

# Influence of the sputtering gas composition on the properties of thin boron nitride thin films

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## Abstract

Boron nitride thin films have been prepared in a radio frequency magnetron sputtering system using different argon–nitrogen gas mixtures and substrate bias values, being deposited on silicon, aluminium and stainless steel substrates. Optical emission spectroscopy was used to monitor the plasma. Under optimal bias, pressure and temperature conditions stoichiometric films can be obtained, their cubic phase content can be controlled by varying the relative amount of nitrogen in the plasma as well as the total flow. The effect of these parameters on intensity ratio between the emission lines for  $N_2^+$  ions and boron atoms is related to the amount of the cubic phase found in the films, as determined by infrared spectroscopy. This gives support to the idea that also in sputtered films the ion to atom arrival ratio controls the amount of cubic phase. Films with up to 60 to 70% of cubic phase content can be deposited on metallic substrates using the same optimum conditions. © 1998 Elsevier Science S.A.

*Keywords:* Boron nitride; Sputtering; D.c. bias; FTIR

## 1. Introduction

Boron nitride thin films have received much attention due to the fact that the cubic phase of this material has some physical properties similar to those of diamond, that is, high hardness, high thermal conductivity and wide optical bandgap, but a better resistance to oxidation and a lower solubility in ferrous materials [1]. There are nevertheless several features of their nucleation and growth still to be elucidated, especially regarding how to control the amount of c-BN and the stress that remains in the films. In this paper we study the properties of boron nitride thin films prepared by radio frequency (r.f.) sputtering and direct current (d.c.) biasing of the substrates, their variation with the amount of argon and nitrogen in the total flow and the effects that different substrates have on them; finding that it is possible by these means to produce stoichiometric, highly cubic material on silicon, aluminium and steel substrates, as well as to control the amount of cubic phase in the material.

## 2. Experimental details

Crystalline silicon with (100) orientation, quartz, stainless steel 316 and commercial aluminium (F1100) plates were used as substrates; these were degreased and cleaned in organic solvents (acetone and iso-propyl-alcohol) in an ultrasonic bath, then dried with nitrogen before introducing them into the reactor by means of a load-lock arm that helped to reduce water vapour contamination. Great care was taken to place the substrates on the same spot under the 10 cm diameter target, made of hexagonal boron nitride (99.95% pure), in order to avoid variations in the ion flow and hence the cubic phase content of the films due to geometrical factors [2]. The substrate holder, distant 4 cm from the target, could be heated by a resistive heater and biased with a direct current (d.c.) power supply. The temperature was set at 350 °C, a  $-150$  V bias was applied to the silicon substrates, through a d.c. power supply, and the radio frequency (r.f.) power was kept at 250 W. For metallic substrates the bias was varied from 0 to  $-150$  V, in order to see if the substrate conductivity affected the biasing effects. The Ar/Ar + N<sub>2</sub> ratio, the  $A$  value from now on, was varied between 0 and 1 by varying the flow of ultra high purity argon and nitrogen gases by means

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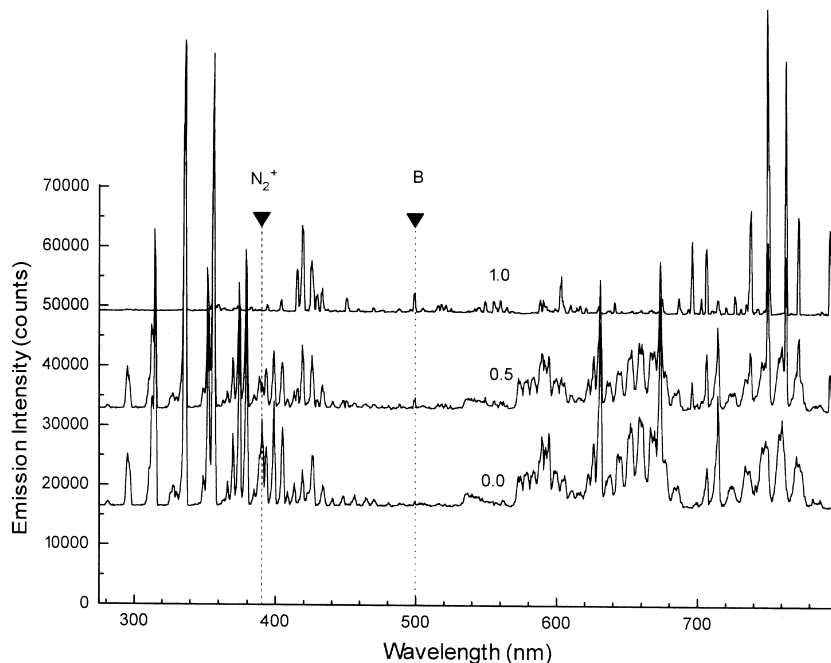


Fig. 1. Emission spectra taken from plasmas prepared using the  $A$  values [Ar/(Ar+N<sub>2</sub>) ratios] indicated above each graph. The dotted vertical lines indicate the peaks from ionized nitrogen molecules and a second order line from boron atoms.

of mass-flow controllers, keeping the total flow set around 17 sccm.

As for the optical emission spectroscopy (OES) measurements, they were taken through a gold coated optical fibre that ran from the chamber inside to a 0.5 m monochromator, using a Hamamatsu photomultiplier tube, both connected to and controlled by a computer. Spectra were taken in the 275–800 nm range with 2.5 Å resolution. Fig. 1 shows spectra for three  $A$  value runs taken during deposition. The peak at 499.5 nm corresponds to a second order boron atom emission, the first order line being at 249.7 nm, and the feature at 390.5 nm can be related to N<sub>2</sub><sup>+</sup> emission.

Vibrational properties were studied by Fourier transform infrared (FTIR) spectroscopy with the aid of a Nicolet 205 spectrometer. FTIR spectra spanned from 400 to 4000 cm<sup>-1</sup> with a 4 cm<sup>-1</sup> resolution, integrating 32 scans in every run for both the transmission and internal reflection modes. Transmission measurements were taken with the beam at normal incidence, whereas those obtained by internal reflection were done at a beam–substrate angle of 45°. From the absorption (both methods actually measure how much radiation is absorbed) spectra the intensities corresponding to the cubic and hexagonal stretching modes were measured and a  $Q$  value calculated according to:

$$Q = I_c / (I_c + I_h) \quad (1)$$

where  $I_c$  is the absorption intensity of the stretching mode of the cubic phase at the 1050–1110 cm<sup>-1</sup> region in the FTIR spectrum,  $I_h$  is the absorption intensity of

the stretching mode of the hexagonal phase at the 1380–1400 cm<sup>-1</sup> region; this parameter overestimates the c-BN content of the films by about 5% [3], but here we are interested more in the trends of this value than in the actual content of the sp<sup>3</sup> bonded phase.

A Gaertner ellipsometer with a 632 nm laser beam was used to determine the index of refraction at such wavelength and to estimate the film thickness; this latter parameter was more accurately determined by a Dektak II profilometer. A Shimadzu 260 UV–vis spectrophotometer with an integrating sphere in the 240–800 nm range was used to study the transmission and reflectance spectra, unfortunately not all the samples could be characterized with these techniques since some of them started to debond from the substrates a few minutes after being taken out from the preparation chamber. The composition was determined by energy dispersion spectroscopy (EDS) in a Leica-Cambridge Instruments scanning electron microscope (SEM) with a 10 keV beam, using a boron nitride standard supplied by the microscope manufacturers, yielding measurements with a 2% error in the B/N ratios determined.

### 3. Results and discussion

In Fig. 2 the Fourier transform infra-red absorption spectra of three different samples are shown. It is rather obvious that varying the gas ratio or  $A$  value has some important effects on the structure of the films. The use of a direct current (d.c.) power supply for biasing

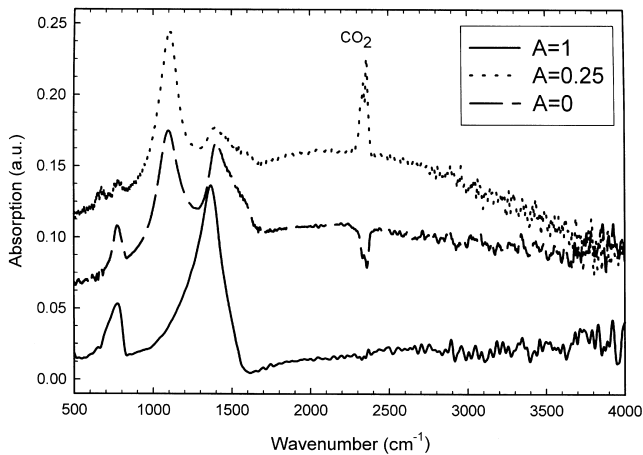


Fig. 2. Fourier transform infrared absorption spectra from three different samples prepared with the  $A$  values [ $\text{Ar}/(\text{Ar} + \text{N}_2)$  ratios] indicated in the legend. The band corresponding to the TO mode of cubic boron nitride is in the  $1060$  to  $1100\text{ cm}^{-1}$  region, the corresponding mode for hexagonal boron nitride is in the  $1360$  to  $1405\text{ cm}^{-1}$  region. The carbon dioxide feature is a doublet in the  $2300$  to  $2400\text{ cm}^{-1}$  region. The graphs have been shifted for clarity.

substrates has been used in the past [4,5] to produce c-BN; it is interesting to notice though, that even with the use of d.c. bias it is possible to obtain relatively large amounts of cubic phase by balanced magnetron sputtering, without additional ionization enhancers such as confining coils [6,7] or electron cyclotrons [4]. This would seem to confirm the view [8] that the bombardment intensity needed during the growth stage is lower (in terms of momentum per condensing atom) than during the nucleation stage of cubic boron nitride, since the direct bias would drop across a highly insulating layer (the silicon, aluminium and steel used have conductivities at least seven orders of magnitude higher than boron nitride) diminishing at least the energy of the impinging ions and hence their momentum as the films grew.

In Fig. 3a–c the B/N ratio and the  $Q$  value [as defined in Eq. (1)] of BN layers prepared under different  $\text{Ar}/(\text{Ar} + \text{N}_2)$  ratios are shown along with the corresponding values of the index of refraction determined for the films before they debonded from the substrates. These results strongly suggest that the absorption peak observed in the  $1060$ – $1100\text{ cm}^{-1}$  region of the FTIR spectra (Fig. 2) is due to c-BN and not to  $\text{SiO}_2$  since a large amount of this material would imply an index of refraction close to  $1.4588$  [9]. As can be seen, both the B/N ratio and  $n$  seem to lock in to values reported for highly cubic material [10] at low or null argon flows, whereas at larger Ar flows the values of boron in the film go up and are associated also with larger values of the index of refraction; the films with the larger B/N values were dark or light brown, whereas the stoichiometric material was transparent in the visible. A similar behaviour has been observed by other authors [6,7] but

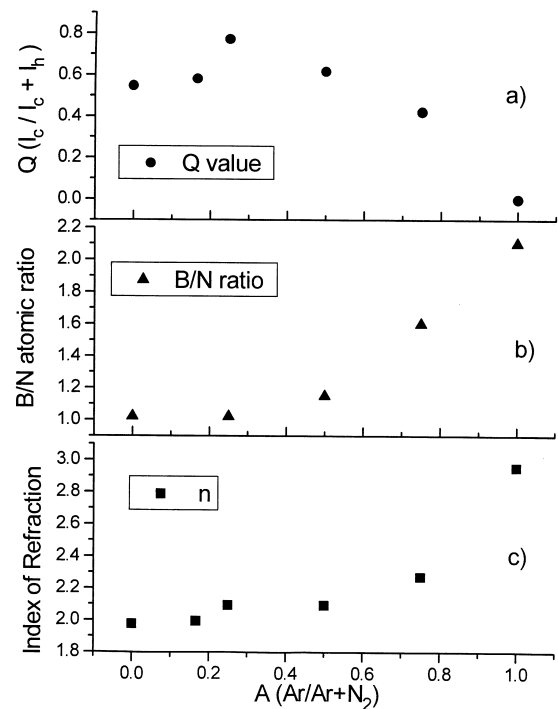


Fig. 3. Film characteristics of samples prepared at different  $A$  values [ $\text{Ar}/(\text{Ar} + \text{N}_2)$  ratios]: (a) the  $Q$  value as determined from FTIR measurements; (b) the boron to nitrogen ratio as determined by EDS; and (c) the index of refraction at  $632.6\text{ nm}$  as determined by ellipsometry. Values that correspond to a predominantly cubic film are found for  $A=0.25$ .

at different  $\text{Ar}/(\text{Ar} + \text{N}_2)$  ratios. This discrepancy is produced by the difference of ion density and flow since, apart from geometrical differences, the equipment utilized in ref. [6,7] was biased by r.f. power sources and had an electromagnet that could increase the magnetic field felt by electrons, and hence their mean free path, and with this enhance ionization of both argon and nitrogen. Following Hahn's model of relating ion flux with momentum per condensing atom ( $p/a$ ) [8], a larger ionization would imply a larger flux and hence larger a  $p/a$  value. This implies that there is a critical flux [2] above which cubic BN is produced in sputtering systems independently of the type of substrate biasing (d.c. or r.f.), sputtering method (d.c. or r.f.) and plasma production. At low  $A$  values, say when only nitrogen is used, the amount of nitrogen ions is increased [11] (there are reports stating that the electron temperature rises [2] and with it ionization), hence a larger ion flow is expected to arrive into the growing layers and reach the resputtering regime. Indeed, using only nitrogen as the sputtering and reacting gas, the deposition rate goes down noticeably; from  $46$  to  $50\text{ \AA}/\text{min}$  when  $A > 0$  to only  $32\text{ \AA}/\text{min}$  for  $A = 0$ , suggesting that the resputtering regime is being reached.

The film properties can be correlated with another parameter measured during deposition: the ratio

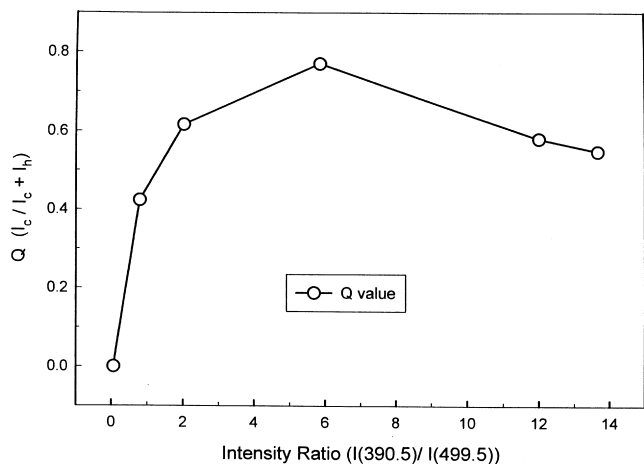


Fig. 4. The  $Q$  value as a function of the intensity ratio between the emission lines of ionized nitrogen molecules and from boron atoms at 390.5 and 499.5 nm respectively, as determined from OES. The lines are only a guide to the eye.

between the boron emission line and the  $N_2^+$  emission line ( $I_{499}/I_{390}$ ). If this intensity ratio is plotted against the  $Q$  value, like in Fig. 4, a maximum is achieved within certain range and then decreases. This graph resembles the relation between ion/atom ratio and c-BN content found by Mirkarimi et al. [12], so this  $I_{499}/I_{390}$  ratio might be related to the ratio of impinging ions and condensing atoms, since at relatively low powers most ions should be ionized nitrogen molecules and boron atoms are considered to control the deposition rate [2]. There are several examples where ion bombardment is mainly through  $N_2^+$  ions, most noticeably those where a Kaufman ion source has been used to irradiate the growing layers of BN, where the  $N_2^+$  ions represent an important fraction of the ions in the beam (over 70%, e.g. refs. [12–14]); as these ions are obviously related to the emission line at 390.5 nm, it is not unrealistic to think that its intensity is some measure of their abundance under our preparation conditions. Even if the ionized nitrogen molecules are likely to split after colliding with the surface, making available nitrogen atoms for BN formation, they will transfer momentum to the growing layer. It has been reported that, in the deposition of BN by boron evaporation with nitrogen ion-beam assistance, as the ion current is decreased (and hence the amount of  $N_2^+$  ions hitting the growing surface), the B/N ratio of the resulting films is larger [10]; at a constant arrival rate of boron this means a larger B atoms to  $N_2^+$  ions ratio. The fact that in our case boron rich films are produced when the intensity of the ionized nitrogen molecule line is small, compared with the line intensity of the boron atom, supports the idea that lower nitrogen bombardment is being supplied to the growing surface, reducing both nitrogen availability and momentum transfer. Hence monitoring the emission intensity ratio ( $I_{499}/I_{390}$ ) might be a useful tool in

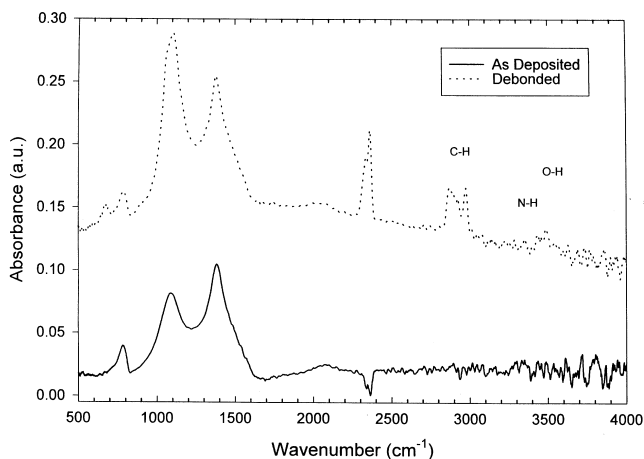


Fig. 5. FTIR spectra of a BN sample prepared with  $A=0.75$  before and after the film was debonded from the substrate. Notice the appearance of hydrogen impurities and the increase of the cubic boron nitride feature intensity. The large shift in the position of this peak may be due to the formation of silicon oxide after the exposed material reacted with water after delamination. The graph was shifted for clarity.

varying film composition and microstructure, especially if, in order to improve adhesion, graded composition layers are to be deposited.

As in other BN films produced by sputtering, delamination occurred after being exposed to air [7,15], and a shift in the FTIR absorption peaks was observed as can be seen in Fig. 5. The c-BN feature not only moves, but also increases its size in relation to the h-BN stretching band. It has been shown that debonding occurs through the reaction of BN with water [16], so oxides and hydroxides should be observed, and silicon dioxide might form, contributing to the enhancement of the feature near  $1065\text{ cm}^{-1}$ . On the other hand, the reaction of non-cubic material [15] gives place to the presence of other radicals that produce absorption features at the high energy region (C–H, N–H, O–H) of the spectrum and to a reduction in the h-BN absorption band. Although a small presence of carbon (1 to 3 at%) was detected in the films, the presence of C–H after delamination may be explained if the carbon was mainly at the film–substrate interface. Oxygen was also present (2 to 4 at%) but few O–H bonds were formed after debonding, so it could possibly have been distributed more evenly across the film.

In Fig. 6 the positions of the h-BN and c-BN IR absorption peaks before and after delamination are plotted as a function of the  $A$  value. Little or no change is observed in the position of the hexagonal material absorption peak after delamination occurs, although it is interesting to see that the highest blue shifts of the cubic material absorption band coincided with the highest peak frequencies of h-BN; the position of the h-BN band can also be correlated with the  $Q$  value that is found for the films, so it may be concluded that the

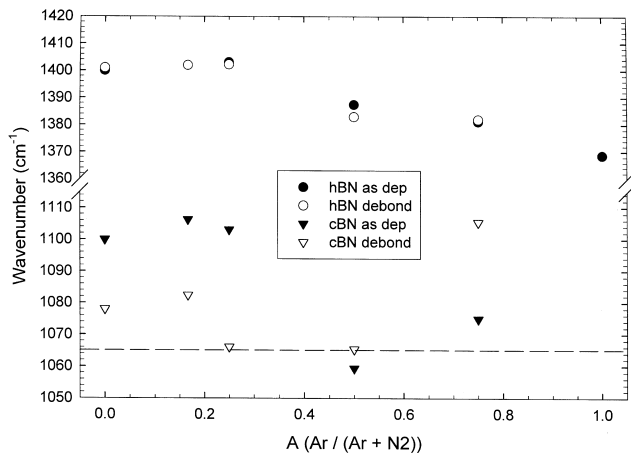
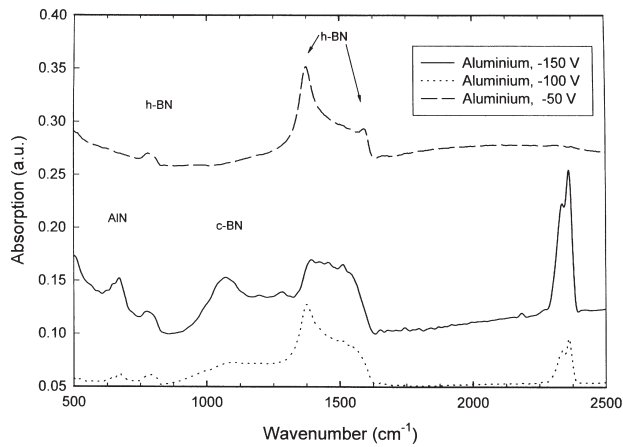


Fig. 6. Position of the peak of the FTIR absorption bands corresponding to hexagonal (circles) and cubic (triangles) boron nitride, as a function of the relative argon flow or  $A$  value  $Ar/(Ar + N_2)$  before (full symbols) and after (empty symbols) the films debonded from the substrate. The bulk value for the c-BN TO mode is indicated by a dashed horizontal line. Notice that in the case of the hexagonal feature some of the symbols almost coincide and hence are overlapped.

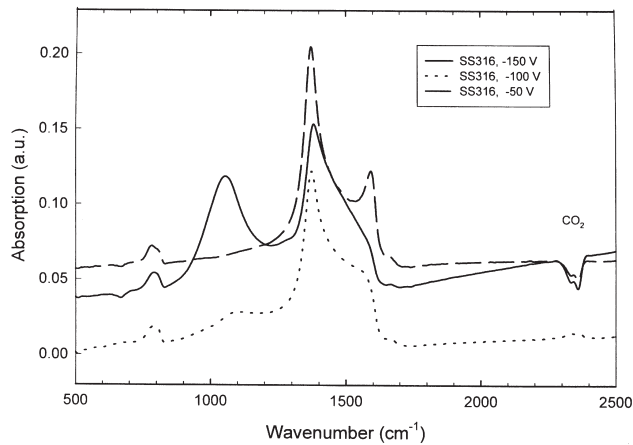
shift of this feature from one sample to another is related to the microstructure of the films and not to the biaxial stress present in them as little or no shift is observed after delamination. For  $A=1$  there are no values for c-BN since no cubic phase was present and actually no delamination was observed after 3 months of storage in air; in fact the film with the largest  $Q$  value took only a few hours to delaminate completely, whereas for lower  $Q$  values and boron rich films the delamination time ran into several weeks. It is also clear from Fig. 6 that the largest cubic phase content is related to the largest compressive biaxial stress present in the films (about 24 GPa according to ref. [17]) as has been found by other researchers [18]. This was confirmed when examining the flakes of the delaminated layers through the SEM used to obtain the EDS spectra for composition determination; the samples with lower  $Q$  values had larger flakes with longer radius of curvature, whereas those with high  $Q$  values had small and highly curled flakes. These facts suggest that the stress related to film debonding is directly related to the presence of relative large amounts of c-BN in an almost stoichiometric material; although argon was incorporated in the films (0 to 2.5 at%), those that had higher inclusions of this gas were the ones prepared with  $A=1$ , since no debonding occurred in these films, the stress cannot be solely related to the presence of argon in the films. For  $A=0.5, 0.75$  the shift is negative, indicating that the excess of boron creates a tensile stress before delamination, although in the second case the large red shift might have been caused by the creation of a silicon dioxide layer on exposed silicon. Notice though, that after debonding, the c-BN absorption peak position does not return to the bulk value wavenumber, this may be due

to residual stress left in the curled flakes of the debonded material, to crystal size effects or — in the case of boron-rich films — to a vibration frequency shift caused by the presence of excess boron [10]. Fahy et al. [19] have reported that shifts to higher energies in the TO mode peak of c-BN might be caused by the polarization of small, dispersed c-BN grains; we unfortunately could not measure the size of the crystallites present in the sample; however, if they were small enough and embedded in a hexagonal and amorphous boron nitride layer, after debonding their relative separation could have increased, giving place to such a shift.

Finally, using the conditions that yielded the largest  $Q$  value for the films deposited on silicon, which were  $A=0.25$  and a slightly lower pressure of 3.6 mTorr [20], samples were prepared on metallic substrates, namely aluminium and stainless steel with a rough surface ( $RA=2000 \text{ \AA}$ ). Internal reflection FTIR was used to study their bonding structure and examples of such spectra are shown in Fig. 7a,b for the two different substrates. It can be observed that at higher biases some mixed phase is produced in the aluminium substrates, since bands are found at wavenumbers not associated with boron nitride; still c-BN is formed. It is obvious that a certain bias voltage is needed to obtain a cubic phase, but what is most important is that, regardless of the mechanical properties of the substrate material [ $HV(Al)=50$ ,  $HV(SS)=220$ ] it is still possible by this method to produce highly cubic material; since the internal reflection method is most sensible at the substrate film interface, where hexagonal and amorphous boron nitride are dominant [8], the  $Q$  values underestimate the cubic phase content, hence following Mirkarimi's results [3] the  $Q$  value for these films should be equivalent to a 60 to 70% c-BN content. This is in contradiction to previous results by the same researchers who reported  $Q$  values scaling with substrate hardness, but nevertheless did not report the average roughness of their metallic substrates [3]. Thus these apparently contrasting results might imply that surface morphology does play a role in the nucleation of c-BN. There is a report by Ikeda et al. [21] stating that when rough silicon surfaces are used as substrates, the ion plating method they use yields mainly h-BN, whereas when their surface is flat, mainly c-BN is obtained. However, the method is highly directional, as boron has to travel through an arc-like plasma after being evaporated by an electron gun, and the material source might have been somewhat far from the substrate; whereas in our case the target is only 4 cm away and hence makes less directional the arrival of boron atoms and nitrogen ions at the substrate surface. The effect of surface morphology could be reflected in how the stresses, that apparently give rise to the c-BN nucleation [13], are distributed along the growing surface. A systematic



(a)



(b)

Fig. 7. FTIR internal reflection spectra (they are actually measures of surface enhanced absorption) for samples deposited on (a) aluminium substrates and (b) stainless steel substrates, at different d.c. bias voltages indicated in the legend. Notice that the LO mode of hexagonal boron nitride can be observed in all cases.

study of substrate roughness and composition versus cubic phase content is under way.

#### 4. Conclusions

Boron nitride thin films have been produced by radio frequency sputtering of a hexagonal BN target at different argon to nitrogen gas ratios, optical emission spectra of the plasmas were obtained by an optical fibre. Films with different compositions and cubic phase content were deposited. The amount of cubic phase can be related to an intensity ratio of the emission lines of atomic boron and  $N_2$  ions. Below certain  $Ar/Ar+N_2$  flow ratio the films lock into stoichiometry, then the amount of cubic phase is dependent on the ion bombard-

ing conditions determined by the amount of nitrogen ions present in the plasma. The films prepared on rough metallic substrates under optimal conditions show large cubic phase content regardless of the substrate mechanical properties.

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