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PULSED LASER ABLATION OF BORON NITRIDE

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I. Introduction

The laser ablation of solid targets has been a research topic of interest since the invention of lasers. With developments of high power lasers in the ultraviolet region, pulsed laser deposition using laser ablation has been intensively studied aiming at the deposition of high quality thin films of wide range including superconductors, semiconductors, ferroelectrics, and dielectrics. Laser ablation technique has been proved to be especially powerful in the stoichiometric deposition of multi-element materials like YBCO superconductors. Another potential application of current interest is the deposition of refractory nitride materials such as boron nitride, silicon nitride, carbon nitride, and titanium nitride.

In pulsed laser deposition, the quality and properties of films are expected to be highly dependent on the characteristics of the plume generated in the laser ablation process. The information on the production and evolution of laser induced plume from the target and the transport of the ablated species to the substrate will be of critical importance in understanding the dynamics involved in the pulsed laser deposition of materials. Several diagnostic methods including probe beam deflection, laser induced fluorescence, time-of-flight, optical time-of-flight, resonance absorption, resonance ionization, and ultrafast photography have been employed to study the plume in the laser ablation. To our knowledge, however, there is still no reliable model to describe the optical and thermal attributes of the laser ablation.

II. Experimental

In this work, we present experimental results on the optical, photoacoustic, and photothermal studies of laser ablation of pyrolytic boron nitride (pBN). Probe beam deflection and optical time-of-flight technique have been adopted to investigate the dynamics of the formation and expansion of the laser induced plume. Also attempted is the deposition of BN film on the silicon substrate by laser ablation. The laser ablation of pyrolytic boron nitride (Union Carbide) was done by the fourth harmonic of Nd:YAG laser (266 nm, Quanta-Ray GCR 150) with pulse duration of 5 ns operating at 10 Hz.

For the probe beam deflection experiment, a HeNe laser (5 mW) was used as probe laser and a quadrant cell photodiode (UDT SPOT 9D) was employed as a position-sensitive detector. Each two outputs of the quadrant photocell were hooked together such that it worked as a bicell. The output signals were amplified by a fast difference amplifier. The HeNe laser beam was focused by a planoconvex lens with focal length of 25 cm. A color filter and an interference filter of bandwidth 3 nm were placed in front of the photodiode to avoid the scattered Nd:YAG laser photons and room light. The photodiode signal was stored in a storage oscilloscope (170 MHz, LeCroy 9304). The target was rotated by a stepper motor which was mounted on a translational stage, allowing adjustment of the distance between the target and the focused HeNe laser beam. The Nd:YAG laser beam was focused by a S1UV lens with focal length of 20 cm. The ablation experiment was performed in air or in nitrogen atmosphere. The pressure in the chamber ranged from 15 mTorr to 1000 Torr, as measured by the thermocouple gauge or capacitance manometer.

In the optical time-of-flight (TOF) experiment, optical emission from the plume generated by the laser ablation was imaged into an optical fiber by a lens with focal length of 15 cm and sent to a monochromator (SPEX 500M) detected by a photomultiplier. The photomultiplier signal was averaged in real time and stored in the oscilloscope. The emission spectrum was obtained with the monochromator, where a boxcar averager (PAR 162) was used for signal processing.

The deposition of BN film was done in the same chamber in nitrogen atmosphere. Si(100) was used as a substrate. The substrate was indirectly heated by a BN block heater up to 900 ℃ and the temperature of the substrate was controlled by a programmable temperature controller (Eurotherm 903). The deposited film was analyzed by FT-IR, XRD, and SEM.

III. Results and Discussion

The probe beam deflection occurs due to the time-dependent density gradient that diffuses through the HeNe laser beam used as the probe laser. Fast photoacoustic signal is followed by a slow photothermal signal. The distance between the target and the focused HeNe laser beam with diameter of 60 μm was 1.5 mm in this experiment.

Upon irradiation of the pulsed laser beam, shockwave is generated due to the material ablation and plasma formation. The shock velocity was obtained by measuring the arrival time of the acoustic wave (the acoustic transit time) as detected by the probe beam deflection. The acoustic signal magnitude increased nonlinearly and then decreased at above 1.5 J/cm^2. As the laser intensity is increased, surface starts melting, and then material evaporation occurs causing the increment of the slope thereby. At laser intensities above 1.5 J/cm^2, the magnitude decreased because of the formation of optically dense plasma which absorbs HeNe laser beam.

The measurement of time delay in the photothermal deflection signal to cross zero was used in the time-of-flight analysis giving the flow velocity of the ambient gas after laser ablation. The laser intensity dependence of the velocity was quite linear. Emissions from the excited B and B^+ were observed and the vibrational progressions from molecular BN ($A^3\Pi \rightarrow X^3\Pi$) were also observed near the target. The emission intensities from N and N^+ were not strong enough for optical TOF studies hidden under molecular emissions.

Real time emission intensities at a B line (249.7 nm) at different distances along the plume axis were obtained. Most probable velocities of B and B^+ were obtained by plotting the distance versus delay between the laser pulse and the emission intensity maximum, where the emission from B^+ was measured at 345.1 nm. The most probable velocities thus obtained indicate that B^+ is much faster than B. Due to the long-range Coulomb forces, ions move faster than neutrals in general. The most probable velocities of B and B^+ were 1.7×10^6 cm/sec and 3.6×10^6 cm/sec, respectively. The velocities of B, however, decreased at distances longer than 1 mm. Near the target, faster velocity of B was observed as in the case of laser ablation of Ge. This can be explained as fast ions that recombine with electrons or just fast neutral species near the target implying that the earlier species in the plume are mainly charged specie.

Most probable velocities of B obtained from the data point near the target (from 0 to 1 mm) increases as the laser intensity increases. For distances longer than 1 mm, the expansion of neutral atoms could not be explained in a simple kinetic concept since there was no appreciable trend found in the dependence of velocity on the laser intensity. The velocity of ions, however, increased with the laser intensity up to 4 mm away from the target. The ion-to-neutral population as measured from the emission intensities of B^+ and B increased by a factor of up to 2.6 times as the laser intensity was increased from 3.5 to 12 J/cm^2. Therefore, enhancement of ion bombardment during film growth is expected with increase of laser power.

Infrared spectroscopy was employed to analyze the BN deposits on the silicon surface. The cubic phase of BN (cBN) is indicated by the transversal mode at 1100 cm^{-1} and the absorption band of hBN (hexagonal BN) occurs at 1380 cm^{-1}. The existence of cubic phase of BN on silicon surface grown by laser ablation of pBN was confirmed by IR absorption spectrum. According to the intensity ratio of cBN and hBN peak, BN film deposited on the silicon was observed to be mostly composed of hexagonal phase.

IV. Conclusion

Photoacoustic, photothermal, and optical time-of-flight spectroscopic technique have been employed as an attempt to elucidate the mechanism of laser ablation process. These techniques proved to be powerful in the dynamic study of pulsed laser ablation under real deposition conditions. Shockwave generation and its velocity increase with laser intensity incident on the target were clearly demonstrated by probe beam deflection method. Real time analysis of the emission intensities observed at different distances from the target gave dynamic informations on atoms and ionic species produced by laser ablation. The deposits of BN on Si substrate under nitrogen atmosphere by laser ablation at 266 nm included both cubic and hexagonal phase of BN.