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Effect of Nitrogen Plasma after glow on Amorphous Boron Nitride Thin Films deposited by Laser Ablation

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Abstract: In this study, we aim to determine the spectral characteristics of the Boron Nitride thin films which are prepared by laser ablation method through analyzing the measurements data conducted by using optical absorption spectroscopy, FTIR spectroscopy and Raman spectroscopy for all prepared samples, In addition to illustrating the impact of each Nitrogen Plasma after glow and the position pressure of on the spectral characteristics of BN thin films.
Keywords: Effect of Nitrogen Plasma, Amorphous Boron Nitride, Thin Films, Laser Ablation.

1. Introduction

Boron Nitride is one of the heat-resistant ceramic substances. It has structures in which the covalent bonds are the prevalent ones. Amorphous Boron Nitride Thin films are characterized by a mix of BN bonds with different patterns of SP^2 and SP^3 hybridization. Thin films characteristics depend mainly on the percentage of these two phases [1]. Interest arose in this phase because developing cubic phase c-BN requires applying high degrees of heat, which does not fit most applications such as optical coating, where thin films with smooth surfaces and homogeneous structure are produced in low degrees of heat. Therefore, it is resorted to produce amorphous Boron Nitride thin films a-BN with high content of BN bonds with SP^3 hybridization, which have characteristics similar to the ones contained in phase c-BN, which can be prepared also at room temperature [2]. The importance of the amorphous phase appears as well during preparing the cubic phase c-BN. In order to get this phase, a primary thickness of amorphous Boron Nitride should exist to provide a limit value of interfacial stress required for the process of cubic phase growing [3].

BN bonds can be monitored in Boron Nitride thin films by FT-IR spectroscopy, where distinct peaks positions of these bonds depend mainly on t he terms of deposition conditions.

Raman spectroscopy can be used to determine the different bonds in Boron Nitride thin films. Cubic phase can be recognized by emergence of distinct peaks at the wave numbers 1055 cm^{-1} and 1304 cm^{-1}. The first peak emerges as a result of the dispersal due to transverse oscillations of BN bond, while the second peak emerges due to longitudinal oscillations [4] for the same bond.

Crystallized Boron Nitride thin films have wide indirect energy gap (Eg>5ev) [5]. While in amorphous Boron Nitride thin films, the thin films optical response depends on the different optical responses for bonds SP^2 and SP^3, which are related to the percentages of these bonds [6].

2. Experimental

Amorphous Boron Nitride films were deposited onto non-heated polished *n*-type Si (100). The Q-switched Nd:YAG pulsed laser (RD-YG-300) was operated at 1 Hz repetition rate and of emission at the fundamental line (λ = 1064 nm) with a 20 ns pulse duration. The laser beam was focused on the Boron target at an incidence angle of 45^{o} and a laser fluence of 12.8 $J\,cm^{-2}$.The substrates were installed on an aluminum holder at a distance of about 2 cm from the target. Two series of Boron Nitride films were prepared in two di▪ erent atmospheres. One (series I) is a deposition in an atmosphere of pure nitrogen molecular gas (purity 99.999%). The Other (series II) is a deposition in a NPA generated by Microwave SAIREM GMP 20 KEDS at fixed transmitted power of 1000 W. The deposition was performed in N_2 or NPA pressures changing from 10 to 100, to 300, to 500, and to 1000 Pa. The schematic and a photo of the experimental setup are shown in Fig (1) More details about the technique and deposition procedures are explained in previous works.

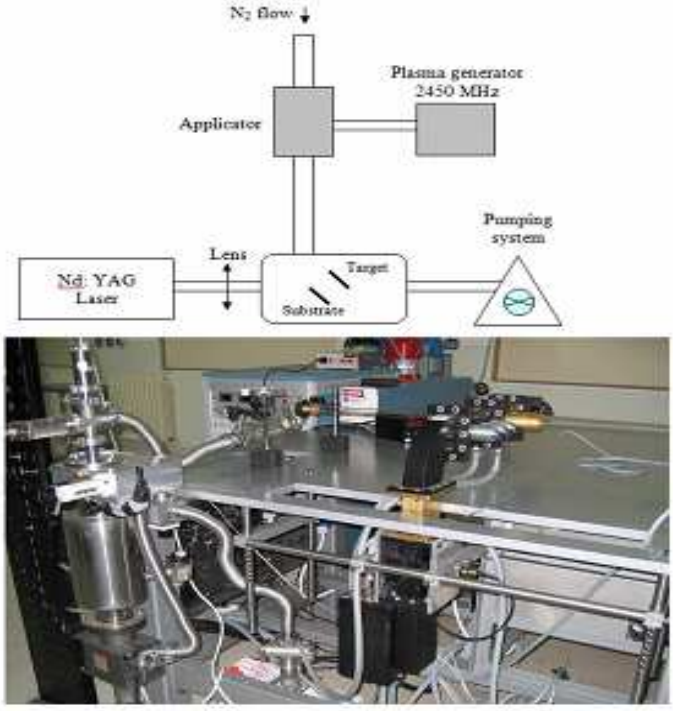

Fig (1): Schematic and photo of the experimental setup.

To investigate the structure and composition of the films, di▪ erent techniques are used.

3. Results and discussion

X-ray diffraction Spectra of Boron nitride thin films on Silicon substrates precipitated were recorded by grazing angle. XRD photos analyzing showed that prepared thin films have an amorphous structure. Figure (2) showed a model of spectra of X-ray diffraction of these thin films, belongs to the prepared sample at positioning pressure of 100Pa from Series B. It is notified that there is no featured peak indicating crystallization.

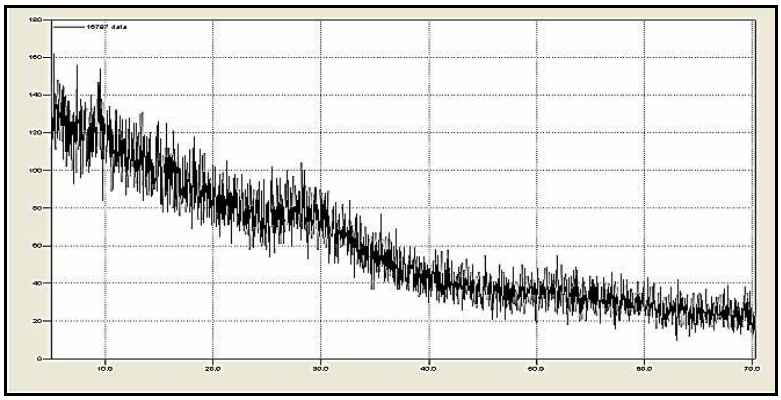

Fig (2): X-ray diffraction spectrum of the prepared series at positioning pressure of 100 Pa from Series B.

In order to study the impact of the substrate, the prepared sample has been re-prepared at positioning pressure of 300Pa of Series B, but on a slice of silicon substrate (111), with a layer of AIN precipitated on it. This substrate was chosen because of the promising results that have been obtained when precipitating Carbon Nitride thin films [7]. Figure (3) contains an XRD spectrum for this sample. Emergence of three peaks indicating formulation of the hexavalent phase h-BN at the values of 2θ (13.20, 26.68, 41.49) is notified. The rest of the appearing peaks are for Aluminum Nitride substrate.

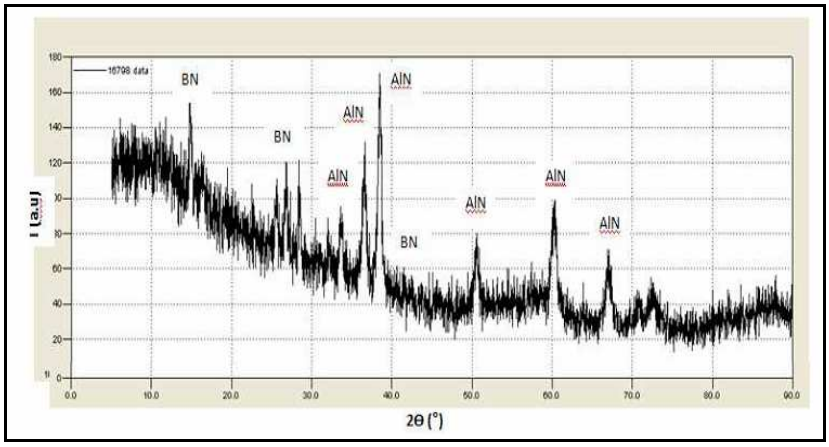

Fig (3): XRD spectrum of BN sample prepared on AIN substrates

Figures (4) and (5) contain the optical transmittance curves for A and B Series. The general form of spectra is similar to the transmittance spectra obtained from previous studies [10].

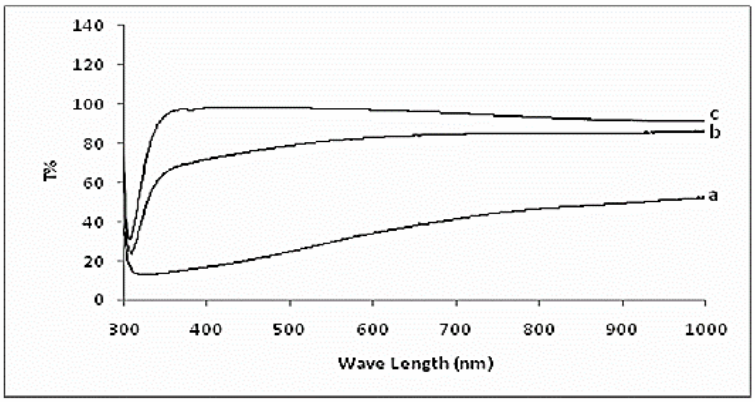

Figure (4): The optical transmittance curves for series A: (a) 10 pa (b) 100 pa (c) 1000 pa.

Increase in transmittance with increase in positioning pressure for both types of samples is notified. It is noted also that using plasma after glow will results in increased transmittance of sample a and decreased transmittance of sample c, whereas there were no impact upon sample b.

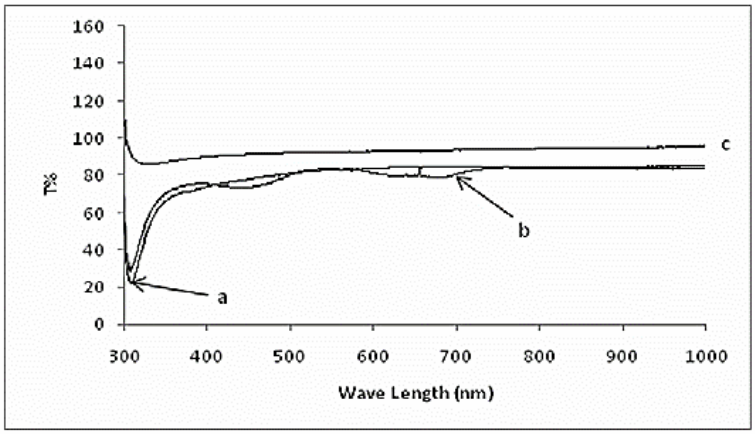

Figure (5): the optical transmittance curves for series B: (a) 10 pa (b) 100 pa (c) 1000 pa.

Ripples noted in the curve b of figure (5) resulting from the slight thickness of this membrane. These ripples are overlap cilia resulting from interference of optical waves reflected from the both sides of the thin film.

The optical energy gap of precipitated samples on the glass substrates was calculated by using Tauc method. The resulting values were included in Table (1), which contains the values of the optical energy gap for all samples in A and B series.

Eg(ev)	P(pa)	
0.755	10	Series A
0.470	100	
3.335	1000	
0.381	10	Series B
0.608	100	
1.194	1000	

Table (1) : The values of the optical energy gap for all samples in A and B series.

The numeric values of optical energy gap decrease by the impact of optical absorbance spectra due to formulation of energy sub-levels within optical energy gap resulting from stress and deformations happened during the growth of the membrane [8]. Stress and deformations occurred due to entry of SP^3 hybridization carbon atoms to the issue arranging SP^2 hybridization bonds.

Figures (6) and (7) contain FT-IR curves of BN samples prepared in different pressures. For Series A samples, it is noticeable that finding NB (sp^2)/LO bonds is feasible through the pack located in the filed 1550-1600 cm^{-1} (The peak shifts toward the low wave numbers when increasing pressure to 1000Pa). In addition, we can notes the existence of NB (sp^3) bonds located at 1132-1244 cm^{-1}, which appear clearly in sample b spectrum.

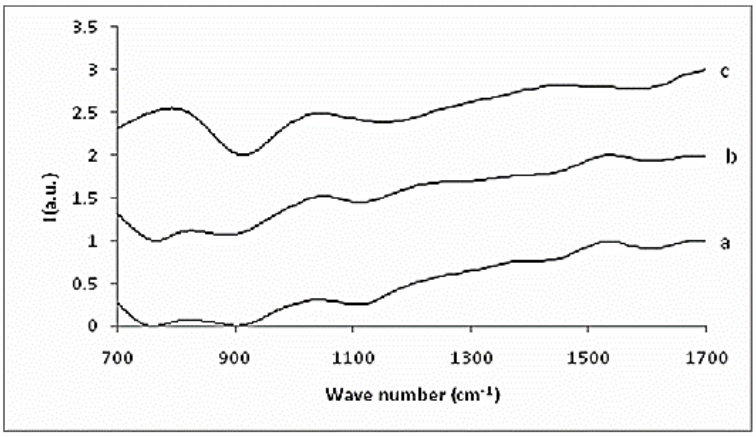

Figure (6): FT-IR curves of series A samples : (a)10 pa (b) 100 pa (c) 1000 pa.

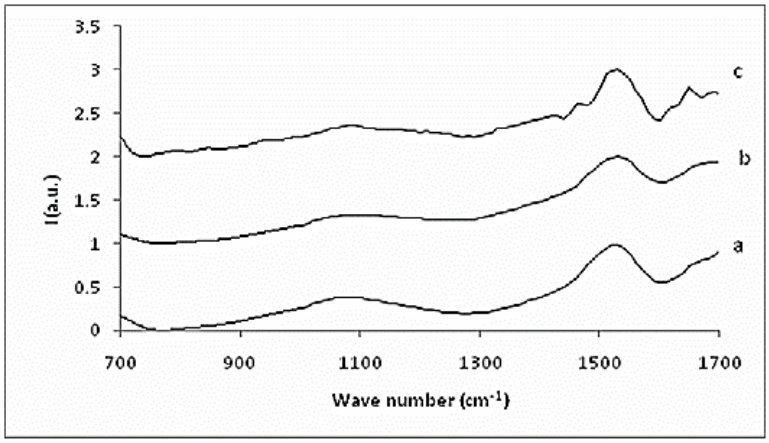

Figure (7): FT-IR curves of Series B samples: (a)10 pa (b) 100 pa (c) 1000 pa.

In Series B samples, it is noted that using after glow microwave plasma results in disappearance of the peak located in the field 760-990 cm^{-1} for samples a and b, and possession of weak intensity for c sample. Plasma results in increase in the intense of pack located in the field 1550-1600 cm^{-1}, indicating the existence of NB (sp^2)/LO bonds over other peaks and the drift in the peak indicating existence of NB (sp^3) bonds toward high wavelike numbers. In figure (5), emergence of new peaks can be noted at wave numbers 1650 cm^{-1} and 1450 cm^{-1} (sample c).

Figure (8) illustrates the BN (SP^3) peak area as a function of pressure for both types of samples A and B . It is noted that increasing the positioning pressure results in increasing the content of the membranes of these bonds for both types of samples. Moreover, using plasma will cause a decrease in the percentage of SP^2 hybridization bonds.

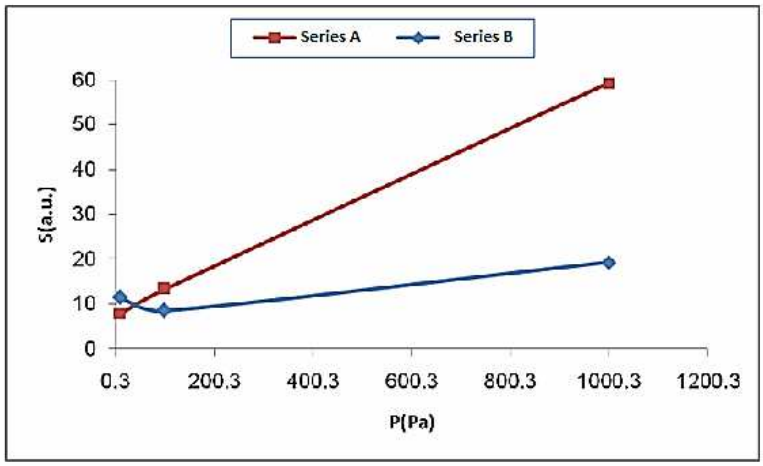

Figure (8): The BN (SP^3) peak area as a function of pressure for both types of samples A and B.

The peak located at the wavelike number 961.29 cm^{-1} belongs to silicon substrate [9]. The wide pack located at the field 1150-1550 cm^{-1} belongs to NB (sp^2)/LO bonds. This pack connect with another less intense pack located at wavelike number 1590 cm^{-1}, which are belong to bonds similar to those in EBN phase. Two small peaks can be also notified to the lift of silicon peak, located at wavelike numbers 808 cm^{-1} and 651 cm^{-1}; the first one belongs to NB (sp^2) bonds (similar to r phase bonds), while the other occurred because of B_2O_3 formulation [10]. Emergence of Oxygen in the membrane can be attributed to O_2 and H_2O molecules adsorbed at the membrane surface, in addition to Oxygen remnants remained after vacuuming.

http://journals.aps.org/prb/abstract/10.1103/PhysRevB.87.035101

4. Conclusion

We have deposited amorphous Boron nitride films by microwave remote nitrogen plasma afterglow assisted pulsed laser deposition. It was found that, using after glow microscopic plasma will results increased transmittance of sample a and decreased transmittance of sample c, whereas there were no impact upon sample b. The numeric values of optical energy gap decrease by the impact of optical absorbance spectra due to formulation of energy sub-levels within optical energy gap resulting from stress and deformations happened during the growth of the membrane.

In FT-IR spectrum we notes that using after glow microscopic plasma results in disappearance of the peak located in the field 760-990 cm-1 for samples a and b, and possession of weak intensity for c sample. Plasma results in increase in the intense of pack located in the field 1550-1600 cm^{-1}, indicating the existence of NB (sp2)/LO bonds over other peaks and the drift in the peak indicating existence of NB (sp3) bonds toward high wavelike numbers. Also we notes, emergence of new peaks at wave numbers 1650 cm^{-1} (sample c) and 1450 cm^{-1} (sample c). Moreover, using plasma will cause a decrease in the percentage of SP2 hybridization bonds. In addition we found that, using layer of Aluminum nitride on a piece of silicon as a substrate, leads to form both of EBN links and hBN small crystals.

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