MOCVD Growth of Boron Nitride Films from Single Source III–V Precursor†

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The sp[2] and sp[3] phases of boron nitride (BN) have been deposited on Si and Ni substrates by low pressure MO-CVD (metal organic chemical vapour deposition) at 450 °C from diethylaminoborane and the films were characterised by Fourier transform infrared (FTIR) and X-ray diffraction (XRD); a plausible mechanism of CVD is proposed from gas-phase decomposition studies, and to our knowledge this is the first report of the growth of BN by MO-CVD using a single source.

Recently, thin film deposition of cubic boron nitride has been studied intensively because of its similarities to diamond and diamond-like carbon. Many variants of the physical vapour deposition[1,2] and chemical vapour deposition[3–9] conditions have been manipulated to selectively obtain cubic boron nitride (c-BN) over hexagonal boron nitride (h-BN). The results are often serendepitous and no clear mechanism has yet been described.

Recent studies of the metal organic chemical vapour depositions (MO-CVD) of III–V and II–VI compounds have established that a molecular level understanding of the deposition process is mandatory in controlling the selectivity parameters.[10] This led to the concept of using a single source organometallic precursor, having the constituent elements in stoichiometric ratio, for MO-CVD growth of the required binary compound.[11] A similar strategy is warranted in the CVD of boron nitride to switch the balance from hexagonal to cubic phase by tailoring the organometallic precursor having boron and nitrogen in 1 : 1 stoichiometry. Here, we report the low-pressure MO-CVD growth of BN using diethylaminoborane (DEAB) as the single source precursor.

CVD is carried out in a vertical silica reactor, the details of which are described elsewhere.[12] The reactor is equipped with a substrate holder, internal pressure monitor gas inlet and outlet, the latter being connected to the vacuum manifold through cold traps. The deposition zone is provided with selective internal- as well as external-heating facilities. Silicon substrates used in the present study were cleaned and etched using standard procedures.[13]

In a typical run the precleaned‡ substrates were transferred into the substrate holder under a nitrogen atmosphere. The vapour of DEAB (b.p. 84 °C at 4 mmHg) was transported into the reactor and the deposition was carried out for 12 h after which the substrates were slowly brought to ambient temperature under nitrogen and finally stored *in vacuo*. Several independent experiments were carried out between 350 and 550 °C and by replacing the nitrogen carrier gas with a mixture of ammonia and nitrogen (1 : 1 ratio).

The deposited films of BN were characterised by XRD and FTIR.§ A typical FTIR spectrum of BN film on Si is shown in Fig. 1. In most cases the distinct features of the spectrum are a strong asymmetric band near 1380–1400 cm^{-1} and two sharp peaks at 1022 and 1097 cm^{-1}. These peaks and the bands always distinguish h-BN and c-BN. The position of these absorption peaks are practically the same for all the deposited layers. The two peaks at 734 and 796 cm^{-1} are considered to be those of the h-BN. The strong peaks at 1400 and 1380 cm^{-1} correspond to B–N band stretching vibrations and the weaker at 734 and 796 cm^{-1} bands assigned to B–H stretching mode is observed, the peak at 3225 cm^{-1} is attributed to O–H stretching. The two sharp peaks observed at 1022 and 1097 cm^{-1} are considered to be corresponding to B–N stretching vibration of c-BN. In addition, we observed a peak at 602 cm^{-1} which is due to Si–Si bonding. Assuming the c-BN bands appear in the region between 1022–1097 cm^{-1} and h-BN band around 1380–1400 cm^{-1}, the relative proportions of these two phases are found to be 1 : 3 ratio in the films deposited on Si substrate at 450 °C.

In Fig. 2, a typical XRD (Fe-Kα radiation) pattern of the film prepared at 450 °C is shown, in case of the reactant gas flow rates were kept constant at the optimum deposition conditions. A diffraction peak which appears at an angle $2\theta = 57.1°$ (d = 2.06 Å) is due to the line of JCPDS h-BN. This phase is considered to be a highly crystalline BN which has a lattice constant 3.61 Å with the c-axis elongated slightly. Another diffraction line but less intensive is found at the same angle $2\theta = 33.4°$ as that of JCPDS c-BN.

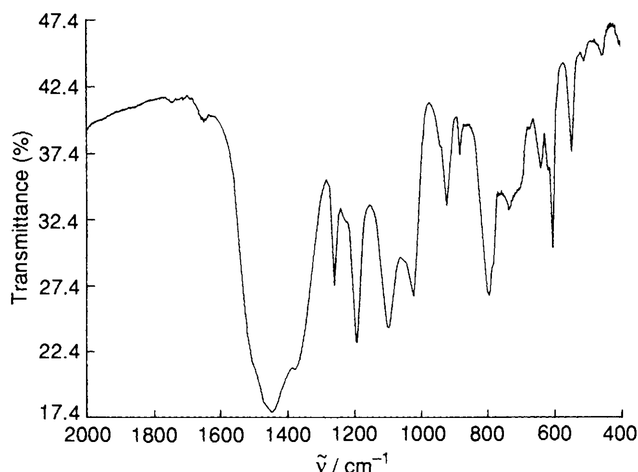

Fig. 1 FTIR spectrum of BN deposited on Si at 450 °C

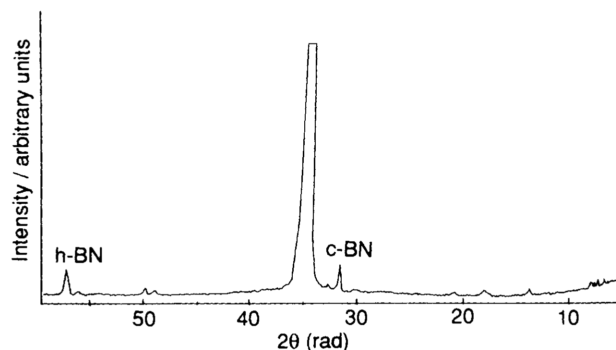

Fig. 2 XRD pattern of BN deposited on Si at 450 °C

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‡ *Experimental conditions*: Internal substrate temperature = 450 ± 2 °C; external deposition zone temperature = 400 ± 5 °C; internal pressure before the introduction of DEAB = 1 mbar (1 bar = 10^5 Pa); during the deposition = 200 mbar; Carrier gas extra pure N_2 (containing less than 4 ppm of total impurities), flow rate = 65 ± 5 ml min^{-1}.

§ XRD was performed on Philips PW 1140 Fe-Kα radiation, FTIR, was recorded on a Nicolet 740 spectrometer and GC was performed using Sigma Instrument.

The XRD profile of the film on Ni substrate at 450 °C consists of three sharp peaks and two relatively weak lines. The sharp diffraction peak centred at d = 3.16 Å and a small peak at d = 1.59 Å are attributed to the (100) and (103) orientations of hexagonal symmetry, respectively. The (111) reflection of c-BN correspond to the diffraction centred at d = 2.08 Å. Two sharp diffraction peaks due to Ni substrate have also been observed at d = 2.03 and 1.76 Å correspond to (111) and (200) orientations, respectively. However, from the XRD data it appears that the content of c-BN phase in the film deposited on Ni substrate is low as compared with that of Si substrate, which is attributed to the surface energy of the substrate. It is obvious that the arrival of h-BN and c-BN molecules during the film growth must be controlled by the substrate surface. The exact role of substrate in the growth mechanism is being studied and the results will be reported later. Although we have not obtained a single-phase crystalline film, the c-BN and h-BN phases of these samples rank the highest among the reported to have been grown from the vapour using a single source precursor, with regard to the crystallinity as revealed by XRD.

Growth mechanism of BN: The mechanism of MO-CVD is an area that is very little understood.[14] Earlier studies on the CVD of BN was confined to the reaction of NH_3 and B_2H_6, and suggested the pre-formation of aminoborane intermediate H_2BHH_2 with finally decomposes to BN liberating hydrogen.[15] In our preliminary studies to understand the mechanism of MO-CVD of BN from DEAB, the latter was subjected to *ex situ* decomposition under the CVD conditions and the volatile products were analysed by GC against authentic samples. Under such experimental conditions DEAB results in the formation of a mixture of C_2H_6 and C_2H_4 in 1:2 relative ratio. The fact that no free amine or borohydride could be observed, therefore, suggest a unimolecular decomposition pathway. The initial steps of mechanism would involve (*i*) β-hydrogen elimination of ethylene and (*ii*) reductive elimination of ethane from DEAB. Towards a total description of the mechanism, *in situ* monitoring of decomposition products are underway in our laboratory.

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