PLASMA IMPLANTATION

Plasma source ion implantation (PSII) (1, 2) is an electrical discharge method for modifying the surface properties of materials so as to increase their value for a variety of applications. As such, PSII is one of a class of electrical discharge surface treatment technologies, including cathodic arc vapor deposition (3), magnetron sputter physical deposition (4), plasma-enhanced chemical vapor deposition (5), and ionized physical vapor deposition (6). These electrical discharge surface treatments can be compared in several respects with conventional plating (chemical or electrolytic), but are free of the hazardous chemicals or contaminated fluids typically associated with commercial plating processes (acids, cyanide compounds, contaminated process water, etc.). In electrical discharge surface treatments, ions are formed and transported to the treated object's surface by placing a voltage bias on the target and immersing it in an ionized gas discharge (plasma) rather than in a liquid chemical or electrolytic bath.

Surface modification by PSII has been shown to be effective at increasing wear resistance and corrosion resistance of metals, while advantageously altering the electronic, magnetic, or electromagnetic surface properties of semiconductors, glasses, or other materials. In the PSII process, a plasma is generated in a vacuum chamber and a series of negative voltage pulses (-500 to $-100{,}000$ V) are applied to the target immersed in the plasma. As the negative voltage pulse is applied, electrons are repelled and ions in the plasma are attracted to the surface of the target at very high velocities and penetrate the surface of the target material. The implantation of energetic ions into the near surface regions of the target results in chemical and microstructural changes at the surface leading to corresponding changes in the surface properties (mechanical, chemical, electrical, magnetic) of the target. A significant advantage of the PSII process is its non–line-of-sight nature, which makes it highly effective for the implantation of three-dimensional targets. In addition to implantation, the PSII process can be used in combination with thin film deposition techniques to realize superior mixing at the film-target interface, thereby ensuring good adhesion.

Following its invention (1) and initial demonstration (2) by Conrad, PSII has grown to a world-wide activity that is under development in approximately 120 laboratories. During its expansion, it has been referred to by a variety of names, such as plasma immersion ion implantation (*PIII*), plasma implantation (*PI*), and plasma doping (*PLAD*), in addition to the acronym PSII used in this article. The proceedings from the Workshops on Plasma-Based Ion Implantation (7–9) and other publications (10, 11) provide extensive reviews of the scope of plasma and materials issues related to the science and technology of the PSII process.

COMPARISON OF PSII WITH BEAMLINE IMPLANTATION

The critical attributes of PSII that make it desirable as a materials modification tool can be best appreciated by comparison with conventional beamline ion implant processes. Conventional ion implantation (see Fig. 1) is a line-of-sight process in which ions are extracted from an ion source, accelerated as a directed beam to high energy, and then raster-scanned across the target. The acceleration voltage is high enough to bury the ions below the target's surface. Depending on the application, the accelerated ion energies can range from a few kilo-electron-volts (*keV*) to several mega-electron-volts (*MeV*).

Ion implantation was first developed as a means of doping the semiconductor elements of integrated circuits. Because of the speed, accuracy, cleanliness, and controllability of the process, it has become the standard for this type of work. In the early 1970s, it was found that ion implantation of metal surfaces could improve their wear, friction, and corrosion properties. Ion implantation of specific tools is now preferred over other types of coating technologies because the ion-implanted layer does not delaminate, does not require high processing temperatures to produce, and does not add more material on the surface (which would change the dimensions of critical components). Unfortunately, conventional beamline implanters are large, complicated, and expensive instruments. Because of the capital costs involved with setting up an ion implant capability and the significant operating expenses that it incurs, ion implantation is now used regularly only to implant specific tools and equipment with a high value-added potential (e.g., score dies for aluminum can pop-tops and artificial knee and hip joints). Studies have shown that a considerably greater number of applications would benefit from ion implantation, but that the expense of the process prevents it from becoming cost effective for those applications.

PSII is essentially a modified method for ion implantation (see Fig. 1). As mentioned above, in PSII, the target is placed directly in the plasma source and pulsed to a high negative potential relative to the chamber walls. Pulses typically last for tens of microseconds at a duty cycle that may range from about 0.1% to a few percent. No ion beam is extracted and none needs to be manipulated or focused. PSII thus achieves ion implantation in a compact bell jar environment without the need for the complex beam optics and sample manipulation necessary for a conventional implanter.

The high-voltage negative pulses applied to the target in PSII attract positive ions in the plasma which naturally tend to strike all parts of the target at normal incidence. Fortuitously, this normal incidence is indeed the optimal angle for ion implantation, because the physical process of sputtering occurs simultaneously with ion implantation. Sputtering is the removal of material from a surface due to transfer of momentum from an atom or ion in the gas phase to an atom (or several atoms) in a surface. It is characterized by a parameter known as the sputter yield, which is defined by the ratio of the mean number of emitted atoms per incident ion on the surface (12). The sputter yield depends on a number of factors, with the most important being (a) the structure and composition of the target, (b) the mass and energy of the incident atoms or ions, and (c) the experimental geometry. Thus, for a given accelerating voltage and ion species, a nonplanar target will present a range of incident angles if it is fixed in a beamline implanter. At

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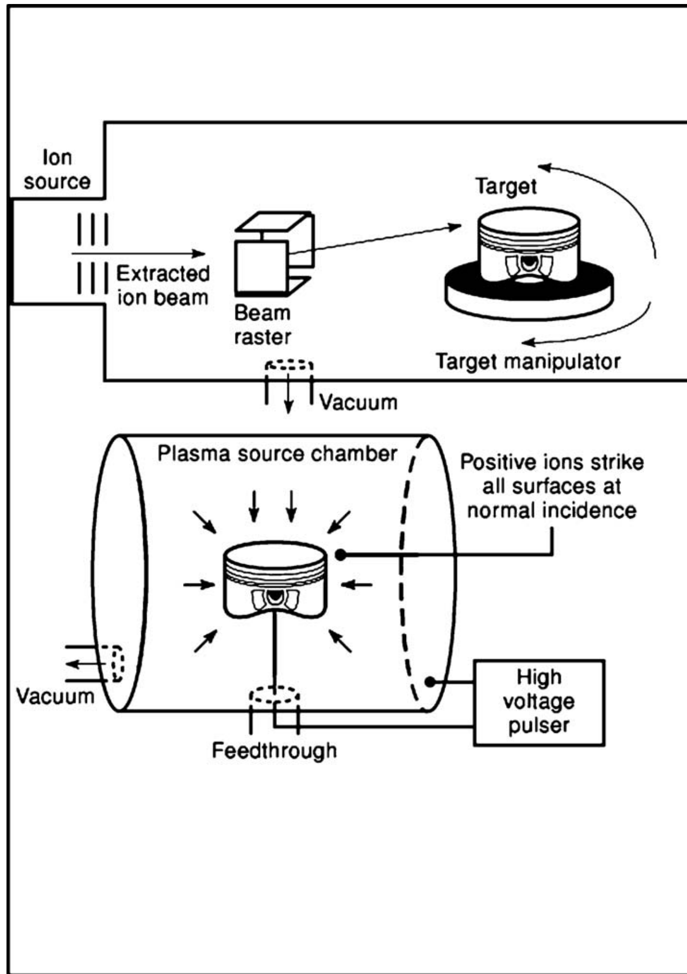

Figure 1. Comparison of (upper) conventional beamline and (lower) plasma source ion implantation.

the off-normal angles of incidence to the surface, the rate of material removal by sputtering can be high enough to equal the delivered dose to the substrate—in other words, the surface is eroded as quickly as ions are implanted into it. The dependence of the retained dose on the incident angle θ (with normal incidence given by $\theta = 0$) can be expressed as (13)

$$D = N\frac{R_p}{S}\cos^{8/3}\theta \tag{1}$$

where

D= the retained dose
N= the target atomic density
R_{p}= the projected ion range
S= the sputter yield

In a conventional beamline implanter, the only reliable solution to the "retained dose problem" is to ensure that the incident ion beam maintains an approximate normal incidence to the surface. This is accomplished by (a) rastering the beam across the surface being implanted, (b) partially masking the surface to prevent the ions from striking the target at incidence angles greater than approximately 30° off-normal, and/or (c) rotating or otherwise manipulating the sample to maintain a near normal incidence. Since these last two operations must be performed within the vacuum environment of the implanter, they result in a significant increase in the complexity and expense in the modification of nonplanar surfaces by ion implant. With PSII, however, the near-normal trajectory of the incident ions greatly reduces the retained dose problem, thus allowing higher doses to be delivered to complex workpieces in shorter times.

PHYSICS OF PSII PLASMA

An understanding of the physics of the plasma discharge during PSII is useful for designing and optimizing the process. A rather sophisticated understanding of the plasma physics has been developed and the interested reader is encouraged to consult Refs. 14 through 15–27 and the references cited therein. Here, a simplified description of the basic phenomenology will suffice to impart an appreciation for the most crucial factors for process adoption and implementation.

The process starts with immersion of the target object in a relatively low-density plasma discharge, with densities typically between 10^8 cm^{-3} and 10^{11} cm^{-3}. Lower-density plasmas would be associated with unacceptably long process times (because of a slow average supply rate for ions)

and higher-density plasmas are difficult to sustain in large volumes and are more susceptible to arcing during the application of the high-voltage pulse. The treatment then consists of the repetitive application of negative voltage pulses to the target object, until the desired number (or dose) of ions have been implanted.

At the beginning of each negative voltage pulse, electrons are repelled from the region immediately surrounding the target toward the walls of the vacuum chamber, which are usually held at ground potential. Since the ions are more massive and move more slowly than the electrons, this initially results in an "ion matrix sheath" or "cathode fall" region surrounding the target which is populated almost exclusively by ions, the electrons having been expelled. Almost all of the applied voltage difference occurs across this region, as indicated in Fig. 2. During this transient ion matrix phase of the sheath evolution, it is possible to determine the extent of the sheath in various geometries from Poisson's equation

$$\frac{d^2\phi}{dr^2} + \frac{a}{r}\frac{d\phi}{dr} = -4\pi e(n_i - n_e) \tag{2}$$

where ϕ is the potential, $n_{\rm i}$ and $n_{\rm e}$ are the ion and electron densities, and $\alpha = 0$, 1, and 2 for planar, cylindrical, and spherical geometries, respectively. If it is assumed that, before the potential is applied to the substrate, the plasma has a uniform density $n_0 = n_{\rm i} = n_{\rm e}$, then the thickness of the ion matrix sheath s can be expressed in a normalized form for a planar geometry by

$$\tilde{s} = \sqrt{2\tilde{\phi}_0} \tag{3}$$

where $\tilde{\phi}_0 = e\phi_0/T_e$, $\tilde{s} \equiv s/\lambda_{\rm D}$, and the Debye length $\lambda_{\rm D} = \sqrt{kT_e/4\pi n_0 e^2}$ (with $T_{\rm e}$ being the electron temperature and k equal to the Boltzmann constant). Similar expressions can be derived for cylindrical and spherical geometries.

Following the ion matrix phase (typically several microseconds), positive ions begin to accelerate within and across this sheath, attracted to the negative potential at the target. The rate at which the ions are drawn from the edge of this sheath region to the target increases with increasing applied voltage and decreasing sheath thickness is described by the Child–Langmuir relation (27):

$$j = \frac{4\epsilon_0}{9n}\sqrt{\frac{2q}{m}}\frac{\phi^{3/2}}{s^2} \tag{4}$$

where j is the Child–Langmuir space charge limited current, q is the ion charge, m is the ion mass, and n is the plasma density. The rate of ion transport across the sheath is typically faster than the rate at which ions flow to the sheath edge from the surrounding plasma. Hence, at the edge of the sheath—as within the sheath itself—the ion and electron densities are markedly reduced (as they are drawn in toward and repelled away from the target, respectively), and the effective sheath edge expands outward. The expansion rate for the sheath can be calculated by using the expression from Lieberman (19) that equates the current density to the sheath expansion by

$$j = nq\left(\frac{ds}{dt} + v_d\right) \tag{5}$$

where $v_{\rm d}$ is the ion drift velocity. If it is assumed that the drift velocity of an ion is zero until the sheath reaches it, then the two expressions given above can be combined to form a differential equation for the sheath edge position (18):

$$\frac{ds}{dt} = \frac{4\epsilon_0}{9n}\sqrt{\frac{2}{qm}}\frac{\phi}{s^2} \tag{6}$$

This expression can be integrated (18) to yield

$$s = s_0[(2/3)\omega_{pi}t + 1]^{1/3} \tag{7}$$

where $\omega_{\rm pi}$ is the ion plasma frequency and s_0 is the sheath thickness at $t = 0$. This sheath expansion continues until the inward flux rate of ions across the sheath decreases to equal the rate at which ions flow from the surrounding plasma to the sheath edge. At this point, the sheath boundary becomes stationary, assuming that the source for the surrounding plasma discharge can globally replenish the plasma ions as quickly as they are "consumed" by implantation into the target. In the event that the plasma replenishment rate is relatively slow (e.g., low-density plasma discharges), the sheath boundary will continue to expand until the negative voltage pulse is terminated or the sheath edge reaches the vacuum chamber walls (i.e., complete consumption of the plasma ions into the target surface).

Knowing the spatial extent of the plasma sheath at the end of each voltage pulse is important for selection of spacing between multiple targets for batch processing (28). If the targets are spaced too closely, then the sheath boundaries will overlap in the regions between the targets before the end of each pulse. This would result in reduced implantation dosage on those interior regions of the target surfaces. Careful selection of multiple target spacing based on an ability to predict maximum sheath thickness for each pulse has been shown to yield good uniformity of implantation in batch processing (29).

Limitations of the PSII Process

When compared directly with beamline implantation, PSII has a number of potential problems that need to be addressed. First, the PSII implant has an inherent energy inhomogeneity because the ions that are first to be accelerated across the sheath experience a different spatial potential distribution than do the ions accelerated at the end of the voltage pulse. In addition, the complex nature of the plasma means that a variety of ionized species are likely to be implanted during a given voltage pulse. These factors combine to make an accurate theoretical prediction of the profile of the implanted ion much more difficult than is the case with monoenergetic beamline implantation of a particular species. Comparisons of beamline versus PSII implant profiles consistently show both qualitative and quantitative differences (30, 31).

In addition to knowing the implant profile, determination of the exact dose delivered to the substrate during PSII implant is somewhat complicated (32, 33). The simple expedient of monitoring the current delivered to the substrate is not a reliable indicator of ion dose, since the current consists of two contributions, namely, the (positive) ion flux

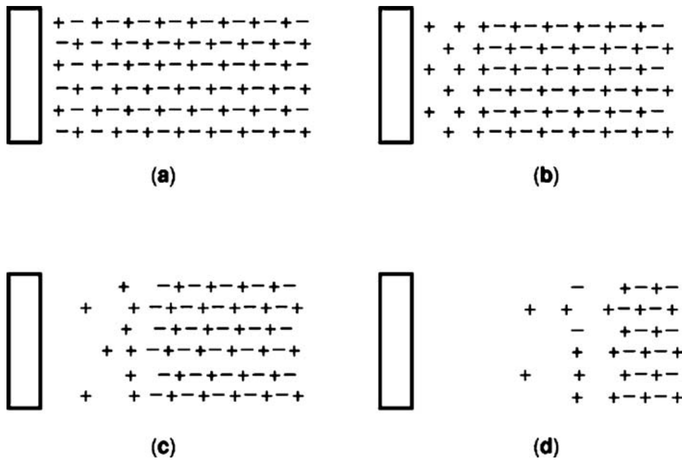

Figure 2. Time evolution of plasma sheath during a PSII pulse.

into the target and the (negative) flux of secondary electrons ejected by the target due to ion irradiation. While it may appear possible to measure the secondary electron current by collecting them as they impinge on the chamber wall, the fact is that the secondary electrons will (as they hit the wall) generate tertiary electrons, which then can produce quaternary electrons, and so on. While an alternative scheme for monitoring the dose during plasma implant has been proposed in Ref. 33, accurate dosimetry remains a significant issue in PSII.

Secondary electron emission poses other problems for PSII. First, it represents a significant electrical inefficiency, since the secondary current can be many times larger than the ion current. This increases the size (and cost) of the high voltage modulator that will be required to attain a particular dose in a specified time. More seriously, when the secondary electrons hit the internal walls of the vacuum chamber, they create bremsstrahlung X rays. This X-ray production may require personnel exclusion or additional shielding for operation at high applied voltages (in excess of 20 kV), depending on the thickness and the materials used in the construction of the vacuum chamber (34). Finally, the secondary electrons sheath the vacuum chamber walls, desorbing gases and contaminants and thus requiring active cooling of the chamber in high dose, high voltage applications.

Uniformity of the implant over large areas is an obvious concern for PSII (as well as for other implant technologies) for semiconductor applications in particular, since silicon wafer diameters are expected to increase to 300 mm in the near future. The uniformity of a plasma implant over a large area would be expected to be a function of all of the factors that influence the spatial properties of the plasma, including chamber geometry, the electric field generated by the voltage pulse, and the characteristics of the gas used to generate the plasma. By careful consideration of chamber design and the specifics of the implant process, doping uniformity of better than 2% across a six-inch diameter wafer has been demonstrated (35).

Contamination due to the unintentional incorporation of impurities during implantation is, like uniformity, a perennial concern in all implant processes, but especially so when PSII is used for semiconductor doping applications. Since there is no mass analysis of the implanted species in PSII (unlike that in beamline implant processes), any impurity that exists or can be inserted into the process gas can appear as a contaminant. Thus contamination can arise either from the starting impurities present in the gas supply or from unintentional sputtering from chamber components onto the implant target. The latter source is of particular concern to PSII, since everything that is biased during the voltage pulse is subject to implantation and thus can become a potential sputter source of impurities. Fortunately, like uniformity, concerns about contamination have largely been mitigated by studies that have shown very low levels of unintentional impurity incorporation in well-designed implant systems (35, 36).

A final concern with PSII is the possibility that the plasma environment (which is obviously in contact with a wafer being processed) may cause undesired changes to the substrate through either etching or charging. For shallow *p*-type implants into silicon (discussed below), BF_3 gas is typically used to supply the implant species. In the plasma environment above the wafer substrate, BF_3 typically decomposes to $BF^{+}{}_2$ and F^+, with the ionized fluorine being a very effective silicon etchant. Thus early attempts at PSII doping from a BF_3 plasma were complicated by the etching of the silicon simultaneously with implantation (37, 38). Fortunately, by altering conditions such as the gas pressure and plasma power, it is possible to reduce the etch rate to essentially zero under PSII conditions (38). In a similar vein, the rich mix of ionized atoms and radiation that is characteristic of a plasma environment could be a source of damage to sensitive structures such as metal–oxide–semiconductor (*MOS*) transistors. Extensive studies using antennae test devices have confirmed that radiation and charging damage are minimal in the PSII environment, presumably because of the rapid neutralization of charge imbalance by the ionized species in the plasma (39).

APPLICATIONS

Materials Systems

Many studies have demonstrated the effectiveness of the PSII process for improving the surface hardness, wear, and corrosion characteristics of engineering materials. When

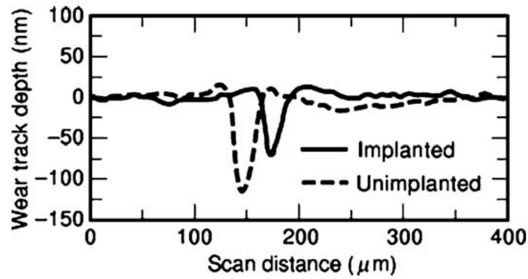

Figure 3. Weak-track profile for PSII nitrogen-implanted S-1 tool steel.

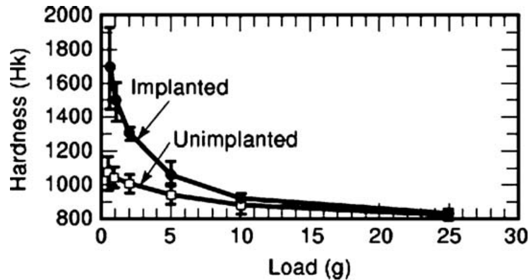

Figure 4. Microhardness profiles for untreated and PSII nitrogen-implanted A-2 tool steel.

performed with gaseous implant species (e.g., nitrogen, oxygen, or carbon-containing vapors), these unique surface properties are obtained primarily through the formation of nitrides, oxides, and carbides. For example, PSII nitrogen ion implantation of American Iron and Steel Institute (*AISI*) S-1 tool steel (40) at a target bias of −50 kV and a dose of 3×10^{21} atoms per square meter results in an implanted layer approximately 100 nm thick. The corresponding increase in wear resistance as measured with a pin-on-disk wear tester is shown in Fig. 3. Under similar conditions, implantation of an AISI A-2 tool steel (41) increases hardness by more than 50% (Fig. 4), while the friction coefficient drops by a factor of two. In field tests of A-2 tool-steel score dies used for stamping tabs in aluminum cans, PSII nitrogen implantation improved service life from 8.5 million to 14 million hits (39). Corrosion resistance of aluminum and bearing steel alloys has been substantially improved by nitrogen PSII (42, 43), and the orthopedic alloy *Ti-6Al-4V* (used for artificial replacement joints) has shown a significant increase in wear resistance after nitrogen ion implantation (44). PSII of Ni-Ti shape memory alloy has been investigated for the improvement biocompatibility and corrosion resistance in biomedical applications (45, 46). Carbon ion implantation using methane precursor gas has been shown to increase the surface hardness of stainless steels (47, 48) and wear and galling resistance of AISI 52100 bearing steel (49). It has been noted that for an austenitic stainless steel, depending on dose and dose rate, the near-surface structure could be altered from crystalline to amorphous or a combination of the two phases (47).

An enormous range of adherent, high-value-added coatings and surface treatments can be realized by combining PSII with plasma or physical vapor coating deposition treatments for an “ion beam enhanced deposition” treatment mode. Examples of coatings deposited using this technique include *W*, *Pt*, *Cr*, *TiN*, *TaN*, *CrN*, and *Cr–Mo* alloy films. The implant characteristics of PSII result in ion-enhanced mixing at the substrate-film interface, thus leading to superior adhesion of the deposited layer (50, 51). PSII nitrogen ion implanted metallic films have been shown to have superior diffusion barrier characteristics. For example, nitrogen ion implanted Ti and Ta films has been shown to exhibit superior high temperature diffusion barrier characteristics between Cu and Si, a materials system of considerable relevance in microelectronics applications (52, 53). Finally, in materials where the implanted species can diffuse, PSII at elevated temperatures can produce a substantially thicker diffusion zone supporting the implanted layer, leading to major increases in hardness and load-bearing capacity (discussed in Ref. 10). Many other examples and detailed studies of the materials science of metallurgical applications of PSII have been conducted at many institutions throughout the world as shown in Refs. 7 through 9.

Diamond-like Carbon (DLC) Films

PSII has been used for depositing diamond-like carbon (DLC) films. DLC films are being considered for a variety of applications because of their high hardness and low friction, wear resistance, biocompatibility, chemical inertness, and optical transparency. DLC films have been traditionally synthesized by ion beam processes and high temperature CVD methods (54, 55). PSII is a near room temperature, non-line-of-sight method for depositing DLC films [56]. A significant advantage of PSII in regards to DLC films is the ability to implant carbon at higher energies (>10 keV) to form a carbide seed layer followed by deposition of DLC at lower energies (1 to 5 keV). Commonly, methane has been used as precursor gas for carbon ion implantation and acetylene has been used for DLC deposition. This approach has been shown to enhance the adhesion of DLC films to a variety of metallic substrates (57, 58), and has been trademarked by General Motors (Ionclad^{TM}). The hardness and elastic modulus of DLC films synthesized by PSII range from 5 to 25 GPa and 50 to 200 GPa, respectively depending on the process parameters and the hydrogen content of the films. Film thicknesses are usually limited to about 3μm due to limitations imposed by film stresses. DLC films elementally modified by with silicon and fluorine can be produced by PSII using appropriate precursor gases (e.g., Si-DLC with hexamethyl-disiloxane and F-DLC with tetrafluoro-ethane). Si-DLC films have a higher hardness, lower surface energy, and greater high temperature stability compared to unmodified DLC films, whereas the F-DLC films are softer. Elementally modified DLC films synthesized by PSII are similar to those that have been successfully produced using the CVD technology (59). Finally, DLC films produced by PSII have been examined for nanoscience and technology, particularly in the study of friction and tribology on a near-atomic level by the conformal deposition of these films on AFM tips (60). DLC films produced by PSII could have potentially wide range of applications in tools and components, MEMs devices and computer hard disks (61).

Semiconductor Systems

PSII has a number of unique and important applications to the processing of semiconductor materials; excellent reviews regarding the application of PSII to semiconductors have been published in Refs. 62–67.

As mentioned before, during each voltage pulse the ions are accelerated across the ion sheath and implanted into the surface. It is important to note that this process can proceed at arbitrarily low accelerating potentials, implying that the PSII implantation process has no limit at low energies. In contrast, a decrease in accelerating voltage reduces the efficiency of beamline implanters as the accelerating voltage is decreased, thus reducing the dose that can be delivered in a given process time. PSII has an added advantage in a semiconductor manufacturing environment in that the space requirement of a typical implant system (i.e., the "footprint" of the installation) is much smaller than that of a typical beamline implanter. Given the escalating costs of typical Class 1 cleanroom space, a decrease in footprint offers the prospect of significant cost-of-ownership advantages for a PSII-based system. A third advantage of PSII for semiconductor applications is that the implantation can be performed (in principle) into substrates of arbitrary sizes. There has been great interest, for instance, in using PSII for the implant step in the fabrication of thin film transistors (*TFT*) in flat panel displays (*FPD*). As mentioned above, beamline implanters typically require complex and expensive target rotation and manipulation mechanisms in order to achieve uniform implantation over large areas.

Since PSII is a plasma process, it shares many of the characteristics of these processes as they are used in the semiconductor industry. This means, for instance, that a PSII implanter can be integrated along with other processing stations into a "cluster tool" environment. Also, it is conceivable that the implant capabilities of PSII could be combined with other plasma processes such as sputter deposition or reactive ion etching to achieve new process capabilities.

PSII has long been recognized for its potential for shallow junction doping, where its combination of high ion flux at low energies makes it ideally suited. This is especially true in the case of *p*-doping (impurity doping that generates acceptor sites or "hole" carriers) of silicon by boron, where the low mass of the boron ion results in a relatively long projected ion range. Boron implantation thus requires very low energies in order to achieve the shallow junction depth anticipated for advanced device geometries [viz. 100 Åto 300 Åfor 0.07 μm process according to the National Technology Roadmap for Semiconductor Processes (62)]. Numerous studies (described in Refs. 63–69) have therefore been conducted on the formation of shallow junctions by PSII doping. For instance, 0.5 kV PSII implantation from a BF_3 plasma yielded a junction depth of less than 400 Åafter a 10 s anneal at 950°C (69). In preamorphized samples, transient-enhanced diffusion and dopant trapping was observed at low temperature (550°C) anneals (69). High-resolution transmission electron microscopy and x-ray diffraction analyses of the as-implanted silicon has shown the expected formation of a thin (5 nm) amorphous layer in silicon implanted from a BF_3 plasma at 3.5 kV. Dislocations or other extended defects are not observed (70, 71).

Other variants on the PSII process show promise for semiconductor materials processing. For instance, instead of implanting boron directly into the silicon and then activating the implant by an anneal process, it is possible to sputter deposit boron onto the silicon surface and then use ion-assisted mixing to incorporate the boron into the silicon lattice (72). An improvement in properties of polysilicon TFT transistors following PSII implant has been reported (73). PSII has also been used to synthesize *TiN* diffusion barriers (74).

PSII has been shown to be useful for the fabrication of silicon-on-insulator structures via the *SIMOX* (*s*eparation by *im*plantation of *ox*ygen) process (75, 76). SIMOX materials are typically synthesized by performing a high dose silicon implant ($>10^{17}$ cm^{-2}) to form a subsurface layer that is supersaturated with oxygen; a subsequent high-temperature anneal converts this layer to a buried oxide. Cheung and coworkers have shown that PSII can effectively form a high-quality SIMOX structure by performing an oxygen implant at 60 kV followed by an anneal at 1270°C (75). Moreover, it was claimed (75) that the high ion doses that can be achieved by PSII could make SIMOX fabrication by this method more cost effective than conventional beamline implant synthesis.

While one of the main advantages of PSII over conventional beamline implantation is the natural near-normal incidence of the accelerated ions, it has been shown (77) that conformal doping of deep silicon trenches can be performed by this method. For trenches with aspect rations as great as 12:1, very good doping uniformity was observed. Since the uniformity depended primarily on the implant bias while the pressure had relatively little effect, the conformal doping was attributed primarily to collisional scattering of the incident ions as they crossed the plasma sheath (62).

OTHER MATERIALS AND PLASMA SYSTEMS

While metallurgical and semiconductor applications of PSII have garnered the greatest attention, other materials can be treated as well by use of this process. One of the more intriguing applications has been in the implantation of polymer films to improve their wetting characteristics. The exposure of polymer surfaces to a plasma in order to improve their wetability is an established practice; however, generally the contact angle of a liquid placed on the surface increases with time (minutes to hours) after the plasma treatment is completed. If polymer surfaces are implanted with oxygen by PSII, the degradation of the wetability can be significantly retarded, or, in some cases, eliminated (78).

Modification of glass surfaces to induce changes in optical or magnetic properties has also been investigated. For example, it has been demonstrated that adding oxygen into iron-doped magnesium aluminosilicate glasses results in near-surface precipitation of nano-scale magnetic spinel domains of potential interest for high storage-density mag-

netic recording media (79). Similar possibilities exist for modifying optical transparency characteristics of specialized window glass by formation of buried TiN layers. This technology has been demonstrated using conventional ion implantation (80), and is considered a reasonable candidate for PSII technology as well.

While the original PSII concept utilized low pressure, weakly ionized gas discharges, other approaches have been investigated (81, 82). In particular, cathodic arcs have been successfully employed as a source of metal ions for PSII processes. By pulsing a cathodic arc in synchronization with the PSII pulse bias it is possible to perform pure metal ion implantation without deposition. Although the directional nature of the cathodic arc may obviate the advantage of treating the entire workpiece simultaneously, excellent conformality can be achieved on surfaces facing the arc. This is due to the fact that cathodic arcs can produce very dense plasma (typically 10^{12} cm^{-3}) which will result in a subcentimeter sheath thickness.

COMMERCIALIZATION ISSUES

Cost effectiveness for high-volume, low-cost-per-part commodities favors large-batch processing, which, in turn, implies large processing chambers and corresponding vacuum systems (28). If the capital costs are amortized, then the annual operating expenses become dominated by personnel costs, and are therefore competitive with other processing technologies. However, the potentially large equipment investment may mean that the time for return on investment is significantly longer than that of competing coating technologies, such as electrolytic plating or vacuum arc deposition. This, of course, depends on the rate of treated parts (or total treated surface) that the market for that product is expected to consume in a year. Therefore, the best opportunities for commercial adoption include large-volume-consumption-rate commodities whose customers are willing to pay premium prices for a high-value-added process. The most obvious candidate, therefore, is plasma doping or related PSII treatments for next generation (ultra-large-scale integrated) microelectronic devices. Other possibilities include niche applications where the wear stress on the material surface is so severe as to cause adhesion failure of more conventionally deposited coatings. A semiempirical model for the cost of a commercial PSII system has concluded that such a facility should be able to treat a surface area of 10^4 m^2/year at a cost of \$0.01 per cm^2 (83). Opportunities exist for commercial adoption in the automotive or fine-finish architectural coatings markets, especially as restrictions on wet chemical plating processes arise from environmental regulations on disposal of hazardous or polluted fluids conventionally used in that industry (84, 85).

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