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TITLE: **PREPARATION OF DIAMOND-LIKE CARBON AND BORON NITRIDE FILMS BY HIGH-INTENSITY PULSED ION BEAM DEPOSITION**

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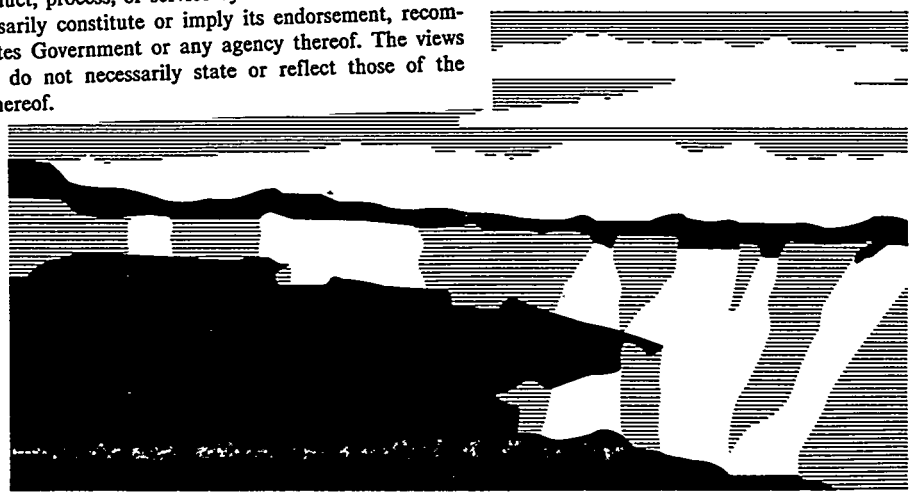

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PREPARATION OF DIAMOND-LIKE CARBON AND BORON NITRIDE FILMS BY HIGH-INTENSITY PULSED ION BEAM DEPOSITION*

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Key words: boron nitride, diamond, diamond-like carbon (DLC), high-intensity pulsed ion beams, thin film deposition

Abstract

Intense ion beams (300-keV C^+, O^+, and H^+, 20-30 kA, 50 to 400-ns pulsewidth, up to 0.3-Hz repetition rate) were used to prepare diamond-like carbon (DLC) and boron nitride (BN) films. Deposition rates of up to 25±5 nm/pulse were obtained with instantaneous rates exceeding 1 mm/s. Most films were uniform, light brown, translucent, and nonporous with some micron-size particulates. Raman and parallel electron energy loss spectroscopy indicated the presence of DLC. The films possessed favorable electron field-emission characteristics desirable for cold-cathode displays. Transmission electron microscopy (TEM) and transmission electron diffraction (TED) revealed that the C films contained diamond crystals with 25 to 125-nm grain size. BN films were composed of hexagonal, cubic and wurtzite phases.

1. Introduction

There has been considerable progress recently in the development of high-intensity pulsed ion beams (HIPIB)[1]. While a primary application driving this development is inertial confinement fusion energy research[2], several materials processing applications have emerged. Because of the short range of ions in matter, applications usually involve material surface modification, *e.g.*, implantation, alloying, or deposition. The high-intensity pulsed ion beam deposition (HIPIBD) process[3-6] is illustrated in Fig. 1. When a beam is propagated into a target, substantial amounts of target material may be evaporated and ionized. For example, an energy fluence of 100 J/cm^2 deposited over a 0.5 μm ion range will heat a target surface

about 5×10^5 K. The ablated plasma may then be condensed at phenomenal rates onto an adjacent substrate. HIPIBD is similar to pulsed laser deposition enabling the congruent evaporation and deposition of complex stoichiometric films. There are added benefits since energetic ions penetrate deeper into a target than a laser beam and couple better with surface plasmas and metallic targets. HIPIBD may allow an economical pathway for bulk deposition of advanced coatings, since the efficient HIPIB accelerarators cost orders of magnitude less than lasers with comparable output. An American-Russian collaboration is underway to study HIPIBD. In this paper we present results of C and BN deposition studies.

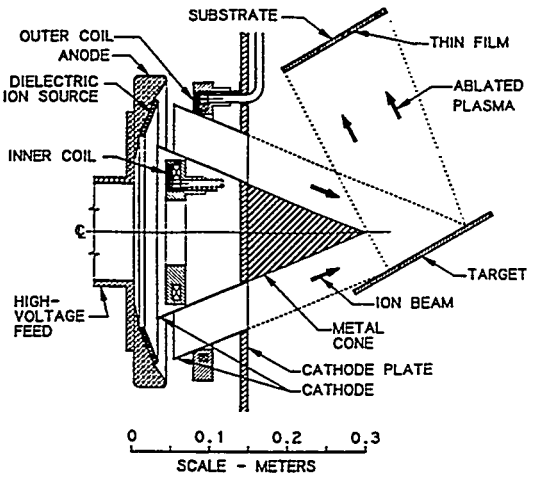

Fig. 1: Experimental arrangement for HIPIBD.

2. Experimental

Experiments were performed on the Los Alamos Anaconda[7] and the Tomsk TEMP accelerators[8]. Beam parameters are listed in Table I. Both accelerators utilized magnetically-insulated ion diodes driven by Marx generators. In Anaconda, an applied-radial magnetic field extraction diode geometry was configured for ballistic focusing of the beam (Fig. 1)[5]. An acrylic dielectric attached to the anode electrode was used as the ion source. The beam converged to a 75-mm-diam focus located approximately 300 mm from the diode. A $203\times152\times2.5$ mm graphite target was positioned near the beam focus with its surface 25° from the beam axis. Deposition was performed onto glass, Cr, and Si substrates which were not preconditioned and initially at room temperature. Substrates were placed at either 150 or 225 mm from the target, at angles θ between 0° (Fig. 1) and 90° from target normal. Substrate heating from the condensation of ablated vapor was examined with thin film Pt thermometers capable of measuring substrate temperature during deposition with nanosecond time resolution[9,10]. Experiments were performed at a base pressure of approximately 1×10^{-6} torr.

Table I: Beam parameters

Device	Energy (keV)	Current (kA)	Pulsewidth (ns)	Species	Power density on target (MW/cm^2)	Repetition Rate
ANACONDA	350	30	400	H,C,O	80	1 pulse/ 3 min
TEMP	300	20	50	H, C	75	0.3 Hz

The TEMP accelerators utilized two innovations that enabled simple and reliable operation at repetition rates of up to 0.3 Hz. First, the magnetic insulation field was generated by a coil connected in series with the diode load. Second, the ions were produced directly from a conducting anode electrode by a preliminary negative prepulse applied before the main positive diode pulse. The beam was focused to a 20-cm^2 cross-section onto a 45-mm-diam C or BN target aligned 45° to the beam axis. Substrates included (100) Si, (100) MgO, and glass, initially at room temperature, and positioned 35 to 50 mm from the target, at $\theta = 0°$.

3. Results

Approximately 10 mg of graphite was ablated with each Anaconda pulse, which was in good agreement with a one-dimensional heat-transport model[11]. From visible framing photography[12], the ablated plume front was observed to expand at approximately 2×10^4 m/s. Deposition rates ranged from 12 to 25 nm/pulse, depending on substrate position relative to the target, while the thin-film Pt resistor calorimeter measurements inferred instantaneous deposition rates of greater than 1 mm/sec. The measured power density incident onto the substrate decreased with increasing angle or target-substrate separation, from 70 kW/cm^2 over approximately a 10 μs period at the 0.1-m separation and $\theta = 0$, to 5 kW/cm^2 over 20 μs at 0.2-m separation and $\theta = 30°$. At the highest heating power, the inferred temperature rise of a glass substrate was about 1500°C, which was above the stability temperature for DLC. The Raman spectra of films deposited at this condition showed a glassy-C characteristic, with DLC characteristics only present at larger target-substrate separations or angles where substrate heating was lower[5]. More complete discussion of the substrate heating measurements may be found elsewhere[10]. Many film properties have already been published[5]. The films were light brown and translucent. A typical stylus profilometry profile is shown in Fig. 2. The films displayed amorphous XRD spectra, while SEM micrographs revealed a uniform, non-porous morphology with feature sizes of ~100 nm, with micron-sized particulates at concentrations of about ten particles per 100 μm^2. Parallel electron energy loss spectroscopy indicated a 25% concentration of sp^3-bonds. Film electrical resistivity ranged from 0.01 to 10 Ω-m. The films possessed favorable electron field-emission characteristics, with good adherence to Fowler-Nordheim theory. Emission was observed at applied electric fields E of 10 V/μm. A reasonably high current was achieved at low applied voltages. This suggests that these films may prove promising for dislay applications.

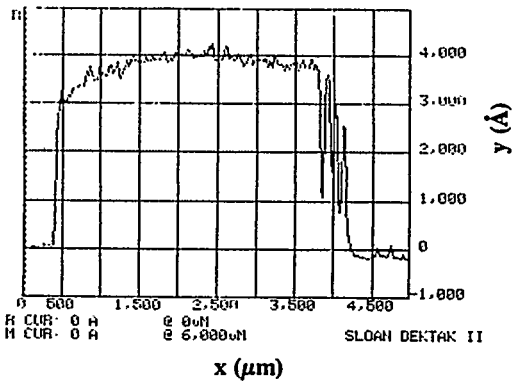

Fig. 2: Profilometry profile of C film, prepared with 20 HIPIB pulses.

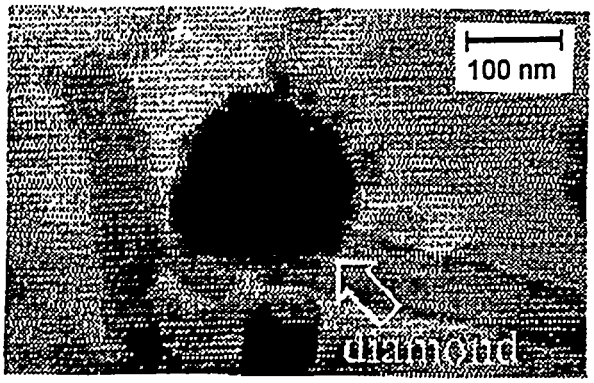

Fig. 3: TEM of C film deposited on a MgO film substrate with Tomsk beam.

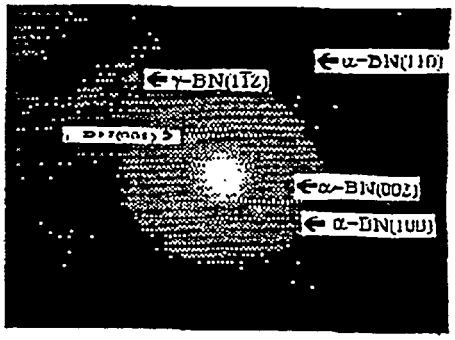

Fig. 4: TED pattern of BN deposited on a glass with Tomsk beam.

Carbon deposition rates on TEMP ranged from 10 to 15 nm/pulse. TEM, TED, and X-ray diffraction indicated the presence of amorphous carbon, crystalline graphite, and diamonds (Fig. 3). Dark field imaging with diffraction analyses showed that the diamonds were 25 to 125 nm in size with a population of up to 10% in the film. The average size of the diamond particles was estimated to be about 63 nm[13].

Boron nitride deposition with the Tomsk beam onto crystalline substrates gave a mixture of hexagonal (α), cubic (β), and wurtzite (γ) phases. Films deposited at room temperature consisted mainly of amorphous α-BN (up to 70 %), with tens of percent concentration of β-BN[14]. With glass substrates, TED indicated the presence of amorphous α-BN and single crystalline γ-BN only (Fig. 4). There was no evidence of β-BN formation.

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