Reduction of particulate density in BN films prepared by pulsed laser deposition

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Abstract. Various measures to reduce the incorporation of particulates (droplets) into boron nitride films prepared by pulsed laser deposition were investigated. These measures include the use of magnetic fields aimed at the separation of the ionized atomic species and the particulates on their way from the target to the substrate and the use of a second laser beam aimed at the destruction of the particulates by evaporation.

1. Introduction
Recently, we have demonstrated that ion-assisted pulsed laser deposition is a method for the preparation of cubic boron nitride (c-BN) films at high growth rates [1]. The production of µm-thick c-BN films as needed for wear reduction applications requires, however, the reduction of the incorporation of particulates of several 100 nm size into the films. Those particulates are ejected from the h-BN targets in solid form resulting in increasing hexagonal film portions with increasing film thickness, which is due to the fact that at high growth rates only hexagonal BN grows on the hexagonal particulates.

One method that has already been shown in the literature [2, 3] and by us [4] to effectively reduce the particulate density in pulsed laser deposited films is the use of magnetic fields for the separation of the ionized atomic species and the particulates on their way from the target to the substrate. In this paper, we report on the use of different arrangements for the generation of the magnetic fields, using permanent as well as electromagnets, and compare them with respect to their applicability. Moreover, we present results of our investigations on the destruction of the particulates by evaporating them above the target surface using pulses of a second laser beam.

2. Experimental Details
The investigations have been carried out in a high vacuum system illustrated previously [5]. A KrF-excimer laser with 1.2 J pulse energy, 50 Hz maximum pulse repetition rate, and 30 ns pulse duration was used for the ablation of the film-forming species from a pyrolytic h-BN target. The laser pulse energy fluency at the target surface was some 30 J/cm² and the laser spot size some 1 mm × 2.5 mm, where the laser pulse energy arriving at the target was 750 mJ. All films were deposited on polished silicon substrates of 660 µm thickness.

Magnetic fields were used with either the field lines parallel or perpendicular to the target surface, where in the second case the field lines were curved with the intention that the ablated ionised species move in spirals to the substrate which is arranged such that non- or weakly deflected particles cannot...
reach it (see Fig. 1). A magnetic circle with gap was used for the generation of the field lines parallel to the target surface resulting in a relatively homogeneous field between the pole plates. The curved field lines were produced with either an arrangement consisting of permanent magnetic rings polarized in axial direction or magnetic coils with inside diameters of 42 mm and 50 mm, respectively. In both arrangements the axial symmetrical magnetic fields inside the rings or coils were used for guiding the ionised species to the substrates. Inside the permanent magnetic rings the inductivity of the magnetic field was 250 mT at the centre line increasing up to 400 mT in the immediate vicinity of the wall. Inside the magnetic coils it can be varied up to a maximum value of 240 mT at the centre line, at which it decreases down to 200 mT in the immediate vicinity of the wall. In the experiments performed so far, the targets and the substrates were placed at a distance of 5 cm from the entrance and the exit, respectively, of the ring or coil arrangements.

For the investigations on the destruction of the particulates by evaporation, a second KrF-laser beam operating at the same repetition rate as the ablation laser was additionally directed onto the ablation spot on the target with only a slightly different angle of incidence (some 45°). Thereby, the time delay between the pulses of both beams was varied in the range of 0 to 50 ns that is a pulse from the second laser hits the ablation spot after each ablation pulse with the set time delay.

3. Results and Discussion
3.1. Characterisation of ablated particle flux
In order to obtain information needed for the conception of the magnetic field arrangements and for the explanation of the results, we have at first characterised the ablated particle flux. The ablated species show a \( \cos^2 \) -distribution, where the total number of ablated species (atoms and ions) per laser pulse was measured to be in the range of \( 10^{16} \text{ pulse} - 10^{17} \text{ pulse} \) at laser pulse fluencies in the range of 25 up to 40 J/cm², respectively. The mean kinetic energy of the atoms and ions was calorimetrically measured to be 60 to 150 eV at laser pulse fluencies in the range of 10 up to 40 J/cm², respectively. The fraction of ions is 55 % at 30 J/cm², as measured by using a Langmuir probe. It can be assumed that the ablated ions and electrons move together and that the common mean velocity, which is some 42 000 m/s at 100 eV ion energy, is attained nearly immediately after they started with a common kinetic energy of 50 eV due to the strong Coulomb interaction. The calculated length of the particle pulses immediately above the target surface is 0.2 cm corresponding to a duration of 30 ns and, due to the velocity distribution of the ablated species, 4 cm corresponding to 2.4 \( \mu \text{s} \) at a distance of 5 cm from the target surface, the latter being in good agreement with our experimental finding of some 2 \( \mu \text{s} \). Accordingly, the maximum ion pulse current in our experimental conditions is some 26700 A immediately above the target surface and 330 A at a distance of 5 cm (assuming \( 5 \times 10^{15} \) ions per pulse).
3.2. Reduction of particulates by deflection of ablated ions using magnetic fields

First investigation on the deflection of ablated ions using magnetic fields have been directed to the application of a magnetic field with the field lines parallel to the target surface produced either by using permanent magnets or a magnetic circle with the target placed in the gap. However, according to our estimations shown in the previous section, the high ion and electron densities result in extraordinarily strong Coulomb interaction. This, along with the deflection of the ions and electrons in opposite direction and the very small radii of the electron trajectories, is the reason why it is nearly impossible to separate the ions from the electrons by using a magnetic field with the field lines parallel to the target surface. Accordingly, nearly no deflection was observed using up to 100 mT field strength. Such an arrangement cannot be used to deflect sufficiently the ions so that a separation from the particulates would take place. There occurred, however, a strong increase of the growth rate from 50 to 120 nm/min due to the collection of sideways ablated ions, resulting in a decrease in particulate density in films of the same thickness. Simultaneously, the mean kinetic energy of the species measured at the substrate decreased from 130 down to 40 eV, which is unsuitable for the growth of cubic boron nitride films at high growth rates, as we have shown recently [1].

In consequence, we used in the following axial symmetrical magnetic fields with the field lines going from the target to the substrate, which are arranged relative to each other in the way shown in Fig. 1. The ablated ions and electrons move in spirals along the field lines and, though the radii of the spirals of ions and electrons differ strongly, there is no spatial charge separation. As can be seen in Fig. 2, an effective reduction of the particulate density in the films is achieved in consequence of the separation of ablated ions from particulates by means of the magnetic field. In Fig. 2 a the relatively high particulate density in a 300 nm thick h-BN film deposited without magnetic field at a growth rate of 50 nm per minute is shown. A significantly lower particulate density is seen in Fig 2 b. This 1 µm thick h-BN film was deposited with magnetic field using the arrangement consisting of permanent magnetic rings. Due to the collection of sideways ablated ions a higher growth rate of 90 nm per minute was obtained using the same deposition parameters. A similar reduction in particulate density as well as increase of growth rate was obtained by using the magnetic coils (see Fig. 2 c).

Apparently, both arrangements are suitable for particulate reduction in pulsed laser deposited h-BN films. For the deposition of c-BN, however, ion bombardment of the growing films is needed requiring a greater distance of the substrates from the exit of the magnetic arrangements. Additional coils or permanent magnets about the substrate are necessary for this in order to guide the field lines to the substrate. Such arrangement is also shown in Fig. 1, has, however, not been used, so far.
3.3. Reduction of particulates by using two laser beams

Another method for the reduction of particulate density in BN-films which we have investigated is the use of two target laser beams. The idea is to evaporate the emitted particulates immediately above the target surface by a second laser beam. The following three conditions have to be fulfilled. There must be complete geometrical overlapping of the two laser beams on the target. The fluence of the second target laser beam must be sufficient to evaporate completely the particulates, but on the other hand be below the BN-target ablation threshold of 2.5 J/cm². The second laser pulse must arrive at the proper time after the ablating laser pulse in order to hit the particulates.

Temperature field calculations show that ablation starts after some 10 ns and lasts several 10 ns. Hence, it can be assumed that the time delay of the second target laser pulse is in that range. Our experimental investigations using a fluence for the second laser beam of 2 J/cm² and time delays from 0 to 50 ns in steps of 5 ns confirmed this and have shown that a time delay of 30 ns is optimum for the reduction in particulate density. The optimum fluency at this optimum time delay was found to be the ablation threshold fluency. Apparently, particulates can be evaporated effectively at laser fluences below or just at the ablation threshold of solid pyrolytic BN targets. This can be explained by the small size of the BN particulates, the majority being only several 100 nm in diameter, which results in the direct heating of the nearly entire volume by the photon absorption without any energy dissipation.

Optical micrographs of h-BN films with thicknesses of 240 nm prepared without and with second laser beam, using optimum parameters with second laser beam, are presented in Fig. 3. It can well be observed that the method turns out to be effective and that nearly particulate-free h-BN films can be prepared by it. This is confirmed by the strong decrease of the surface roughness measured with a DEKTAK profilometer (see also Fig. 3). Thereby, the curvature in those profiles is attributed to the bending of the substrate due to the internal mechanical film stresses.
4. Conclusions

A reduction in the incorporation of particulates in pulsed laser deposited boron nitride films can be achieved by using magnetic fields for the separation of ablated ions from particulates. Thereby, the magnetic field lines must ideally go homogeneously from the target to the substrate and be curved such that only the ablated ions deflected by the magnetic field can reach the substrate surface. A secondary effect of the magnetic field is the collection of sideways ablated ions resulting in increased growth rates.

Particulate reduction can also be achieved by the destruction of the particulates immediately after their emission, which can be attained by using a second target laser beam with its pulses having appropriate time delay to the pulses of the ablating laser beam. The optimum fluency of the second laser pulses was found to be in the vicinity of the ablation threshold fluency and the optimum time delay to be 30 ns.

Acknowledgments

The authors gratefully acknowledge financial support of the present work by the Sächsisches Ministerium für Wissenschaft und Kunst (Project No. 4-7531.50-03-5140-98/3).

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