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# Surface Hardening with LAPPS

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**Introduction:** LAPPS (Large Area Plasma Processing System) was invented[1] in NRL's Plasma Physics Division and Materials Science and Technology Directorate. It uses a 2-5 keV electron beam to ionize and dissociate gas molecules, species that are then used to modify the surface properties of various materials. This novel approach to plasma generation provides a direct scalability of the system and higher control over reactive chemical species compared to conventional plasma processing systems used in the semiconductor and coatings industries. The scalability is simply dictated by the dimensions of the electron beam, allowing unprecedented surface areas to be treated uniformly. The process/chemical control is provided by the electron beam/molecule interactions, which ensures that all chemical reaction pathways are accessible, as opposed to conventional plasma systems.

The ability to increase the hardness of a material while preserving its intrinsic properties provides tremendous advantages in choosing materials for demanding applications. Thin layers of well-known hard coatings are frequently used, but adhesion problems (lattice and temperature coefficient matching) limit their utility. For metals, incorporating nitrogen into the surface's lattice (surface nitriding) is highly desirable because the nitrided layer is physically part of, yet significantly harder than, the bulk material. Equally important in surface nitriding is maintaining sufficiently low temperatures to preserve the properties of the bulk material.

**Technical Approach:** The unique plasma chemistries provided by LAPPS are ideal for surface nitriding; large amounts of atomic nitrogen species ($N^+$ and N) are produced[2] in these plasmas, independent of workpiece or system configuration. Figure 4 (top) shows the generalized layout of LAPPS, including a voltage/temperature controlled substrate stage. The middle photo of Fig. 4 shows the working device with a $0.5^2$-m active area, generated by a 2 keV e-beam that is 1-cm thick by 50 cm wide (into photo) and travels 1 m in the vacuum chamber. The bottom picture shows an end-on view of the device interior configured for wafer processing (wafers in photo are 150 mm in diameter).

To produce nitrided surfaces in stainless steel, pieces of stock architectural material (3-mm thick)

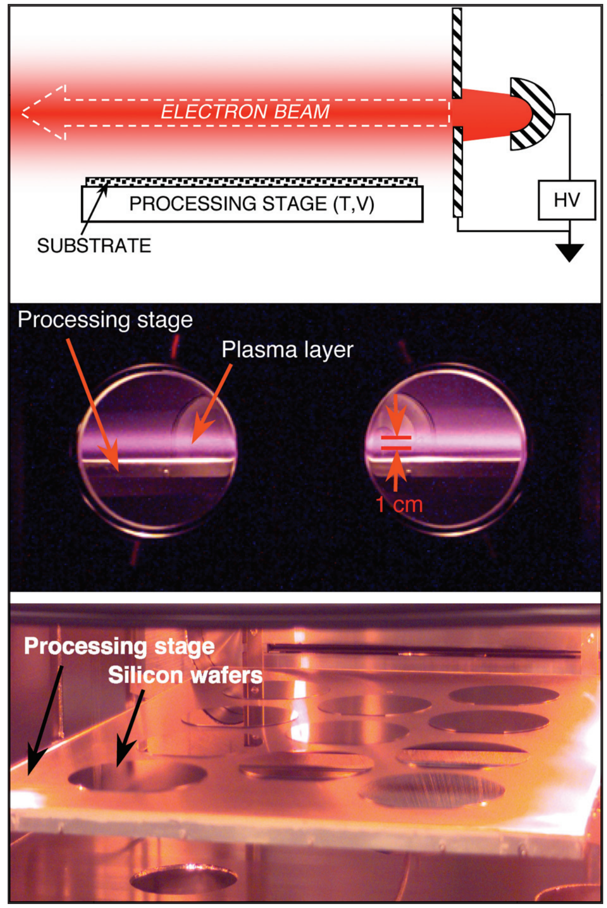


**FIGURE 4**
Large Area Plasma Processing System (LAPPS) layout(s). Top figure is schematic representation of electron beam, plasma source, and materials' processing stage. Middle photo is 0.5 × 1 m (×1 cm) LAPPS, with nitrogen working gas. Bottom photo is end-on-view of LAPPS (electron beam would emerge from slot at top of photo) showing multiwafer processing capability.

were exposed to nitrogen-based plasmas produced in a smaller (15 × 30 cm active area) system. To improve nitrogen diffusion into the surface, the substrate was heated to temperatures between 325 and 462 °C, and biased to –350 Vdc to reduce oxide formation via ion bombardment (sputtering). This nitriding rate increased with temperature, however, at 462 °C the corrosion resistance of the bulk material was compromised because of chromium nitride precipitation in the stainless steel.

Nitriding in LAPPS allows a chemical activation energy of 1.4 eV/atom, which is lower than any previously reported nitriding process and means that high nitriding rates occur at low temperatures. The hardness of the surface was also increased by a factor of six at all of the temperatures. Further scientific studies[2,3] showed that these dramatic improvements were correlated with the high flux of atomic nitrogen ($N^+$ and N) generated in LAPPS. These critical species, particularly the atomic ion, are more abundant in these plasmas because of the availability of the appropriate reaction pathways. By incorporating more atomic ion flux in this process, the reactive chemical (atomic nitrogen) component is used in conjunction with the additional localized energy (ion kinetic energy from the external bias), effectively delivering species to the surface that both sputter clean and promote surface diffusion.

Figure 5 shows the results of stainless steel nitriding at 462 °C in LAPPS. The top photograph is a cross sectional view of a sample that was chemically etched to clearly show the interface between the nitrided surface layer and bulk material. The bottom plot is the surface hardness measured along the workpiece cross section, showing the transition from the bulk material (2.6 GPa) to the nitrided surface (>15 GPa). The inset photo shows the impression left by the indenter (hardness measurement). The bulk stainless steel material shows significant deformation by the indenter while the nitrided surface was only slightly marred. From the thickness of the nitride layer and assuming a diffusion-controlled nitride layer growth mechanism, an average growth rate of 6.5 $\mu m/h^{1/2}$ is obtained for this LAPPS process, the highest value reported for a plasma-based stainless steel nitriding process.

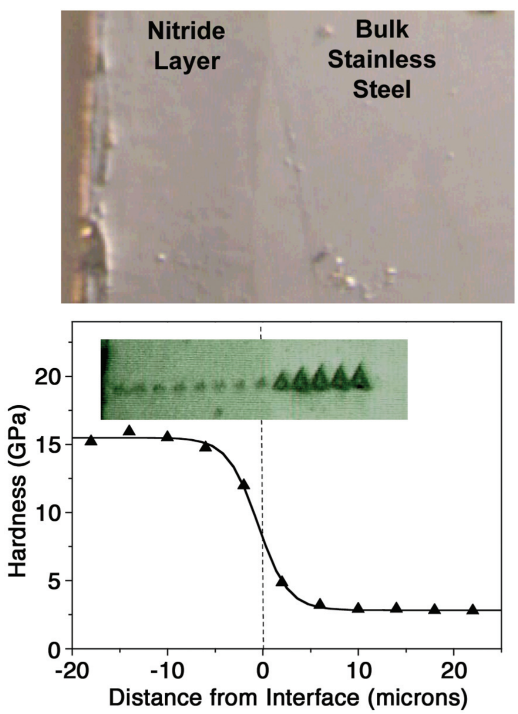


**FIGURE 5**
Cross sectional views of stainless steel surface nitrided in nitrogen-based LAPPS. Top photo shows chemically etched cross section where the interface between the nitrided surface and bulk material can be clearly seen. Bottom plot shows the variation in surface hardness across interface; inset photo shows indentations left behind from hardness measurements.

**Summary:** The ability to improve the surface wear of critical components without changing a material's desirable characteristics is of paramount importance in many military and commercial applications. The LAPPS tool has demonstrated tremendous capabilities in nitriding the surface of stainless steel, primarily due to the large flux of useful nitrogen species it can produce. The increased ion flux to the surface, along with a large nitrogen atom flux, allowed nitride layers to be produced at low processing temperatures (< 460 °C), preserving the intrinsic corrosion-resistant properties of the bulk stainless steel throughout the material. Applying this technique to other metals offers promising capabilities to the Navy's present and future forces.

[Sponsored by ONR]

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[2] C. Muratore, S.G. Walton, D. Leonhardt, R.F. Fernsler, D.D. Blackwell, and R.A. Meger, "The Effect of Plasma Flux Composition on the Nitriding Rate of Stainless Steel," *J. Vac. Sci. Technol. A* **22**, 1530-1535 (2004).

[3] C. Muratore, D. Leonhardt, S.G. Walton, D.D. Blackwell, R.F. Fernsler, and R.A. Meger, "Low Temperature Nitriding Rate of Stainless Steel in an Electron Beam Generated Plasma," *Surf. Coat. Technol.* **191**, 255-262 (2005).