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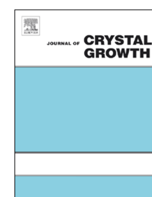

Metalorganic chemical vapor deposition of few-layer sp^2 bonded boron nitride films

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A B S T R A C T

A systematic study of the growth of atomically smooth few-layer sp^2 bonded BN on 50 mm sapphire substrates by metalorganic chemical vapor deposition (MOCVD) using Triethylboron (TEB) and NH_3 as precursors is described. Based on the experimental results obtained using Raman spectroscopy, atomic force microscopy (AFM), X-ray reflectance measurements and transmission electron microscopy, we explored the growth parameter space and identified three different growth modes: random three-dimensional (3D) growth, a self-terminating few-layer growth mode, and a very slow layer-by-layer mode. The growth mode depends on the temperature, pressure, V/III ratio, and surface nitridation conditions, as follows: 3D island growth is dominant in the low V/III range and is characterized by a decreasing growth rate with increasing deposition temperature. When the V/III ratio is increased this 3D island growth mode transitions to a self-terminating few-layer growth mode. An additional transition from self-terminating growth to 3D growth occurs when the growth pressure is increased. Very slow layer by layer growth is found at high temperature and low pressure. Finally, substrate surface nitridation promotes self-terminating growth that results in atomically smooth films.

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1. Introduction

Scalable growth of two dimensional (2D) materials on insulating substrates would be a major step towards realizing commercial scale 2D devices. In particular, sp^2 bonded BN is of interest as the insulating substrate or dielectric because of its structural similarity to graphene, wide band gap, good dielectric properties and excellent thermal conductivity. However, achieving this goal presents a variety of challenges: scalable uniform growth, growth on insulating substrates, and precise thickness control down to the monolayer level, all of which require a thorough understanding of the mechanisms and process space involved in growth of a 2D van der Waals material on a 3D substrate.

Chemical vapor deposition (CVD) of BN on catalyzing transition metal substrates (Ni, [1] Cu, [2,3] Pt, [4] Rh, [5] Ru, [6]) has been well-demonstrated for scalable growth of few to mono-layer material. CVD growth on single-crystal transition metals under UHV has been shown to be a surface-limited process [1,7,8]) – that is, after a full mono-layer is formed, the growth rate significantly decreases or stops completely. However, these films require transfer to insulating substrates for device fabrication, which can introduce defects and contamination. On the other hand, metalorganic chemical vapor deposition (MOCVD) has demonstrated scalable epitaxial growth of BN films on sapphire and other substrates [9–11]), but lacks precise thickness control and uniformity. Recently, our group described a MOCVD technique for producing ultra-thin films with uniform thickness over 50 mm diameter substrates [12–14]. We demonstrated that for certain V/III ratios, substrate temperatures, and growth pressures, the growth mode could be changed from random 3D nucleation to 2D self-terminating growth, resulting in 5 monolayer thick films.

In this context, our previous studies focused on process condition effects in isolation. Herein we investigate the overall process space, providing a cogent summary of the growth modes within that space. We expand on earlier work to detail the interacting effects of deposition temperature, pressure, V/III ratio, and sapphire substrate nitridation conditions. By exploring a wide process space we are able to develop correlations between multiple process parameters and the different growth modes. Characterizations by reflection high energy electron diffraction (RHEED), X-ray reflectance (XRR), atomic force microscopy (AFM), Raman, transmission electron microscopy (TEM) and optical spectroscopy were used to identify the structure, surface/layer properties and phase of the BN films.

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2. Experiment

Boron nitride films were grown at low pressure by MOCVD in a reactor with an actively cooled, close-coupled showerhead. For this work the growth temperature was varied from 1000 to 1100 °C and the pressure was varied from 20 to 500 Torr. Films were grown using hydrogen as the carrier gas and Triethylboron (TEB) and NH_3 as the boron and nitrogen precursors. The V/III ratio was controlled by varying either the TEB flux at a constant NH_3 flow of 500 sccm, or the NH_3 flow at a constant TEB flux of 10 μmol/min. More details can be found in our previous work [12]. To examine the film thickness vs. growth time, the deposition time was varied from 1 to 60 min. Standard epi-ready c-plane sapphire substrates were used as delivered and heated in hydrogen to growth temperature for 5 min. prior to deposition. Most of the results described below were obtained without a pre-growth nitridation step. In the cases used to study nitridation, a low temperature low ammonia-to-hydrogen ratio (~1%) anneal was carried out at 300 Torr for 10 min. producing a ~1 nm thick AlON layer as described in our previous work [14].

The BN film thickness was characterized by X-ray reflectance (XRR) using a PANalytical Empyrean X-ray diffractometer at a grazing incidence angle. Proper alignment was carefully checked before each measurement, and film thickness was obtained by fitting to the measured reflectance using a layered model with the BN density constrained between 2 and 2.9 g/cm^3. The surface structure was investigated by RHEED, which was used to determine the relationship between film and substrate in-plane orientation. Samples were transferred to a separate vacuum system and then a 20-keV electron beam was used to examine the surface. The surface morphologies of the BN films were analyzed by AFM using a Bruker Dimension Icon in tapping mode. Cross sectional TEM was used to examine the microstructure of BN layers. The TEM-ready samples were prepared using the in-situ FIB lift out technique on an FEI Dual Beam FIB/SEM. The samples were then imaged with a FEI Tecnai TF-20 FEG/TEM operated at 200 kV in high-resolution (HR) TEM mode. To characterize the optical properties of resulting ultra-thin BN films, optical transmission spectra were obtained using a PerkinElmer Lambda 900 UV/visible scanning spectrophotometer in the wavelength range of 200–800 nm. To correct for the sapphire substrate, the measurements were performed using a sapphire substrate in the reference leg. In addition, Raman measurements were performed using a Renishaw inVia system under a backscattering geometry with scattered radiation collected along the sapphire [0001] direction. An accumulation of 120 scans, each of 30 s duration, was collected using a 4 mW 488 nm excitation source, 20 μm slits, and a 3000 line/mm grating for each measurement. For nitridation experiments, the sapphire surface before and after nitridation was characterized using XRR, X-ray photoelectron spectroscopy (XPS), and AFM to establish a baseline for BN measurements.

3. Results and discussion

It was apparent from the beginning that V/III ratio had an important influence on BN growth [14]. In this study, 30 min depositions were performed at different V/III ratios in temperatures range from 1000 to 1100 °C, and at first, with a fixed reactor pressure of 20 Torr. Typical XRR curves for BN films on sapphire grown at 1050 °C and various V/III ratios are shown in Fig. 1a. The XRR curves are very similar until V/III ratio is reduced below 1800; below this ratio, the XRR curves shift dramatically as V/III is reduced to 450. This corresponds as an increase in average film thickness, which is notable for V/III ratios from 900 to 450. BN thicknesses deduced from fitting XRR curves for growth

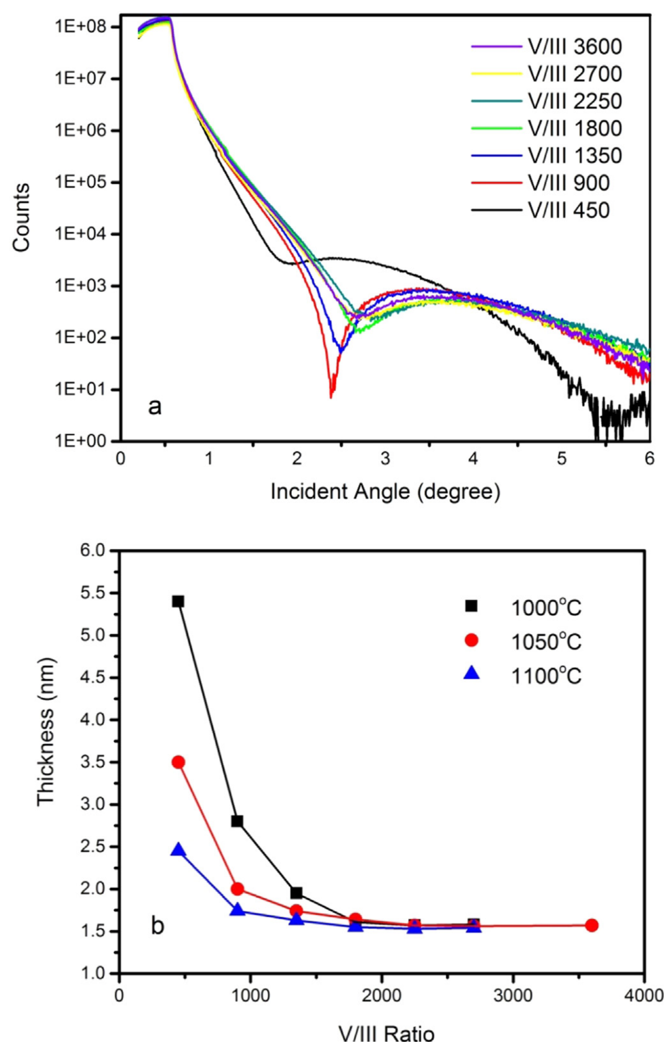

Fig. 1. BN film thickness measured by X-Ray reflectance (XRR) as a function of V/III ratio. (a) XRR curves of a series of BN films grown at 1050 °C using various V/III ratios. (b) BN film thicknesses derived from XRR fitting vs. V/III ratio for three different growth temperatures. All growth processes were conducted under 20 Torr for 30 min.

temperatures of 1000 °C, 1050 °C and 1100 °C are shown in Fig. 1b. An average layer thickness of ~1.6 nm was consistently observed on all films grown using V/III ratios greater than 2250, corresponding to a thickness of ~5 atomic layers. Below a V/III of 2250, thickness increases as V/III ratio is reduced, with the effect being more pronounced at lower deposition temperatures. At the lowest V/III ratio (450), and for some samples at a V/III of 900, films become very rough at low temperature. XRR fitting results cannot represent the real film thickness, since roughness could be greater than the average film thickness. In these cases, we used the average value of the peak-to-valley difference measured from AFM as an approximate film thickness.

Fig. 2 shows film thickness as a function of deposition time for different deposition temperatures and V/III ratios, all under a deposition pressure of 20 Torr.[1] At low V/III ratios (450 and 900), fairly constant growth rates are observed, with a strong dependence on growth temperature. The results show a nearly linear increase of film thickness with time when at a V/III of 450; this is typical behavior for continuous 3D island growth. The growth rate decreases as V/III ratio is increased to 900 and 1800; that is, the

[1] The 'error bars' in Fig. 2a for a V/III of 450 indicate the maximum and minimum peak-to-valley difference from AFM measurements, since the roughness prevents reliable estimates of thickness from XRR.

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