Recent developments and applications of plasma immersion ion implantation

Paul K. Chu

Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong

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Plasma immersion ion implantation (PIII) is an established technique in some niche microelectronics applications, such as synthesis of silicon on insulator. In other applications, such as shallow junction formation by plasma doping, trench doping, and others, PIII possesses unique advantages over conventional techniques. In the last few years, there have been significant breakthroughs in these areas. Recent developments in plasma doping, direct-current plasma immersion ion implantation that excels in planar sample processing, PIII of insulating materials, as well as plasma surface modification of biomaterials are reviewed in this article. © 2004 American Vacuum Society. [DOI: 10.1116/1.1632920]

I. INTRODUCTION

Plasma immersion ion implantation (PIII) was first introduced in the 1980’s to circumvent the line-of-sight restriction of conventional beamline ion implantation.1–3 PIII also offers advantages, such as high efficiency, large area, and batch processing, as well as small instrument footprint. Figure 1 illustrates some of the processes occurring in the PIII chamber demonstrating the versatility and potential problems of the technique. In addition to metallurgical engineering, PIII excels in semiconductor and microelectronics processing as well as biomedical engineering.4,5 The most widely studied semiconductor applications of PIII are shallow junction formation by plasma doping (PD),6–11 production of silicon-on-insulator (SOI) substrates by either PIII/ion-cut or separation by plasma implantation of oxygen,12–19 conformal trench doping,20 hydrogenation of polysilicon thin films used in flat-panel displays,21 as well as fabrication of thin oxide on SiGe, low dielectric constant (low-k), and III-nitride materials.22–24 In this article, recent developments and applications of PIII in semiconductors and nonsemiconductors are reviewed.

II. PLASMA DOPING

Figure 2 shows some other typical PIII applications in ultralarge-scale integrated silicon processing. Examples shown here include sidewall doping of deep trench-based and stack capacitor-based dynamic random access memory, gate oxide processing, as well as polysilicon gate doping. PIII is a competing doping technique in ultralarge-scale integration (ULSI). Modern silicon microelectronic devices require ultrashallow source/drain extensions to reduce short-channel effects and enhance the performance. Shallow junctions can be accomplished using low-energy conventional beamline ion implantation and rapid thermal annealing. In spite of recent progress on hardware improvement,25 conventional beamline ion implantation still suffers from small throughput and poor beam performance as a low-energy tool.26,27 Hence, PIII, also called PD, has attracted much attention. As an ultrashallow junction fabrication technique, PIII (PD) has been demonstrated for both n-type and p-type ultrashallow junctions. In order to improve the process, much work is being conducted on related issues, such as high activation efficiency, reduction of damage, improvement of dopant profile steepness, and enhancement of transistor performances. However, PD is still not a mature technique from the commercial perspective and a few practical issues, such as dosimetry accuracy, glancing angle implantation underneath gate structures, precision, and plasma–surface interactions must still be addressed.28 More details on the current status and development of PD can be found in other articles in this special issue.

III. SILICON-ON-INSULATOR SYNTHESIS AND DIRECT-CURRENT PLASMA IMMERSION ION IMPLANTATION

Hydrogen ion implantation is, at present, used commercially to produce SOIs29,30 and has been extended to perform layer transfer in other materials.31,32 As shown in Fig. 3, the ion-cut process requires high dose hydrogen ion implantation to create microcavities along the projected range of the implant. Upon annealing, the stress imposed by the expansion and coalescence of these microcavities causes delamination of the wafer along the projected range of the implanted ions. In the silicon ion-cut process illustrated here, the implanted or donor wafer is bonded to another silicon or acceptor wafer before annealing and the cleaved silicon film is transferred to the acceptor film. If the acceptor film has a surface oxide layer, the resulting structure becomes a SOI. As the required hydrogen dose for the layer transfer process is quite high, typically in the mid-1016 atoms/cm², PIII is more economical than conventional beamline ion implantation. In addition to innovations in hardware, the success of PIII stems from intensive research and subsequent improvement on the uniformity of ion dose and implant energy as well as processing issues, such as contamination.33–35
In the ion-cut process, the important parameter is the depth of the hydrogen implant provided that a critical dose has been implanted. Hydrogen PIII is typically performed in mTorr or sub-mTorr pressure to ensure noncollisional conditions in which the ion mean-free path is much larger than the ion-matrix sheath thickness. However, low-energy ions implanted during the rise and fall times of the voltage pulses can introduce defects affecting the yield of the ion-cut process. During the short but finite rise and fall times of each voltage pulse, the ion acceleration energy is reduced, resulting in a low-energy component in the implant distribution. In addition, when a negative high-voltage pulse is imposed, the vacuum chamber, sheath, and circuit inherently induce an equivalent capacitive load on the power modulator and give rise to a displacement current. This displacement current generates extra heating to the wafer and sample stage, and metal impurities can diffuse from the contact interface and sample stage into the wafer, and are subsequently driven into the wafer at a higher temperature. Therefore, cooling is sometimes required in the implantation process. These effects are deleterious in the PIII-ion cut and PIII-SIMOX techniques. Hence, in order to reduce the effects of the voltage pulse rise and fall times, dc PIII has been proposed.

Figure 4 displays a dc-PIII apparatus consisting of a radio frequency (rf) plasma source. A conducting grid, made of a compatible material to avoid contamination (e.g., a silicon-coated mesh for implanting silicon wafers), divides the chamber into two halves. In the lower part, a strong electric field is formed between the negatively biased wafer stage and the grid.
and the boundaries created by the grid in the lower part of the chamber walls. The upper part confines the plasma since the grounded grid stops the expansion of the ion sheath. In this way, a continuous low-pressure discharge can be maintained in the volume above the grid without plasma extinction even at high sample voltage. Without the grid, the plasma sheath may propagate all the way to the top of the PIII chamber thereby extinguishing the plasma. Positive ions diffuse into the lower part through the grid and are implanted into the top of the wafer.

The dose and energy uniformity along the implanted wafer are important issues for PIII, and as aforementioned, there are many low-energy ions introduced into the wafer during the rise and fall times of each negative voltage pulses. In the dc-PIII mode, the ion impact energy is constant since the ions are accelerated directly from the grid to the wafer stage. The uniformity of the ion dose on the wafer depends on two factors: The uniformity of the incident ion current and impact angle. In the dc mode, the implantation area is totally determined by the ratio of the radius of wafer stage, the radius of the vacuum chamber, the distance between the wafer stage and grid \( H \), and diameter of the wafer stage. The projected area from the grid to the wafer stage determines the incident dose into the wafer. Actually, the smaller \( H \) is, the closer the ratio of the projected area to the implanted area is to 1 and the better the incident dose uniformity. However, the shorter the distance between the anode (grid) and cathode (wafer stage), the higher the electric field that may lead to breakdown at high implantation voltage. The impact angle at the edge can be made normal by changing the dimension of the wafer stage. For instance, a larger wafer stage can smooth out the electric field at the edge. In PIII, the ions are accelerated from the ion sheath and the impact angle is determined by the topography of the sheath. Hence, the retained dose and impact energy in the dc mode can be made more uniform by choosing the suitable internal dimensions of the lower part.

PIII experiments are usually conducted at very low gas pressure to achieve high impact energy, for example, lower than 0.1 mTorr, and so energy loss and charge transfer/neutralization arising from ion collisions are minimal. Hence, a high intensity plasma source such as an electron cyclotron resonance (ECR) plasma source is necessary for high ion dose dc-PIII. Such an apparatus is displayed in Fig. 5. Rutherford backscattering spectrometry analysis shows excellent lateral implant dose uniformity. The calculated doses at the center and side of the 75 mm wafer are \( 3.0 \times 10^{16} \) cm\(^{-2} \) and \( 2.5 \times 10^{16} \) cm\(^{-2} \), respectively.\(^{36} \) The uniformity value is not adequate for commercial semiconductor application which is typically \( \leq 1\% \) over 200 or 300 mm, but it can be improved by using a more uniform plasma source and better chamber geometry. The results unequivocally illustrate that the dose rate and electrical power efficiency are improved by dc-PIII. For instance, the dose rate can be as high as \( 1 \times 10^{17} \) cm\(^{-2} \) min\(^{-1} \) and the electrical power consumption can be reduced to about one quarter of that in pulsed PIII.

To enhance the efficacy of the dc-PIII process, the grid separating the vacuum chamber can be biased. The process changes the plasma density in the upper chamber and modifies the plasma topography along the grid surface. Our results show an enhanced extracted ion current density from the plasma and suggest specific optimal process windows.\(^{47} \) In a recent study,\(^{48} \) the implanted area is shown to increase with the radius of the extraction hole and wafer stage, but decreases with a larger distance between the grid and sample. The effects of the extraction hole radius are the largest, followed by the placement of the sample to the conducting grid. The wafer stage poses the smallest influence but a proper wafer stage dimension improves the lateral implant dose and incident angle homogeneity. Simulation and experimental results suggest optimal ratios of these parameters for each wafer size.

A method to control the ion current in dc-PIII has recently been reported for low-pressure magnetized inductively coupled plasma.\(^{39} \) The ion current can be conveniently adjusted by applying a bias voltage to the conducting grid separating the plasma formation and implantation (ion acceleration) zones without the need to alter the rf input power, gas flux, and other work conditions. The acceleration currents \( I_a \) versus the grid bias voltages at acceleration voltage \( V_g = -50 \) kV with and without the external magnetic field are depicted in Fig. 6. Here, the grid mesh size is \( 2 \times 2 \) mm and the grid diameter is 250 mm. Our results show that the current only increases by about 25% without the external magnetic field when \( V_g = 70 \) V. The current diminishes with increasing grid bias voltage when the plasma is magnetized, from 48 mA to 1 mA by simply adjusting the grid bias voltage from 0 V to 70 V at \( I_c = 0.8 \) A without needing to alter
other macroscopic plasma parameters. Hence, high implantation voltage and monoenergetic immersion implantation can now be achieved with control of the ion current without varying the macroscopic plasma parameters. The experimental results and interpretation of the effects are presented in this article. This technique is very attractive for PIII of planar samples requiring on-the-fly adjustment of the implantation current at high implantation voltage but low substrate temperature. In some applications, such as hydrogen PIII-ion cut, it may even obviate the need for complicated sample cooling devices that must work at high voltage.

IV. PLASMA IMMERSION ION IMPLANTATION OF INSULATING MATERIALS

Attempts to implant dielectric substrates using PIII have encountered intrinsic technical problems. The common PIII approach is to place the dielectric sample on a conductive substrate holder and apply high-voltage pulses to the holder. However, the magnitude of the potential at the dielectric–plasma interface, induced by applying a potential to the rear surface of the dielectric, is reduced by a combination of capacitive voltage division and charge accumulation due to the introduction of positive ions and emission of secondary electrons. The insulating substrate that is positioned on a conductive target holder cannot rise to the full (negative) pulse bias potential and, consequently, the energy of the incident ions is less than the full pulse voltage. As a result, the effective dielectric thickness of the substrate and applied pulse length and frequency that can be used in practice are limited. In severe cases involving large pieces of bulk insulators, the surface potential is significantly reduced and instrumental arcing may become too difficult to overcome. For thinner dielectric samples, surface charging broadens the energy distribution of incident ions in addition to the effects of the rise or fall times of the negative pulses. Surface charging is also brought about by secondary electron emission. The discharge time scale of the charged insulator surface can be on the order of 20 μs, and a combination of short pulse duration, high pulse frequency, and low plasma density can be beneficial from the viewpoint of increasing the ion implantation energy.

In cases where the insulating substrates are thick, alternative approaches must be adopted. The obvious one is the use of a sacrificial conductive surface layer. In this method, thin conducting films are deposited on the insulating surfaces connected to the power modulator and ions are implanted through the conductive layer to modify the underlying materials. The conductive films can be etched in the end if desired. This technique is useful if the deposited metallic film does not introduce detrimental effects to the substrates. In cases when the use of a sacrificial conductive surface layer is not feasible, for example, in gas ion PIII, when the existence of the metallic layer causes deleterious effects, or when the surface film is so thick in order to accomplish the necessary surface electrical conductivity that the implant projected range into the insulating materials is insufficient, Matossian et al. have proposed “mesh-assisted” PIII. This technique utilizes a conducting grid placed several mm or cm above the insulating substrate and connected to the high-voltage modulator. In the configuration illustrated in Fig. 7, ions accelerated across the sheath toward the grid pass through the holes and are implanted into the insulator surface. Our initial results are quite positive showing improvement in the implantation energy. Figure 8 depicts the nitrogen depth profiles of nitrogen-implanted SiO2 with and without the grid acquired by secondary ion mass spectrometry (SIMS). The sample voltage is −40 kV, but simulation results show that the maximum voltage is 30 kV and 23 kV for the grid and without-grid samples, respectively. Broad ion distributions are observed due to coimplantation of low-energy ions and ions of different types (e.g., N+1, N2+ etc.). The surface potential drop on the sample implanted without the grid is consistent with simulated capacitance effects. Even though the nitrogen profile is deeper using the grid indicating better coupling of the implantation voltage on the surface of the insulating sample, the maximum voltage is still lower than the applied one and it may be due to factors, such as ion deceleration, between the grid and sample surface. The size of the grid holes is critical because if they are too large, ions implanted through the center region of the holes will not have high impact energy and secondary electrons, which would be otherwise reflected back to the samples to neutral-
ize surface charging, may pass through into the overlying plasma. Hence, proper placement of the grid with respect to the insulator surface as well as correct dimensions and shape of the grid holes are crucial to the ion energy and dose uniformity. Moreover, shadowing effects due to the grid are quite apparent and can affect the lateral ion dose uniformity. In principle, sample rotation is a possibility and more work is being done to fathom the sheath evolution process as well as to optimize the process. More work is being conducted to mitigate the effects of grid sputtering and surface contamination. All in all, the ability to plasma implant insulating samples broadens the applications tremendously and the primary beneficiaries are the biomedical and polymeric industries.

V. RECENT BIOMEDICAL APPLICATIONS

Plasma surface modification of biomaterials has recently become a hot topic. One of the advantages is that mechanically sturdy materials that are not very biocompatible can be plasma treated to render the surface more biocompatible while retaining the favorable bulk attributes. This provides a faster track to generate biocompatible artificial materials when compared to the synthesis of new materials. One of the recent applications of PIII deposition (PIII-D) is to enhance the blood compatibility of artificial materials used in medical transplants, such as artificial heart valves. Low-temperature isotropic pyrolytic carbon (LTIC) is currently the most widely accepted material used in artificial heart valves. However, the materials are quite brittle and its blood compatibility is still not sufficient. As a consequence, patients with heart transplants made of LTIC must take medication to prevent blood coagulation and there is an urgent need to develop new artificial heart valve materials that possess better blood compatibility and mechanical durability. Thin films that have been successfully fabricated by PIII-D and possess improved blood compatibility include TiN, Ti(Ta$_{1-x}$O$_2$, and diamond-like carbon thin films. Several recent studies are reviewed here.

Figure 9 depicts the blood clotting behavior of TiN, Ta, TaN, and LTIC. The absorbance of the hemolyzed hemoglobin solution varies with time, and the higher the absorbance, the better the thromboresistance. The time at which the absorbance is equal to 0.1 is generally defined to be the clotting time, and a longer clotting time implies that the materials have better blood compatibility. The data shown here unequivocally demonstrate that the clotting tendency of tantalum nitride is smaller than that of TiN, Ta, and LTIC and tantalum nitride thus possesses the best blood compatibility among the four materials. The platelet adhesion study illustrates that the number of adhered platelets is highest on LTIC and smallest on tantalum nitride, as shown in Fig. 10, and the difference is quite substantial for an incubation time of 10 min. Figure 11 displays the morphology of the adhered platelets on tantalum nitride and LTIC, and the number of platelets adhered onto the tantalum nitride film is markedly lower than that on LTIC. The degree of deformation (pseudopodium) and aggregation of the adhered platelets are also less on tantalum nitride. The observation is consistent with the results of the clotting time measurement corroborating that the blood compatibility of tantalum nitride is better than that of the TiN, Ta, and LTIC.
The *in vitro* and *in vivo* blood compatibility of Ti(Ta\(^{+5}\))O\(_2\) films synthesized by PIII-D has been studied.\(^{62}\) The morphology of the adhered platelets on Ti(Ta\(^{+5}\))O\(_2\) and LTIC after 3 h of external incubation is displayed in Fig. 12, which is the result of a scanning electron microscope (SEM) field chosen at random. The platelets on Ti(Ta\(^{+5}\))O\(_2\) form a single layer and are isolated [Fig. 12(a)]. There is no sign of accumulation and only slight pseudopodium can be observed. In contrast, platelet accumulation and pseudopodium are very serious on the LTIC surface, as indicated by the three-dimensional structures connected by pseudopodium. Quantitatively, the number of adherent platelets on LTIC is about two orders of magnitude higher than that on Ti(Ta\(^{+5}\))O\(_2\). The results thus unambiguously impart that platelet adhesion is mitigated significantly on Ti(Ta\(^{+5}\))O\(_2\) and the film thromboresistance is much better than that of LTIC.

*In vivo* investigation of the Ti(Ta\(^{+5}\))O\(_2\) films is conducted by implanting the coated CPTi and LTIC (control) into the ventral aorta and right auricle of the same dog. Two holes with a diameter of about 0.5 mm are made at the edge of the test samples. The samples are then affixed onto the wall of the ventral aorta or right auricle by a prolene thread passing through the sample hole. The experiments are repeated three times (one in the ventral aorta and two in right auricle) in the same dog, and three dogs weighing 10 to 15 kg are tested in the experiments to obtain more reliable results. After the samples are implanted into the dogs, no medication is used. After 17 days, each sample is taken out carefully not to remove the thrombus formed on the tested samples, and the thrombus formed on the surface of the sample is subsequently observed visually and using a SEM. Results from *in vivo* experiments conducted on seven of the nine specimens show that the amount of thrombus on Ti(Ta\(^{+5}\))O\(_2\) is less than that on LTIC. On the remaining two Ti(Ta\(^{+5}\))O\(_2\) specimens, no thrombus formation is revealed. The SEM micrographs showing the microstructure of the adhered blood components are depicted in Fig. 13. On the surface of Ti(Ta\(^{+5}\))O\(_2\) film, all of the SEM fields chosen at random show that the adherent red blood cells are not only small in quantity, but also its morphology is quite normal, and almost no fibrin and adherent platelets can be found on the surface. That is to say, the red blood cells exhibit a circular disk-shaped structure with a concave center [Figs. 13(a) and 13(b)]. On the other hand, the adherent red blood cells on the LTIC surface appear to be damaged [Fig. 13(c)] because they do not exhibit the biconcave morphology indicative of normal red blood cells. Moreover, on the LTIC surface, platelet aggregation can be observed and there is much fibrin on the surface as shown in Fig. 13(d). Based on the *in vitro* and *in vivo* experiments, Ti(Ta\(^{+5}\))O\(_2\) films exhibit attractive blood compatibility exceeding that of low isotropic pyrolytic carbon and material characteristics, such as surface energy and semiconductivity, play important roles. The results also suggest that the smaller surface energy \(\gamma_s\) and blood/film interfacial tension \(\gamma_c,\text{blood}\) are partially responsible for the enhancement of hemocompatibility. These factors result in
thinner protein layers on the film surface as well as less distortion and denaturing of protein.

VI. CONCLUSION

PIII has found a number of exciting applications. PD is a potential alternative to conventional beamline ion implantation in trench doping and shallow junction formation. Hydrogen PIII, as practiced in the layer transfer technology, has gained acceptance due to recent improvement in the ion dose and energy uniformity as well as contamination control. The advent of dc-PIII obviates the need for the complicated and expensive power modulator and significantly reduces the instrument cost and footprint. This technique may find its way into commercial SOI fabrication and other semiconductor processes. The use of mesh-assisted PIII greatly expands the applications to insulating materials and plasma surface modification processes are being used to improve the biocompatibility of artificial materials used in animals and human beings.

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