Thin Solid Films, 236 (1993) 96–102

Properties of mixed-phase BN films deposited by r.f. PACVD

D. C. Cameron and M. Z. Karim

School of Electronic Engineering, Dublin City University, Dublin 9 (Ireland)

M. S. J. Hashmi

School of Mechanical and Manufacturing Engineering, Dublin City University, Dublin 9 (Ireland)

Abstract

A hot filament activated plasma-assisted chemical vapour deposition (PACVD) technique was developed to deposit BN films under a wide range of conditions. Using this technique, mixed-phase boron nitride (BN) films, containing crystallites of the cubic phase embedded in a hexagonal matrix, were deposited from a non-toxic source material, borane–ammonia (BH_3–NH_3) at a substrate temperature of up to 350 °C. These films showed good thermal and chemical stability, with smooth surface topography. It was found that the increased ion bombardment at higher r.f. power contributed to increasing the volume fraction of the cubic phase in the film. The film properties, *e.g.* refractive index and stress, are directly correlated with the increasing cBN content of the film produced by higher activation energy. Hardness of the film measured by ultra-low load indentation showed an improvement over the silicon substrate. The electronic properties of these films were measured, and exhibited high resistivity and breakdown field strength, and a low level interface state density.

1. Introduction

Boron nitride (BN) shows unique structural, mechanical, optical and electronic properties that make it ideal for a variety of industrial applications. Interest in diamond deposition and subsequent constraints has diverted curiosity to growing cubic boron nitride (cBN) films: cBN is a sister-material to diamond. With respect to diamond, cBN is a favourable superhard material that resists oxidation even at elevated temperatures up to about 1400 °C. BN exhibits an excellent inertness to hot steel surfaces under conditions where diamond is dissolved violently and therefore cannot be used. As well as having superior mechanical properties to those of diamond, cBN could be useful for electronic and optical coatings. The low atomic number combined with transparency and mechanical strength give BN potential as an optical coating; the high resistivity, high dielectric strength and thermal conductivity, along with the possibility of doping the semiconducting cBN with both *n* and *p* type impurities, make cBN a strong competitor to diamond-based electronics.

The promise cBN holds, and the success in growing diamond or diamond-like films, have revitalized the interest in cBN films worldwide for the past few years. After extensive research worldwide in the past three years, numerous experimental and theoretical problems remain, and successful synthesis of well-crystallized cBN films has been very difficult compared with that of diamond films. Most of the reported films are highly defective, with many experiments showing the presence of nanocrystalline and pyrolytic (hexagonal) material. In particular, researchers are facing considerable difficulties and different views in characterizing cBN films. This was discussed recently by the present authors [1]. Notwithstanding the high number of works motivated by the realization of some properties of cBN thin films that are superior to those of diamond, there has been no report, since the pioneering work by Sokolowski [2], on the growth from vapour of cBN whose crystallinity is comparable to CVD diamond films.

We have deposited thin films of mixed-phase BN using the non-toxic material borane–ammonia (BH_3–NH_3) by the PACVD technique incorporating a hot filament activation. The structural and physical properties of these films are described using various characterization techniques.

2. Experimental details

The experimental system has been described elsewhere [1, 3]. As was reported previously, a non-toxic crystalline solid, BH_3–NH_3, was used to produce BN films. The evaporation procedure of BH_3–NH_3 is also described in ref. 1, and procedures for cleaning and etching the substrates immediately prior to the deposi-

0040-6090/93/$6.00

© 1993 — Elsevier Sequoia. All rights reserved

TABLE 1. Deposition conditions

Reactant	Borane–ammonia (BH_3–NH_3)
Carrier gas	Nitrogen (N_2)
N_2 flow rate (sccm)	18–100
Working pressure (mbar)	0.26–0.9
R.f. power (W)	50–400
Substrate temperature (°C)	350
Filament temperature (°C)	≈1300–1600
Deposition time (min)	45–90
Film thickness (nm)	≈100–300

tion have been reported [1, 3]. Table 1 lists the deposition conditions.

3. Characterization techniques

The N_2 plasma was studied by using an optical emission spectrometer (DIGITWIN from Sofie Instrument). The detector has two changeable grids with 200–600 nm (UV) and 500–900 nm (VIS) range. The light emitted from the plasma was guided to the monochromator through the quartz wall by means of an optical quartz fibre which was located just above the substrate holder.

The thermal stability of the films was determined by thermogravimetric analysis (TGA), which was carried out in a Stanton Redcroft TG 750/770 instrument. The morphology and topography were studied using a Leica-Cambridge S360 SEM.

The films on Si or KBr were studied using IR spectroscopy which was carried out on a Perkin-Elmer 983G spectrometer in the transmittance mode in the range 600–4000 cm^{-1}, using a bare silicon wafer as a reference where necessary. The silicon wafer was etched just before introducing it in the deposition chamber and the reference silicon was also etched just before the IR study, which was conducted immediately after each deposition.

The relative content of cubic to hexagonal phase was obtained by the intensity ratio of the IR absorption bands at about 1065 cm^{-1} and about 1365 cm^{-1} respectively, since the absorption intensity is a function of film thickness. The intensity was evaluated by the peak height common tangent base line method [4]. The intensity ratio of cBN and hBN, A_{cBN}/A_{hBN}, is independent of the film thickness. A Rudolph ellipsometer with an He–Ne laser (633 nm) beam incident at 70° was used to determine the thickness and refractive index of the films on silicon substrates.

The stress in the BN films was measured by the curvature method, which is most commonly used. The deflection was measured by optical microscopy on a 5 mm long path in the middle of the substrate. A 4 in optically flat microscope slide was used to calibrate the system, and initially an uncoated silicon wafer was evaluated to establish the initial curvature before deposition.

The hardness of the films was measured using a Nanotest instrument manufactured by Micro Materials Ltd. The principle of this instrument has been discussed by Pollock *et al.* [5]. The Nanotest, unlike conventional hardness testers, produces continuous curves of load *vs.* indentation depth. For each run, the load was increased to a predetermined level and then automatically reversed. The loading and unloading curves were obtained and the resulting hysteresis curve was produced. The depth values therefore contain both plastic and elastic contributions. In order to eliminate the elastic contributions, the elastic recovery parameter (ERP) [5] was determined for each run. This was found from the unloading branch of the hysteresis curve, with the intercept at zero load representing the plastic depth. The load was varied for each sample from 20 to 0.2 mN, and at each load a hysteresis plot of load *vs.* depth was obtained. The resulting hardness values for each run were plotted against plastic depth.

In order to examine the insulating properties and stabilities of BN films, Al/BN/Si metal–insulator–semiconductor (MIS) structures were fabricated on ⟨100⟩ Si substrates. The experimental procedure of capacitance *vs.* voltage ($C-V$) and current *vs.* voltage ($I-V$) measurements are described in ref. 3.

4. General properties of the films

BN films up to 300 nm thick were deposited directly onto silicon, KBr and steel substrates with controlled evaporation of the borane–ammonia adduct. Films were grown with various combinations of pressure, substrate temperature, filament temperature and r.f. power.

As the evaporation of the borane–ammonia adduct was not even, the deposition rate was difficult to determine, but was about 20 Å min^{-1}. The density of the films measured by gravimetric techniques was in the range of 1.8–2.7 g cm^{-3}.

The films consisted of a mixture of the hexagonal and cubic phases, whose ratio depended on the deposition parameters. Most of the films were not attacked by water. There were no visible changes in the appearance of the films after exposing them to 40% dilute HCl acid. No weight loss or gain was observed for the BN samples in the TGA curve. The temperature range was 100–1000 °C; the rate was 15 °C min^{-1}. The samples were cooled down in an N_2 dominant atmosphere. Their thermal stability was excellent. However, a colour change was observed in the case of hBN films.

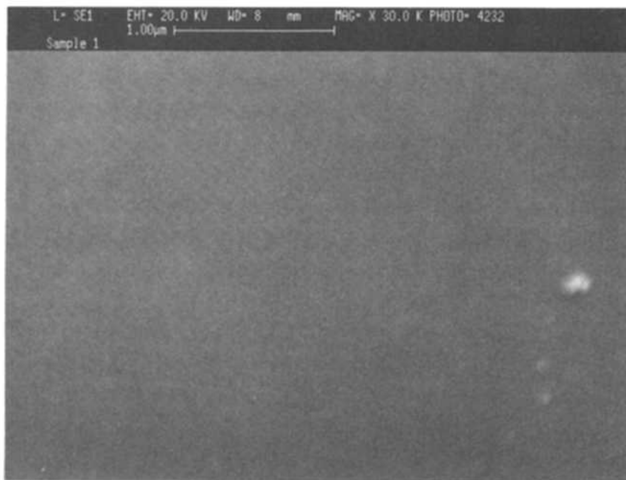
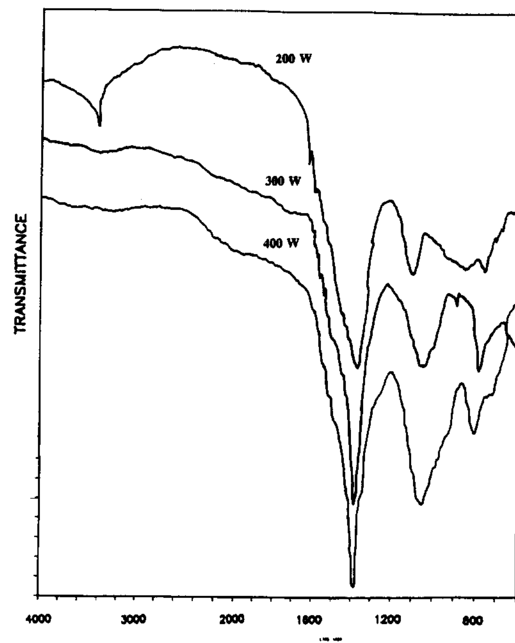


Fig. 1. SEM image of mixed-phase BN thin film showing smooth surface topography.

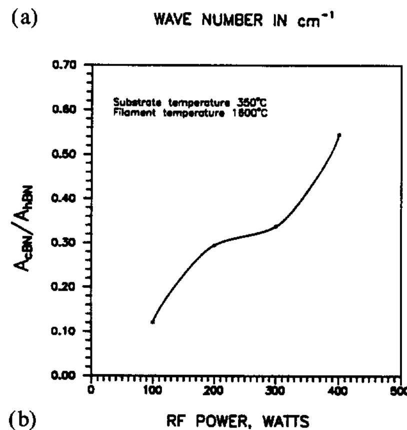
SEM images of most of the mixed-phase films showed a smooth and essentially featureless surface with an occasional nodule projecting above the surface. These nodules may have been initiated when the r.f. power was momentarily turned off during the deposition to check substrate temperature and/or reactant temperature. When the r.f. power was momentarily turned off, it is likely that the evaporated reactant was deposited on the film as a nodular form. Such a film grown at 400 W r.f. power, a substrate temperature of 350 °C and filament temperature of 1600 °C (pressure 0.3 torr) is shown in Fig. 1. Most of the boron nitride films grown with a substrate temperature of 350 °C and at higher r.f. power (>200 W) on properly cleaned Si substrates adhered well to the substrates.

5. Structural properties of the films

The cBN content of the films depended strongly on the deposition temperature, filament temperature and capacitively coupled r.f. power. Without substrate heating (the lowest substrate temperature was about 150 °C with 400 W r.f. power on) and filament activation, the cBN peak was very small. As the substrate temperature was increased, an absorption band at nearly 1054 cm^{-1} was normally obtained after 250 °C, though no functional relation could be determined between increasing substrate temperature and cBN content of the films. Moreover, the adhesion of the films to the substrate was good and the peak at 3220 cm^{-1} attributed to N–H stretching vibrations disappeared in most of the cases after 300 °C. For this reason, we kept our substrate temperature always at 350 °C, which is suitable for most substrates, including high speed steel and GaAs. A filament temperature of greater than 1400 °C



(a)



(b)

Fig. 2. (a) IR absorption spectra of BN films prepared by varying the r.f. power at a substrate temperature of 350 °C and filament temperature of 1600 °C; (b) intensity ratio of cubic to hexagonal phases in BN films as a function of r.f. power coupled to the substrate.

had a considerable effect on the cBN peak shape and height. A value of 1600 °C of the filament was therefore adopted in our experiments.

Radiofrequency power has an important effect on the cBN content of the films. With less than 100 W r.f. power, and at a substrate temperature of 350 °C, virtually no cBN peak could be detected. At 100 W, maxima in absorption appear near both the hexagonal and cubic vibrational frequencies, but the hexagonal in-plane peak is stronger and wider than the tiny cBN peak. The hexagonal in-plane peak position varies widely from film to film, ranging from 1265 to 1350 cm^{-1}. After 160 W, there is a sharp increase in the cBN reststrahlen band. Figure 2(a) shows the IR spectra of the deposited films at 200, 300 and 400 W respectively, at a substrate temperature of 350 °C and a

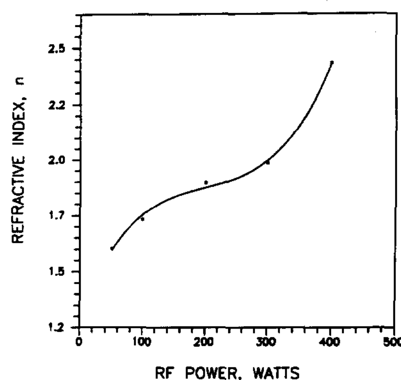


Fig. 3. The effect of r.f. power on the refractive index of the BN films grown at a substrate temperature of 350 °C and filament temperature of 1600 °C.

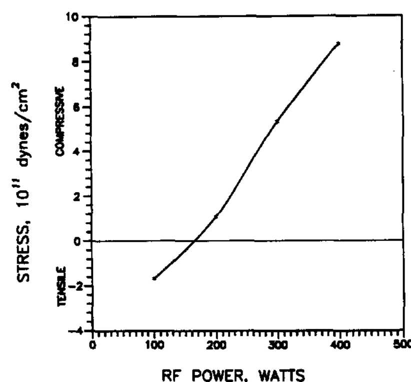


Fig. 4. The effect of r.f. power on the stress of BN films.

filament temperature of 1600 °C; Fig. 2(b) shows the intensity ratio of the cBN and hBN peaks with respect to the r.f. power. In addition to the peak-height change, there was a change of the peak position of the reststrahlen band. The reststrahlen band related to sp^3 BN bonds shifts from 1096 cm^{-1} at 100 W to 1054 cm^{-1} at 400 W. For films grown at >300 °C and >200 W, no peaks exist at around 3220 cm^{-1} (which would be designated as N–H peaks) or at around 2400 cm^{-1} (which would be designated as B–H peaks), confirming the film as hydrogen free.

The refractive index of the films grown at 400 W and at a deposition temperature of 350 °C and a filament temperature of 1600 °C was 2.29. The value of refractive index with a good cBN reststrahlen peak in the IR spectrum did not show any value lower than 1.93. Values for the refractive index for cBN-containing films are usually 1.8–2.3, whereas the refractive index for the hBN films grown show values in the range 1.55–1.77. Run-to-run variations in the refractive index are usually within ± 0.05.

The variation of refractive index with plasma power is shown in Fig. 3. After 200 W, the refractive index showed a sharp increase with r.f. power. This correlates with the increasing cBN content of the films as measured by the IR absorption peak. It should be noted that the indices of the films with cBN content are substantially higher than those for hBN (1.7–1.8) [6] and are close to the reported values of 2.0–2.3 for cBN [6].

Structural characterization was also conducted by Siemens D-500 X-ray diffractometry. Other than a large peak due to the Si substrate, no peaks due to BN phases were found.

6. Mechanical properties of the films

The stress of the hBN films grown at lower r.f. power ($\leqslant 100$ W) was seen to be tensile. The average of this stress for five films at 100 W and 350 °C is 1.6×10^{11} dynes cm^{-2}. However, films grown at higher r.f. power are under compressive stress and this stress is seen to be increasing with r.f. power. The stress at 400 W r.f. power and 350 °C was about 8.6×11^{12} dynes cm^{-2}. The uncertainty in the stress measurement is $\pm 10\%$. The data also show large scatter at lower r.f. power. The scatter is thought to be due to thinness of the films.

With increasing r.f. power, the stress crosses over from tensile to compressive between 100 and 200 W and remains compressive up to 400 W, the maximum power investigated. Figure 4 shows the variation of the film stress with r.f. power at a deposition temperature of 350 °C. The annealing of the film at 400 °C at 10 mtorr for 15 min did not produce significant stress variation.

Figure 5(a) shows the hardness *vs.* depth curve for sample 1 grown at 400 W r.f. power with a substrate temperature of 350 °C and filament temperature of 1600 °C. Figure 5(a) also shows the curve for uncoated and etched silicon for a comparison of composite hardness and substrate hardness. For higher indentation loads, the films begin to display a trend in hardness values which approaches that of the underlying material (Si), as expected. There is an increase in the hardness of the coated substrate. All the films are approximately 300 nm thick.

It is often most practical simply to compare specimens by normalizing one set of data to another. This approach effectively eliminates questions of the diamond geometry. Figure 5(b) shows the hardness data from sample 1 normalized to the hardness data obtained from the substrate material. An improvement by a factor of approximately 1.5 is apparent from the figure. The hexagonal film coated substrate did not show an improvement in the hardness as compared with silicon substrate.

7. Electronic properties of the films

The MIS structure was used as the vehicle by which the electronic and interfacial properties could be

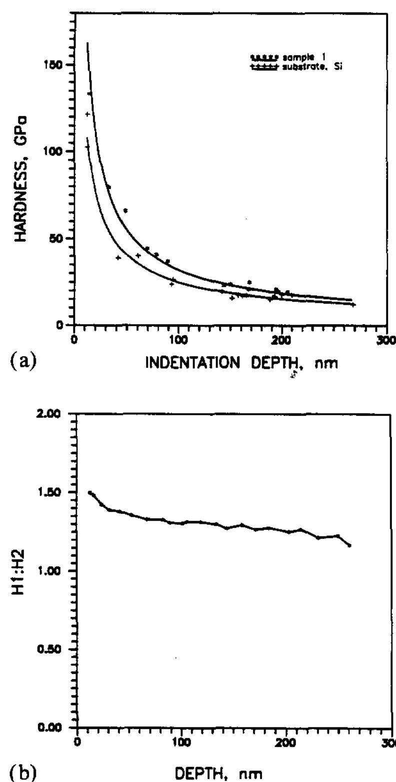


Fig. 5. (a) Apparent hardness *vs.* depth curves for sample 1 and substrate Si (sample 1: mixed-phase BN films grown at r.f. power of 400 W, substrate temperature $T_s = 350$ °C and filament temperature $T_F = 1600$ °C); (b) normalized hardness data (sample 1, H_1:substrate Si, H_2) *vs.* depth curve derived from Fig. 5(a).

analysed. These included the dielectric constant ϵ_i of the BN insulator, the flat band voltage V_{fb}, the surface-state density N_{ss} and its distribution and the fixed charge density Q_{fc} in the insulator. The $C-V$ and $I-V$ curves are described in ref. 3.

As determined from the $C-V$ curves [3], the dielectric constant of mixed-phase BN films was in the range 2.2–4.41. These values are close to the reported values for BN films in ref. 7, where they have a value greater than 4.2 for cBN films.

The approximate surface state density and flat-band capacitance was determined using Terman's method [8]. The surface state density was approximated by a U-shaped curve with a minimum interface state density of 1.8×10^{12} states cm^{-2} eV^{-1}.

From the measured $I-V$ characteristics [3], the resistivity of the films was measured and varied from 3.24×10^{12} to 3.3×10^{13} Ω cm. The dielectric breakdown strength of our films ranged from 8×10^5 to 4×10^6 V cm^{-1}.

Table 2 lists some of the electro-physical properties of mixed-phase BN films.

TABLE 2. Electro-physical parameters for MIS structure

Property	Al/BN/nSi
Refractive index n	1.55–2.3
Dielectric constant ϵ_i	2.2–4.41
Flat-band voltage V_{fb}	26 V (for $\epsilon_i = 4.41$)
Surface-state density N_{ss} (states cm^{-2} eV^{-1})	$(1.75–7) \times 10^{12}$
Resistivity ρ (Ω cm)	$(3.24–33) \times 10^{12}$
Fixed charge density Q_{fc}	7×10^{12}
Breakdown field (V cm^{-1})	$(8–40) \times 10^5$

8. Discussion

The increase in the cBN peak at higher r.f. power is due to the increased ion bombardment on the growing film. The nitrogen ion concentration, as determined by optical emission spectroscopy (OES), increased in the plasma with increasing r.f. power. At 160 W, the plasma colour changed and peaks attributed to N_2^+ ions in the OES study appeared which then increased further with r.f. power. This increased ion bombardment is responsible for selective etching of the hexagonal phase and the supply of sufficient energy for the conversion to the metastable cBN phase. The shift of the cBN peak to lower frequency was also observed by other authors [9, 10], and explained as an effect of internal stress, with the lower frequency signifying lower stress. At higher r.f. power, our film showed higher stress, which does not comply with this stress reduction hypothesis. Moreover, no shift was observed between the film just after deposition and the same film which had debonded from the substrate after atmospheric exposure. Kessler *et al.* [11] published an IR spectrum of a wurtzite BN (wBN) thin film with an absorption centred at 1100 cm^{-1}. This leads to the suggestion that under conditions not appropriate for cBN growth, the wBN is formed by a similar mechanism with high temperature and high pressure growth. The formation of cBN occurs when we supply just enough energy to convert the wBN to cBN, *i.e.* at temperatures greater than 300 °C and an r.f. power of 160 W. This phenomenon will be explained in a later publication.

The determination of the characteristic bonds using IR data is an important tool to characterize BN films, but on Si, the cBN reststrahlen band is very close to the Si–O bond at 1103 cm^{-1}, which is typical for silicon dioxide film IR spectra. However, this peak is very sharp compared with the broad peak due to the cBN reststrahlen band. To identify the peak unambiguously, we deposited BN films on KBr substrates. In addition to the hexagonal peaks, the cBN peak at 1100 cm^{-1} can be seen in the IR study.

As the refractive index showed very little increase with substrate temperature, the increase in refractive index with r.f. power is directly related to the cBN content of the films. From the X-ray diffraction, it cannot be concluded that the films are totally amorphous; as B and N are poor X-ray scatterers and the films are thin (100–300 nm), getting no diffraction peaks from the BN films was not unexpected.

High stress and poor adhesion of cBN thin films are common and widely reported [9, 10]. Films are generally under compressive stress. Therefore, the origin of tensile stress of our films needs to be explained. It has been found that films deposited under conditions of low adatom mobility (low deposition temperature relative to the melting point) or in the absence of energetic particle bombardment generally develop a porous zone 1 microstructure [12]. These films are usually under tensile stress due to attractive atomic forces acting across grain boundaries or the voids pulling the film columns together. The tensile stress in the hBN films grown at lower r.f. powers can be understood from the above explanation. The origin of the intrinsic compressive stress is more or less established. The compressive stresses are produced by energetic particles striking the film. The good adhesion of the mixed phase BN films may be due to the support the hexagonal region gives to the cubic region for stress relaxation.

No absolute value of hardness was estimated from the nano-indenter measurements. Several effects tend to complicate the interpretation of submicroscopic test results in addition to experimental limitations such as vibrations, surface roughness, contamination, and imperfect indenter geometry. First, the value of hardness depends on the strain rate at the time when the measurement is made: even at ambient temperature, time-dependent effects can be significant at submicron depths and at low loads. Also, surface roughness affects the measurements. The quantity of scatter associated with each set of data was noticeable at low loads; this may be due to the result of slightly poorer surface roughness of the BN films. Films were also too thin to have a reliable absolute hardness. In addition, vibration effects were significant during the measurement, sometimes giving spurious results. However, most of the measurements were consistent.

Fast interface state density values are comparable with the value for plasma deposited SiN (2×10^{11}–7×10^{12} states cm^{-2} eV^{-1}) and SiO_2 (2×10^{11} states cm^{-2} eV^{-1}). It is likely that the exposure to the plasma in the BN process, in common with other plasma processes, has a disruptive effect on the silicon surface, giving rise to a rather higher interface state density not achievable with thermal oxide on silicon. The precision of Terman's method is rather poor; it gives information only on a restricted part of the gap.

9. Conclusions

The deposition of hydrogen-free BN films containing cubic phases was achieved by a filament activated PACVD system using the non-toxic material borane–ammonia. An excellent correlation between the plasma diagnostics and deposition parameters with the properties of the cubic phase containing film was obtained.

It was found that ion-bombardment plays an important role in forming the sp^3-microstructure of BN films. In addition to bombardment, substrate and filament temperatures are important factors in film growth. A substrate temperature of more than 300 °C and a filament temperature of more than 1400 °C were necessary for enhancement of the growth of the cubic phase in the films.

The stress of the films crossed over from tensile to compressive between 100 W and 200 W, and remained compressive up to 400 W. There is a very close parallel between the film containing a higher amount of the cubic phase and the higher level of compressive stress. Hardness of the mixed-phase film measured by near-surface ultra-low load indentation testing showed an improvement as compared with the substrate.

These mixed-phase BN films showed potential for use in electronic circuits. However, pure cubic boron nitride films were not achieved; the growth region derived suggests the possibility of depositing cBN films with additional activation energy into the system, *e.g.* by increasing the substrate temperature, and/or higher plasma ionization. It was difficult to evaporate the reactant material evenly and with good control, since borane–ammonia tends to polymerize and does not have a definite vaporization temperature. Precursors with better defined vaporization properties may improve the deposition process.

Acknowledgments

This work on the deposition of cBN films was partially supported by the EC BRITE programme under contract BRITE RI1B.0221.C(H). Grateful acknowledgment is also made to EOLAS for nano-indenter measurements.

References

1 M. Z. Karim, D. C. Cameron and M. S. J. Hashmi, *Surf. Coat. Technol., 54/55* (1992) 355–359.
2 M. Sokolowski, *J. Cryst. Growth, 46*(1) (1979) 136–138.

3 M. Z. Karim, D. C. Cameron and M. S. J. Hashmi, *Proc. 3rd Int. Conf. on Plasma Surface Engineering, Garmisch-Partenkirchen, Germany, October 25–28, 1992.*

4 G. L. McClure, in H. A. Willis, J. H. van der Maas and R. G. J. Miller (eds.), *Laboratory Methods in Vibrational Spectroscopy*, Wiley, Chichester, 1987.

5 H. M. Pollock, D. Maugis and M. Barquins, STP 889, American Society for Testing and Materials, Philadelphia, PA, 1986.

6 P. Lin, C. Deshpandey, H. J. Doerr, R. F. Bunshah, K. L. Chopra and V. D. Vankar, *Thin Solid Films*, *153* (1987) 487–496.

7 J. Szmidt, A. Jakubowski and A. Balasinski, *Thin Solid Films*, *110* (1983) 269–277.

8 L. M. Terman, *Solid State Electron.*, *5* (1962) 285–299.

9 T. Ikeda, Y. Kawate and Y. Hirai, *J. Vac. Sci. Technol.*, *8A*(4) (1990) 3168–3174.

10 M. Murakawa and S. Watanabe, *Surf. Coat. Technol.*, *43/44* (1990) 128–136.

11 G. Kessler, H.-D. Bauer, W. Pompe and H.-J. Scheibe, *Thin Solid Films*, *147* (1987) L45.

12 J. A. Thornton, *J. Vac. Sci. Technol.*, *11* (1974) 666.