

Laser physico-chemical vapour deposition of cubic boron nitride thin films

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A laser physico-chemical vapour deposition (LPCVD) technique was developed based on the interaction of an ultraviolet laser beam with a boron nitride target and borazine gas to synthesize cubic boron nitride (CBN) thin films on silicon substrates. The process involved a hybrid of pulsed laser ablation (PLA) of a solid HBN target and chemical vapour deposition (CVD) using borazine as a feed stock. The films were characterized with scanning electron microscopy, X-ray diffraction and infrared spectroscopy. Results indicate that the thin films consisted of almost single-crystalline CBN structures and that the film quality in terms of adherence, particulate density and smoothness was excellent. The purity and crystal structure of target material, laser beam wavelength and energy fluence were the key variables that controlled the film characteristics. In contrast to LPCVD, the conventional PLA method did not generate CBN films.

1. Introduction

New and novel materials are required for advanced electronics, radar and communication systems because the currently used Si and GaAs materials are not able to meet the demands of high frequency, high speed and high temperatures in these systems. Recent interest in advanced electronic materials includes diamond, cubic boron nitride (CBN) and SiC. Diamond thin films, preferably single-crystal diamonds, have been actively researched over the past decade. Little attention, however, has been paid to CBN, the material that is comparable to diamond in density, thermal conductivity and resistivity. In fact, CBN is a better semiconductor than diamond at high temperatures (800–1200 °C). CBN and diamond also have common tribological properties and are chemically inert. CBN is an attractive substrate for diamond growth because of the small mismatch in lattice constants.

Several methods have been investigated to synthesize BN thin films in cubic form. Most of these methods, however, produced mostly amorphous BN and HBN structures. A promising method for CBN deposition is based on the utilization of a laser beam for physically ablating a target by pulsed laser ablation (PLA). In this technique an intense source of laser radiation is employed to ablate the target material, leading to a highly directional flux of energetic species which are then deposited on to a substrate positioned at some distance away. PLA is a clean, fast process and is useful for producing a wide range of thin films. PLA has been successfully employed in the preparation of high-quality dielectric films, epitaxial semiconductor layers, superlattices and high-temperature superconducting oxides [1–6].

PLA offers unique benefits when compared with other physical vapour deposition (PVD) methods [2]

and hence has the potential to synthesize new and novel thin films:

(i) congruent ablation: rapid heating of the target and rapid cooling of the film on the substrate do not allow dissociation of source material, even though the constituents have different vapour pressures leading to stoichiometric films;

(ii) high kinetic energy species: the ionized and excited species ablated by the laser have high kinetic energy and velocities (10^6 – 10^7 cm s^{-1}) and thereby promote film crystallinity and dense packing;

(iii) uniformity: the plume developed during the ablation is in a narrow cone and assists in attaining films of uniform thickness;

(iv) high-purity films: low heat input followed by local evaporation tends to produce high-purity films; high energy fluence “burn” the impurities; and

(v) simple: since the method is optical, it is operationally simple.

Although our understanding of laser–material interactions has been significantly improved over the last decade, progress in PLA for thin-film deposition is slow. This may partly be due to the concurrent and successful developments in competing techniques such as molecular beam epitaxy, metal-organic chemical vapour deposition (CVD) and sputtering. In addition, the problem of particulate emission which degrades the optical and electrical properties has severely reduced the acceptance of the PLA technique.

Although PLA techniques for the growth of CBN films have been reported [7–9], continued analysis [10] of the laser-grown films revealed that the films were predominantly amorphous in nature rather than in cubic form. However, it has been clearly demonstrated [7] that laser ablation has the superior potential among other techniques including plasma, ion

beam etc. to grow CBN films. In this work, we have combined the PLA technique with a CVD method, designated LPCVD, to synthesize BN in cubic form.

1.1. Previous research

Boron nitride, one of the most interesting III–V compounds, is favoured as a thin film for several electronic devices because of its broad forbidden band, high temperature stability, resistance to radiation, high electrical resistivity, chemical inertness, high hardness and low density. Some applications of BN thin films are as follows:

- (i) high-quality insulating films for high-frequency device applications;
- (ii) thin films in integrated circuits for their stability, strongly non-ohmic high field conducting properties;
- (iii) thin-film capacitors, and thin insulating layers to increase the stability of field-effect transistors and tunneling in metal–insulator–metal structures;
- (iv) transparent substrates for X-ray lithography masks;
- (v) an insulator in metal–insulator–semiconductor memory diodes for controlling capacitance–voltage characteristics;
- (vi) films used as restricted-area boron diffusion sources for fabricating planar diodes using only one photomask;
- (vii) high-power microwave devices and optoelectronic devices;
- (viii) exoatmospheric solar blind detectors;
- (ix) substrates for diamond nucleation and growth;
- (x) wear- and erosion-resistant protective coatings; and
- (xi) high-temperature insulation and high-temperature capacitors.

The BN films prepared by CVD and PVD techniques have a refractive index in the range 1.6 to 2.0, optical band-gap from 3.6 to 6 eV, dielectric constant from 3.5 to 8, electrical resistivity 10^{14} to 10^{17} Ω cm and dielectric strength 10^6 to 10^7 V cm⁻¹ [7–27].

BN crystallizes in three structures: hexagonal, wurtzite and cubic. Hexagonal BN (HBN) is often known as white graphite because of its colour and layered structure. It has low density (2.3 g cm⁻³), low hardness (200 H_V), low electrical conductivity and high thermal conductivity. Cubic BN (CBN), on the other hand, is extremely hard (4000–6000 H_V) and possesses even higher thermal conductivity. It is also stable in air up to 1400 °C (compared to only 800 °C for diamond), making it an effective high-temperature semiconductor. Wurtzite BN (WBN) is close to CBN but is highly unstable.

Among the three forms of BN, CBN is the most attractive material for electronics because it is an excellent thermal conductor and resistor. The techniques used by many researchers to prepare CBN films include thermal CVD, low-pressure CVD [11], plasma-enhanced CVD [20, 21], sputtering [16], electron beam evaporation [22, 27], reactive evaporation [17–19], ion-beam deposition [13–15] and pulsed laser ablation [7–10, 23]. Sokolowski *et al.* pioneered

CBN synthesis [11] under low pressure by a pulsed plasma method using a gas mixture of N₂ and H₂ and a sintered boron electrode. Hirano *et al.* [12] produced CBN from borazine by gas-phase pyrolysis and pressure pyrolysis. Weissmantel *et al.* [27] reported the formation of CBN films by electron beam evaporation of boron in an NH₃ plasma. Satou and Fujimoto [14], on the other hand, used an ion beam to ionize nitrogen and bombard the substrate with nitrogen ions in the presence of boron to produce CBN films. Shanfield and Wolfson [13] deposited CBN films from borazine in an r.f.-excited ammonia plasma. They found the structure of ion-beam PVD films to be mostly amorphous with some CBN. Seidel *et al.* [24] have prepared CBN films by reactive diode sputtering; a variation of that technique using r.f. excitation produced lower growth-rate films that were not highly insulating and contained a large number of pinholes [22].

Bunshah [25] developed a process based on activated reactive evaporation that uses a non-toxic boric acid (instead of borazine or diborane) as a starting material. Bunshah's process, involving the evaporation of boric acid in an NH₃ plasma, was capable of depositing CBN films at substrate temperatures as low as 400 °C with a deposition rate of 150 nm min⁻¹. Lin *et al.* [17] used H₃BO₃ in an NH₃ discharge and Inagawa *et al.* [18] used boron in N₂ + Ar in the reactive evaporation process to synthesize CBN. However, such activated reactive evaporation and various ion-beam techniques yielded films with significant amounts of impurities such as carbon and oxygen which make the films inappropriate for applications in electronic devices [22].

Films grown by CVD techniques involving the reaction between NH₃ and B₂H₆ at high temperatures were hexagonal in structure [18]. Plasma CVD techniques using a mixture of B₂H₆ and N₂ [20] or NaBH₄ + NH₃ + H₂ [21] were used to deposit CBN films but resulted in mostly amorphous structures. Recently, Komatsu *et al.* [26] found that the impingement of a 193 nm ArF beam in plasma CVD resulted in improved crystallinity of the film. The chemisorption of BH₂ radicals, growth reactions and the migration of precursor radicals were photochemically enhanced by the use of a laser.

PLA techniques for CBN synthesis have not yet been fully explored. Kessler *et al.* [28] used a Q-switched Nd:YAG laser to evaporate wurtzite BN on to a KBr substrate, resulting in the formation of wurtzite BN film. Murray *et al.* [29] used a Q-switched Nd:YAG laser in the frequency-doubled mode (532 nm) to evaporate an HBN target on to Si <111>, producing stoichiometric HBN film. Paul *et al.* [30] used a Q-switched ruby laser (694 nm) to deposit HBN on to an InP substrate using an HBN target. Doll and his research group [7–10] reported the deposition of epitaxial CBN film on Si <100> using hexagonal BN sources and a 248 nm excimer laser. However, the films were very thin (120 nm) and contained mostly amorphous structures [10].

It is appropriate to review the work by two Japanese research groups on the laser deposition of CBN

films. Mineta *et al.* [31] used a hybrid technique combining a continuous-wave, high-power CO₂ laser and an ion-beam source to produce CBN films. Essentially, the CO₂ laser was used to evaporate the target while the ion source caused the ionization of nitrogen which subsequently imparted high energy to the film. The films obtained were predominantly cubic but they were not well ordered or epitaxial. In Mineta's process, a 1000 W continuous-wave CO₂ laser was used to evaporate a sintered HBN rod rotating at about 30 r.p.m. A Kaufman-type ion source was used to ionize and accelerate the nitrogen ions to the substrate. The substrate temperature was 800 °C. ESCA and i.r. absorption spectroscopy analysis revealed that the N/B ratio is less than 1 for films prepared without the ion supply and is close to 1 for films prepared with ion supply. In addition, X-ray diffraction and i.r. spectroscopy showed a mixture of CBN and HBN in the films. Takemoto *et al.* [32] have been investigating CBN film synthesis by laser techniques. Initially they attempted CO₂ laser ablation but found the films to consist mostly of boron with a trace of HBN. They then combined r.f. plasma and CO₂ laser ablation to deposit films composed of a mixture of CBN and HBN. After several years of research, a combination of electron cyclotron resonance with the laser ablation method proved to be the most reliable technique, yielding films that consisted of 90% CBN with a surface film of HBN that could be etched away by the Ar-ion.

2. Experimental procedure

2.1. Materials

A major factor in pulsed laser ablation is the physical characteristics of the target (purity, density and crystal-line form) which may determine the production of ionized and excited species with high velocities and thereby affect the nucleation and growth of the film. Hence four different types of BN target were studied in this work. These targets were obtained from Union Carbide (UC) and General Electric (GE) and were as follows:

1. Sintered, hexagonal BN (HBC grade from Union Carbide).
2. Pyrolytic, hexagonal BN (pBN grade from Union Carbide).
3. 92% CBN, 8% Co (BZN 6000 from General Electric).
4. 99% CBN experimental grade (B8199 from General Electric).

HBC grade is a high-purity HBN produced by the powder metallurgy technique. pBN is an extremely pure material with a laminar type of structure. pBN, produced by a patented CVD process, has improved density, thermal shock resistance, oxidation resistance, outgassing, and porosity over the HBC grade. Cubic BN targets were obtained from General Electric Superabrasives division. BZN 6000 grade contains 8% Co while B8199 is an experimental grade of cubic BN where most of the cobalt is leached out by a chemical reduction process.

For laser CVD, borazine (B₃N₃H₆) was used as a precursor and was obtained from Callery Chemical Co. Pennsylvania. Borazine consists of a six-membered planar ring containing alternate boron and nitrogen atoms, each bonded to a hydrogen atom. Since borazine itself has the same stoichiometry as BN, it is an excellent starting material for CBN synthesis. Borazine, the six-membered benzene ring type, contains significant number of B-N structural units to form high-purity films at high deposition rates. Borazine, being a liquid at room temperature, has a vapour pressure of 70 mtorr. Borazine can be thermally decomposed by the condensation reaction, which indicates the potential for laser pyrolysis to open the six-membered ring to form a linear molecule at reduced pressures in a CVD reactor.

The substrate materials chosen were Si <100> and Si <111> wafers with thicknesses of 1.6 and 0.6 mm, respectively. The surfaces of the silicon substrates were degreased in trichloroethylene and ultrasonically cleaned in methanol, followed by acid etching in HF (49%), and then dried in nitrogen. The presence of a monolayer of oxide is expected to reduce the adhesion of the film and therefore the substrates were etched long enough in HF to eliminate the oxide formation prior to deposition.

2.2. Lasers

Two lasers, the specifications of which are listed in Table I, were used to perform the deposition of CBN on silicon substrates. These lasers were a pulsed excimer laser operating at two wavelengths and a pulsed Nd:YAG laser.

2.3. Laser techniques

Two different laser procedures were employed to deposit thin films of CBN:

1. Single-beam pulsed laser ablation (SPLA).
2. Laser physico-chemical vapour deposition (LPCVD).

The experimental set-up is schematically illustrated in Fig. 1 and a photograph is shown in Fig. 2. The arrangement involved a six-way vacuum chamber which can be evacuated to less than 10⁻⁷ torr by means of diffusion and mechanical pumps. This chamber has provision for the laser beam window, gas flow, heating the substrate up to 600 °C and mounting the target. The target can be spun within the chamber using a magnetic device external to the chamber. The rotation is needed to prevent cratering of the target by the laser beams and to minimize particulate formation. The rod can rotate at various speeds up to a

TABLE I Pulsed laser specifications

Wavelength (nm)	193/248	1064
Pulse energy (J)	0.2/0.4	3
Pulse width (ns)	17/23	150000
Repetition rate (Hz)	1-100	1-10
Average power (W)	15/30	10

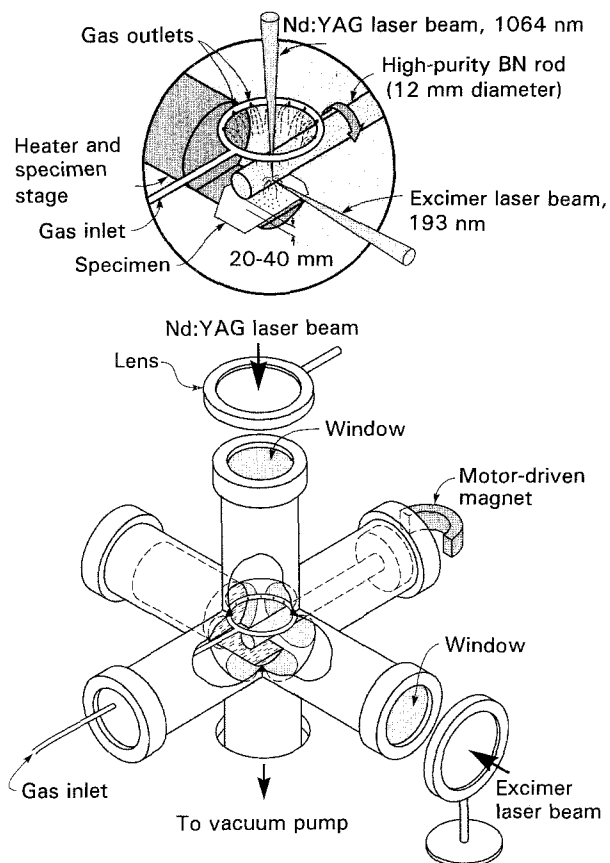


Figure 1 Schematic diagram of PLA-LPCVD deposition of CBN thin films.

maximum of 50 r.p.m. The substrate-to-target distance was varied from 5 to 25 mm. An inlet for gas flow into the chamber is also provided. A lens behind the window is located in order to focus the beam on the target. The variables for study included energy fluence ($1-6 \text{ J cm}^{-2}$), substrate temperature (100 to 550°C), target-to-specimen distance (5 to 20 mm) and environment (vacuum, nitrogen or borazine).

In SPLA, either an excimer laser operating at wavelengths 193 and 248 nm or a pulsed Nd:YAG laser was used to ablate the target. In the LPCVD technique, an excimer laser beam for simultaneously ablating the solid HBN target and dissociating the borazine gas was used. The rationale for choosing the excimer laser is due to its higher photon energy that allows the breakdown of borazine molecules. Borazine was fed at a rate of 0.3 sccm for a pressure of 0.1 torr.

2.4. Analysis of BN films

Following the experiments, the specimens were examined visually, and in scanning electron microscopy (SEM) for surface morphology, flaws and microstructural features. Crystallographic characterization of the films was carried out by X-ray diffraction (XRD) and infrared (IR) spectroscopy. For XRD the Bragg-Brentano powder method, thin-film mode and materials research diffractometer (MRD) were employed. The Bragg-Brentano method is the usual symmetrical configuration of the powder method in

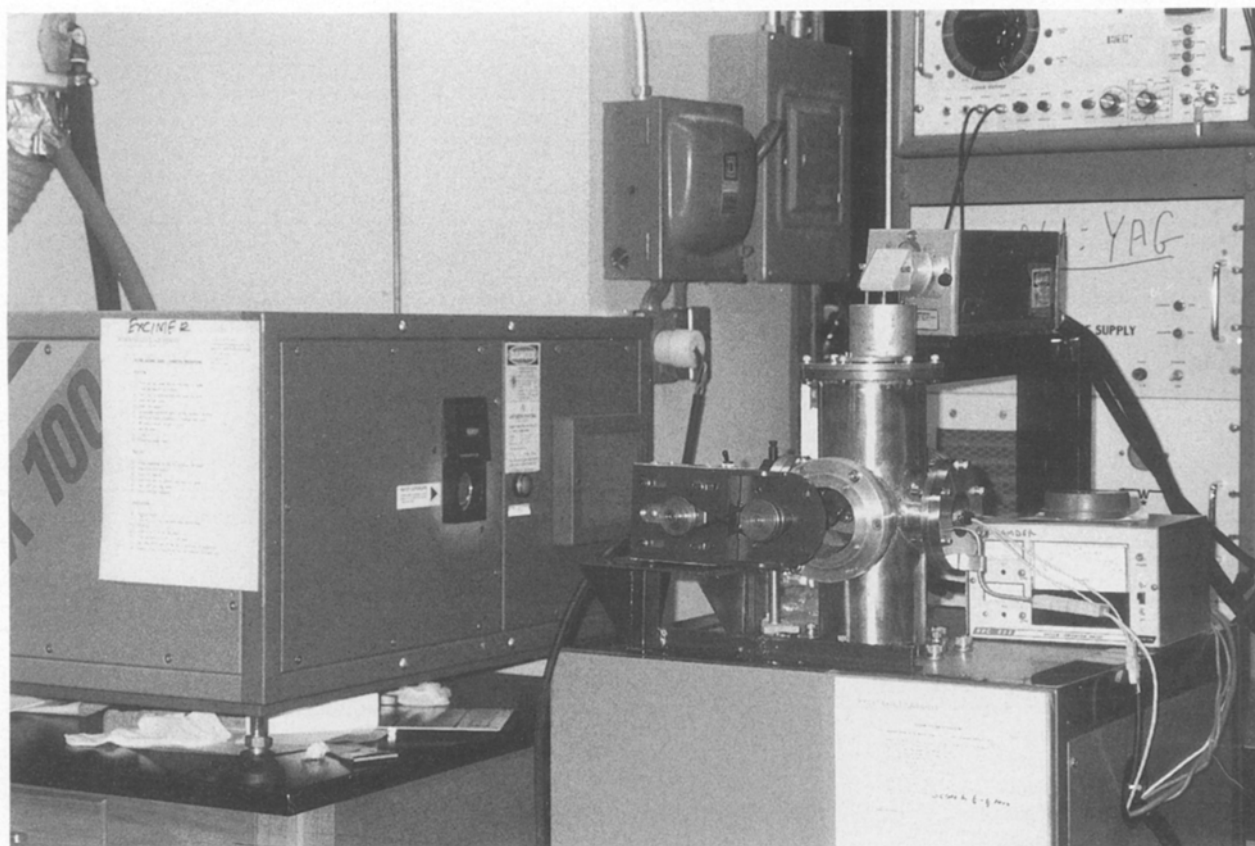


Figure 2 A photograph of PLA-LPCVD showing the excimer laser, Nd:YAG laser and vacuum chamber.

which a flat sample rotates by an angle θ while the detector rotates by an angle 2θ from the incident beam. Incident and diffracted beams are within the same plane as the diffracting normals (the diffraction plane). The focusing geometry improves resolution and intensity. In our powder diffractometer, the sample θ can be offset or decoupled from the 2θ rotation of the detector.

In contrast to the powder method, the thin-film mode is an asymmetric XRD with a constant low angle of incidence which is particularly useful for the study of thin films, since X-ray penetration is limited to a depth controlled by the angle of incidence. A parallel beam detector system is scanned over 2θ within the diffraction plane. This technique is found to be optimum for polycrystalline films. For single crystals or very textured materials, the orientation limits the patterns to very specific angles and planes. The angle of incidence is of the order of 6° . The MRD is a texture machine which can orient the sample with three angles in three perpendicular planes and, hence, is suited to single-crystal studies in which the sample

can be rotated within the diffraction plane independently of the 2θ scan, in addition to the usual rotation of the sample in two planes perpendicular to the diffraction plane. The pole figures were obtained in symmetric diffraction geometry with the 2θ angle set for the Bragg reflection with no correction.

3. Results and discussion

3.1. Single-beam pulsed laser ablation

Tables II to IV provide the experimental parameters and observations of SPLA ablation of BN targets. The significant results are as follows:

1. The Nd:YAG laser generated mostly HBN films with a large number of particulates.
2. Excimer lasers deposited a film consisting of amorphous BN and boron. ArF-excimer beam ablation deposition yielded better quality films over a KrF-excimer beam.
3. An increase in excimer laser energy fluence resulted in thicker films but produced a large number of

TABLE II SPLA of sintered, hexagonal BN target

Sample No.	Substrate-target distance (mm)	Energy density (J cm^{-2})	Deposition time (min)	Observations
4	6	5.5	60	Film fracture
5	18	4.4	30	Smooth uniform film
6	18	4.4	30	Smooth uniform film
7	18	4.4	30	Smooth uniform film
9	18	2.9	30	Extremely thin film
10	18	3.7	30	Smooth thin film
11	18	4.0	30	Smooth thin film
12	18	5.0	45	Smooth thin film
14	18	6.0	20	Smooth thick film

Laser: 248-nm KrF excimer, lens: 100 mm focal length, spot size: $4.5 \text{ mm} \times 1.5 \text{ mm}$, target: hexagonal BN rod rotated at 50 r.p.m., pulse width: 23 ns, pulse rate: 5 s^{-1} , substrate temperature: 100–500°C, vacuum: $< 10^{-7}$ torr, substrate: silicon, polished and etched in HF.

TABLE III SPLA of pBN target

Sample No.	Environment	Excimer laser parameters	Deposition time (min)	Observations
16–19	Vacuum	248 nm, 270 mJ, 10 Hz	20	Smooth film
21	Vacuum	248 nm, 400 mJ, 10 Hz	5	Smooth film
22	Vacuum	248 nm, 400 mJ, 10 Hz	10	Film fracture
26	Nitrogen	248 nm, 250 mJ, 10 Hz	15	Smooth film
30	Nitrogen	193 nm, 200 mJ, 10 Hz	60	Smooth film
33	Nitrogen	193 nm, 150 mJ, 10 Hz	60	Smooth film

Lasers: pulsed excimer at 193 and 248 nm, target-to-substrate distance: 18 mm, target rotation: 50 r.p.m., substrate temperature: 500°C.

TABLE IV SPLA of CBN targets

Sample No.	Environment	Excimer laser parameters	Deposition time (min)	Observations
20	Vacuum	248 nm, 250 mJ, 10 Hz	60	Poor ablation
24	Vacuum	248 nm, 400 mJ, 10 Hz	30	Film fracture
25	Vacuum	248 nm, 400 mJ, 10 Hz	15	Smooth film
27	Nitrogen	248 nm, 400 mJ, 10 Hz	15	Smooth film
31	Nitrogen	193 nm, 200 mJ, 10 Hz	60	Thin film

Lasers: pulsed excimer at 193 and 248 nm, target-to-substrate distance: 18 mm, target rotation: 50 r.p.m., substrate temperature: 500°C.

particulates. In addition, film cracking and fracture were observed with an increase in energy fluence.

4. When the distance between the target and the substrate was decreased, thicker and loosely attached films with a large number of particulates were obtained.

5. Substrate temperature did not affect the film properties including the adherence.

6. The film thickness was about 1 μm or less. In all the experiments, the film exhibited fringes of multiple colours indicating the variations in thickness.

7. A nitrogen environment changed the film to be more transparent.

Visual examination of the samples indicated a brown/blue film distributed over 350 mm^2 area of the sample. In thick films (greater than 1 μm), the deposit was not adherent at the centre and, in fact, was stripped off. In those films produced from the sintered, hexagonal BN target (HBC grade), SEM analysis revealed that the films contained 2–5 μm sized particles (Fig. 3). Wavelength-dispersive X-ray analysis (WDAX) identified the particles to be boron and BN compounds. Although the purity was satisfactory, the HBC grade target was flaky in nature and had a strong tendency to disintegrate into particles due to thermal stresses caused by the laser beam. The particulate formation was attributed to the sintered form of target, the short distance between the substrate and target, and high energy fluence. When the target was switched to pBN, the films were strongly adherent and contained very few particulates. Fig. 4 shows the film morphology of sample 21 deposited from the pBN target. Changing the environment of film growth from vacuum to nitrogen minimized particulates (Fig. 5) and also improved the film transparency.

The film morphology obtained using CBN targets appears to be no different from those obtained from pBN targets. Among all the targets attempted, the pBN target had the best ablation efficiency. For a pulse energy of 400 mJ and a pulse rate of 10 Hz, it required only 5 min to deposit a micrometre-sized film on silicon without any film fracture. In contrast, it required 20 min for HBC grade and over 30 min for CBN targets. The optical band gap for a CBN target is about 6.3 eV and hence the ablation rate is substantially lower than for pBN. pBN and CBN targets

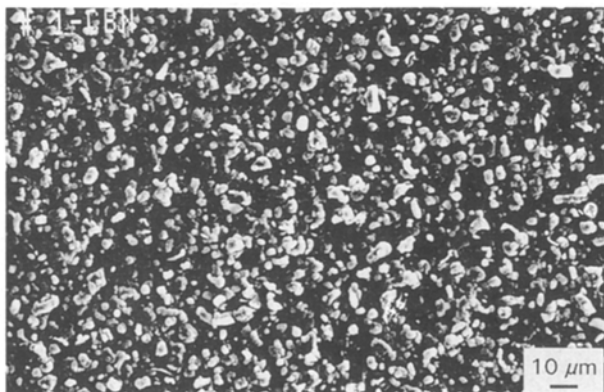


Figure 3 Scanning electron micrograph of SPLA deposited film using sintered HBN target, showing large number of particulates.

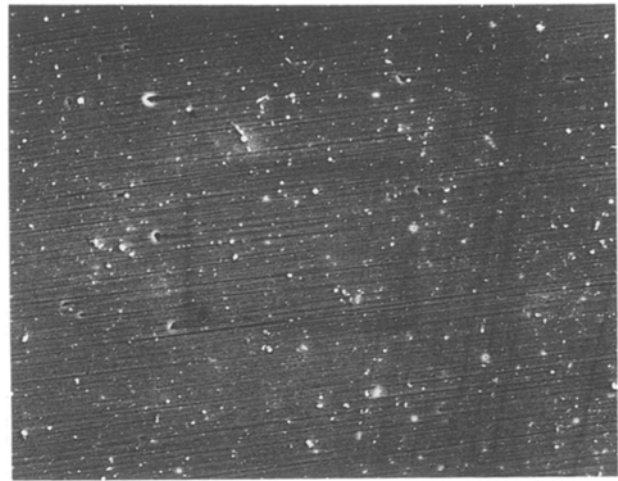


Figure 4 Scanning electron micrograph of SPLA deposited film using pyrolytic BN target, showing few particulates.

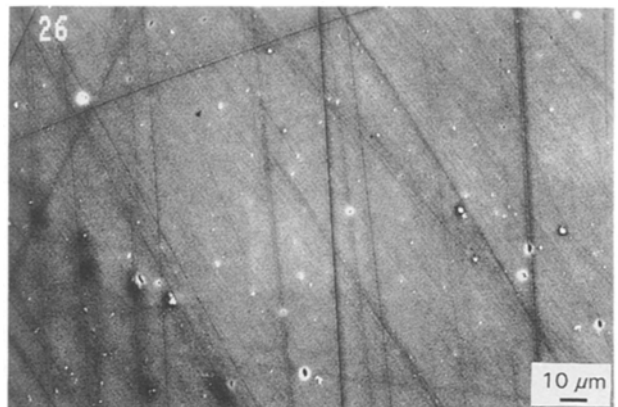


Figure 5 Scanning electron micrograph of SPLA deposited film using pyrolytic BN target under nitrogen environment.

resulted in very little particulate formation. However, film fracture occurred once a threshold or critical thickness of film was reached irrespective of the type of target. A comparison between samples 21 and 22 clearly indicates that thick films of BN could not be obtained without film fracture. The film fracture is attributed to the strain associated with the growth of BN on Si. It may be added that BN has a five times higher shear modulus than Si.

XRD and IR spectroscopy did not indicate evidence for CBN in the samples listed in Tables II to IV. The films exhibited broader, diffuse peaks in XRD, confirming the amorphous nature of the films (Figs 6 and 7). B and HBN were also detected in the films. IR spectra of these films (Figs 8 and 9) confirmed the absence of the growth of CBN.

3.2. Laser physico-chemical vapour deposition

Laser CVD using borazine in conjunction with SPLA was conducted to synthesize CBN films. The excimer beam at 193 nm was used in the parallel radiation mode (1–2 mm above the specimen surface) to cause photolysis of borazine while ablating a pBN target. The combined processing generated a transparent

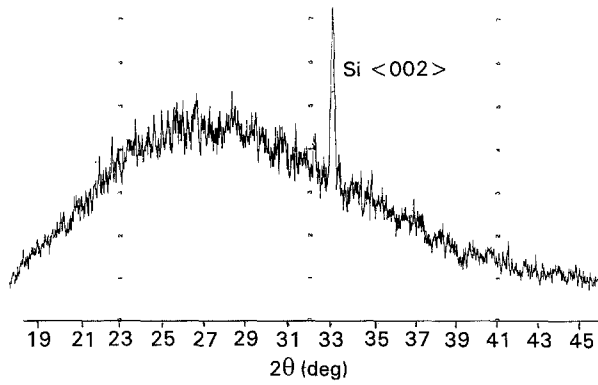


Figure 6 Powder XRD pattern of SPLA samples showing peaks for B, HBN and amorphous BN (sample 12).

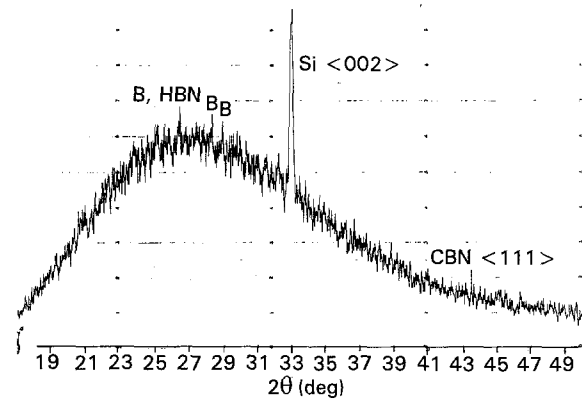


Figure 7 Powder XRD pattern of SPLA samples showing peaks for B, HBN and amorphous BN (sample 14).

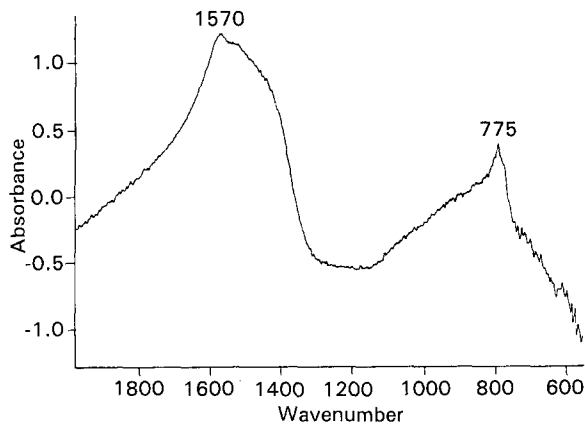


Figure 8 IR spectrum of SPLA deposited film showing the peaks for HBN (sample 12).

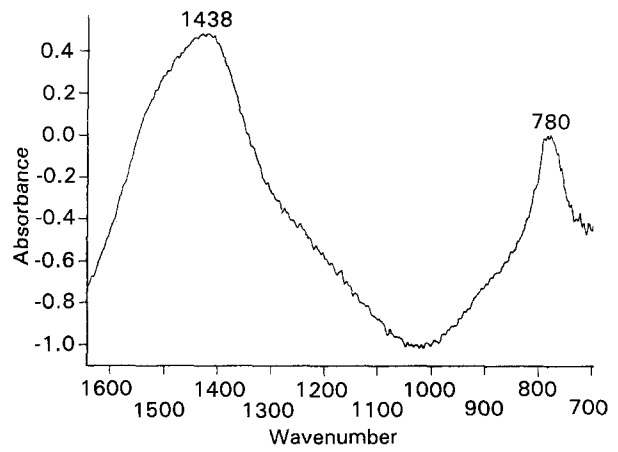


Figure 9 IR spectrum of SPLA deposited film showing the peaks for HBN (sample 14).

blue film. Table V lists the most successful experimental parameters. Extensive characterization of these films was carried out using XRD and IR spectroscopy and the results are presented below.

Using the thin-film mode on the powder diffractometer and on the MRD texture machine, five lines were generated which could not be explained by the silicon substrate (Table VI). Two of those lines with $d = 0.208$ and 0.1086 nm correspond respectively to the (1 1 1) and (3 1 1) of CBN. The other three lines do not belong to the CBN and may be an intermediate phase. Great efforts were made to determine the pole figures for the film but they were not successful.

Figs 10 and 11 show the XRD patterns in thin-film mode which revealed the main line of CBN for samples 28 and 29. However, this line would disappear if the angle of incidence was changed by $\pm 1^\circ$, indicating a very strong texture. The abrupt dependence of the patterns on the angle of incidence in the thin-film mode suggests that the film is a single crystal. As the powder diffractometer stage was rotated manually, the main line was observed at four positions at 90° from each other and at angles of incidence varying from 5.5 to 6.5° . It occurred over 10 – 15° of rotation within the plane of the film. In Figs 10 and 11, the lines at 0.208 nm are well defined and the other two lines do not belong to CBN. A remarkable fact is the complete absence of the (0 0 4) line for silicon which was always dominant in the powder mode of XRD (Bragg–Brentano). With the higher angle of incidence of 10° , the pattern in the thin-film mode has changed dramatically as shown in Fig. 12. The dominant lines in the

TABLE V LPCVD results

Sample No.	Pulse energy (mJ)	Repetition rate (Hz)	Deposition time (min)	Observations
28	200	10	15	Smooth film
29	200	10	30	Smooth film

Laser: 193 nm ArF (17 ns pulse), target: hexagonal BN rod rotated at 50 r.p.m., initial vacuum: $< 10^{-7}$ torr, substrate: silicon, polished and etched in HF, beam-to-target distance: 18 mm, substrate temperature: 500°C , gas: borazine at 0.3 torr.

TABLE VI XRD data for LPCVD deposited films

<i>d</i> (nm)	Identifying phase
0.209–0.2077	CBN
0.161	X
0.149	X
0.1167	X
0.10865	CBN

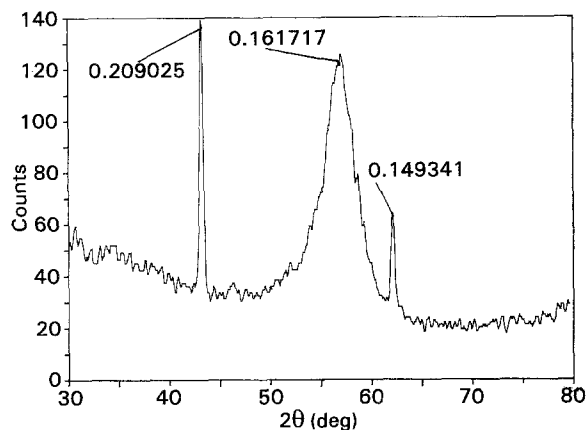


Figure 10 Thin-film mode XRD pattern of LPCVD deposited film (sample 28).

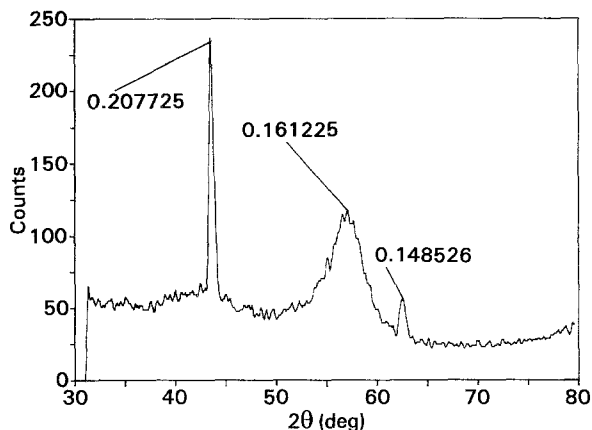


Figure 11 Thin-film mode XRD pattern of LPCVD deposited film (sample 29).

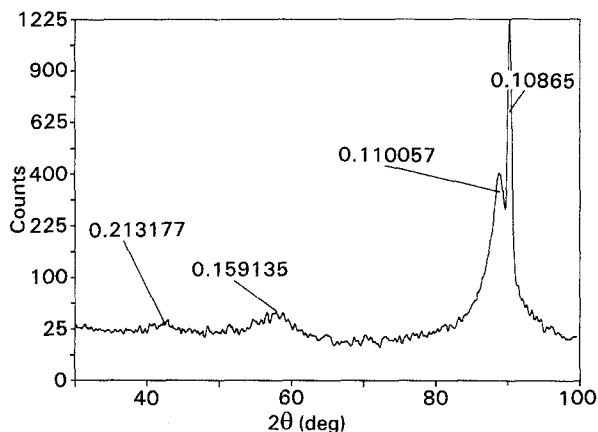


Figure 12 Thin-film mode, using higher angle of incidence, of LPCVD deposited film (sample 29).

pattern are a doublet at $d = 0.1100$ nm which corresponds to the (4 2 2) line of Si and $d = 0.1086$ nm which belongs to the (3 1 1) line of CBN. With the thin-film collimator on the texture (MRD) machine, it was possible to orient the film (in rotation) and run another scan in the thin-film mode (Fig. 13).

The broad peaks at 0.159–0.161 nm in Figs 10 and 13 were thought to be due to the (3 1 1) of silicon which has a d spacing of 0.16375 nm (JCPDS). However, the d spacing was consistently 0.002 nm too small. This was checked in detail and the MRD produced peaks at $2\theta = 57.13$ and 56.175° . At 56.175° the intensity was very high in the Bragg–Brentano mode ($> 100000^\circ\text{Cs}^{-1}$). The two peaks displayed in Fig. 14 were obtained in the thin-film mode with an incidence angle of about 3° . At this low incidence, the (3 1 1) peak of silicon is strongly attenuated.

Difficulties were encountered in the interpretation of the result because it was proved that the lines of the single-crystal silicon substrate could generate β -diffraction lines even though we have monochromators on both machines – some of the peaks are very close or overlap β peaks corresponding to the major lines of silicon. In the Bragg–Brentano mode used for pole figure determination, the β lines dominated (four out of five lines) and no pole figures could be obtained when a nickel filter was used (in addition to the monochromator). The pole figure reproduced in Fig. 15 was obtained for the one line at $d = 0.161$ nm.

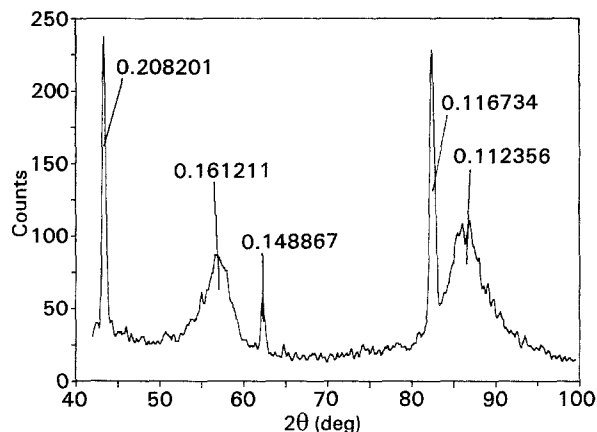


Figure 13 Thin-film mode (MRD) of LPCVD deposited film (sample 29).

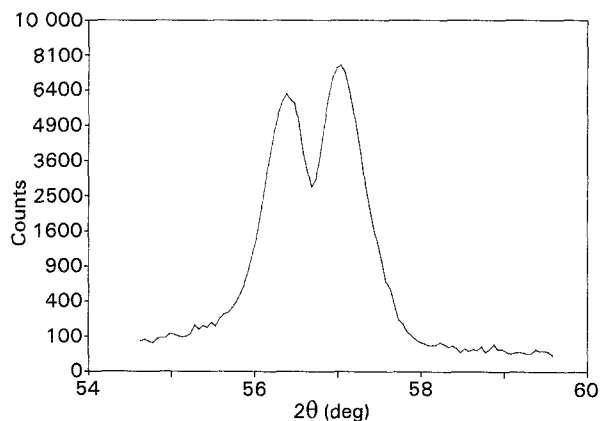


Figure 14 Thin-film mode (MRD) of LPCVD deposited film (sample 29).

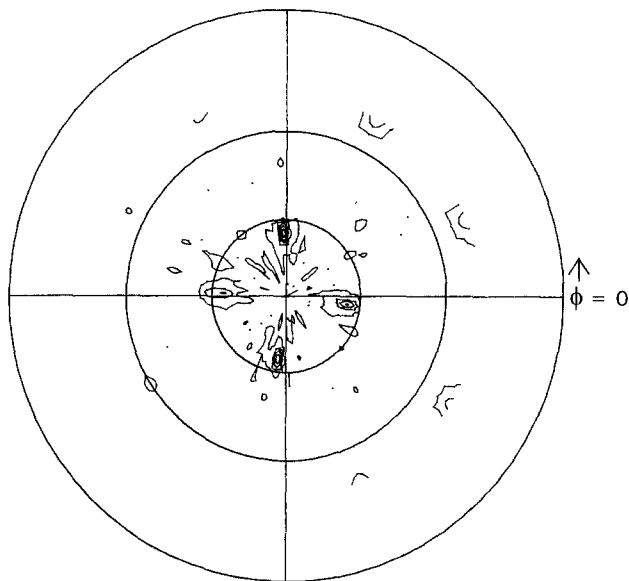


Figure 15 Pole figure obtained for sample 29 at $d = 0.161$ nm.

It has fourfold symmetry and the poles make approximately 25° with the normal to the film. The other lines which did not give satisfactory pole figures were not believed to be due to the substrate. Since the silicon K_α reflections are strongly attenuated in the thin-film mode, the corresponding K_β lines which tended to interface with the BN film lines in the Bragg-Brentano mode were not expected to show up in patterns of the thin-film mode. To confirm this statement, XRD patterns were obtained in thin-film mode with a nickel filter (in addition to monochromator) and are shown in Figs 16 and 17. Figs 18 and 19 show the IR absorption spectra of samples 28 and 29, confirming the presence of CBN structures in the films.

3.3. Discussion

The unique feature of PLA is the generation of high-energy particles from the coupling of a large optical field with the solid target. Measurements in PLA indicate that the ablated species have kinetic energies in the range 10 to 10 000 eV and velocities in the range 10^6 to 10^7 cm s^{-1} [2]. These energies are large in comparison with the translational kinetic energy of

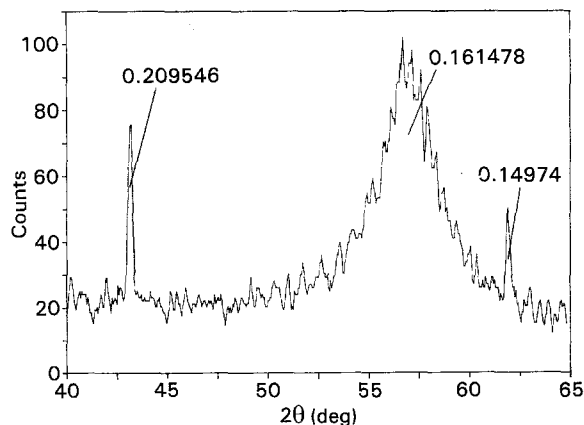


Figure 16 Thin-film mode XRD of LPCVD deposited film using an Ni filter (sample 28).

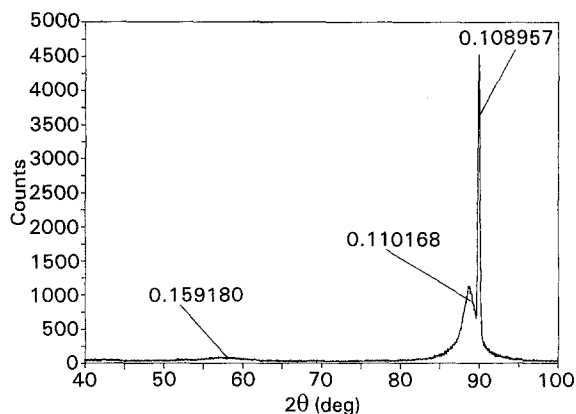


Figure 17 Thin-film mode XRD of LPCVD deposited film using an Ni filter (sample 28).

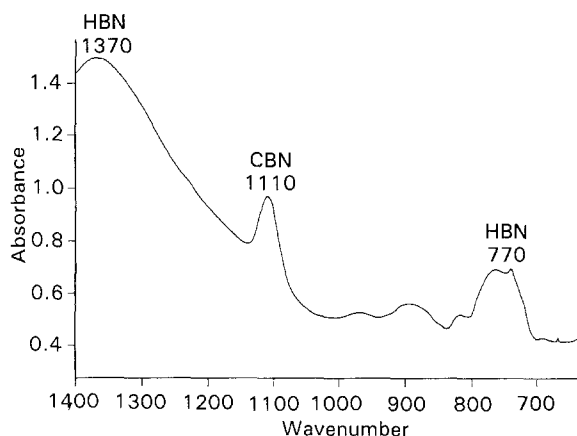


Figure 18 IR spectrum of LPCVD deposited film showing the peaks for CBN and HBN (sample 28).

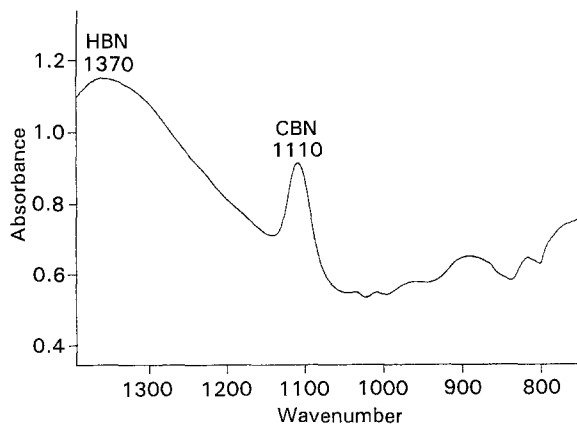


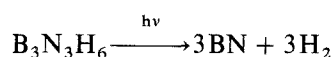
Figure 19 IR spectrum of LPCVD deposited film showing the peaks for CBN and HBN (sample 29).

vapours (0.1 to 0.2 eV) from thermal evaporation. The energy distribution of these particles largely depends both on the absorption characteristics of the target and on the plasma. For a solid BN target, the threshold ablation value for a 248 nm KrF excimer laser is experimentally determined to be 0.31 to 0.34 J cm^{-2} [7]. A time-of-flight analysis of excimer laser-ablated solid BN indicates a velocity of 2×10^6 cm s^{-1} and the energy to be 22 eV [8]. In the present study, the laser fluence using an excimer laser and a 100 mm focal

length lens can be as high as 6 J cm^{-2} . Thus ablative photodecomposition can easily occur even in solid BN, and the ablated material is expected to have high velocity and high energy.

Although the scientific evidence appears to be sound, results obtained in SPLA were not satisfactory. Although we could not obtain the CBN films using SPLA, reports from other researchers indicate the growth of CBN. Doll and co-workers [7–10] have grown CBN films on silicon using single-beam excimer laser ablation of an HBN target to a thickness of about 120 nm which they claimed as epitaxial CBN film on Si $\langle 100 \rangle$ based on X-ray diffraction data. Transmission electron microscopy and IR spectroscopy confirmed the presence of CBN in their samples. Kanetkar *et al.* [23] also reported the heteroepitaxial growth of CBN on Si $\langle 100 \rangle$ using pulsed excimer laser ablation of HBN targets. Both research teams used X-ray diffraction to confirm the presence of CBN. Specifically, a very strong peak at CBN (004) corresponding to a d spacing of 0.0904 nm ($2\theta = 46^\circ$ using Mo radiation and 116.6° using Cu radiation) and a very weak line at CBN (002) were observed. A careful examination of JCPDS for Si indicates that Si (006) has also a peak at $d = 0.0905$ nm corresponding to the (006) reflection. Since the reflections CBN (004) and Si (006) are nearly identical, it is impossible to confirm the heteroepitaxial growth of CBN on Si. It appears that heteroepitaxial growth of CBN should be based upon (002) texture rather than (004) of CBN. Kanetkar *et al.* [23] found that the growth of CBN in pulsed laser ablation requires the presence of nitrogen. In our work, the presence or absence of nitrogen did not make any difference on the X-ray diffractograms.

The difficulties in obtaining CBN by SPLA in our study may be attributed to one or both of the following two reasons: the stoichiometry of the films may not be appropriate to form CBN or the energy of ablated species is not high enough to convert the amorphous or hexagonal form into cubic form. Previous studies by Doll and co-workers [7–10] clearly indicated that the stoichiometry of the laser deposited film is $\text{BN}_{0.8}$ and that there is a deficiency of nitrogen ions. Although the flow of nitrogen during PLA enhanced the nitrogen content of the films in their work, it was still not possible to obtain films with perfect BN stoichiometry. In the LPCVD method, the ability of the excimer beam to dissociate borazine into BN stoichiometry is believed to be responsible for the formation of CBN films. Borazine readily provides BN by photothermal dissociation as given below:



The energy of ablated species is a function of the wavelength of the laser beam. In the present study, the formation of CBN was made possible with the use of an 193 nm excimer beam rather than a 248 nm beam, which implies that the coupling of 193 nm radiation with the pBN target is more efficient. Consequently highly energetic, excited species traveling at supersonic velocities were obtained and assisted in synthesizing CBN films because high energetic species can

break atomic bonds, cause thermal spikes, generate subsurface vacancies, enhance adsorbed atom mobility, and generate nucleation centres. Surface diffusion of adsorbed atoms is also enhanced by the impact of highly energetic species, resulting in smoother film morphology.

4. Conclusions

Single-beam pulsed laser ablation and laser physico-chemical vapour deposition techniques were investigated to deposit thin films of cubic boron nitride (CBN) on silicon substrates. The purity and crystal structure of target material, beam wavelength, pulse width and energy fluence were the key variables studied in this work. Results indicated that the films grown by SPLA at high energy fluence and using dense targets exhibited boron, HBN and amorphous boron nitride. SPLA experiments to produce CBN films were not successful and results were not in agreement with those reported in the literature, namely the heteroepitaxial growth of CBN $\langle 004 \rangle$ on Si $\langle 004 \rangle$. However, the newly developed LPCVD method was capable of producing almost single-crystalline films of CBN. The mechanism is believed to be due to the laser dissociation of borazine into BN and subsequent bombardment of BN by the laser-ablated species.

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References

1. D. C. PAINE and J. C. BRAVMAN, (eds), "Laser Ablation for Materials Synthesis", MRS Symposium Proceedings Vol. 191 (Materials Research Society, 1990).
2. H. SANKUR and J. T. CHEUNG, *Appl. Phys. A* **47** (1988) 271.
3. J. T. CHEUNG *et al.*, *J. Vac. Sci. Technol.* **A4** (1986) 2086.
4. D. LUBBEN *et al.*, *ibid.* **B3** (1985) 968.
5. H. SANKUR *et al.*, *ibid.* **A5** (1987) 15.
6. H. SANKUR *et al.*, *ibid.* **A5** (1987) 2869.
7. G. L. DOLL *et al.*, *Phys. Rev. B* **43** (1991) 6816.
8. G. L. DOLL *et al.*, in "Laser Ablation for Materials Synthesis", edited by D. C. Paine and J. C. Bravman (Materials Research Society, 1990) p. 55.
9. G. L. DOLL *et al.*, presented at International Conference on Metallurgical Coatings and Technology, San Diego, April 1991.
10. G. L. DOLL, private communication (1991).
11. M. SOKOLOWSKI *et al.*, *J. Cryst. Growth*, **52** (1981) 165.
12. S. HIRANO *et al.*, *J. Amer. Ceram. Soc.*, **73** (1990) 2238.
13. S. SHANFIELD and R. WOLFSON, *J. Vac. Sci. Technol.* **A1** (1983) 323.
14. M. SATOU and F. FUJIMOTO, *J. Appl. Phys.* **22** (1983) L171.
15. T. IKEDA *et al.*, *J. Vac. Sci. Technol.* **A8** (1990) 3168.
16. M. MIENO and T. YOSHIDA, *Jpn J. Appl. Phys.* **29** (1990) L1175.
17. LIN *et al.*, *Thin Solid Films* **153** (1987) 487.
18. K. INAGAWA *et al.*, *J. Vac. Sci. Technol.* **36** (1988) 621.
19. S. KOMATSU and Y. MORRIYOSHI, *J. Appl. Phys.* **64** (1988) 1878.

20. A. CHAYAHARA *et al.*, *Jpn J. Appl. Phys.* **26** (1987) L1435.
21. H. SAITOH and W. A. YARBROUGH, *Appl. Phys. Lett.* **58** (1991) 2482.
22. S. P. S. ARYA and A. DAMICO, *Thin Solid Films* **157** (1988) 267.
23. S. M. KANETKAR *et al.*, *MRS Symp. Proc.* **201** (1991) 189.
24. K. H. SEIDEL *et al.*, *Thin Solid Films*, **151** (1987) 243.
25. R. F. BUNSHAH, in "Plasma and Laser Processing of Materials" edited by K. Upadhy, Proceedings of TMS Symposium, New Orleans, February 1991 (The Metals and Materials Society, 1991) p. 257.
26. S. KOMATSU *et al.*, *J. Phys. D: Appl. Phys.* **24** (1991) 1687.
27. C. WEISSMANTEL *et al.*, *Thin Solid Films* **72** (1980) 9.
28. G. KESSLER *et al.*, *ibid.* **147** (1987) L45.
29. P. T. MURRAY *et al.*, *MRS Symp. Proc.*, **128** (1989) 91.
30. T. K. PAUL, P. BHATTACHARYA and D. N. BOSE, *Appl. Phys. Lett.* **56** (1990) 2648.
31. S. MINETA *et al.*, *Thin Solid Films*, **189** (1990) 125.
32. M. TAKEMOTO, N. SUZUKI and T. ANZAI, in Proceedings of Conference on Laser Advanced Materials Processing, edited by A. Matsunawa and S. Katayama, Nagaoka, Japan, June 1992 (High Temperature Society of Japan, 1992) p. 903.

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