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Dose and energy uniformity over inner surface in plasma immersion ion implantation

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The absence of the line-of-sight restriction makes plasma immersion ion implantation an excellent interior surface treatment technique. In our experiments, we implanted both the outside and inside surfaces of a set of hollow cylindrical samples with and without a grounded conductive electrode positioned along the center of the bores to evaluate the impact energy as well as dose uniformity along the specimens. Our experimental results show that the use of the coaxial electrode increases the impact energy by 43% and retained dose by 71%. The nonuniformity is 20% to 30% and is worse with larger bore length. © *1998 American Institute of Physics.* [S0021-8979(98)01116-5]

I. INTRODUCTION

Plasma immersion ion implantation (PIII) has no line-of-sight restriction and is superior to conventional beam-line ion implantation when dealing with specimens of irregular shape.[1] The potential of implanting the interior surfaces of industrial components by PIII has aroused the interests of plasma scientists and engineers because the treatment process is otherwise very difficult by beam-line implantation. There have been a number of theoretical papers investigating the feasibility of implanting the interior of a hollow cylindrical bore and the conclusion is that a grounded, conductive electrode positioned along the axis of the bore will increase the impact energy significantly.[2–9] Recently, Malik *et al.*[10] used a grounded coaxial electrode to deposit TiN_x and diamond like carbon thin films onto the interior of a hollow cylindrical sample. Their preliminary results show that the coaxial electrode is indeed helpful, but the film thickness is not very uniform. It therefore remains to be proven that deposition using PIII can emulate conventional coating techniques. On the other hand, high energy PIII by which ions are implanted into the specimen to change the surface properties shows more promises as there are very few alternative techniques. In addition, as the ions are implanted and become a part of the materials, there is no film adhesion issue and the dimension of the treated specimens is the same as the untreated ones thereby requiring no re-engineering. The latter factor is quite important in the industry. For example, stainless steel pistons and sleeves treated by PIII can be readily put back into oil pumps used in an oil field.

In this work, we conduct a systematic investigation on inner surface PIII with and without a coaxial electrode. Our objective is to determine experimentally the degree of improvement and to study the implantation uniformity.

II. EXPERIMENT

Implantation was performed in a multipurpose plasma immersion ion implanter.[11] Two sets of stainless steel hollow cylindrical bores, $\Phi 100$ mm×200 mm and $\Phi 100$ mm×400 mm, were prepared. The thickness of the wall was 1.5 mm and 3 mm×3 mm stainless steel sheets were affixed at regular intervals on both the exterior and interior surfaces of each bore. The bore was connected to the sample stage in the vacuum chamber by a 260 mm long aluminum rod for electrical contact and minimizing the influence of the stage. A stainless steel tube 6 mm in diameter was inserted coaxially along the bore and connected to the sidewall of the chamber which was grounded during the PIII experiment. The schematic of the experimental setup is shown in Fig. 1 and a picture of the apparatus is displayed in Fig. 2. The chamber was pumped down to a base pressure of 9.1×10^{-4} Pa and a nitrogen plasma was generated using a filament source. The implantation parameters are listed in Table I. The experiment was repeated without the coaxial electrode. After PIII, the 3 mm×3 mm sheets were taken out to perform Auger depth profiling to determine the implanted dose and elemental in-depth distribution.

III. RESULTS AND DISCUSSION

Under the selected implantation conditions, the calculated ion-matrix sheath thickness is more than 5.5 cm and larger than the radius of the bore samples. Figure 3 shows the nitrogen depth profiles acquired on the outside surface and on the interior surface 50 mm from the edge of the bore with and without the auxiliary electrode (deflecting field) for sample 1 ($\Phi 100$ mm×200 mm). The peak depth without the auxiliary electrode is 210 A or 33% of that on the outer surface and that with the auxiliary electrode is 300 A which corresponds to 48% of that on the outer surface. The improvement when using the auxiliary electrode is 43%. The retained dose without the auxiliary electrode is 1.6×10^{16} atoms/cm^2 or 19% of that of the outer surface, and 2.7×10^{16} atoms/cm^2 or 32% of that of the outer surface when an auxiliary electrode is in place. The retained dose is improved by 71% in the presence of deflecting electric field caused by the grounded electrode. It should be noted that all three samples were implanted under the same conditions and

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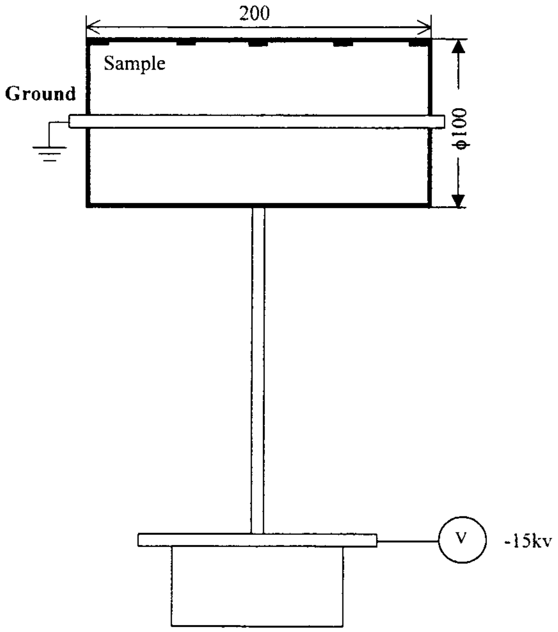

FIG. 1. Schematic of experimental setup.

TABLE I. Instrumental parameters.

Implantation voltage	-15 kV
Pulsing frequency	200 Hz
Pulse width	15 μs
Voltage rise time	$<1\mu$s
Measured plasma density	1.1×10^9/cm^3
Measured electron temperature	1.4 eV
Electron saturation current	10.9 mA
Pressure	0.15 mTorr
Implantation time	3 h
Nitrogen flow rate	14.5 sccm

the results thus reflect the difference between outer and inner surface implantation. Even though inner surface PIII is not as efficient as outer surface PIII, it is quite obvious that the deflecting field created by the auxiliary electrode does indeed give rise to a higher retained dose as well as impact energy. The nonzero nitrogen concentration after the peaks is due to nitrogen diffusion.[12]

To evaluate the dose and energy uniformity along the specimens, Figs. 4(a) and 4(b) plot the projected ranges and retained doses calculated at various interior locations on the two bores of different lengths in the absence of the auxiliary electrode. Since the experimental setup is symmetrical about the center, only results obtained from one half of the bores are presented for simplicity. The results indicate some nonuniformity in the impact energy (peak depth) and retained dose for inner surface PIII. Both the impact energy and retained dose reach maximum values at the end of the bores. For the bore 200 mm in length, the peak depth changes from 240 A at the end to 180 A at the center, while the retained dose decreases from 1.7×10^{16} to 1.6×10^{16} atoms/cm^2. The maximum nonuniformity of the implantation depth and dose is 14% and 4%, respectively. For the longer bore (400 mm), the implantation depth decreases from 240 A at the end to 180 A at the center, whereas the retained dose drops from 1.9×10^{16} to 1.5×10^{16} atoms/cm^2. The maximum variation in the implantation depth and dose is 21% and 25%, respectively. As the diameter of both bore samples is 100 mm and equal to the half length of the smaller bore, the difference observed in the implantation energy and dose between the two samples can be explained as follows. Under our experimental conditions, the mean free path is estimated to be 48 cm based on our simple collision model compared to an ion-matrix sheath thickness of 5.5 cm. For outer surface implantation, ions can attain the full acceleration across the sheath and are implanted at the voltage applied to the target as long as the mean free path is larger than the sheath thickness. However, inside the bore, the electric field is quite weak and ions inside the bore cannot gain the full potential. There is a small contribution from ions attracted from the region immediately outside the bore and having the right ion trajectories to impact the inner wall. Hence, ions implanted into the region between the end to about 100 mm from the edge originate from those already existing in the bore before the voltage pulse is applied and also from the adjacent region outside the bore. These outside ions are drawn in by the electric field and implanted into the interior side walls at glancing angles. Therefore, the implantation depth is shallower towards the center of the bore. However, few outside ions are implanted into the center region of the bore as most of them do not have the right ion trajectories (some of them will go straight through the bore and exit on the other side). Hence, in the center regions, only ions originally present inside the bore before the voltage pulse is applied are im-

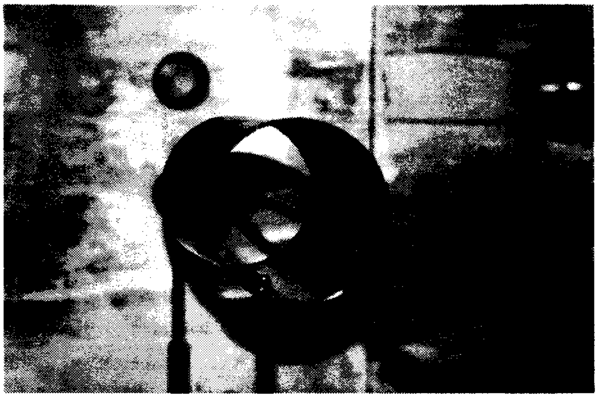

FIG. 2. Picture of the experimental setup showing the elevated hollow cylindrical sample with a zero potential coaxial electrode.

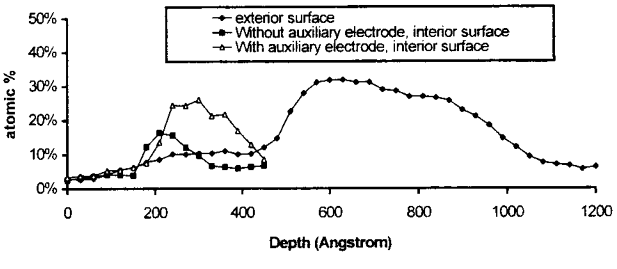

FIG. 3. Auger depth profiles comparing the nitrogen profiles on the outside surface and interior surface with and without the coaxial electrode.

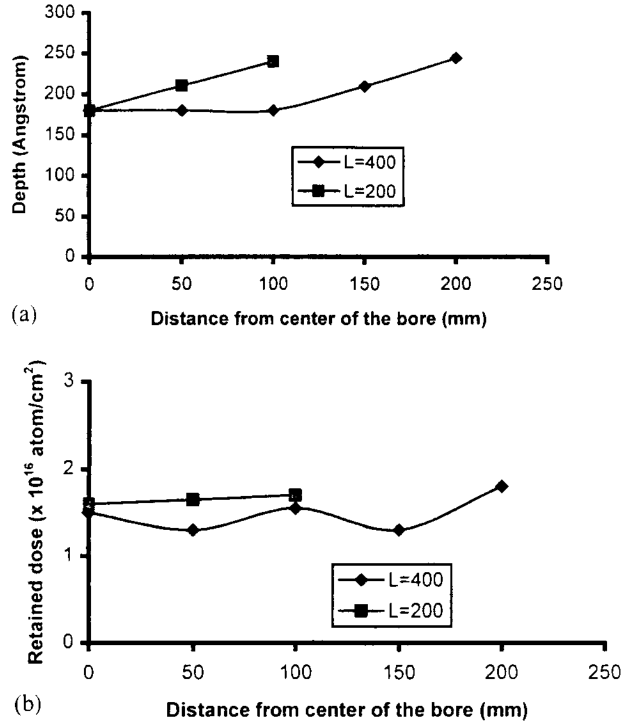

FIG. 4. (a) Variation of implantation depth along the interior of the two samples without the auxiliary electrode. (b) Variation of retained dose along the interior of the two samples without the auxiliary electrode. The center of the bore is at $x=0$.

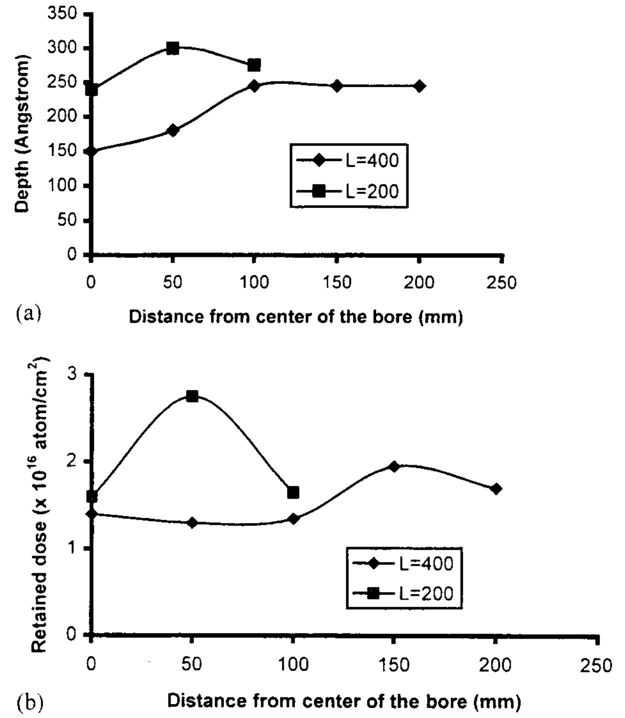

FIG. 5. (a) Variation of implantation depth along the interior of the two samples with the auxiliary electrode. (b) Variation of retained dose along the interior of the two samples with the auxiliary electrode. The center of the bore is at $x=0$.

planted and there is very little replenishment from the outside. The discrepancy is higher for a longer bore length, but the degree of nonuniformity is expected to reach a steady state with increasing bore length. It should be mentioned that the implantation depth depends on both the impact energy and incident angle. As shown in Fig. 4, similar implantation depths are observed at the midplane of both the long and short tubes. It therefore appears that the shallower implantation depth at the center of the bores is primarily due to a smaller average impact energy but not the ion impact angle which would have been shallower toward the center of the bore.

Computer simulation has shown that the use of a grounded coaxial electrode will improve both the implantation energy and dose.[2–9] The results obtained in the presence of the deflecting field sustained by the auxiliary electrode are shown in Fig. 5. The higher electric field inside the bore in the presence of the electrode gives rise to better ion acceleration, i.e., larger implantation depth or energy. Outside ions that would have exited through the other side are deflected by the electrode and implanted into the inner wall, and consequently, the retained dose is improved. Our data show that for the 200 mm bore, the implantation depth and retained dose nonuniformity is 11% and 37%, respectively. The values for the 400 mm bore are 29% and 28%, respectively. The length of the bore affects the degree of improvement and the enhancement effects at the center regions are smaller for a larger bore length. The results also reveal a very interesting phenomenon. Without the auxiliary electrode, the highest retained dose and energy are observed at the edge, but when the auxiliary electrode is present, the deepest implantation depth and highest retained dose occur at a certain distance from the edge. We believe that when ions enter the bore from the outside, they gain a certain velocity determined by the sheath voltage drop. As they enter the bore, the radial electric field created by the auxiliary electrode changes the ion trajectories and pushes the ions toward the inner surface. Hence, the ions tend to preferentially bombard the inner surface within a certain area that varies according to the radius of the bore, implantation voltage, ion mass, etc. In fact, when using an auxiliary electrode, we always observe a colored ring-like feature on the inner surface that indicates localized higher implantation doses. The position of the ring correlates with the Auger results (Fig. 5) that show a higher retained dose 50 mm from the edge in both samples.

IV. CONCLUSION

Based on our experimental results, the implantation energy and retained dose are lower for inner surface PIII when compared to outer surface PIII. The implantation depth and retained dose are 33% and 19% of those achieved on the outer surface, respectively. Positioning a grounded electrode along the center of the hollow bore improves the implantation depth by 43% and the retained dose by 71%. Nonuniformity in both implantation energy and retained dose is observed for inner surface PIII and it increases with larger bore length. The overall variation is about 30% with or without the auxiliary electrode. Without the auxiliary electrode, the edge of the bore receives the highest dose, but the region moves inward under the influence of a deflecting electric field caused by the presence of the auxiliary electrode.

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