

OMCVD Growth of Boron Nitride Films from Single Molecular Precursors

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1. Introduction

Recently, the deposition of cubic boron nitride (cBN) has been intensively studied because of its similarities to diamond and diamond-like carbon. cBN is an interesting material since it has almost the same hardness and thermal conductivity as diamond, and is a III-V compound semiconductor. Therefore, cBN film is promising not only as a hard coating, but also as a heat sink for electronic devices and as a semiconductor material.

There are two crystalline phases of BN that are analogous to phases of carbon. hBN has a layered structure which is sp^2 -bonded structure similar to that of graphite, and is the stable ordered phase at ambient conditions. cBN has a zinc blende structure with sp^3 -bonding like diamond, and is the metastable phase at ambient conditions. Also like carbon, there are amorphous and poorly crystalline forms of BN having sp^2 -bonding. Conventionally, significant progress has been made in the experimental techniques for synthesizing cBN films using various methods of physical and chemical vapor deposition. But the major disadvantage of cBN films is that they are much more difficult to synthesize than diamond films due to its narrow stability phase region, high compression stress, and problem of boron or nitrogen source control.

Recent studies of the organometallic chemical vapor deposition of III-V compounds have established that a molecular level understanding of the deposition process is mandatory in controlling the selectivity parameters. This led to the concept of using single source organometallic precursors, having the constituent elements in stoichiometric ratio, for OMCVD growth of the required binary compounds. A similar strategy is warranted in the CVD of BN to switch the balance from hexagonal to cubic phase by tailoring the organometallic precursor having boron and nitrogen in 1:1 stoichiometry.

In this study, therefore, we have carried out the low pressure OMCVD growth of hBN films on Si(100) substrates using $\text{Et}_3\text{BNH}_2(\text{tBu})$, $\text{Et}_3\text{BNH}_2(\text{tPr})$, and $\text{Et}_3\text{BNH}(\text{tPr})_2$ as single source precursors.

2. Experimental

CVD was carried out in a simple vacuum chamber made of quartz. Si(100) substrates used in the present study were cleaned and etched using standard procedure. The precleaned substrates were mounted on the sample holder and then the precursors were admitted into

the deposition chamber. The deposition was carried out for 5 ~ 14 hours after which the substrates were slowly brought to ambient temperature. Several independent experiments were carried out between 850 and 1,000 °C without carrier gas. The temperature of substrate/film was detected by an optical pyrometer and the pressure during deposition was adjusted between 50 and 90 Pa. The films produced were characterized by XPS, XRD, SEM, FT-IR, and Raman spectroscopy.

3. Results and Discussion

CVD was carried out using $\text{Et}_3\text{BNH}_2(^i\text{Bu})$, $\text{Et}_3\text{BNH}_2(^i\text{Pr})$, and $\text{Et}_3\text{BNH}(^i\text{Pr})_2$ as single source precursors in the temperature range of 850 ~ 1,000 °C. Fig. 1 shows the X-ray diffraction pattern of the BN film deposited on a Si(100) substrate using $\text{Et}_3\text{BNH}_2(^i\text{Bu})$ at 850 °C. The diffraction pattern shows a hint of hexagonal boron nitride (*h*BN) formation, since the *h*BN coating exhibits a relatively intense BN(002) peak at $2\theta = 26.8^\circ$. There is no other detectable phase in the diffraction pattern. However, the quality of the film is judged poor, and the film surface consists of minute grains.

Fig. 2 shows the X-ray photoelectron survey spectrum of the BN film deposited on a Si(100) substrate at 850 °C using $\text{Et}_3\text{BNH}_2(^i\text{Bu})$. The survey spectrum clearly shows the photoelectron peaks of Si 2s, Si 2p, B 1s, and N 1s which indicate formation of hexagonal boron nitride (*h*BN) film on the Si(100) surface. From the survey spectrum and high resolution XP spectra of the BN films, we believe that the films deposited on Si(100) substrates have hexagonal structure. Both the B 1s and N 1s core level spectra of the BN films show loss features at ≈ 9 and 25 eV higher binding energies than the main peaks, which are characteristic of *h*BN. Besides these relevant peaks, there also appear C 1s and O 1s photoelectron peaks and C(KVV) and O(KVV) Auger electron peaks. Surface carbon and native oxygen can be attributed to surface contamination of the newly formed films by air and the precursor during sample transfer and deposition, respectively. But, with increasing the substrate temperature, B_4C is strongly formed along with *h*BN.

In Fig. 3, a typical X-ray diffraction pattern of the BN film deposited using $\text{Et}_3\text{BNH}(^i\text{Pr})_2$ at 900 °C is shown. The result indicates that the film is also *h*BN because the characteristic peaks due to *h*BN are seen at a 2θ value of $\approx 27^\circ$. But Fig. 4 indicates that the BN films are more polycrystalline than Fig. 1.

Fig. 4 shows the X-ray diffraction pattern of the BN film deposited on a Si(100) substrate using $\text{Et}_3\text{BNH}_2(^i\text{Pr})$ at 1,000 °C. In this case, the X-ray diffraction pattern shows that amorphous BN films are obtained.

4. Conclusions

We have grown hexagonal boron nitride (*h*BN) films on Si(100) substrates by low pressure organometallic chemical vapor deposition using $\text{Et}_3\text{BNH}_2(^i\text{Bu})$, $\text{Et}_3\text{BNH}_2(^i\text{Pr})$, and $\text{Et}_3\text{BNH}(^i\text{Pr})_2$ as single molecular precursors in the temperature range of 850 ~ 1,000 °C. This growth temperature is much lower than those of previous reports, and this is also the first report of *h*BN films formed from these precursors. With increasing the substrate temperature, however, B_4C films are strongly formed along with *h*BN, and the BN films obtained from $\text{Et}_3\text{BNH}_2(^i\text{Pr})$ and $\text{Et}_3\text{BNH}(^i\text{Pr})_2$ are mostly polycrystalline.

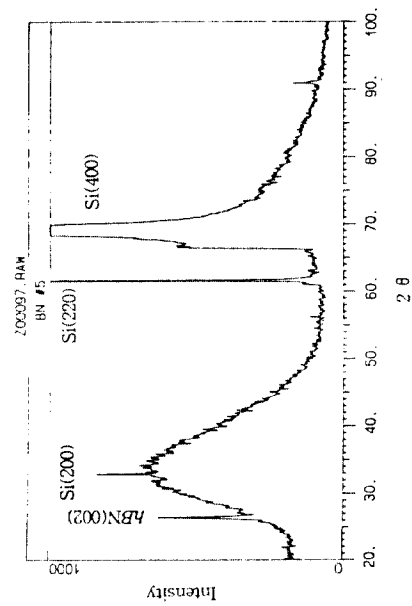


Fig. 1. X-ray diffraction pattern of the film deposited using $\text{Et}_3\text{BNH}_2(i\text{Bu})$ at 850 °C on a Si(100) substrate.

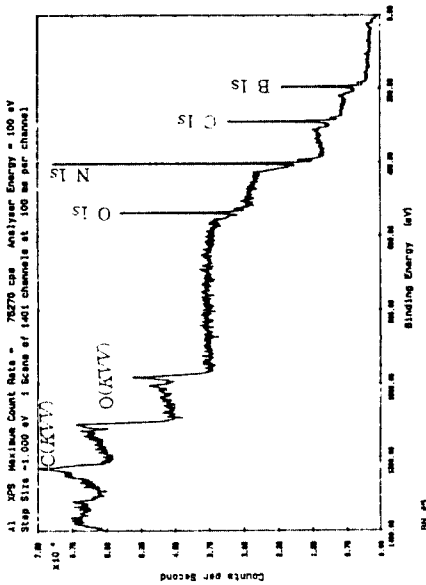


Fig. 2. X-ray photoelectron survey spectrum of the film deposited using $\text{Et}_3\text{BNH}_2(i\text{Bu})$ at 850 °C on a Si(100) substrate.

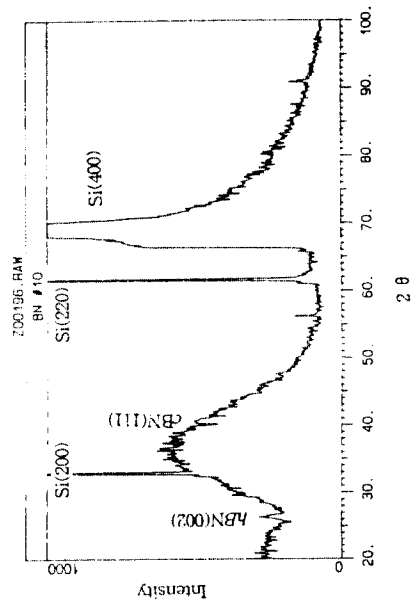


Fig. 3. X-ray diffraction pattern of the film deposited using $\text{Et}_3\text{BNH}_2(i\text{Pr})_2$ at 900 °C on a Si(100) substrate.

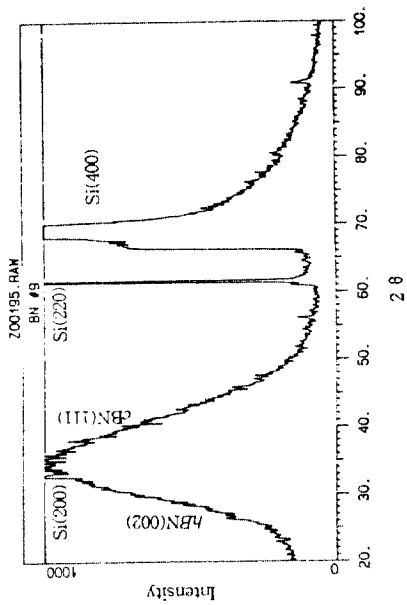


Fig. 4. X-ray diffraction pattern of the film deposited using $\text{Et}_3\text{BNH}_2(i\text{Pr})$ at 1000 °C on a Si(100) substrate.