NANOSTRUCTURES BASED IN BORO NITRIDE THIN FILMS DEPOSITED BY PLD ONTO Si/Si$_3$N$_4$/DLC SUBSTRATE

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Abstract. Diamond-like carbon and boron nitride were deposited like nanostructured bilayer on Si/Si$_3$N$_4$ substrate, both with (100) crystallographic orientation, these films were deposited through pulsed laser technique (Nd: YAG: 8 Jcm$^{-2}$, 9ns). Graphite (99.99%) and boron nitride (99.99%) targets used to growth the films in argon atmosphere. The thicknesses of bilayer were determined with a perfilometer, active vibration modes were analyzed using infrared spectroscopy (FTIR), finding bands associated around 1400 cm$^{-1}$ for B – N bonding and bands around 1700 cm$^{-1}$ associated with C=C stretching vibrations of non-conjugated alkenes and azomethinic groups, respectively. The crystallites of thin films were analyzed using X-ray diffraction (XRD) and determined the h-BN (0002), α-Si$_3$N$_4$ (101) phases. The aim of this study is to relate the dependence on physical and chemical characteristics of the system Si/Si$_3$N$_4$/DLC/BN with gas pressure adjusted at the 1.33, 2.67 and 5.33 Pa values.

1. Introduction

Pulsed laser deposition (PLD) is a conceptually simple technique that generates reactive species under highly non-equilibrium conditions, which cannot be produced by any other technique. This leads the way to the growth of materials having unique properties, and indeed, PLD is proving to be one of the most attractive techniques to synthesize amorphous carbon-based thin films such as diamond-like-carbon (DLC) [1] and nitride thin films. The physical properties of carbon-based materials, such as hardness and electrical conductivity, depend to a large extent on the deposition conditions such as gas pressure and substrate temperature as well as on the structural arrangement of the atoms in the films.

Boron nitride (BN) is a synthetic ceramic compound, which crystallizes in crystallographic structures similar to the allotropic forms of carbon. Two most important crystalline forms are hexagonal (h-BN) and cubic (c-BN) one, which are similar to graphite and diamond respectively. Graphite-like phase (h-BN) is a soft chemically inert and stable in air atmosphere insulator, what makes it suitable compound for insulating protective and self lubricating coatings, while cubic phase (c-BN) is the second hardness compound after diamond. Cubic form has also special advantage with

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respect to diamond like its inertness with respect to iron even at high temperatures. Therefore c-BN thin films can be applied as super-hard wear-resistant corrosion resistant coatings for cutting tools, optical and electronic devices etc. [1-2]. The most important advantages of PLD are high deposition rate in laser pulsed, stoichiometry transfer, possibility to deposition without substrate heating and easy preparation of multilayer coatings [3].

In this paper, we report on low-temperature preparation of BN thin films, using pulsed laser deposition method. We prepared BN films on top of the DLC layers and DLC thin films were grown on silicon and silicon nitride as Si/Si$_3$N$_4$ substrates, through pulsed laser ablation of a sintered BN target, in the environment of Argon. The composition and chemical structure of the prepared films were studied using X-ray spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy.

2. Experimental Details

The experiments have made in usual PLD configuration consisting of laser system, a multi-port stainless steel vacuum chamber equipped with a gas inlet, a rotating target and a heated substrate holder. We used a Nd:YAG laser that provides pulses at the wavelength of 1064 nm with 9 ns pulse duration and repetition rate 10 Hz, the laser fluence kept to 8 J/cm$^2$. The laser beam was focused with an f=23 cm glass lens on the target at the angle of 45°, with respect the normal. The target was rotating 2.2 rpm to avoid fast drilling. The distance between the target and the substrate was 6.5 cm. Before deposition the vacuum chamber was evacuated down to 2 x 10$^{-5}$ Pa by using rotary pump and turbo-molecular pump, then a continuous flow of argon, 99.99% purity, was introduce and the argon pressure was fixed from 1 to 20 Pa by changing the argon flux. Fig. 1 shows a schematic diagram of the PLD system used in this study [4]. The DLC films were grown at room temperature and under different argon pressures on the Si$_3$N$_4$ substrate, whereas the BN films were grown on top of the DLC layers with the same experimental parameters of growth. For all thin films the deposition time was 10 min. IR absorption was investigated using the Fourier transform infrared (FTIR) spectrophotometer (Shimatsu model prestige 21). The crystallinity of the films was evaluated by using a X-ray diffraction (XRD) apparatus (Bruker, D8 Advance) with a Cu Kα radiation. The nano-structural analysis of film morphology and crystal nucleation was performed on a Cambridge 360 SEM/EDS.

Figure 1. Schematics of the laser ablation setup.
3. Results and discussion

When prepared PLD for 10 min, the film has a thickness of approximately 350 nm. The BN and DLC films prepared on Si substrates show a very smooth appearance, and are stable and adherent to the substrates under ambient conditions.

3.1. X-ray diffraction analysis

X-ray diffraction patterns of DLC/BN for different gas pressure are shown in Fig. 2. All spectra reveal crystalline structures. XRD patterns showed that the major phase in all the three samples was β-Si₃N₄, which indicated that adding h-BN did not hinder the α→β phase transformation of Si₃N₄. The c-BN phase was not detected in XRD patterns, which may due to either the amounts being too small to be detected or forming the intergranular amorphous phase. In samples grown at 2.67 and 1.33 Pa, additional peak that is close to (0002) peak of h-BN was observed, suggesting the presence of a strong local boron nitride structure [8]. The (0002) diffraction peak in the XRD spectra of the Bₓ-Nᵧ samples suggests the presence of an h-BN-like phase. The amount of this hexagonal Bₓ-Nᵧ phase in the samples can be expected to be proportional to the intensity of the (0002) diffraction peak.

![Figure 2. X-ray diffraction patterns of DLC/BN films grown by PLD at three different gas pressure on Si3N4 substrates.](image)

3.2. FTIR analysis

We show in Fig. 3, typical IR absorption spectra obtained in the range 500–3600 cm⁻¹, at three values of nitrogen partial pressure. In spectrum, two strong absorption bands with dips at approximately 1400 cm⁻¹ and 768 cm⁻¹, are clearly identified. These two bands can be interpreted as the in-plane B–N, stretching vibration and the out-of-plane B–N–B bending vibration [2,3,5], respectively. This indicates a characteristic of the h-BN phase, with a sp² bonding structure. In addition, there is also a small but distinct absorption near 1080 cm⁻¹ corresponding to the transverse optical mode (TO) of c-BN. However, this absorption might also be due to B–C bonds [6]. The film prepared at 2.7 Pa exhibits a strong absorption characteristic of the in-plane B–N stretching vibration at 1400 cm⁻¹ and its out-of-plane B–N–B bending vibration gets weaker. The maximum of peak of the tensile vibrations of B-N bond is observed to be shifted towards lower frequencies (the peak appears at 1371 cm⁻¹ in the reference h-BN crystal). This suggests that there is tensile stress in the BN layer [7]. Such stress could improve the overall layer adhesion by compensating compressive stress, usually encountered in the areas with the sp³-type phase obtained by PLD method and frequently responsible for layer delamination. The spectrum obtained from the layer produced at 5.3 Pa is characterized by a reduced intensity of the signals received from the sp²-BN form and contains only a small intensity peak with the maximum at about 1388 cm⁻¹. This could have been caused by the decrease of amount of...
crystalline h-BN and the tendency of amorphous BN to increase its share in the entire layer volume. The broadening in the absorption band suggests that the film is highly disordered.

**Figure 3.** Typical infrared spectra of DLC/BN thin films for different values of argon partial pressure grown by PLD.

3.3. SEM Characterization

SEM investigations were carried out to observe the surface morphology of the deposited films. Fig. 4 shows the SEM micrographs of the surface of the BN films deposited at different pressures. The deposited films have small droplets and crystallites. It is thought that the droplets consist of elemental boron, ejected from the melt, due to the inhomogeneity of the power density distribution of laser beam on the target. Fragment consists of h-BN, which are typically ejected in ablation process of the soft targets such as h-BN. For films deposited at 5.3 Pa the surfaces contain mostly small size (few tens of nanometer) boron droplets. At 1.33 Pa, the size of the melted boron droplet increases on the surface and the films deposited at 2.67 Pa have a rougher surface. In summary the surface morphology, however, becomes smoother and grain size smaller with increasing the gas pressure.

**Figure 4.** Typical SEM images of the surface of the BN films deposited at the a) 1.33, b) 2.66 and c) 5.3 Pa of Ar gas pressure by Nd:YAG laser ablation at 8 J/cm².

4. Conclusion

DLC/BN bilayer films were deposited PLD using simultaneously graphite and h-BN as targets in Ar atmosphere. The gas pressure in the vacuum chamber was varied from 1.33 Pa to 5.33 Pa changing the argon flux. The pressure changes induce important variations on formation of crystallographic structures of h-BN(0002) and h-BN(0004) phases. The Films grown at 2.67 Pa has shown a shift of the absorption band of B-N and B-N-B phases around 1400 cm⁻¹ and 768 cm⁻¹ respectively, indicating a high influence of gas pressure on the molecular
formation of DLC/BN films. The SEM analysis of the film grown at 5.33 Pa showed more regularity and continuity on its surface than the other bilayer films grown.

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