Bull. Mater. Sci., Vol. 17, No. 3, June 1994, pp. 219–224. © Printed in India.

Thin films of boron nitride grown by CVD

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MS received 11 May 1993; revised 15 March 1994

Abstract. For the first time, thin films of boron nitride were deposited by chemical vapour deposition on to polished silicon and other metal substrates using the inorganic compound H_3BNH_3 (aminodiborane) and ammonia as carrier gas. The substrate temperature was varied from 400 to 600°C. The films were chemically inert and adherent to the substrates. The FTIR spectrum of the film showed B–N–B absorption at $800\,cm^{-1}$, B–N stretching at $1056\,cm^{-1}$, and also a weak absorption at $1340\,cm^{-1}$ corresponding to B–N–B bending vibration. Deposited films also exhibited X-ray diffraction pattern with interplanar spacing with (002) plane of hexagonal boron nitride.

Keywords. Aminodiborane; chemical vapour deposition; boron nitride.

1. Introduction

Boron nitride (BN) possesses high thermal stability, is chemically stable in aggressive media and can exist as cubic BN (C–BN), hexagonal BN (h-BN) and rhombohedral BN (r-BN). The crystalline form of c-BN is known as an abrasive. Thin amorphous nitride films are used in microelectronics as a source of boron diffusion in silicon. Hexagonal BN is known to form corrosion-resistant and insulating film which can be used in a high-temperature molten salt or corrosive gaseous environment. A relatively high resistance of the film to thermal shock also gives possibility of its use as a refractory container where rapid heating or cooling is required. Chemical vapour deposition (CVD) of BN has been studied by many investigators using thermal decomposition of BCl_3 using NH_3 (Powell *et al* 1962; Sano and Aoki 1981; Motojma *et al* 1989). Apart from CVD, many other techniques to deposit c-BN films have been investigated. These include activated reactive evaporation with a gas activation nozzle (Inagawa *et al* 1987), arc-like plasma-enhanced ion plating (Ikeda *et al* 1991), ion beam deposition (Ikeda 1992), plasma chemical transport (Saitoh and Yarbrough 1991a), electron beam-assisted hot filament CVD (Chaudhari *et al*, submitted), and r.f. plasma CVD (Saitoh and Yarbrough 1991b). However, the obtained films consist of c-BN and h-BN. The content of c-BN phase in the film was not very high. Of all the techniques employed so far, CVD is the most common and involves formation from reactive compounds by thermal means. These techniques generally require a high substrate temperature. For BN deposition by the thermal CVD technique handling of toxic and hazardous starting materials such as B_2H_6, BCl_3, BBr_3, etc. is often required. In our present investigation, BN films were deposited on polished Si wafers and Ni substrates by using a single-source precursor containing both boron and nitrogen.

2. Experimental procedure

Aminodiborane (ADB), the single-source precursor, is a solid that can be volatilized under vacuum. This material is prepared by treating sodium borohydride ($NaBH_4$) with ammonium carbonate in the presence of tetrahydrofuran (THF) solvent for about 14 h in N_2 atmosphere. The contents are filtered to obtain H_3BNH_3 which is slowly soluble in THF. THF is distilled out to obtain crystalline white solid of H_3BNH_3.

BN was deposited by CVD using ADB with ammonia as carrier gas in a flow system. A schematic diagram of the apparatus is shown in figure 1. At the centre of the horizontal quartz reactor, substrates were kept slanted and located downstream of the NH_3 outlet. The inorganic compound ADB was kept outside the furnace and was heated by using a coil heater (up to 200°C slowly). The distance between the substrates and the source was 5 cm. Silicon substrates used in the present study were degreased with warm isopropyl alcohol, washed with deionized water and etched with HF acid followed by rinsing with running deionized water, and finally blown dry with N_2 and quickly loaded into the reactor. Ni substrates were cleaned similarly except that HF acid was replaced with HCl.

Prior to reaction, the reaction tube was flushed with N_2 and the substrates placed in the deposition zone and heated to the deposition temperature at a pressure of 1 mbar. The vapours of ADB were transported by ammonia as carrier gas at a flow rate of 40 ml/min, the total internal pressure being adjusted to 500 mbar. The deposition was carried out for 12 h after which the substrates were slowly brought to room temperature under N_2 atmosphere and finally stored *in vacuo*. The films were characterized by FTIR (Nicolet 740), XRD (Phillips PW 1140 with FeK_α radiation) and SEM (Hitachi S 520).

3. Results and discussion

3.1 *FTIR spectra*

Films deposited on polished silicon wafer at two different temperatures were studied by FTIR. The distinct features of the spectrum of samples deposited at 500°C are strong asymmetric bands near 800 cm^{-1} and 1056 cm^{-1} and weaker bands at 1312 cm^{-1}. The positions of these absorption peaks were practically the same for the

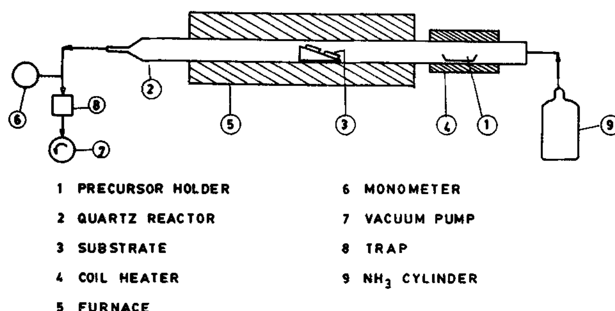

Figure 1. Schematic diagram of CVD reactor for BN deposition.

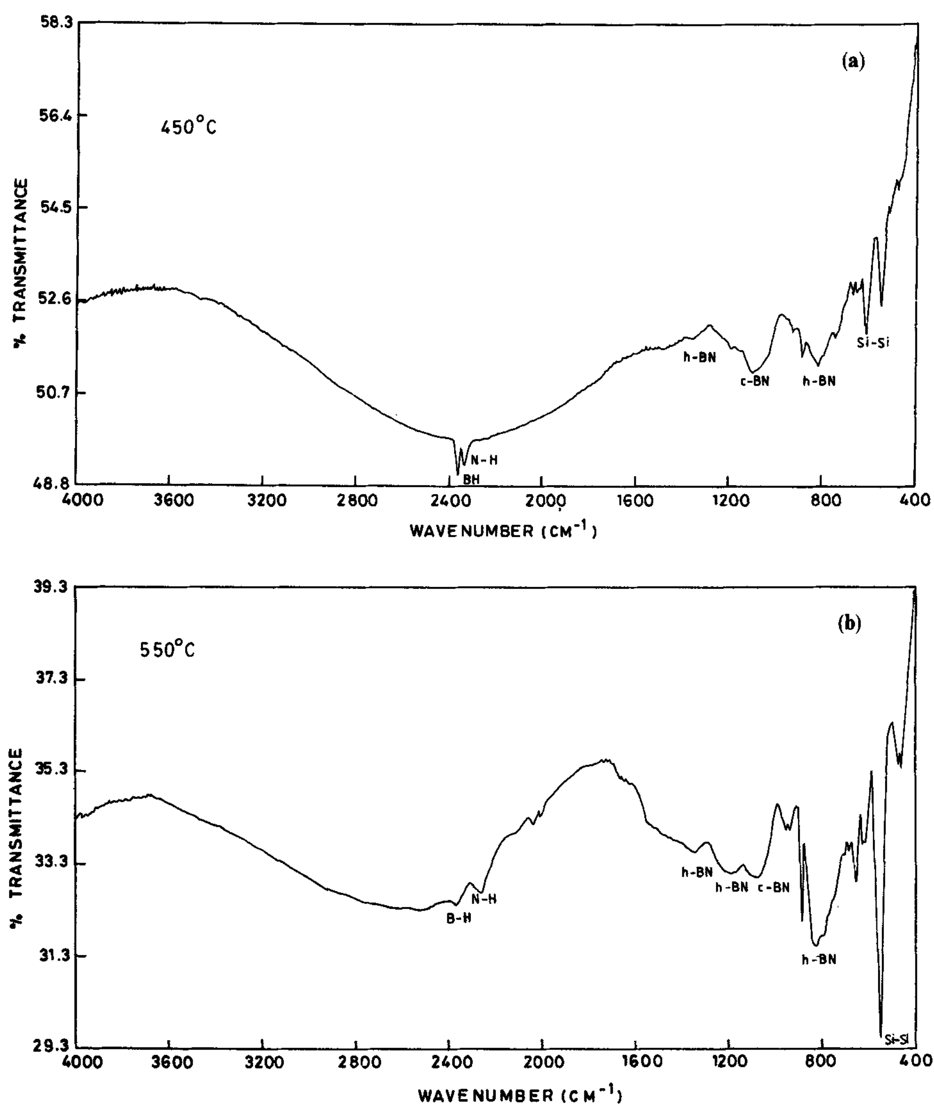

Figure 2. FTIR spectra of BN films on Si.

samples deposited at 450°C, as shown in figure 2. FTIR absorption measurements on BN films have been published by several workers (Takahashi *et al* 1979; Paul *et al* 1990; Bath *et al* 1991; Maya and Haugh 1991). The two peaks observed at $1056\,cm^{-1}$ and $800\,cm^{-1}$ correspond to those of c-BN and h-BN respectively. The strong peak at $800\,cm^{-1}$ corresponds to B–N bond stretching, and the weaker band at $1312\,cm^{-1}$ is attributed to B–N–B bending. Small peaks at $2430\,cm^{-1}$ have been assigned to N–H stretching mode, while no peaks were observed at $3300\,cm^{-1}$ for O–H bending.

In the light of the above we conclude that, in our case, the deposited BN films contain both the phases of BN, i.e. h-BN and c-BN. It is also noteworthy that films deposited on silicon substrates at 550°C and 450°C show absorption at $624\,cm^{-1}$

due to Si–Si bond vibration along with peaks of very weak intensities at 544, 878 and 1168 cm^{-1}. Besides the above, we have also analysed the unreacted compound by FTIR, which shows peaks at 790 and 1400 cm^{-1} attributed to B–N stretching, and 1045 and 1575 cm^{-1} attributed to B–N–B bending.

3.2 *XRD characteristics*

X-ray diffractograms of BN films deposited at 550°C on silicon and nickel substrates are shown in figure 3. The XRD of BN/Ni (at 550°C) film shows distinct peaks due

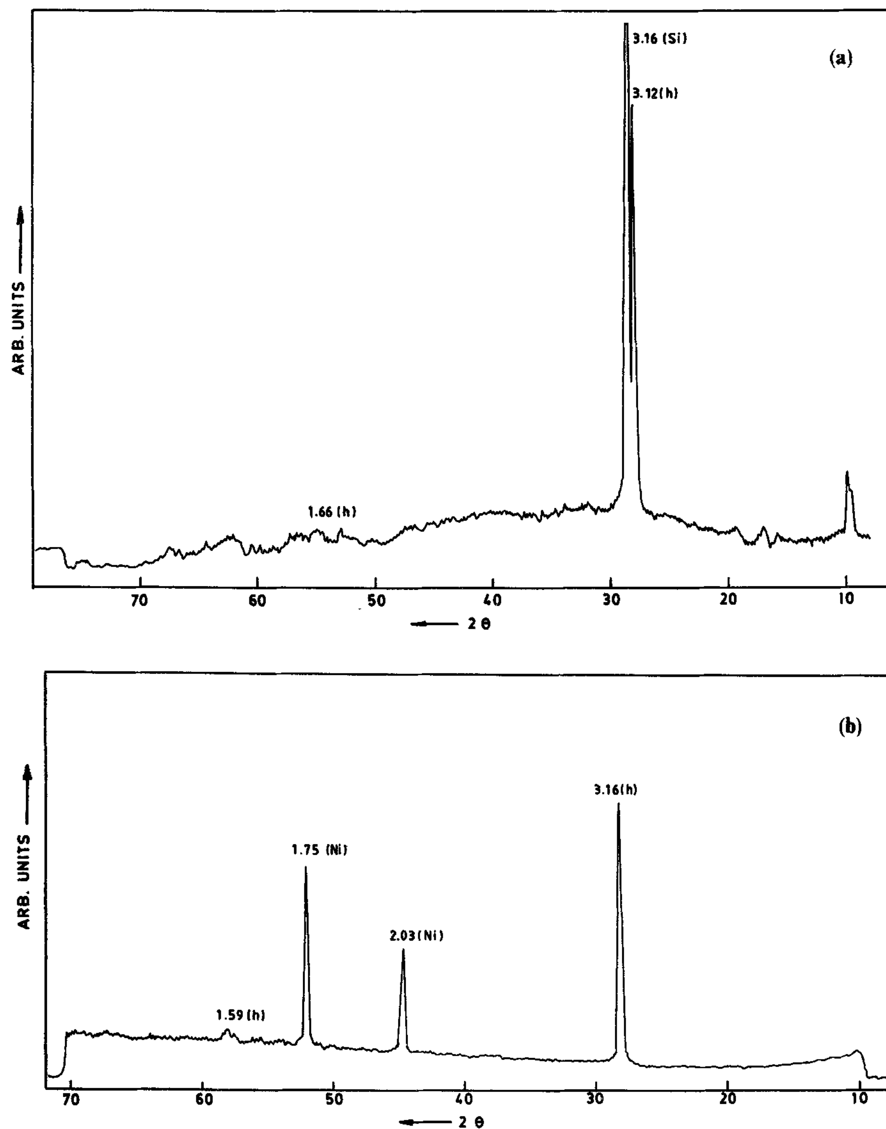

Figure 3. X-ray diffractograms of BN films: (a) BN/Si at 550°C; (b) BN/Ni at 550°C.

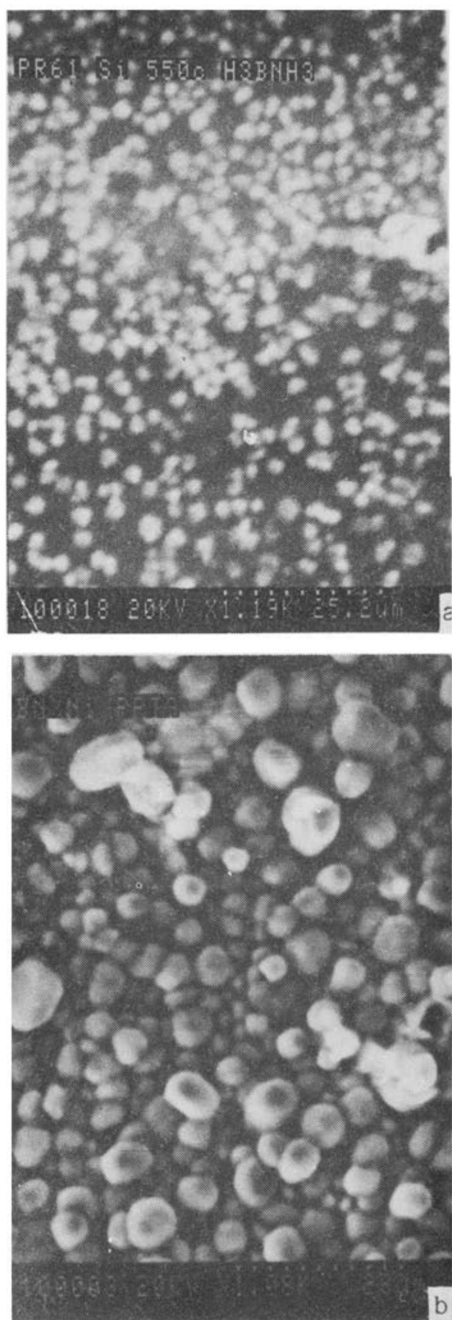

Figure 4. Scanning electron micrographs of BN films deposited on **(a)** Si and **(b)** Ni at 550°C.

to h-BN at $d = 3{\cdot}33$ Å. Similarly the XRD pattern of BN/Si film shows h-BN peaks at $d = 3{\cdot}12$ Å and $d = 1{\cdot}66$ Å. In both the above cases, peaks due to Ni and Si are observed, which suggest that the thickness of the BN films is low. However, the peak at $d = 3{\cdot}33$ Å, corresponding to (002) plane of 100% relative intensity in h-BN, is present in the case of Si/Ni films obtained by us. It suggests that FTIR information on h-BN present in film deposited on Si as described earlier may correspond largely to its amorphous nature. An XRD pattern of the precursor collected from the boat after the reaction was also taken. The XRD pattern shows distinct peaks at angles corresponding to lattice constant values of 3·08 Å and 2·202 Å representing the (002) and (100) crystallographic planes of h-BN and c-BN respectively.

3.3 *Surface morphology*

SEM of deposited films is shown in figure 4. The films deposited at 550°C show highly crystalline BN particles. The nucleation of the crystal grains has been so initiated that they look like pebbles.

4. Conclusions

BN films were deposited by CVD from aminodiborane at 550°C in the presence of NH_3 gas. FTIR and XRD data reveal the presence of BN phases. SEM shows well-formed crystallites with uniform size for films grown on Si and Ni substrates at 550°C. Further investigations on structure and other parameters are being carried out.

Acknowledgement

The author wishes to thank Dr V J Rao for his constant encouragement and many helpful discussions.

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