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TITLE: **PLASMA AND ION BEAM PROCESSING AT LOS ALAMOS**

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**Los Alamos**
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# PLASMA AND ION BEAM PROCESSING AT LOS ALAMOS

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**Abstract**

*Efforts are underway at Los Alamos National Laboratory to utilize plasma and intense ion beam science and technology for the processing of advanced materials. A major theme involves surface modification of materials, e.g., etching, deposition, alloying, and implantation. In this paper, we concentrate on two programs, plasma source ion implantation and high-intensity pulsed ion beam deposition.*

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**INTRODUCTION:** Over the past 25 years, plasma technologies have found increased use in a wide variety of industrial processes.[1] Manufacturing applications include reactive ion etching and cleaning, ion implantation, thin film deposition, polymerization, bulk chemical processing, and spray coatings. Efforts are underway at Los Alamos National Laboratory (LANL) to utilize plasmas and beams for the processing of advanced materials. These activities are outgrowths of U.S. Department of Energy defense and energy research programs. A major theme of our effort is the surface modification of materials. Magnetized coaxial plasma guns, originally developed for magnetic fusion and space propulsion programs, are being used for polymer and metal etching.[2] Novel rf sources are under development for semiconductor implantation and film growth.[3] Cleaning and decontamination[4] processes are being studied on a large scale.

In this paper, we briefly review two LANL programs involving high-energy ion currents: plasma source ion implantation (PSII) and high-intensity pulsed ion beam deposition (HIPIBD). Further details about these two projects can be found in the cited references.

**PLASMA SOURCE ION IMPLANTATION (PSII):** PSII (Fig. 1) is an innovative technique[5] to generate high dose implants into complicated shapes in a simple, efficient, and cost-effective manner. A negative high-voltage pulse is applied to a workpiece which is immersed in a plasma. Ions are accelerated by the electrical potential and are implanted into the surface of the workpiece. PSII offers several improvements over conventional techniques. Particle accelerators are eliminated. PSII is a non-line-of-sight process enabling conformal implantation, *i.e.*, ions are accelerated from all directions simultaneously into all exposed surfaces of the workpiece. Consequently, cumbersome workpiece manipulation fixtures and beam rastering are unnecessary. Efficiencies are high since the perpendicular trajectories into the workpiece eliminate the need for masking. Implant times are short since high-current, pulsed-power supplies compatible with this process can provide two orders of magnitude higher average currents than conventional accelerators. Since large areas can be implanted concurrently, ion current densities to the workpiece can be kept low to avoid overheating problems sometimes encountered in beam-line implants. PSII processing cost of approximately $\$0.01/cm^2$ have been projected.[6]

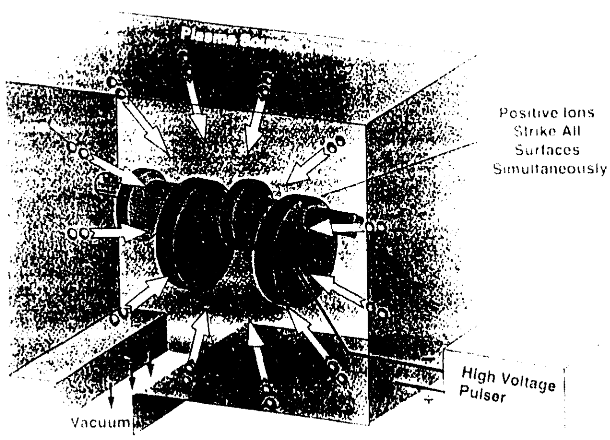


**Fig. 1 Plasma Source Ion Implantation (PSII)**

In collaboration with the General Motors Corp. and the U. of Wisconsin, the PSII process is being investigated on a large scale.[7] The LANL PSII facility[8,9] can accommodate large, heavy parts in a 4.6-m-long, 1.5-m-i.d. chamber. Argon, nitrogen, methane, acetylene, ethane, or oxygen plasmas have been produced by a $\leq$ 1 kW capacitively-coupled 13.56-Mhz rf discharge. Experiments are conducted in relatively low density ($n = 10^{14}$-$10^{15}$ $m^{-3}$) plasmas produced in background fills of 0.3 mtorr or less. Ions are accelerated by a high-voltage pulser capable of producing 125-kV, 60-A pulses with a 4% duty cycle.[10] Similar hardware have achieved operating lifetimes of 70,000 hours in particle accelerator and radar installations.

First tests were performed at 50 kV with nitrogen implants into M2 tool steel.[11] Both coupons and manufactured components, with surface areas of 4 $m^2$, were processed. Implanted doses $D_i$ between 1 and $1.5 \times 10^{17} cm^{-2}$ were estimated from the total time-integrated modulator current and workpiece area, correcting for the secondary electron emission. Since the plasma consisted of unknown proportions of $N_2^+$ and $N^+$, the actual implanted nitrogen dose was between 1 and $2D_i$. Nitrogen contents were determined by resonant non-Rutherford back scattering of 8.9 MeV He ions to be $(1.0 \pm 0.1) \times 10^{17} cm^{-2}$. In addition, oxygen was detected in both the implanted (with dose $1.1 \times 10^{17} cm^{-2}$ and unimplanted (with dose 0.6 $\times 10^{17} cm^{-2}$) samples.

Surface mechanical properties were evaluated with a Knoop microhardness tester at loads ranging from 2 to 10 grams. A modest ($\sim$ 20%) improvement in microhardness was observed.[11] The improvement became more apparent at low loads since the indentation depth approached the implanted layer thickness. However, even at the lowest load employed, the indentation depth was large enough to include substrate effects; thus, the improvement in hardness in the near surface regions was underestimated. Large scatter in hardness data were observed at low loads because of inherently large uncertainties associated with the measurement of smaller indents, the second phase carbide distribution in the steel, and the surface roughness. The principal hardening mechanism is speculated to be due to nitride formation with iron and the alloying elements present in the steel.

Secondary electron emission is an important issue in PSII. As each ion is implanted, electrons are liberated from the workpiece and are rapidly accelerated through the sheath potential. In most experiments to date, the energetic secondaries stream along collisionless trajectories until they strike and are stopped by grounded objects such as the processing chamber walls. For many metallurgic applications, the secondary electron emission coefficient $\gamma$ is large,[12] typically ranging between 5 and 20. Consequently, uncontrolled loss of secondaries can significantly reduce system efficiency, while the bremsstrahlung x-rays produced by energetic electron bombardment of the chamber walls poses a potential safety hazard. Methods to suppress secondary losses, such as magnetic insulation[13] or negative ion implants with positive applied voltages, have been proposed.

PSII implants are conformal as long as the plasma sheath dimensions remain small compared to the workpiece feature sizes. For certain applications, this condition may not be easily attained because of hardware limitations described below. During the quasi-steady, space-charge limited current phase, the plasma acts as a resistive load to the high-voltage pulsed power supply. This load impedance $Z_p$ for an expanding planar sheath is obtained by combining the Child-Langmuir equation with Ohm's law,

$$Z_p = [9/4\varepsilon_0]\,[M/2e]^{1/2}\,\{s^2/[A(\gamma+1)V^{1/2}]\} \quad ,$$

where M is the ion mass, A is the workpiece area, V is the magnitude of the applied voltage, and s is the plasma sheath dimension which for planar geometries is given by[14]

$$s(t) = [2\varepsilon_0 V/en]^{1/2}\,[(2/3)\omega_{pi}t + 1]^{1/3} \quad .$$

Present-day high-voltage switching technology can drive load impedances of approximately 100 $\Omega$ or more.[10,15] For a specified voltage and workpiece area, this limit corresponds to a minimum sheath dimension (or plasma density). For $A = 5\ m^2$, $\gamma = 7$, $Z_p = 100\ \Omega$, and $V = -100$ kV, relatively large sheaths, $s \geq 0.1$ m, are mandatory for an $N_2^+$ plasma and planar geometry.

Implant conformality and dose uniformity into practical geometries were estimated with multi-dimensional particle-in-cell computations of plasma electron and ion dynamics, and Monte Carlo simulations of ion transport in solids.[11] Simulations were performed for a 100-kV $N_2^+$ implant into an elongated workpiece geometry corresponding to the Pierce punch that was PSII treated and reported in Ref. 5. At an early times ($t < 0.3\ \mu s$), the cylindrical shape of the punch is still roughly retained. After about 2 $\mu$s, the expanded sheath becomes spherical and any shape information about the punch has been "washed out." Ions are always accelerated toward the part, in the direction normal to the sheath.[11]

**III. PULSED ION BEAM DEPOSITION:** The congruent evaporative deposition of polycrystalline and amorphous thin films (illustrated in Fig. 2) appears especially well suited for intense ion beams. When the ion beam strikes a target, substantial amounts of target material may be evaporated and ionized. For example, an energy fluence of 1 kJ/cm$^2$ deposited over a 5 $\mu$m ion range will heat the target surface about $5 \times 10^5$ K or approximately 40 eV per atom. The ablated plasma may then be condensed at phenomenal rates onto an adjacent substrate as a film.[16-19]

Experiments were performed on the Los Alamos Anaconda HIPIB generator.[20] The magnetically-insulated diode was configured in an extraction geometry shown in Fig. 2. The ions were formed by the flashover of a conical annulus of Lucite attached to the anode electrode. The field was generated by pulsed electromagnets (configured on the cathode side) and flux-excluding metal components located in the vacuum chamber. The diode was connected directly to the Marx generator and operated to produce 300-keV, 30-kA, 0.4-$\mu$s-pulsewidth beam of H, C, and O ions.[21]

Diamond-like carbon (DLC) films were prepared by ablation of graphite targets. The ion beam removed approximately 10 mg of graphite per pulse, based on weight measurements before and after 20 pulses. This is in approximate agreement with the ~ 7 mg/pulse calculated by a simple thermal model based on one-dimensional heat conduction with mass removal by vaporization. The time evolution of the ablated plume is shown by the framing photographs in Figs. 3 and 4. Time is referenced to the firing of the Marx generator. For clarity, the substrate assembly has been temporarily removed while taking these photographs. Illumination of the target is evident at time t = 200 ns, which corresponds to the arrival of the intense ion beam. A plume begins to emerge at t = 600 ns, which is approximately near the end of the beam pulse. The plume is highly directed with a diameter of 150 mm corresponding to the beam spot size as viewed by the camera. The plume expands at approximately $2.0 \times 10^4$ m/s, which corresponds to a carbon atom or ion directed energy of 24 eV. A broader, slower moving plume emerges later at t ≈ 4 $\mu$sec.

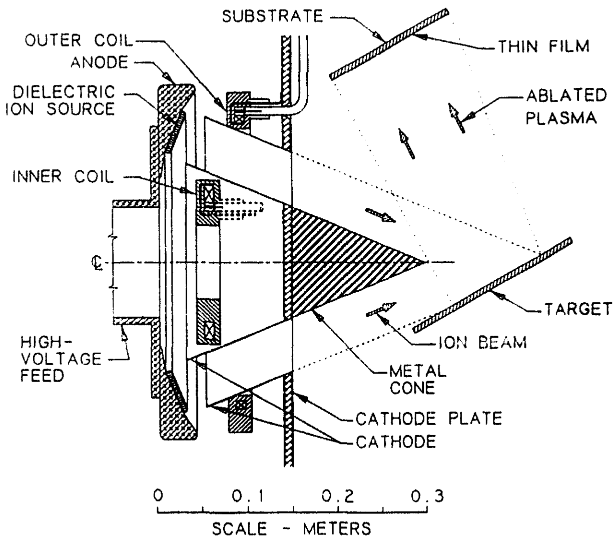


**Fig. 2 Ion diode configuration used in HIPIBD**

Most of the deposited films were uniform, light brown, translucent, and nonporous with some particles in the micron size range. Film deposition rates were 25±5 nm/pulse onto substrates that were 150 mm from and normal to the target. This rate dropped to about 12 nm/pulse at 40° off normal and less than 2 nm/pulse at 80°. For a 225 mm target-to-substrate separation, 15±3 nm/pulse was deposited normal to the target. Fast thin-film calorimetry at the substrate position,[22] revealed instantaneous deposition rates greater than 1 mm/sec. The electrical resistivity varied from 1 to 1000 $\Omega$-cm, increasing with larger target-to-substrate separations. Raman Spectra indicated that most of the films were DLC with significant amounts of sp$^3$-bonded C, detected by parallel electron energy loss spectroscopy.[23]

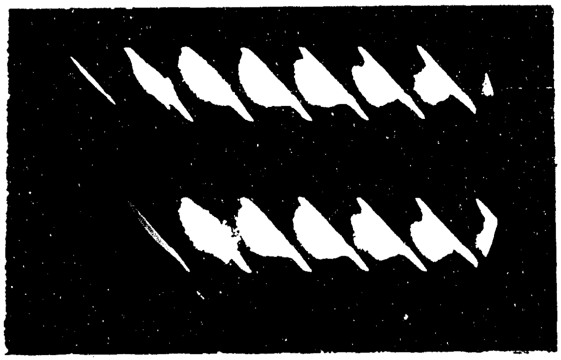


**Fig. 3 Framing photographs of graphite ablation**


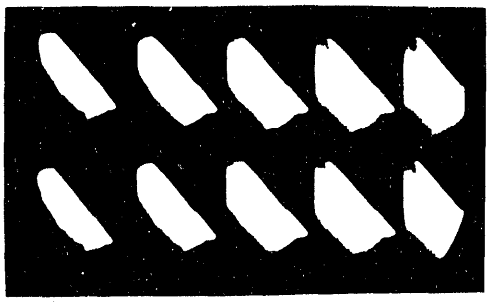


**Fig. 4 Framing photographs of graphite ablation**

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