PLASMA PROCESSING AND ION IMPLANTATION

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Contents

Summary

Various types of plasma processing of the surfaces of materials (cleaning, etching, surface property modification, and coating) are described. Either a processed material is placed in contact with plasma, or plasma is used as a source of ions that interact with atoms in the material itself. The key features, advantages, and technological potential of ion implantation methods are illustrated. Examples of ion implantation applications to improve microhardness, as well as to enhance corrosion, wear, and fatigue resistance properties, are considered, along with implantation/plasma processing types. Experimental equipment is illustrated schematically.

1. Introduction

The great majority of components of modern machines and mechanisms operate under extreme conditions involving heavy loads, corrosive media, and high temperatures. Surface modification represents a useful way of extending the service life and reliability of machines since surface conditions govern many properties of materials, most importantly mechanical and tribological performance, and resistance to corrosion.

One of the coating methods for wear-proofing surfaces that has seen widest commercial development is *diffusion saturation*, which forms the basis for nitriding, cementation, boronizing, sulfocyaniding, and other processes. From the 1930s until recently, ion bombardment of surfaces has been applied widely to improve mechanical, tribological, corrosion resistance, and other properties of surfaces. In 1932, Berghaus took out the first patent for the glowing discharge steel-nitriding method. The 1950s and 1960s saw the start of this method's commercial application to increasing the hardness, wear and score resistance, fatigue limits, and corrosion resistance of steels and alloys.

Since the late twentieth century, studies on the modification of structural material properties by ion-plasma methods have led to active development in this field. Methods for producing vacuum ion-plasma coatings have received wide acceptance; these include the electroarc method, used to produce wearproof coatings, based on modification of nitrides and carbides of refractory metals.

One of the most promising vacuum ion-plasma coating methods is *DC reactive magnetron sputtering*. This method allows synthesis of chemical compound coatings on virtually any structural material with a relatively low temperature at the processed surface, and leads to better adhesion and efficiency properties than the other vacuum ion-plasma methods. New physical methods for surface property modification can prove an efficient means of extending the service life and reliability of machine elements.

Novel technologies and equipment for specific treatments of metal surfaces have developed simultaneously with changes in new fields of science and engineering. For example, the solution to the problem of isotope electromagnetic separation for most of the elements of the Periodic System in the 1950 and 1960s has led to much fuller development of powerful ion sources; this in turn stimulated development and application of ion implantation in semiconductors and metals. Development of ionic propulsors has led to the creation of unique plasma accelerators for surface cleaning and nitriding at low ion energies and high current densities.

Significant interest in modifying metal layer properties by ion implantation arose in the 1970s, as a result of attempts to design a material suitable for use in the inner wall of a fusion reactor, and related problems involved in perfecting structural materials that retain necessary performance properties under extreme operating conditions. Surface modification and doping using ion, electron, plasma, and laser fluxes represents one of the most promising fields of materials science. Combining various methods of surface modification represents a novel line of inquiry for materials science and engineering. The technological processes allowing control of the structure-phase state of surface layers and their composition form a major element in modern approaches to applied materials science.

2. Plasma Processing of Surfaces

2.1. Surface Cleaning; Plasmachemical Etching

Surface cleaning and plasmachemical etching are carried out using low-temperature gas discharge plasma (LTGP) to initiate physico-chemical processes at the solid surface, whose products are gaseous compounds formed by chemically active radicals of plasma with atoms of solids. LTGP can be generated by discharges excited by a DC electric field, as well as by low- (10^2–10^3 Hz), high- (10^5–10^8 Hz), and ultrahigh- (10^9–10^{11} Hz) frequency discharges in rarefied gases.

Plasmachemical etching is the process of removing the surface layers by means of chemical reactions. If the processed material surface is actually in contact with plasma, this treatment is referred to as *plasma etching*. If layers are removed due to sputtering by ions and chemical reactions, *reactive ion etching* takes place; in cases where the processed material surface is actually in contact with plasma, the etching is referred to as *reactive sputter etching*. If the sample surface does not make contact with the plasma, which is used only as a source of energetic (with the energy E_i) chemically active ions, the process is referred to as *reactive ion beam etching.* If E_i <100 eV, plasma etching takes place. At E_i> 100 eV, reactive ion beam etching occurs (for example, etching of silicon in gas containing fluorine). If E_i exceeds the energy threshold of sputtering, and atom displacements take place in the solid state, plasma etching is described as *ion-assisted plasma etching.*

Plasmachemical etching of silicon and its oxides has been studied most comprehensively. The gases most commonly used in the process are halides (CF_4, $CClF_3$, CHF_3, CHF_2C_{l2}, and others).

2.2. Plasma Processing of Metal Surfaces

Plasma processing of the metal surface in the glow discharge is one the most commonly encountered methods for improving the mechanical and tribological properties of surfaces, as well as enhancing corrosion resistance. Plasma nitriding, carbidizing, boronizing, and titanizing of metals and alloys are all processes widely used by industry. A treated material may be placed in the immediate plasma zone; alternatively it may not make contact with plasma, which is used as a source of ions interacting with material atoms (Figure 1).

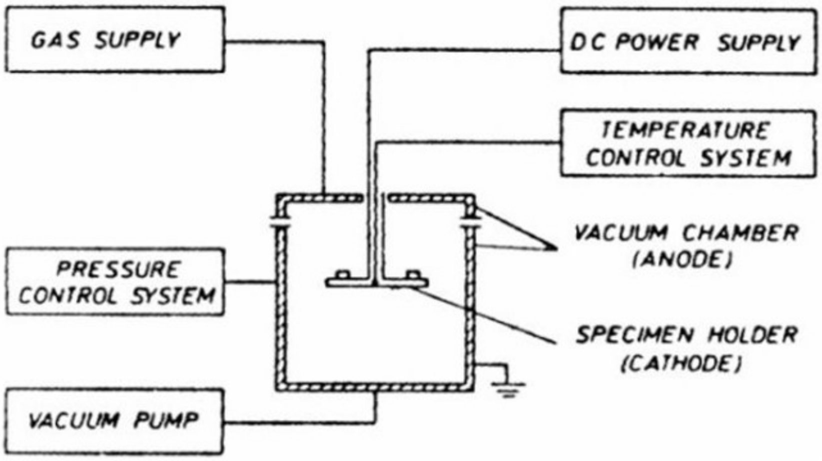
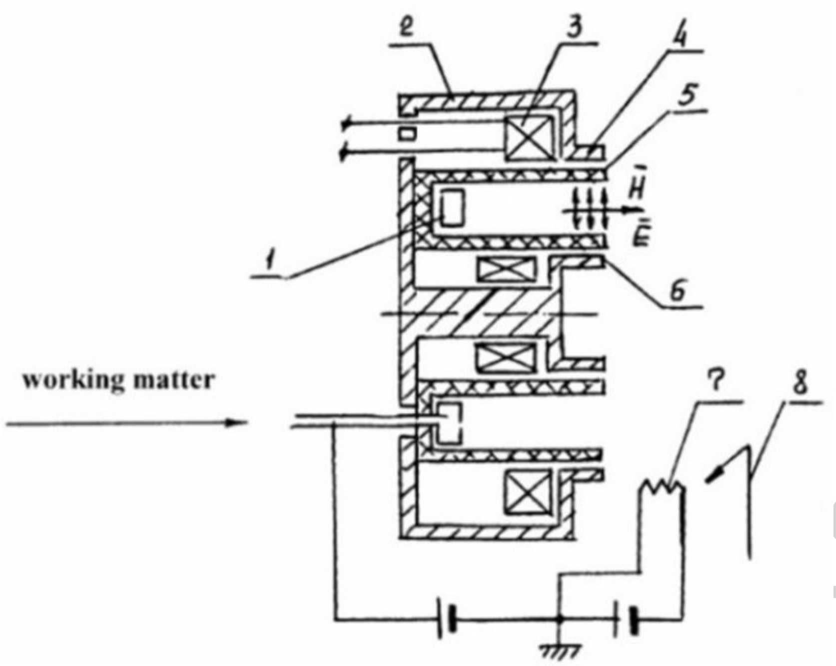


Figure 1. Scheme of plasma processing of a material placed in the plasma zone. Source: Rie and Lampe (1985).

The holder of a treated object is the cathode, while the discharge anode is the grounded vacuum chamber. The glow discharge is maintained by the discharge voltage power (from 1 to 10 keV), Nitrogen ions current density $j \leq 30$ mA/cm^2, and gas pressure of 10–100 Torr (where 1 Torr=133 Пa). The sample temperature depends on the material in question. The modified layer thickness is a function of time and irradiation temperature. The glow discharge is characterized by a low degree of ionization (10^{-6}–10^{-4}). This parameter has a significant effect on the surface properties of an irradiated surface, increasing the probability of a chemical reaction between an adsorbed ion of active gas and an ion of the material lattice.

Plasma processes using closed drift accelerators (CDA) and beam plasma discharge—where the ionization degree is close to 100%, and the plasma density is significantly higher than that in the glow discharge—are much more efficient. In the CDA, ions are generated and accelerated within the crossed longitudinal electric and radial magnetic fields inside a ring-shaped dielectric channel (Figure 2).



1) Anode – gas distributor,
2) Magnetic guide,
3) Magnetizing coil,
4), 6) Magnetic poles,
5) Discharge chamber,
7) Cathode compensator,
8) Igniting electrode

Figure 2. Schematic diagram of the closed drift accelerator

The ion current density in the CDA reaches 50–100 mA cm^{-2} at the average ion energy of 50–300 eV and an operating vacuum of 10^{-3}–10^{-6} Torr.

Figure 3 illustrates change in ferrite-martensite steel microhardness resulting from plasma nitriding. The CDA is used to bombard the surface with low-energy (300 eV) nitrogen ions, at a current density of 25 mA cm^{2} and a target temperature of 350 °C, raised by the ion beam power release.

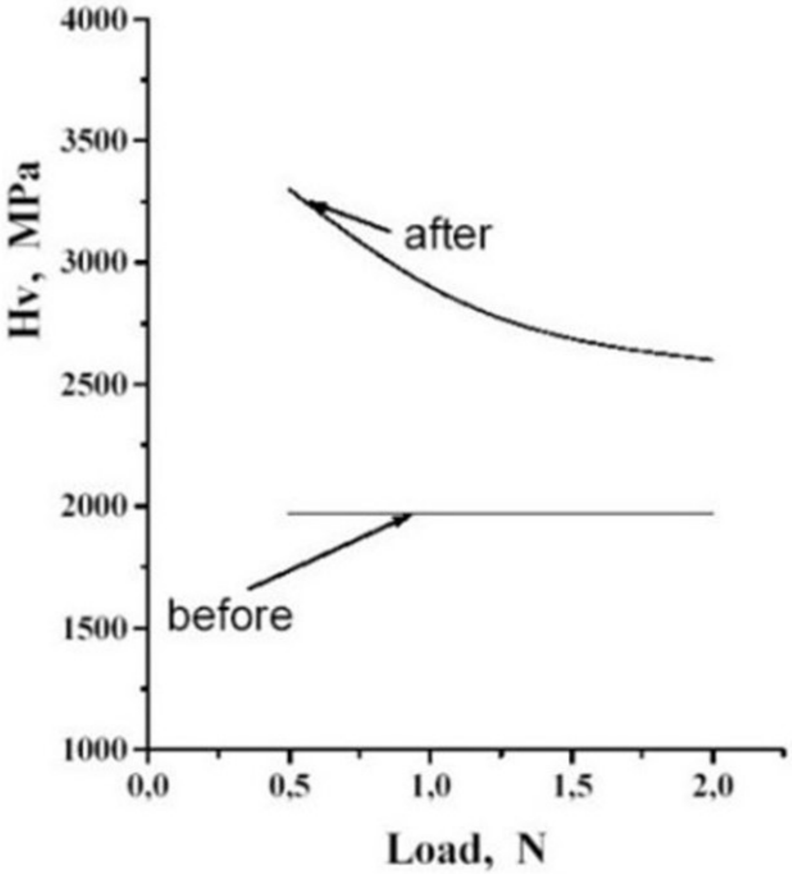


Figure 3. Dependence of the ferrite-martensite steel microhardness on the load (1) before and (2) after treatment by a nitrogen plasma flux

2.3. Coating by the Plasma Method (Magnetron Sputtering in Glowing Discharge Plasma)

In coating processes using the magnetron method, condensation takes place at the atomic level, and the sputtered atom flux contains no drop and cluster phases. This allows coating to proceed without any quality deterioration in the form of initial surface roughness.

In order to produce coatings with a predetermined composition by magnetron sputtering, it is standard practice to employ a cathode prepared from an alloy of this composition, a set of several magnetrons with cathodes from different materials, or a mosaic cathode consisting of inserts of another material.

The operation of the magnetron for coating is based on cathode sputtering in glow-discharge plasma. Sputtered atoms are deposited onto a substrate, forming a coating. As well as sputtering, ion bombardment of a target generates secondary electrons. A magnet is placed immediately under the magnetron target. The magnet poles are positioned at the target center and edge, respectively (Figure 4). The magnetic field parallel to the target surface “magnetizes” electrons, thus confining them near the target surface. The term “magnetized electrons” means that electrons move over a screw line around magnetic field lines with a radius equal to the Larmor radius, $r_L = mv_e c / eB$, where m and v_e are the electron mass and velocity, c is the velocity of light, and B is the magnetic field (gauss). Electrons ionize a working gas, increasing the degree of plasma ionization and the target current, and this results in an increase in sputtering and coating deposition rates. This makes it possible to maintain the discharge at low operating pressures, typically 10^{-3} Torr, and at an operating cathode voltage of about –500 V. The area where there is sufficiently dense plasma typically extends from the cathode over a distance of about 6 mm.

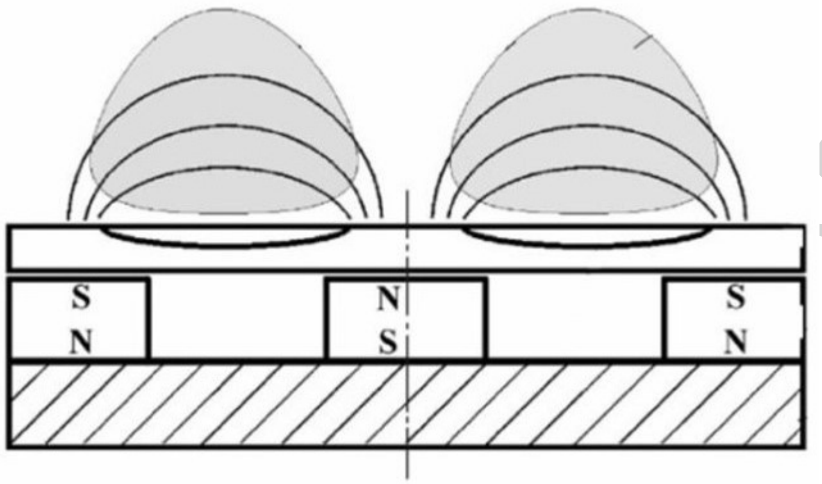


Figure 4. Schematic of plasma confinement in a typical magnetron

If the outer magnetic pole in the magnetron is stronger than the inner, some of the magnetic field lines coming from the outer pole are not closed at the inner pole but come out to the substrate upon which the coating is deposited. Such a magnetron is referred to as an *unbalanced* one. In this case the plasma region extends to the substrate, and its density near the substrate can be controlled by disbalancing the magnetic field. In the unbalanced magnetron, the ion current onto the substrate can reach about 5 mA cm^2: this exceeds the ion current onto the substrate that is conventionally caused by feeding a negative voltage to the substrate by an order of magnitude.

Pulsed magnetron sputtering is used to advantage in the production of oxide insulating coatings in a reactive gas—oxygen. In the course of steady sputtering by oxygen the target is coated with oxide: in other words, it is "poisoned." This lowers the sputtering rate and causes breakdowns and arcs, which in turn give rise to drop erosion and degradation in coating quality. With pulsed sputtering, arcs do not arise, and the sputtering rate is almost the same as in the case of metal coating.

Magnetrons with a variable magnetic field have been designed to extend the capabilities of magnetron sputtering. Displacement of the magnetron's magnetic poles allows variation of the magnetic field configuration from balanced to unbalanced, with a stronger either outer or inner pole. Variation of the magnetic field configuration in the course of coating allows variation in the ratio of the ion current to the flux of deposited atoms, thus varying the coating properties. For example, the coating near the substrate may be characterized by a density that is optimal for adhesion, while the coating near the surface might have another density better suited to other functional properties.

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Biographical Sketch

Maria Il'inishna Guseva is Head of Laboratory at the Russian Research Centre Kurchatov Institute. She obtained her Ph.D. degree in 1984. She is working in the field of plasma and ion beam surface interactions. Her scientific interest was first directed towards the study of sputtering and ion implantation in semiconductors, metals, and other materials. At present, she is interested in plasma-surface interactions in controlled fusion devices, ion-plasma methods of diamond-like film deposition, and long-range effects. She has published about 200 articles in international and Russian scientific journals. She was awarded the 1979 State Prize for her work in the field of ion implantation. She is a member of the New York Academy and the Italian Physical Society. She is currently completing for a long time as expert of International Atomic Energy Agency. Guseva also has proceeded the professor title in 2004 and she was deserved Honoured figure of Scientist