

Optical properties of thin hexagonal boron nitride layers

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Manuscript received 15 Mac 2003
Manuscript revised 20 Sept. 2003

Abstract: *Thin films of hexagonal boron nitride have been deposited at low temperature in a microwave plasma enhanced chemical vapor deposition reactor. They have been characterized by Infrared (FTIR) and micro-Raman spectroscopy (SMR). The films are optically anisotropic, and the IR measurements can be properly modeled when using an uniaxial model for the layers. This description is valid at the macroscopic scale, but gives only an averaged response of the polycrystalline nature of the films. Actually, they are constituted at the atomic scale by a collection of nanocrystallites with a preferred orientation around the normal of the layer. The size of the crystallites can be evaluated by micro-Raman measurements, when taking into account a confinement model. Some thermal annealing have been performed.*

Keywords : Nitrides, h-BN thin film, FTIR, micro-Raman, orientation, crystal size.

Introduction: Boron nitride (BN) is the lighter of the III-V compounds, not found in the nature, its properties being in a major part analogous to those of carbon, its nearest neighbor. Like this one, its orbital can be hybridized whether sp^2 or sp^3 , leading to two generic forms,

respectively the hexagonal (h-BN), and the cubic one (c-BN). The h-BN is constituted by planes of boron and nitrogen alternatively located at the nodes of a hexagonal network, which can be stacked in the form of a hexagonal crystalline structure or of a rhombohedral one [1]. In the case of a random stacking of the planes, the structure is referred as the turbostratic one. The tetrahedral arrangement of the sp^3 hybridization leads to the denser phases, the zinc-blende and the wurtzitic crystalline structures, which present great analogies with diamond and lonsdalite for the carbon. In this paper we will deal only with h-BN thin films, which has a wide gap semiconductor and difference than graphite. It is an optically transparent down to the near UV. By nature all its properties (electrical, optical, mechanical ...) are highly anisotropic, and are distinguished relatively to one of its two major directions. to say parallel or perpendicular to the c-axis.

Boron nitride is a fully artificial compound, and the h-BN has been industrially synthesized into a powder form, with a white aspect, essentially for the metallurgy, due to its chemical inertness against melted metals and its lubricant properties. Its synthesis in the form of thin films has been investigated with a great variety of deposition techniques, including the laser ablation, magnetron sputtering [2], dip coating [3] or chemical vapor deposition [4], the resulting materials being polycrystalline or amorphous. X-ray diffraction (XRD) cannot efficiently be employed for the structural characterization, due to its very low cross-section, with light elements like boron and nitrogen. This is especially true in the case of thin films where the interaction volume is reduced as compared to bulk material. Transmission electron microscopy, can be a valuable method to overcome these problems, but such an apparatus is not found everywhere. Moreover, this method is destructive, and requires a sample preparation which is time consuming and difficult to perform. On the contrary, IR and Raman spectroscopies can give some structural information quickly and easily, and are non destructive and widely spread methods. Infrared spectroscopy is especially attractive to characterize boron nitride, due to its high sensitivity to this compound.

Experimental - The synthesis of the boron nitride layers has been performed at low temperature in a plasma enhanced chemical vapor deposition reactor. A schematic view graph of the experimental set up has already been presented in a previous article [5]. The

walls of the chamber have a conical geometry, and are built in quartz glass. The samples are located on an holder of about 50 mm diameter, made of a sheet of molybdenum. They are radiatively heated through the chamber wall by means of four halogen lamps (250W, 24V), with metallic reflectors, whom bias is manually adjusted with a autotransformer (Variac). The temperature is measured with a thermocouple inserted in the holder, and is kept at 215 to 220°C during the deposition. The true temperature on the front face of the samples is estimated between 250 and 280 °C. The pressure in the reactor is regulated at 0.1 Torr, under a constant flux of nitrogen and argon gas of 0.2 litre each, controlled with mass flow controllers. The boron precursor is an organometallic compounds, the borane-dimethylamine $(\text{CH}_3)_2\text{-NH-BH}_3$ (BDMA), maintained at 37 °C, 1°C above its melting point in a vessel, and introduced in the reactor by bubbling a stream of nitrogen. A microwave plasma is sustained in the upper part of the reactor with a magnetron working at 2.45 GHz, delivering a power generally set between 100 and 1200 W, and coupled to the reactor with a surface wave launcher of 'Surfatron' type. The deposits are done on silicon substrates with (100) orientation, on a optically polished surface. The infrared transmittance measurements are obtained by using a Mattson 3000 FTIR spectrometer, covering the mid IR region from 400 to 4000 cm^{-1} , with a best resolution of 2 cm^{-1} . An optical grid polariser (Graseby Specac IGP-225), covering the same region can be added, to select the S or P component at non-normal incidence.

Another part of the characterizations involve Raman measurements performed with a Jobin Yvon MicroRaman spectrometer (LABRAM system), working in the backscattering geometry, with the red line of an He-Ne laser (632.8nm), through a 100X microscope objective. Some post deposition thermal annealing of 30 min each have been performed at increasing temperatures from 400 to 1000 °C, and pressure of about 300 Torr, under a flow of nitrogen. The oven is previously turned on to the desired temperature, and moved in order to produce a warming up and cooling down with a constant slope of 20 °C.min⁻¹.

Results and discussion: A typical infrared spectrum of a h-BN layer is presented on Figure 1. The two absorption bands at 1370 and 780 cm^{-1} correspond to transversal optical vibrations, respectively the in plane B-N stretching mode (E_{1g}), and the out of plane B-N-B

bending mode (A_{2u}) [1]. We will refer to them as the TO_{\perp} and the TO_{\parallel} modes, with respect to the deformation direction relative to the c-axis of the h-BN structure. Associated with each of them, there are two longitudinal modes, the LO_{\perp} and the LO_{\parallel} , which can be excited when performing the infrared transmittance measurements at oblique incidence, according to the Berreman effect [6].

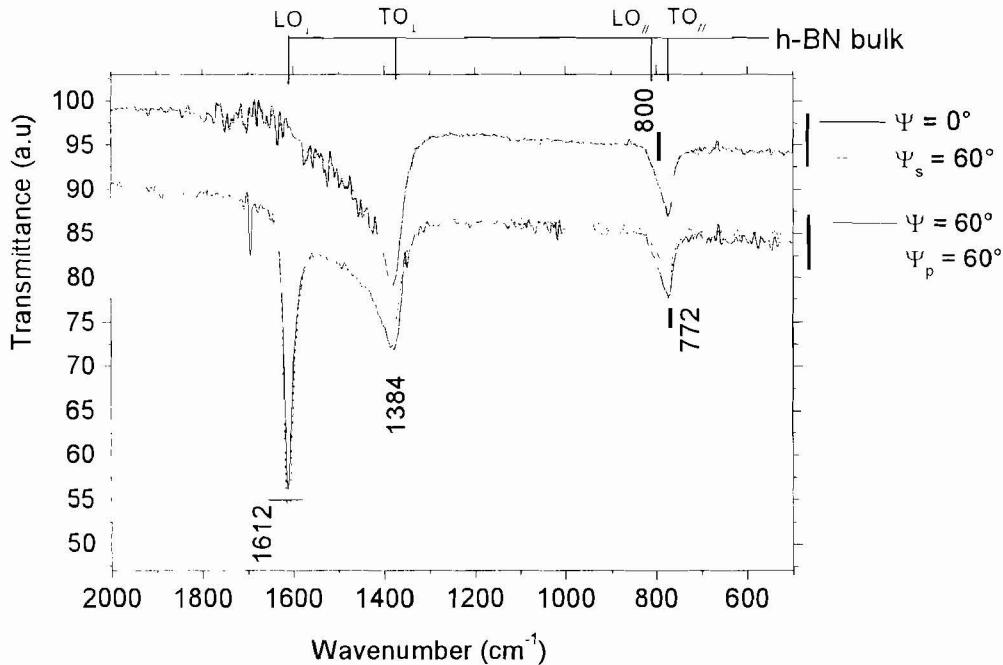


Figure 1 : Infrared transmittance spectra measured at normal and oblique incidence on a film of h-BN205 deposited on a silicon substrate. Ψ is the angle of incidence of the natural light; Ψ_s and Ψ_p is the angle of incidence of the polarized light, respectively S and P.

This latter measurement has established that the LO modes can be activated at oblique incidence in layered media whose thickness is less than the incoming wavelength. It happened only in the direction along the normal of the film, when a LO mode and electric field component of the electromagnetic wave overlap. Also, only the P polarized part of the wave is concerned, and in an anisotropic medium such as h-BN (or else), only the LO mode with a component within the direction of the sample normal can be evidenced.

Experimentally, we observe that between various samples, their IR transmittance spectra recorded at oblique incidence are different, but when considering one of them, it remains the same when it is tilted around its normal. This behavior can perfectly be expressed in the optical model of an uniaxial medium with an extraordinary direction along their normal and an isotropic behavior in the plane of the film, which has been derived by Schubert *et al.* [2]. The effective dielectric function of the h-BN films is described at the macroscopic scale by the averaged response of a collection of crystallites with the same orientation of their *c*-axis relative to the normal of the layer. When it is oriented along the normal, only the LO_{\parallel} is observed, whereas when it is perpendicular only the LO_{\perp} is observed at its position. When this angle varies, the absorption band of the LO mode continuously shifts between their position, and the position of the associated TO mode [2,5] (see Figure 2).

At the same time, its intensity decreases, and drop to zero when it is oriented within the plane of the film, due to the decrease of its overlapping with the electric field. The observation of the LO modes in an anisotropic medium is then a direct indication of the structuration of the film. Experimentally, this set of h-BN samples with various orientations of the *c* axis have been obtained by varying the plasma power in the reaction chamber, between 250 and 700 W. At the lower microwave power, the *c*-axis is oriented along the normal of the substrate, and it rotates at increasing power, to be finally directed in the plane of the sample at 700W. All the other parameters were kept constant, with a pressure regulated to 0.1 Torr, with identical argon and nitrogen flow rates of 20 sscm, and a silicon substrate maintained at about 250 °C. The values of the TO_{\perp} and the TO_{\parallel} have been deduced to be respectively 1612 cm^{-1} and 820 cm^{-1} . These values are in perfect agreement with those reported by Schubert *et al* [2], with samples of h-BN deposited by reactive magnetron sputtering.

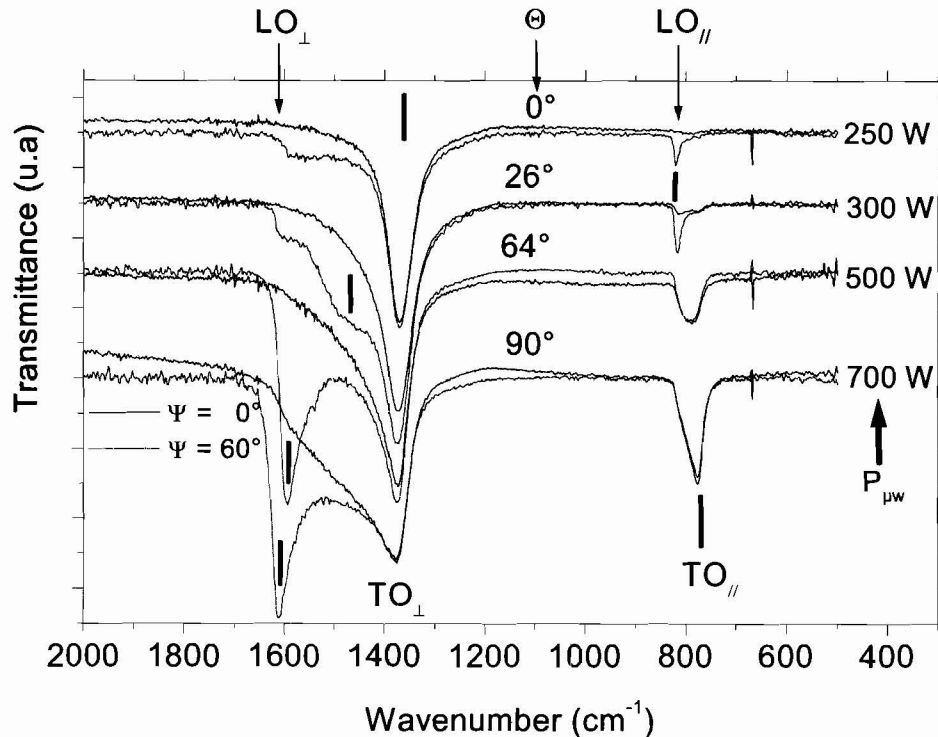


Figure 2 : Infrared transmittance spectra measured with a beam incidence of $\Psi = 60^\circ$ from the normal, on samples h-BN samples with a c-axis oriented from the normal down to the plane of the substrate. The shift of the LO modes can be observed. For various values of the plasma power $P_{\mu w}$ from 250 to 700 W, the c-axis orientation rotates from nearly $\theta = 0^\circ$ to 90° [5]. For each power is associated a curve in incidence normal (— $\Psi = 0^\circ$) and in oblique incidence (----- $\Psi = 60^\circ$).

In Raman spectroscopy of h-BN, there are two E_{2g} modes which are active, one at 1366.2 cm^{-1} which is strong and corresponds to vibrations of B and N moving against each other in the plane, and a mode at 51.8 cm^{-1} , attributed to sliding between whole planes [7]. We have observed this latter at about 57 cm^{-1} , but its observation is difficult because of the vicinity of the Rayleigh diffusion, and to the presence of a fluorescence background. For the high frequency mode, both the Stokes and the anti-Stokes peaks, have been easily observed (see Figure 3). They are positioned at 1375 cm^{-1} , about 8 cm^{-1} above the reference position given

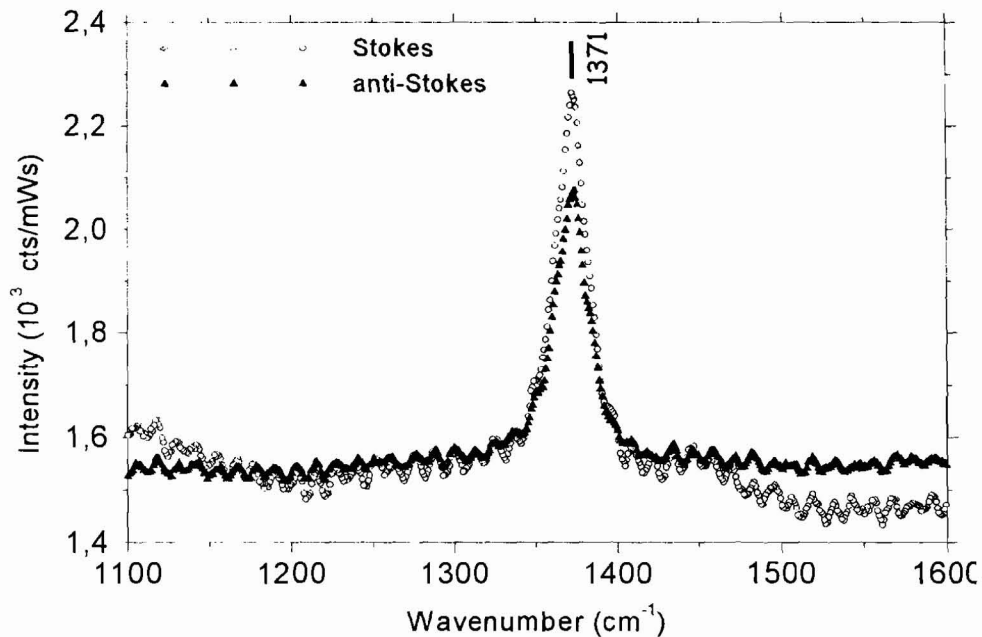


Figure 3 : Micro-Raman measurement on a h-BN233 sample. The Stokes and the anti-Stokes response of the high frequency mode of h-BN233 is evidenced.

previously, with a width at half maximum (FWHM) of 19 cm^{-1} , which is markedly larger than the 2 cm^{-1} resolution of the spectrometer. This shift in the position and the enlargement of the band can be explained by a size effect of the crystallites, according to a confinement model [8]. Due to the polycrystalline nature of the layer, there exists only a limited undisturbed volume where the vibrations are confined, resulting in an uncertainty of the phonon wave vector, owing to interactions not only at the center of the Brillouin zone. The shifting to higher wave number can then be explained by the unusual phonon dispersion curve for the E_{2g} mode of h-BN, which increases from the Γ point. The dimension of the crystallites can be determined, according to the systematic study performed by Nemanich *et al.* [8] on the Raman response of h-BN samples of various sizes. They have derived an expression : $\text{FWHM} = 8.70 + 1417/L_a$, expressing a linear dependence of the FWHM versus ($1/L_a$), respectively given in cm^{-1} and in \AA^{-1} , where L_a is the size of the crystallites measured

by X-ray diffraction. A value of 13 nm can be inferred in our case, when subtracting quadratically the resolution of their apparatus, which is evaluated to 10 nm, on their larger samples.

The effect of a thermal annealing on the Raman response is presented on Figure 4. The temperature was increased from 400 to 1000 °C, and the same sample was successively annealed and characterized with the same acquisition parameters. The intensity of the Raman line has increased with the temperature, especially at 800°C, indicating a better crystallinity of the sample. However no modification of the peak position and of its FWHM has been evidenced. This seems to indicate the presence of a larger number of crystallites rather than an increase of their size. The additional peak at about 1460 cm⁻¹, is also observed on the bare silicon sample introduced as a reference during the annealing, and is probably attributed to an oxidation resulting from a leak in the oven.

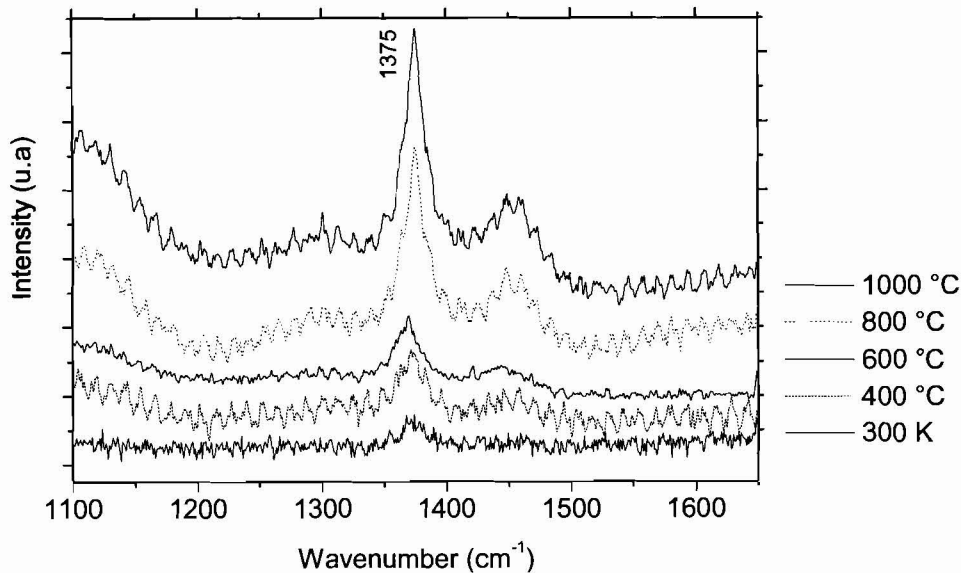


Figure 4 : Successive Micro-Raman spectra performed on a h-BN285 sample thermally annealed during 30 minutes, when increasing the temperature from 400 to 1000 °C.

Conclusion: Thin films of hexagonal boron nitride have been deposited by plasma enhanced CVD, and their optical properties in the infra-red region has been modelled as an uniaxial anisotropic medium. This description in conjunction of the observation of the LO modes in transmittance at oblique incidence allows us to determine the average orientation of the c-axis of the nanocrystallites constituting the layers. The size of the crystallites has been evaluated to 13 nm thanks to Micro-Raman measurements. A better crystallization of the sample has been evidenced by Micro-Raman measurements, when performing a thermal annealing at high temperature.

References

- [1] R. Geick, C. H. Perry, G. Rupprecht, Phys. Rev. **146**, 543-547 (1966)
- [2] M. Schubert, B. Rheinlander, E. Franke, H. Neumann, T. E. Tiwald, J. A. Woollam, J. Hahn, F. Richter, Phys. Rev. **B56**, 13306-13313 (1997)
- [3] L. Chen, B. J. Tan, W. S. Willis, F. S. Galasso, S. L. Suib, J. Am. Ceram. Soc. **77**, 1011-1016 (1994)
- [4] B. J. Choi, D. W. Park, D. R. Kim, J. Mat. Sci. Let. **14**, 452-454 (1995)
- [5] A. Soltani, P. Thévenin, A. Bath, Mat. Sci. & Eng. **B82**, 170-172 (2001)
- [6] D. W. Berreman, Phys. Rev. **130**, 2193-2198 (1963)
- [7] L. Bergman, R. J. Nemanich, Ann. Rev. Mater. Sci. **26**, 551-579 (1996)
- [8] R. J. Nemanich, S. A. Solin, R. M. Martin, Phys. Rev. **B23**, 6348-6356 (1981)