Chemical and Physical Properties of Copper and Nitrogen Plasma-Implanted Polyethylene

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Plasma immersion ion implantation (PIII) is a new technique used to modify the surface physical and chemical properties of polymers for antibacterial purposes. Our previous research work has shown that copper and nitrogen PIII can give rise to excellent antibacterial properties on polyethylene (PE) substrates. In this paper, the effects of the PIII conditions on the chemical and physical properties of the Cu and N plasma-implanted PE are investigated. Elemental depth profiles show that Cu and N PIII results in the formation of C–N, C≡N bonds in the surface region, and that the implanted Cu does not bond with the polymer matrix elements. A longer PIII time increases the concentrations of C≡N, C≡N and C–N bonds formed in the near-surface region, but the elemental chemical states deeper into the sample remain about the same for different PIII time durations. However, if N-PIII and Cu-PIII are not carried out simultaneously, for example, N-PIII following Cu-PIII, the retained Cu dose is affected due to nitrogen sputtering, but the Cu chemical state is not altered. In addition, more C≡N and C≡N bonds are formed in the outer surface region. A longer N-PIII implantation time further enriches these chemical functional groups.

Introduction

Polymer-based materials are widely used in many fields, including biomedical engineering and microelectronics.\textsuperscript{[1–6]} In general, their surface properties such as antibacterial ability, biocompatibility, and hydrophilicity depend on not only the type of polymer, but also on the surface structure and chemistry. Therefore, the proper surface modification techniques can selectively improve one or more of these properties making them more suitable for particular applications, while the favorable bulk attributes of the polymers are not altered.\textsuperscript{[7–10]} For
example, an antibacterial metal coating on polymer surfaces produced by plasma implantation can provide excellent antibacterial properties. Plasma immersion ion implantation (PIII) is a burgeoning technology used to modify the surface of polymeric materials. In our previous research, copper and nitrogen were plasma-implanted into the near surface region of polyethylene (PE). It was observed that N-PIII regulated the release of the plasma-implanted Cu, and prolonged the antibacterial effects of the co-implanted PE, and that this regulation mainly stemmed from functional groups on the surface macromolecules. In this work, we investigate the chemical and physical characteristics of copper and nitrogen plasma-implanted PE under different PIII conditions in an attempt to further understand the copper release mechanism.

Experimental Part

Low density polyethylene (PE) samples with dimensions of $2 \times 2 \times 0.2$ cm were inserted in the plasma immersion ion implanter equipped with a copper cathodic arc plasma source. The arc was ignited using a pulse duration of 300 $\mu$s, repetition rate of 30 Hz, and arc current of 1 A. To conduct simultaneous Cu and N PIII, N$_2$ gas was bled into the vicinity of the copper arc discharge plume at a flow rate of 10 sccm (standard cubic centimeter). The dual PIII process was conducted by applying an in-phase bias voltage of $-5$ kV with a repetition rate of 30 Hz and pulse width of 300 $\mu$s to the PE samples. Another set of PE samples underwent sequential Cu and N PIII. In this case, Cu PIII was first conducted by applying an in-phase bias voltage of $-5$ kV with a repetition rate of 30 Hz and pulse width of 300 $\mu$s to the PE samples, followed by the N-PIII using the same flow rate of N$_2$ and conditions as before, but without triggering the Cu cathode arc source. The working pressure in the vacuum chamber was $1-2 \times 10^{-4}$ Torr. The elemental depth profiles and chemical states were determined by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics PHI 5802. A monochromatic aluminum X-ray source was used, and the elemental depth distributions were determined using an argon ion sputtering. The sputtering rate of 1 nm/min was approximated using that derived from a silicon oxide sample under similar conditions.

Results and Discussion

Influence of Simultaneous Cu and N PIII Time on Chemical and Physical Properties

Figure 1 depicts the in-depth elemental distribution of the PE samples implanted with Cu and N for 10 min and 30 min. Comparing Figure 1a and b, it can be observed that the quantities of Cu and N in the surface region increase with increasing the implantation time. Our TEM results (not shown here) disclose that the implanted Cu and N are located in the top several hundred nanometers. Here, even though the PIII time changes from 10 min to 30 min, the amount of implanted Cu does not increase proportionally. This nonlinearity is believed to stem from the accumulation of positive charges on the PE surface over the course of PIII due to the poor electrical conductance of the materials. Meanwhile, it is observed that the amounts of Cu and N deposited on the surface after 30 min are larger than those on the 10 min samples by more than 3 times. This is because of the lower energy of the incident ions as positive charges build up on the PE surface, making the distribution of the ions skewed towards the surface. The Cu$_2$p XPS spectra acquired from the Cu and N co-PIII samples implanted for different time durations provide information about the chemical states of Cu. Figure 2 shows that the implanted Cu has the elemental (zero
valence) state and does not react with elements in the polymer matrix (S-2 in Figure 2), whereas the surface Cu is oxidized (S-1 in Figure 2).\(^{13,19}\) The similarity in Figure 2a and Figure 2b suggests that the chemical state of Cu is not altered during the implantation process.

Cu ions implanted into the materials cause damage to the polymer chains. Collisions between the incident Cu ions and polymer molecules, and subsequent energy transfer lead to dehydrogenation reactions, dissociation, as well as formation of different functional groups.\(^{21–23}\) The C1s XPS high resolution spectra obtained at different depths can be used to determine the chemical states of C in the two samples implanted for 10 min and 30 min. Both Figure 3a and 3b show that during the Cu and N PIII, dehydrogenation occurs, and new C=C bonds are formed. The dehydrogenated carbon reacts with the implanted N to produce new N-containing functional groups such as C=N, C=N, C≡N. Comparing the fitted XPS spectra (S-2) in Figure 3a and 3b, the implantation time is found to affect the in-depth distribution of these functional groups. Ten minutes of Cu and N PIII produce C=N and C=C bonds in the implantation region. On the other hand, thirty minutes of Cu and N PIII give rise to more C=N, C=N, and C≡N bonds in the near-surface region. Figure 3b indicates that, as the depth increases, the peak gradually moves to a lower binding energy. The fitted S-2 spectrum imparts that the quantities of C=N, C=N, C≡N bonds decrease gradually with increasing the depths, but the opposite is true for the C=C and C≡C bonds. That is to say, the chemical state of the implanted N in the near-surface region is different from that at a larger depth in the 10 min Cu and N PIII sample.

The N1s high resolution spectra are obtained from both samples in order to determine the chemical states of the
implanted N. Figure 4a shows no shift in the N1s XPS spectra throughout the entire implanted depth. The fitted S-2 spectrum suggests that there are mainly C–N and C==N bonds in the near-surface region, and this result is consistent with the C1s spectra. On the other hand, Figure 4b shows a small shift to a lower binding energy in the N1s XPS spectra, suggesting that the N chemical state varies with depth. The fitted S-2 spectrum proves that a longer Cu and N co-PIII time produces more C–N, C==N, –C==N bonds in the near-surface region.[19]

Influence of Sequential Cu and N PIII on Chemical and Physical Properties

Figure 5 shows the elemental depth distributions of the samples plasma-implanted with copper and nitrogen sequentially. The depth profiles are quite different from the simultaneously plasma-implanted samples described in the previous section. Comparing Figure 5a and b with Figure 1a and b, the amounts of Cu in the sequentially implanted samples are less than those in the co-implanted samples. This is because the nitrogen ions sputter the
previously introduced Cu ions. The sequentially implanted samples also have higher concentrations of nitrogen, because nitrogen is sputtered by incident Cu ions during the co-PIII. The effect is more apparent when the N-PIII time is increased to 30 min (Figure 5b). The surface Cu concentration decreases with N-PIII. The Cu2p XPS spectra in Figure 6 show similar copper chemical states in both the sequentially implanted and co-implanted samples. That is to say, the order of implantation has very little effect on the chemical state of Cu in the PE substrate.

The C1s XPS spectra series acquired from the two sequentially implanted samples are shown in Figure 7. The peaks gradually move to lower binding energies with increasing the depth. This phenomenon is similar to that of the longer time co-implanted samples. The shift is a little larger and more C–N, C=N, and C≡N bonds are formed on the surface. A longer N-PIII time introduces more dehydrogenation, resulting in the formation of more C≡N and C≡N bonds.\(^{[19]}\) The end result is that the chemical shift is larger, as indicated in Figure 2a. Similar to the C1s XPS spectra, the N1s high resolution spectra series taken from the two samples shown in Figure 8 also exhibit a larger shift to lower binding energies. This is because of the more abundant C≡N and C≡N bonds on the surface, especially on the 30 min N-PIII sample. The degree of damage and dehydrogenation depends on the nitrogen ion energy which decreases with increasing the depth. Hence, when copper and nitrogen are sequentially plasma-implanted, more C≡N and C≡N bonds are formed in the near-surface region, and more C≡N bonds are formed at greater depths. Similarly, when copper and nitrogen are co-implanted for a longer time, the same chemical state trend can be observed. In comparison, when the implantation time is short, there is less dehydrogenation. Consequently, only a slightly larger number of C–N bonds, but little C≡N bonds
can be observed throughout the implanted depth. These new chemical functional groups are expected to play an important role in the retention of copper and control of Cu release with time observed in our previous experiments.

Conclusion

We have investigated the chemical states of Cu and N in sequentially and simultaneously implanted PE samples and also the effects of the PIII time. Our results show that simultaneous copper and nitrogen PIII produce C–N and C––N bonds, and the implanted Cu atoms exist in the elemental (zero valence) state. If the co-PIII time is longer, more C=N and C=N bonds are formed in the near-surface region, but the elemental chemical states at greater depths do not differ much from those of the shorter time implanted sample. In comparison, when copper and nitrogen are plasma-implanted sequentially, the chemical state of Cu is not altered, but the amount of Cu is reduced due to sputtering by nitrogen ions. More C=N and C=N bonds are formed in the near-surface region compared to the co-implanted sample. A longer N-PIII step increases these functional groups due to more extensive dehydrogenation. Better understanding of the chemistry of the plasma-implanted samples provides more information on how to alter the Cu release rate from Cu/N plasma-implanted PE, and how optimize the long-term surface antibacterial effects.

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