Nitrogen depth profiles in plasma implanted stainless steel

Xiubo Tian a, Dixon T.K. Kwok a, Paul K. Chu a,*, Chung Chan b

a Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong, China
b Department of Electrical and Computer Engineering, Northeastern University, Boston, MA 02115, USA

Received 17 January 2002; received in revised form 15 February 2002; accepted 11 March 2002

Communicated by F. Porcelli

Abstract

Nitrogen plasma immersion ion implantation (PIII) is a useful technique to enhance the surface properties of stainless steels and the in-depth distribution of the implanted nitrogen is a crucial parameter. A comparison of the nitrogen depth profiles in AISI 304 stainless steel reported in the literature and observed in our laboratory with the one simulated using a plasma sheath model and TRIM shows a discrepancy. The simulated profile is non-Gaussian and shallower due to the non-perfect high voltage pulses whereas the experimental profile is a better fit to a Gaussian distribution. Since most PIII equipment is not designed for ultra-high vacuum (UHV) operation and the plasma is highly reactive in this environment, the surface of the implanted samples is easily contaminated by a large amount of atmospheric species such as oxygen and carbon from the residual vacuum in the processing chamber, thereby converting the materials surface into an oxidized and carburized form. The change in the matrix composition in the near surface skews and translates the nitrogen depth profile obtained by Auger electron spectroscopy. By normalizing the nitrogen signal point-by-point with the combined (Fe + Cr + Ni) signal, a more accurate depth profile can be obtained. This type of normalization, albeit common in secondary ion mass spectrometry (SIMS) data quantification, is seldom implemented in the plasma community when dealing with nitrogen depth profiles acquired by Auger electron spectroscopy. Our results indicate that the excessively high surface contamination renders the raw nitrogen depth profile inaccurate and a proper normalization measure must be adopted. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Plasma immersion ion implantation; Depth profile; Impurity

Plasma immersion ion implantation-deposition (PIII-D) has received much interest as a surface modification technique due to its high efficiency, simple instrumentation, and small equipment footprint [1]. One of its biggest advantages is the capability to treat components possessing an irregular shape without requiring complicated manipulation of the target holder due to the non-line-of-sight operation [2,3]. If the processing conditions are optimized, a conformal plasma sheath forms around the sample and uniform implantation can be carried into the entire specimen simultaneously. Owing to the lack of mass selection and beam collimation, all ionized species in the plasma are co-implanted and surface adsorption of neutral and excited species from the plasma can also be significant if the sample has high surface reactivity. To make things worse, metallic contaminants can be sputtered from the exposed sample chuck and re-introduced to the sample as unintentional impurities [4]. Furthermore, since PIII-D equipment is typi-
cally not designed for ultra-high vacuum (UHV) operation and PIII-D is typically carried out at a pressure between $10^{-2}$ and 1.0 Pa, there exists an appreciable amount of atmospheric contaminants such as oxygen and carbon in the plasma due to out-gassing and gas leaks. If they adsorb or are implanted into the samples in large amounts, surface oxidation and carburization can occur altering the surface structure and chemistry of the treated sample [5]. The chemical effects of these atmospheric contaminants have been investigated, but we recently discovered that the change in the surface composition also alters the nitrogen depth profile acquired by Auger electron spectroscopy (AES). Many of the nitrogen depth profiles reported in the literature, including that from our own experiment, exhibit a near-Gaussian shape [6–8], but they deviate from the ones predicted by our one-dimensional plasma sheath model. In this Letter, the discrepancy between the experimental and theoretical nitrogen depth profiles in stainless steel is investigated. Our results indicate that the large amount of surface oxygen and carbon alters the matrix in the near surface region rendering the AES profile inaccurate, but the difference can be compensated by point-by-point normalization to the (Fe + Cr + Ni) signal.

AISI 304 stainless steel samples 20 mm in diameter and 4 mm in thickness were ground, polished and ultrasonically cleaned before loaded into the PIII instrument [9]. The base pressure was $7 \times 10^{-4}$ Pa and working nitrogen pressure was $4 \times 10^{-2}$ Pa. The plasma was sustained by hot filament glow discharge. The implantation parameters were: implantation voltage = 20 kV, pulse duration = 30 µs, rise time = 1.0 µs, and pulsing frequency = 200 Hz. The number of implantation pulses is 720 000. Before nitrogen PIII, Ar ion sputtering was employed to clean the sample surface for 5 minutes at 5 kV. After PIII, the sample was depth profiled using Auger electron spectroscopy (AES) and Ar ion sputtering.

Fig. 1 displays the AES depth profiles of C, N, O, Cr, Fe, and Ni acquired from the nitrogen plasma implanted stainless steel sample. The near surface region has been heavily contaminated by atmospheric species such as oxygen and carbon. The oxygen may be due to incomplete removal of the surface oxide in the Ar sputtering pretreatment, but most likely it arises from plasma surface oxidation and to a lesser extent oxygen co-implantation. The difference between the nitrogen and oxygen profiles suggests oxygen implantation is not substantial. Instead, oxygen atoms (or molecules) mostly adsorb onto the surface and are subsequently knocked into the substrate by the incident nitrogen ions. Carbon contamination similar to that reported in the literature [6–8,10–12] is also observed here but it is mainly confined to the surface and again, surface adsorption appears to be the dominant incorporation mechanism. The peak of the nitrogen depth profile appears at a depth corresponding to about 6 minutes of sputtering time. We have not tried to assign an absolute depth to the peak here to avoid over-interpretation of the depth scale for the sputtering rate in this transient region varies significantly due to the large amount of atmospheric impurities.

As a comparison, the theoretical nitrogen profile is derived using a hybrid simulation program combining plasma sheath simulation described by the Child–Langmuir law [2,13] and TRIM [14,15]. Using the experimental parameters and assuming that the dominant ion species is $N^+_2$, the ion energy spectrum is derived and exhibited in Fig. 2. Owing to the finite rise time of the voltage pulses, broad energy distribution results and less than 80% of the implanted ions impact the substrate with the full energy in this case. In addition, based on the space–charge-limited Child–Langmuir law, $J_i \propto S^{-2}$ ($J_i$ is the ion current and $S$ is the sheath thickness), there is a higher ion flux during this rise-time period due to the relatively small plasma sheath thickness. Consequently, even a 1 µs rise time

![Fig. 1. Elemental depth profiles acquired from nitrogen plasma implanted AISI 304 stainless steel sample using sputtering Auger electron spectroscopy.](image)
impacts the energy distribution significantly [16]. It should be mentioned that the fall time of the voltage pulse is also finite and typically longer than the rise time, but the number of ions implanted during the fall time period is much smaller.

As shown in Fig. 2, more than 20% of ions have energy smaller than 20 keV, and so the depth profile should be skewed towards the surface leading to a distribution shown in Fig. 4 as described in Ref. [17]. The PIII nitrogen distribution is different from the solid curve derived using TRIM for conventional beam-line ion implantation. It is also quite different from the Auger depth profile shown by the open circles in Fig. 3. However, if the ratio of nitrogen Auger intensity is normalized to the (Fe + Cr + Ni) combined intensity point-by-point, the resulting depth profile (solid circles in Fig. 3) resembles that of our theoretically simulated profile (Fig. 4). Our results show that the nitrogen depth profile is influenced by the change in the matrix in the near-surface region and normalization is necessary to derive the correct distribution. The tribological properties of the implanted materials have been found to be very sensitive to the nitrogen distribution [18].

Owing to pulsed and non-UHV operation in PIII, the ion distribution has an appreciable low energy component, and surface adsorption (and knock-on) of atmospheric species changes the surface composition significantly. Because of hardware limitation, a zero voltage rise time is impossible, but a good solution is direct-current (DC) or quasi-DC PIII [19–23]. However, attention must be paid to minimize glow discharge especially at high implantation voltage or high pressure. Surface atmospheric contaminants can only be avoided by adopting UHV conditions, but the measure adds to the equipment cost and makes many PIII hybrid processes such as PIII and ion beam enhanced deposition (IBED) very difficult or commercially impractical. Hence, the anomaly arising from the change in the surface composition must be accounted for when interpreting the nitrogen depth profile under typical PIII conditions. Our study indicates that point-by-point normalization should be performed to eliminate this artifact.
Acknowledgements

The work described in this Letter was jointly supported by Hong Kong RGC CERG #9040498 or CityU 1032/00E and #9040577 or CityU 1013/01E, as well as National Science Foundation (NSF) grant ECE 0001378.

References