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Effect of target temperature on microstructure of aluminum surface layer modified by plasma based ion implantation①

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Abstract: Aluminum (99.6% purity) was implanted with nitrogen ions to a total dose of 6×10^{17} cm^{-2} at different temperatures (from 50 ℃ to 400 ℃) by plasma based ion implantation (PBII). The surface microstructure was investigated by glancing angle X-ray diffraction (GXRD), X-ray photoelectron spectroscopy (XPS) and cross-sectional transmission electron microscopy (XTEM). The results of GXRD and XTEM showed that there was an amorphous layer on the outer surface, and fine dispersion of AlN precipitates was found under the amorphous layer. The size of AlN precipitates strongly depended on the target temperature, with the increase of the target temperature, the size of AlN precipitates became larger. The excess nitrogen atoms can diffuse or migrate to the lower nitrogen concentration regions by radiation-enhanced diffusion. The results of XPS further indicated that it was easier to form AlN precipitates at a higher target temperature, and the depth profile of nitrogen broadened.

Key words: plasma based ion implantation; aluminum; target temperature; microstructure **Document code: A**

1 INTRODUCTION

Apart from the conventional ion implantation technique, the specimens with a complex geometry can be implanted directly at all orientations by the PBII method, so the PBII method owns a wider foreground in industry applications[1].

The AlN precipitates may form in the surface layer after nitrogen ions are implanted into aluminum, and the surface hardness and relative wear resistance can be increased notably. These provide the possibility of using aluminum alloys widely in modern industry[2~4]. It has already been observed that the shape and thickness of the formed layer strongly depend on the implantation dose for a given energy at room temperature, but the effect of implantation parameters, especially the target temperature on the distribution of implanted ions and microstructure of aluminum must be investigated further[5~7]. Since the solubility of nitrogen in aluminum is very low (< 0.001%), and the reactivity of nitrogen with aluminum is high, not only the AlN precipitates but also supersaturated solution of nitrogen is formed after nitrogen implantation[8~10]. Up to now, the effect of target temperature on the supersaturated solution of nitrogen has not been reported.

2 EXPERIMENTAL

The pure aluminum specimens (99.6% purity, d20 mm × 5 mm) were carefully ground with SiC abrasive papers and polished with diamond paste to a grit size of 0.025 μm, then cleaned by an alcohol ultrasonic cleaner before ion implantation. The ion implantation experiment was carried out on a DLZ-01 plasma immersion ion implanter. The sample was biased by negative voltage pulses of 50 kV with a pulse duration of 45 μs and a repetition rate of 100 Hz, and the residual vacuum in the implantation chamber was 1×10^{-4} Pa. This process resulted in a retained dose of about 6×10^{17} cm^{-2}. During the implantation, the sample was heated from 50 ℃ to 400 ℃ by energy transferring of implantated ions. The temperature of sample was measured by a thermocouple fixed in the core of the sample. In order to get samples at different target temperatures (50, 100, 150, 300 and 400 ℃), the average current density and the implantation time were varied.

The phase present in the modified layer was determined by GXRD (D/Max-γβ) with Cu K_α radiation at 30 kV voltage, 80 mA current, 3° glancing angle and 0.005 (°)/s scanning speed.

The depth profile and the binding energy spectroscopy of Al2$p_{3/2}$ were measured by XPS (PHI ESCA 5700) with Mg K_α(1253.6 eV) radiation. A high vacuum of 10^{-7} Pa was maintained throughout the measurement. The C1s line (284.6 eV) was used for the calibration purpose. The Ar ion beam of 3 keV and 30 μA was used for sputtering. For the depth profiling, the current was kept constant (30 μA) while the sputtering time was varied. The sputtering rate was about 3.5 nm/min.

The surface microstructure was investigated by XTEM (JEM 200CX). Firstly, the PBII treated

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sample was carefully thinned from the untreated side to a thickness of 1 mm, with the modified surface carefully protected. Secondly, the thinned sample was sliced into 2 mm wide strips, which were subsequently sandwiched using epoxy, with the treated surfacing each other. The specimen sandwich was then cast into a brass tube of 3 mm outer diameter using epoxy. Thirdly, discs 1 mm thick were sectioned from the tube assembly by spark eroding, then carefully ground with SiC abrasive papers to 80 μm. Finally, the discs were thinned in a chemical solution to 30 μm, then ion-beam thinned to the XTEM specimens.

3 RESULTS AND DISCUSSION

The direct evidence indicating the formation of AlN precipitate was obtained by GXRD studies (incident angle of 3°). Fig. 1 shows the XRD patterns of aluminum surface implanted by nitrogen ions. The diffraction peaks of AlN appeared at 2θ = 33.2°, 35.8°, 37.8° and 65.8°. The corresponding D values are 0.270, 0.249, 0.237 and 0.141 nm, respectively. These D values agree well with the (100), (002), (101) and (103) planes of AlN crystal with hcp structure. Comparing the spectroscopies of the sample implanted at 200 ℃ and 400 ℃, it is clear that the amount of nitride precipitation increased with the increase of temperature. The GXRD pattern also shows diffraction peak is widened because ion implantation can produce large collision cascades which evolve into high density of defects in the matrix.

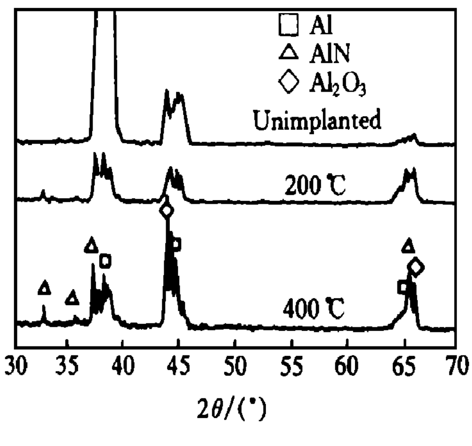

Fig. 1 Glancing angle XRD patterns (incident angle of 3°) obtained from original aluminum and specimens treated at 50 kV, 200 ℃ and 400 ℃

Fig. 2 shows the depth profile of nitrogen at different temperatures, the content of nitrogen in the aluminum matrix presents a Gaussian-like distribution with a peak and the profile became rectangular when implanted at higher temperatures. This indicates that at higher temperatures, the nitrogen can migrate or diffuse to the lower nitrogen concentration regions by radiation-enhanced diffusion. The maximum depth was about 200 nm when implanted at 400 ℃, while 180 nm at 100 ℃. As a consequence, the maximum concentration of nitrogen decreased, and it was about 30% when implanted at 400 ℃, while 38% at 100 ℃. In addition, the peak position of the nitrogen concentration shifted to the surface.

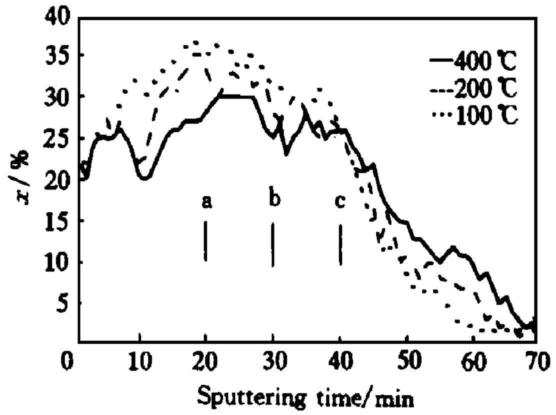

Fig. 2 Depth profile of nitrogen in aluminum implanted at different temperatures

Fig. 3 shows the XPS Montage spectra of $Al2p_{3/2}$, N1s and O1s, it gives the relationship among chemical binding energy, intensity and the depth in the implanted layer. The content of nitrogen in the aluminum matrix presents a Gaussian-like distribution. With the increase of depth, the content of oxygen decreased. It is clear that the binding energy of $Al2p_{3/2}$ was shifted at the depth of 120 nm corresponding to the maximum content of nitrogen. In addition, a little shift of the binding energy of N1s and O1s also takes place. It is revealed that the chemical state of the element changed in the implanted layer.

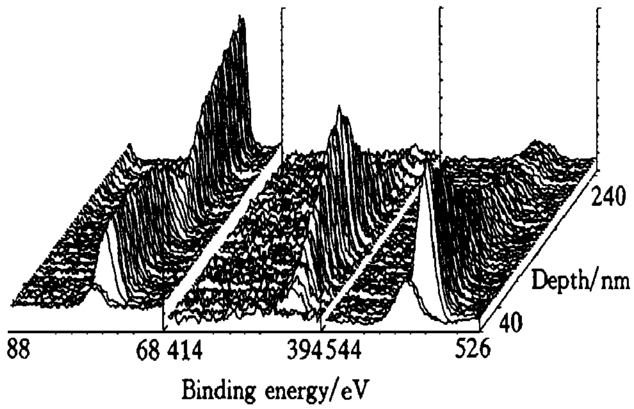

Fig. 3 XPS Montage spectra of $Al2p_{3/2}$, N1s and O1s

Fig. 4 shows the $Al2p_{3/2}$ XPS spectra at different depths of the sample implanted at 200 ℃. Figs. 4(a) ~ (c) refer to different nitrogen concentrations as indicated on the depth concentration profile (Fig. 2) of the corresponding sample. The depths are about 65, 100 and 135 nm respectively. The presence of Al in different chemical states corresponding to Al, AlN and Al_2O_3 at the binding energies of 72.8, 74.3 and

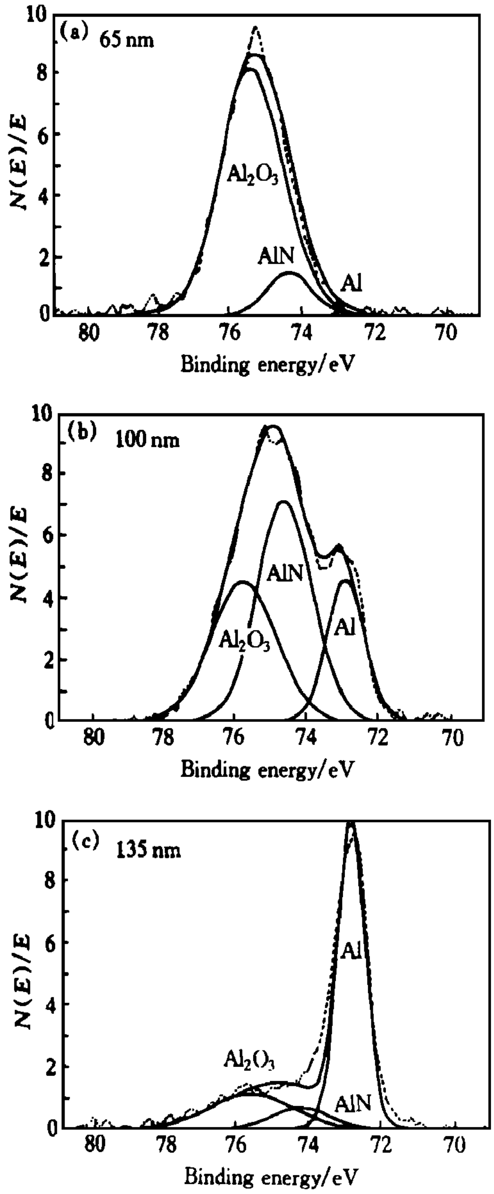

Fig. 4 XPS $Al2p_{3/2}$ spectra at different depths of sample implanted at 200 ℃

75.5 eV, respectively[11].

With the increase of sputtering time, the amount of Al_2O_3 decreases, while that of Al increases. The amount of AlN precipitates is varied, at the depth of 100 nm, the amount of AlN is the largest, which corresponds to the maximum content of nitrogen.

Fig. 5 gives the function between the content of AlN precipitates and the target temperature (about 100 nm in depth). Since the fact that the additional activation energy supplied by the implanted ions is required to form AlN, the amount of AlN increases with the increase of the target temperature. The results of XPS further indicates that it is easy to form AlN precipitates at higher target temperatures.

Fig. 6(a) shows the XTEM image of the implanted layer. The total thickness of the surface modified layer is about 0.2 μm. It is composed of three layers, the outer layer (I) is amorphous, about 20 nm thick. An obvious amorphous diffraction ring is

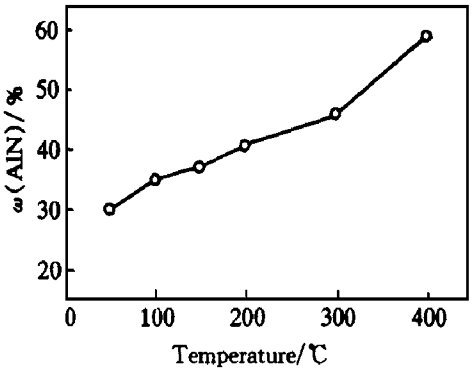

Fig. 5 Relationship between target temperature and content of AlN precipitates

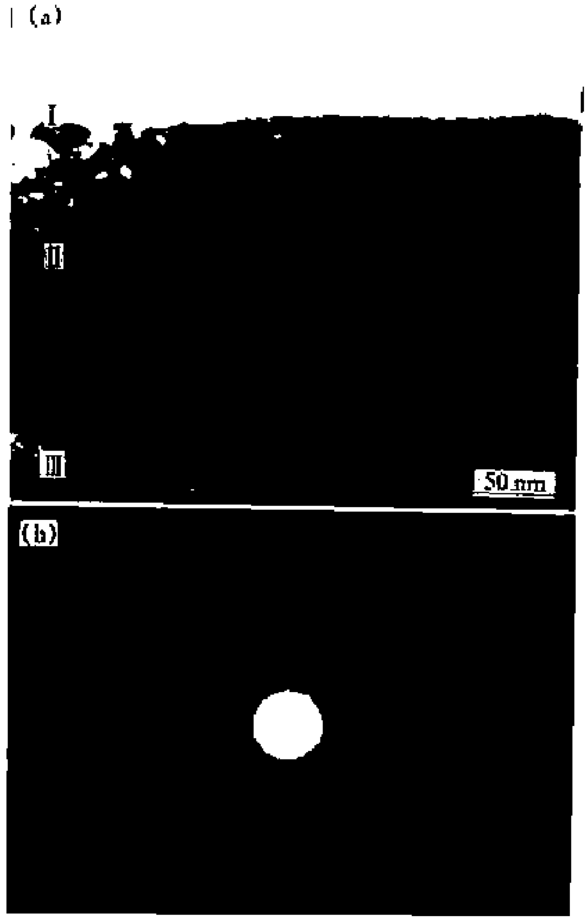

Fig. 6 TEM image of sample implanted with nitrogen at 200 ℃

(a) —Cross-sectional TEM image;

(b) —TED patterns of amorphous layer

observed (Fig. 6(b)), which results from Al_2O_3 phase formed by the surface oxidation. The second layer (II) is about 180 nm thick composed of AlN precipitates and matrix phase α-Al under the amorphous layer. It is identified by transmission electron diffraction that the relationship between the aluminum matrix and AlN precipitates are $\{0001\}_{AlN} // \{111\}_{Al}$, $\langle 11\bar{2}0\rangle_{AlN} // \langle 110\rangle_{Al}$. The size of the dispersive AlN precipitates is about 10 nm, and it strongly depends on the target temperature. With the increase of the target temperature, the AlN precipitates become larger. When implanted at 400 ℃, the size of the AlN precipitates is about 30 nm.

There is no evidence of bubble and void formation under these experimental conditions. It is suggested that the implanted nitrogen atoms are incorporated in the AlN and form supersaturated solution of nitrogen[7]. As shown in Fig. 7, the AlN precipitates always nucleate and grow at the crystal boundary or dislocations, and these precipitates can anchor the crystal boundary or dislocations, as a consequence, it is difficult for AlN phase to migrate at higher temperatures. However the excess nitrogen atoms can migrate to the deeper regions where nitrogen concentration is lowered by radiation-enhanced diffusion. The last layer (III) is aluminum matrix.

Fig. 7 AlN precipitates formed at crystal boundary (400 ℃)

4 CONCLUSIONS

The results of XRD and XTEM showed that after plasma based ion implanting nitrogen into aluminum, there was an amorphous layer on the outer surface, and the fine dispersive AlN precipitates were found under the amorphous layer. It was easier to form AlN precipitates at a higher target temperature. The size of the AlN strongly depended on the target temperature. With the increase of the target temperature, the precipitation of AlN became larger. The excess nitrogen atoms can migrate or diffuse to the lower nitrogen concentration regions by radiation-enhanced diffusion. The results of XPS further confirmed that it was easy to form AlN precipitates at higher target temperatures, and the depth profile of nitrogen was broadened.

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