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High repetition rate deposition of boron nitride films using femtosecond pulsed laser

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Abstract

Cubic (c-BN), and hexagonal (h-BN) boron nitride thin films are of interest in many applications and industries because of their unique mechanical, thermal and chemical properties. In this work, we investigate high repetition rate deposition of BN films using femtosecond pulsed laser deposition. Boron nitride (BN) films were deposited on silicon wafers using 800 nm, 100 fs Ti:sapphire femtosecond laser with 2.4 mJ pulse energy and high repetition rate of 1 kHz using a c-BN target. The deposited films were analyzed using transmission electron microscopy (TEM), scanning electron microscope (SEM), and optical profilometer. Nano-indentation tests were performed to measure the hardness of the adhered film. The results indicate the influence of the high repetition rate on the film growth, crystalline arrangement and adhesion. The experimental work is utilized to identify the process parameters that can be used in pulsed laser deposition (PLD) process to grow thick and adherent BN films.

1. Introduction

Boron nitride (BN) is a compound isoelectronic with carbon, can possess sp2- and sp3-bonded phases. BN has four primary crystalline phases, such as hexagonal BN (h-BN), rhombohedral BN (r-BN), cubic BN (c-BN), and wurtzite BN (w-BN) [1]. In particular, h-BN is occasionally called white graphene because of its likeness and duality. It has received much interest because of its infrequent electronic band arrangement and the nature of its charge carriers that results in high mobility and other incomparable quantum phenomena at room temperature. h-BN is a smart material because its structural properties were quite similar to graphite [2]. c-BN attracts widespread interest as a promising material for many potential applications because of its unique physical and chemical properties, such as the highest hardness lower than diamond, wide bandgap, high thermal conductivity, high electrical resistivity, chemical inertness [3]. Because c-BN has the highest hardness next to diamond, it can be expected to show excellent wear resistance in a frictional environment, and thus it is a natural candidate for hard protective coatings, Zhang and Meng [1]. In comparison to h-BN, c-BN phase presents superior electrical, thermal, optical, and electrical properties, with hardness up to 70 GPa. In addition, owing to its elevated heat chemical stability in machining, c-BN is much better to diamond as a tool for ferrous products. The pulsed laser deposition (PLD) method provides a lot of possibilities in adjusting deposition parameters. The laser wavelength, energy density, pulse duration, target to substrate distance and a substrate temperature could drastically change mechanical and physical properties of thin films [4].

The demand for thin or dense BN film deposition is growing quickly and many researchers are trying to synthesize boron nitride coating not only for cutting but also as protective coating, insulating layers and optical coatings [3]. Reference [6] studied the surface morphology of thin films grown by laser ablation of barium titanate with femtosecond pulses at 620 nm laser wavelength. Reference [7] studied the effect of nitrogen partial pressure on amorphous carbon nitride a-CN_{x} (0.0 \leq x \leq 0.17) and laser fluence on amorphous carbon a-C films prepared by ultrafast high repetition rate PLD. Reference [8] deposited N-doped tungsten carbide thin
films on Si(100) substrates at 500 °C using direct-current reactive magnetron sputtering in a mixture of CH$_4$/N$_2$/Ar discharge. Reference [9, 10] enabled the hardness of polycrystalline cubic/wurtzite boron nitride composite by using surface heating the composite using a continuous wave laser followed by tandem waterjet quenching of the laser beam path to cause stress-induced phase transitions. Reference [11] designed a pulsed laser ablation manufacturing process involving thin film deposition and micro-machining to create hard/soft layered 'brick-bridge-mortar' nacre of AlMgB$_{14}$ (hard phase) with Ti (soft phase). Reference [12] investigated the electronic properties of nitrogen doped amorphous carbon (a-CNx) thin films prepared on silicon substrate by pulsed laser deposition process using methane (CH$_4$) and nitrogen (N$_2$) as source gas. Reference [4] investigated effects of laser wavelength, energy density and postannealing on the films’ properties on rhenium diboride films deposited by PLD. Reference [13] and [14] developed ultrahard boron nitride material through a hybrid laser/waterjet based surface treatment. Reference [15] synthesized nitrogen containing amorphous carbon thin films by femtosecond pulsed laser deposition coupled with plasma assistance through Direct Current bias power supply. Reference [16] studied electronic/micro-structural and mechanical properties of Fe, N and Si-doped alloying DLC thin films. Reference [17] investigated the effects of the arc interlayer, nitrogen doping, and post-annealing process on the adhesion force, electrical, and electrochemical properties of the electrodes. Reference [18] fabricated Graphene nanocrystalline embedded carbon nitride coatings with the mirror confinement electron cyclotron resonance plasma sputtering system under low energy electron irradiation at various N$_2$/Ar ratios.

Reference [19] reported the direct reproducible synthesis of 2%-3% nitrogen-doped 'few-layer' graphene from a solid state nitrogen carbide a-C:N source synthesized by femtosecond pulsed laser ablation. Reference [20] used reactive magnetron sputtering system to synthesis composite Nb–V–C–N films with different carbon content. In this study Ju et al investigated the influence of carbon on the microstructure, mechanical, and tribological properties of niobium vanadium nitride films. Reference [21] demonstrate wafer-scale growth of high-quality h-BN film on Ni(111) template using metal-organic chemical vapor deposition (CVD). Reference [22] employed the laser ablation of boron-nitride (BN) ceramic to prepare of thin films in high vacuum and nanoparticles and nanocrystals generated in water. Reference [23] investigated the production of boron films by femtosecond PLD to be used as converters on bulk semiconductor neutron detectors. Reference [24] studied the deposition of boron/boron nitride (B/BN) composite films at low substrate temperature (275°C–375°C) by alternating pulses of diborane (B$_2$H$_6$) and ammonia (NH$_3$) with argon purging in between to avoid gas-phase reactions of the precursors. Reference [25] modeled tetrahedrally coordinated amorphous BN by molecular dynamics to predict its mechanical and electrical properties. Reference [26] reported that 'the electrical resistivity of the films measured at room temperature for Ni-BN-Ni structures shows a large increase up to the order of 1010 Ω cm when the B-to-N ratio in the film is increased closer to the stoichiometry due to a lower density of defect states related to the boron vacancy'.

Thus, this article presented an investigation to study effects of high repetition rate femtosecond PLD of c-BN target in vacuum and Si substrate in order to produce stoichiometric well adhered film, and to investigate the film growth characteristics under femtosecond PLD. The rest of this article is organized as follows: section 2 presented the experimental procedure to deposit boron nitride particles on thin films using a PLD system that include a vacuum chamber and femtosecond laser source. The experimental analysis also discussed in section 2. The experimental results and obtained data are presented in section 3. However, section 4 is devoted to discussion of the obtained results of section 3. The main points and conclusions are presented in section 5.

2. Experimental methods

2.1. Experiment procedure

Films deposition were carried out using a PLD system that include a vacuum chamber and femtosecond laser source. The vacuum chamber is evacuated using mechanical and turbo-molecular pumps to 10$^{-8}$ Torr. The chamber contains substrate holder that connected to a resistive heater. The substrate is (100) silicon (Si) wafer that kept at 600 °C through all experiments. The chamber also contains a rotational holder for the target material. The target material is 92% c-BN and 8% aluminum which is designated as BZN 6000 (Diamond Innovations, Ohio, USA). The target-to-substrate distance is kept at 5 cm for all experiments. The target and the substrate are cleaned using acetone and methanol before being placed in the PLD chamber.

The femtosecond laser source is 800 nm wavelength, 100 fs pulse width Ti:sapphire (Spectra-Physics Solstice) with 2.4 mJ pulse energy and 1000 Hz repetition rate. The laser beam is focused to project a 0.02 mm$^2$ laser spot on the target material and the spot is steered on the target using stepper motors and optical beam steering mechanisms. The films were deposited for 30 min and 60 min on different Si wafers.
2.2. Experimental analysis

The deposited thin films were analyzed using scanning transmission electron microscopy (STEM model FEI-Tecnai 2-F20) for structural and analytical characterization. Scanning electron microscopy (SEM model JEOL JSM-606LV) and optical profilometer (Zygo NewView 7100) were used to study the surface morphology of the film. Finally, Nanoindentation tests were performed using Hysitron TI 950 TriboIndenter (TriboIndentor™ by Hysitron Inc.) and a Berkovich tip of 100–150 nm tip radius to measure the hardness and the modulus of the film.

3. Experimental results

The film deposited on the Si wafer for 30 min resulted in a very thin film that is not adhered well. The film mean thickness is around 6 nm (figure 1), and surface roughness (Ra) around 3 nm. On the other hand, the film deposited for 60 min using the same conditions produced a thicker film with good adhesion to the Si wafer (figure 2). The film thickness was measured to be 500 nm and surface roughness (Ra) around 150 nm.

The STEM sample of thick films were prepared by gluing two pieces of samples face to face, then mechanically polished and ion-milled with LN₂ cold stage (figure 3). The STEM analysis revealed that the film contains h-BN and amorphous form of BN (figure 4). The electron energy loss spectograph (EELS) analysis of the sample indicated that the deposited films are primarily in h-BN phase. Figure 5 shows the surface morphology of the film using SEM where the film is rough but particulate free. The nanoindentation tests carried out at constant loads in the range of 1000 and 2500 μN so that the indentation depth does not exceed the 1/3 of the film thickness in order to precisely measure ‘film-only’ mechanical properties [27]. The measured film hardness is around as 2.47 ± 0.20 GPa while the elastic modulus is 74.32 ± 7.98 GPa. Figure 6 shows a representative load-indentation depth curve of the examined film. Figure 7 shows the variation of the hardness and modulus of the film with indentation depth. The measurements represent the average film properties, as they are clearly independent of the indentation depth level.

4. Discussions

By using ion-beam-assisted pulsed laser deposition (IAPLD) on h-BN target, the deposition of thick and well adhered c-BN film at high growth rate was achieved on an intermediate layer [28]. It was also found that the ratio of ions (the ion beam to atoms and ions in the ablated particle flux) necessary for cubic film growth can be reduced at high laser fluence, since the ablated boron and nitrogen species themselves have a high mean kinetic energy [28]. In addition, films deposited at high growth rates show relatively high compressive stress, which is governed by the energy of the ablated species [29]. The problem with IAPLD is the maximum achievable thickness of only 500 nm, due to a top layer formation of h-BN, or h-BN/t-BN particles [28]. Ultra-short pulses PLD of BN is expected to improve the film quality and produce thicker films, while alleviating the needs of assisting ion beam. The ultra-short pulses PLD can provide high energetic ablated species and high growth rate that is necessary for c-BN formation [30]. Also, the process typically produces more stoichiometric films that
will overcome the N$_2$ deficiency problem. In addition, the process is known to have less particulate formation problem.

By using ultra-high repetition rate picosecond laser for PLD of h-BN in N$_2$ environment, amorphous-like B-rich phase, h-BN flakes, and nano BN structures were created due to the interaction of BN plume with nitrogen and the laser [31]. On the other hand, the low repetition rate femtosecond pulses pulsed laser deposition of h-BN target in nitrogen environment resulted in particulate formation on the film [32]. The result of these two studies suggest that N$_2$ environment should not be used with ultra-short pulses PLD to produce c-BN film, and c-BN target may create a better condition for BN formation. Studies of low repetition rate femtosecond PLD of c-BN target in vacuum and Si substrate heated to 700 °C, showed the formation of mixed phases of BN, including w-BN [33].
Different from all previous attempts in the literature to deposit BN on Si wafer, this study uses femtosecond pulse duration with high repetition rate to deposit from c-BN target. The small pulse duration in PLD of c-BN is expected to provide the same chemical composition of the target in the deposited film. Also, the small pulse duration reduces the heat affected zone on the target material which in turn lower the possibility of melting material and particulate formation on the film. On the other hand, the high repetition rate is expected to result of high deposition rate and uniform smooth film. The substrate temperature was kept at 600 °C to enhance the deposition of c-BN phase over the h-BN phase. Using Si wafer or substrate with high micro-hardness is expected to enhance the deposition of c-BN phase in the film which is consistent with the model of stress-induces c-BN film formation.

As seen in the results, the BN film deposited for 30 min on Si wafer only produced a very thin poorly adhered film regardless of the high ablation rate of the target material. This could be a result of the deposited material bouncing back from the substrate due to the high energetic materials in the plume. The high energy is a result of the high energy fluence ($\approx 12 \text{ J cm}^{-2}$) used, and the multi photon absorption associated with the femtosecond laser ablation of BN and.

The BN film deposited on Si wafer for 60 min reveled completely different results. The film thickness was around 500 nm which means the nucleation and film growth mechanism has changed after the first 30 min. This indicates the film growth mechanisms occurred with two stages. In the first 30 min, the film growth was...
two-dimensional, layer-by-layer (Frank-van der Merwe); however, the formation of another layer was failing and the film did not grow beyond 5 nm. During the second 30 min duration, three-dimensional island formation (Stranski-Krastanov) was triggered and the lattice matching in the film improved. Such improvement would increase the film growth in the thickness dimension. It is not clear to us what triggers that change and a different study is required to address that. The possible reasons are the increase of the stress in the film which known to increase the deposition of c-BN [29, 39], or the effect of impurities that coming from the 8% aluminum in the target material. Continuing the ablation of the target material beyond the 30 min would saturate the film with more BN material that would increase the stress as well as increasing the aluminum content in the film that will improve the lattice mismatch in the film.

5. Conclusion

Investigation of high repetition rate deposition of BN films using femtosecond pulsed laser deposition is presented through this article. Boron nitride (BN) films were deposited on silicon wafers using 800 nm, 100 fs Ti:
sapphire femtosecond laser with 2.4 mJ and high repetition rate of 1 kHz using a c-BN target. The deposited films were analyzed using transmission electron microscopy (TEM), scanning electron microscope (SEM), and optical profilometer. Nano-indentation tests were performed to measure the hardness of the adhered film. The results indicate the influence of the high repetition. The main conclusions can be summarized as:

High repetition rate deposition using femtosecond pulsed laser of c-BN target on Si wafer was performed for 30 min and 60 min. The process produced BN films with mixed phases: (1) poor adhesion thin film, which is 5 nm thick, in the deposition for 30 min; and (2) good adhesion thick film (relatively), which is 500 nm thick, in the deposition for 60 min. The thick film chemical characterization and nanoindentation tests are presented and the film growth mechanism was discussed.

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