nitride (BN) materials have attracted much attention in recent years [1], due to a wide variety of promising future applications for coating and related technologies [2–5]. Hexagonal boron nitride (hBN) has a structure similar to graphite, in which B and N atoms are bound alternatively in in-plane hexagonal rings forming two dimensional (2D) sheets, which are held together by van der Waals forces, forming the hBN lattice. hBN can be synthesized into nanostructured films, such as nanowalls, with tunable properties depending on the growth parameters, to make it insulating, highly compressible, or to improve its lubricity [1,5]. Grown hBN structures have so far shown a considerable number of defects and disordered BN phases, i.e. amorphous and turbostratic boron nitride (aBN and tBN), particularly at the initial stages of thin film growth. The presence of those phases is largely dependent on dynamics of chemical reactions at the substrate surface [1]. A substrate material that reduces these defective phases, creating a direct interface to the hBN phase, is therefore highly desirable.

Many excellent properties of diamond, such as a negative electron affinity on hydrogen terminated surfaces, mechanical hardness, chemical inertness, and good thermal conductivity [6–9], make nanocrystalline diamond (NCD) thin films an interesting potential substrate material for hBN. For example, field electron emission devices that take advantage of the NEA of NCD thin films and the electric field enhancement factor of hBN nanowall structures, are an exciting potential application for these materials [10]. This work seeks to understand the nucleation and early growth phase of hBN layers on different substrates, including NCD films, by investigating the role of the different substrate surfaces on the crystallinity of the deposited hBN nanowalls at the BN-substrate interface.

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2. Experimental details

2.1. Substrates

Three types of substrates were used for hBN film growth – Si (100), NCD grown on Si (100), and amorphous Si_3N_4 membranes. 1×1 cm^2 Si (100) substrates were cut from a single side polished *n*-type Si wafer 500–550 μm in thickness, with a resistivity of 10–20 Ω cm, obtained from WAFERNET, INC. Si(100) substrates were cleaned using a standard cleaning procedure [11]. The 300 nm thick NCD layers were deposited on the same Si (100) substrates, with deposition conditions that will be given in Section 2.4. The membrane is a 35 nm-thick amorphous Si_3N_4 film supported on a 500 μm-thick silicon frame with a 100×100 μm^2 electron transparent window, obtained from TED PELLA, INC. The samples studied in this work are summarized in Table 1.

2.2. Deposition of the hBN films

hBN thin films were synthesized in a home-built, unbalanced 13.56 MHz radio frequency (RF) sputtering system using optimized process conditions for nanowall formation, as determined in our previous work, i.e. a gas mixture of Ar(51%)/N_2(44%)/H_2(5%) and cathode power of 75 W [12]. A 3 inch diameter pyrolytic BN ceramic target (Kurt J. Lesker) with 99.99% material purity and a mass density of 1.96×10^3 kg/m^3 was used as the sputtering target. The working pressure and target-to-substrate distance were fixed at 2.1×10^{-2} mbar and 3 cm. The samples were unintentionally heated during the thin film deposition, due to reactive gas ion bombardment on the substrate surface [13]. The substrate temperature during growth was monitored through a thermocouple probe with a EUROTHERM 2408 controller, and was measured to be 125 °C for all of the depositions in this work.

2.3. Optical, morphological and TEM characterization

Optical properties of the films were characterized by Raman spectroscopy with a HORIBA Jobin Yvon T64000 spectrometer using a blue laser (488 nm) in backscattering mode [14]. The Fourier transformed infrared (FTIR) transmission spectra of the films were taken at room temperature with a NICOLET™ 8700 spectrometer [15]. The FTIR measurements were performed normal to the film surface from 400 to 4000 cm^{-1} with a resolution of 2.0 cm^{-1}, and the transmission spectrum of a bare Si (100) substrate was used as a baseline. Morphological properties of the films were investigated by electron microscopy using an FEI Quanta 200F field emission gun scanning electron microscope (FEG-SEM).

High resolution transmission electron microscopy (HRTEM) was performed on a JEOL 3000F microscope, equipped with a high-brightness Schottky-field emission electron source, and a high-resolution Gatan Imaging Filter (GIF2000) [16]. 80 kV accelerating voltages were used to minimize knock-on damage to the soft hBN material while retaining high contrast between the C, B, and N elements with similar atomic number (*Z*) [17]. 300 kV FEG accelerating operation voltages were used for annular dark field scanning TEM (ADF STEM) experiments, with the convergence and collection semi-angles in the range of 20–22 mrad. The TEM point resolution is 1.9 Å, and probe current and the energy spread are 0.5 nA and 1.2 eV, respectively.

2.4. NCD film growth

Si(100) substrates were seeded by spin-coating, using a 3.3×10^{-4} kg/L water-based colloidal suspension of detonation nanodiamond particles with average size of 5–10 nm [18]. The NCD thin films were then grown by microwave plasma enhanced chemical vapor deposition (MWPECVD) in an ASTeX 6500 reactor, using a gas composition of 99% H_2 (396 sccm)/1% CH_4 (4 sccm), a working pressure of 25 Torr, and a microwave power of 2500 W. The substrate temperature of 680 °C was constant for all the NCD growth runs and was monitored by single color optical pyrometry, assuming an optical emission coefficient $\varepsilon = 0.3$. The film thickness was measured *in situ* during growth from the interference fringes of the reflection spectrum of a 405 nm diode-pumped solid state laser, and the deposition was stopped when the film thickness reached 300 nm. The resulting diamond film showed well-faceted grains, as seen in Fig. 1. These grains form as a result of the process of evolutionary selection of diamond, which assumes that a cubic diamond crystal consists out of the {001} and {111} faces. The growth of those grains occurs by propagation of these faces, of

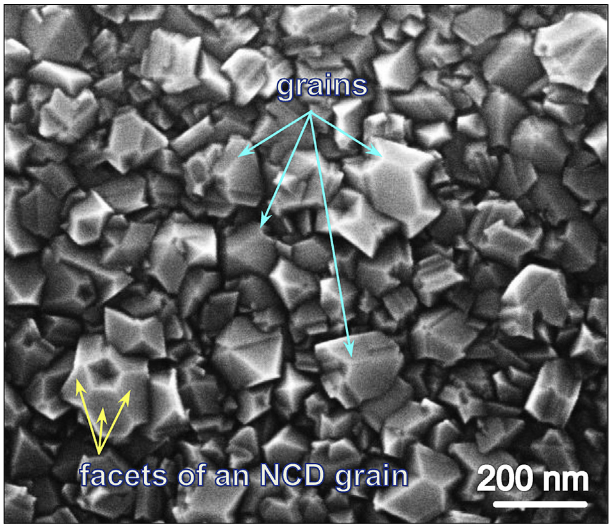

Fig. 1. SEM image of the 300 nm-thick NCD film grown on a Si(100) substrate showing well-faceted grains.

Table 1
Samples studied in this work. TEM preparation methods for the purpose of thinning the samples to electron transparency refer to: gentle ion milling (IM) encapsulation and focused ion beam (FIB) techniques. T3 was only grown to a thickness of 100 nm thus remained electron transparent.

Sample name	Substrate	hBN thickness (nm)	TEM preparation method	Deposition time (t_d) (min)	Average growth rate (R_G) (nm/h)
T1	Si (100)	300 ± 18	IM	79	228 ± 18
T2	NCD	300 ± 25	FIB	54	333 ± 25
T3	a-Si_3N_4 membrane	100 ± 18	–	26	231 ± 18
Si1	Si (100)	250 ± 16	–	66	228 ± 16
D1	NCD	370 ± 27	–	66	336 ± 27
Si2	Si (100)	700 ± 33	–	150	280 ± 33
D2	NCD	800 ± 39	–	150	320 ± 39
Si3	Si (100)	1080 ± 38	–	240	270 ± 38
D3	NCD	970 ± 41	–	240	242 ± 41