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Sputtering of W-Mo alloy under ion bombardment①

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Abstract: The distribution of plasma density in the vicinity of the W-Mo alloy source in the process of double-glow discharge plasma surface alloying was diagnosed using the moveable Langmuir probe. The sputtering law, surface composition and morphological variation of the W-Mo alloy source was studied. The experimental results show that there exists obvious preferential sputtering on the surface of the W-Mo alloy source under the argon ion bombardment; the stable period is reached after a transitional period, and the preferential sputtering occurs in a definite range of composition(mole fraction): 70%~75% Mo, 22%~25% W; there appears segregation on the surface of the W-Mo alloy source.

Key words: metallic cementation; W-Mo alloy; preferential sputtering; ion bombardment
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1 INTRODUCTION

In the surface alloying technologies, the surface quality by laser beam and electron beam alloying is difficult to control and dimensional change follows. The thickness of the alloying layer formed by ion implantation is only about 1 μm, while that produced by ion metallic cementation can reach several ten to several hundred micra. In different surface alloying proceses, the alloying elements are provided in different ways. Take ion metallic cementation as an example, the alloying elements can be provided by glow-discharge decomposition and arc vaporization[1,2]. Because the alloying elements are provided by physical sputtering in the double-glow discharge plasma, the surface sputtering of the alloy target is very important to the ion metallic cementation[3].

In 1969, Sigmund[4] proposed the cascade collision theory which quantitatively describes the sputtering process by assuming the target surface to be a smooth plane. Pons-Cornbeau[5] and Liu *et al*[6] studied the sputtering of Cu-Zn, Fe-Ni, Fe-Cr alloys, while Wang *et al*[7,8] and Zhou *et al*[9] studied the properties of W alloys and Mo alloys, respectively. This article studies the surface composition and morphological variation of W-Mo alloy source in the double-glow discharge plasma surface alloying, and diagnoses the distribution of the plasma density in the vicinity of the alloy source. It aims to provide theoretic foundation for the design of proper alloy source so as to obtain the alloying layer of ideal composition.

2 EXPERIMENTAL

The test was carried out in the self-made double-glow discharge plasma metallic cementation furnace. The W and Mo powders were mixed in a mass ratio of 2∶8, then pressed, sin-

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tered and rolled, and finally made into 200 mm × 80 mm × 5 mm W-Mo alloy source. The test source voltage is adjustable from zero to 1 000 V, the workpiece voltage is 300 ~ 600 V, the gas pressure is 30 ~ 50 Pa, and the distance from the source to the workpiece is 20 mm. The morphological variation was observed by scan electron microscopy and the chemical composition of the surface layer of the alloy source was analysed by X-ray energy dispersive spectrometry. The chemical composition of the top surface was determined by Auger energy spectrometry, and the distribution of plasma density in the vicinity of the alloy source was diagnosed with the moveable Langmuir probe.

3 RESULTS AND DISCUSSION

3.1 Distribution of plasma density in vicinity of W-Mo alloy target

The plasma density in the glow discharge can reach the order of magnitude of $10^{10} cm^{-3}$. Non-equipotential hollow cathod effect[10] is adopted in the double-glow discharge plasma metallic cementation process so as to enhance the discharge between the W-Mo alloy source and the workpiece, increase the current density on the source surface and the workpiece surface, and raise the plasma density in the discharge space, thus on one hand intensifying the sputtering of the W-Mo alloy surface so as to ensure the effective supply of alloying elements, and on the other hand accelerating the diffusion of the alloying elements in the surface layer of the workpiece through the strong bombardment at the workpiece surface. Fig.1 shows the distribution of plasma density in the vicinity of the W-Mo alloy source when there occurs non-equipotential hollow cathod effect. The plasma density in the discharge space reaches the order of magnitude of $10^{12} cm^{-3}$.

3.2 Preferential sputtering of W-Mo alloy target

The sputtering yield is defined as the average number of target particles produced by one incidence ion. According to the cascabe collision theory, the sputtering yield of an element in a multi-constitutional target is not only related to its relative content, but also to its atomic mass and surface binding energy. The ratio of the sputtering yields of two alloying elements can be approximately expressed by[11]

$$Y_1/Y_2 \approx C_1(M_2/M_1)^{2m}(U_{01}/U_{02})^{1-2m}/C_2$$

where m is a potential paramenter($0 < m < 1$), when the energy of the incidence ion is small, the value of m is small; C_1 and C_2, M_1 and M_2, and U_{01} and U_{02} are the mass fractions, atomic masses and surface binding energies of two alloying elements, respectively. It is clear from Eq.(1) that when a multi-constitutional target is bombarded by ions, the element with smaller atomic mass and binding energy will be sputtered preferentially, thus causing the change of the chemical composition in the target surface layer. It has been proved that the bombardment of low-energy(0.3 ~ 3.0 keV) light ions at compounds or alloys will cause the reduction of light elements in the targets[12], thus changing the nature of the target surface.

The voltage exerted on the W-Mo alloy source is about 1 000 V. According to the theory of glow discharge, it is known that the voltage-drop of the cathod mainly occurs in the sheath layer. After accelerated in the sheath layer, the energy of the argon ions can reach several hundred eV ~ 1 keV when they get to the source surface. The atomic mass of Mo is lighter than that of W, therefore Mo is preferentially sputtered. The original chemical composition (mass

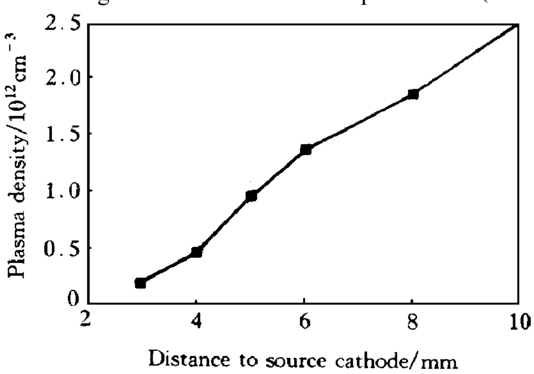

Fig.1 Distribution of plasma density in vicinity of W-Mo alloy source
(Source voltage: 1 000 V; Workpiece voltage: 450 V; Gas pressure: 40 Pa)

fraction, %) in the surface layer of the W- Mo alloy source is 79.56 Mo-20.44 W. After sputtering for different times under the conditions of source voltage = 1 000 V, workpiece voltage = 400 V and gas pressure = 40 Pa, the changes of chemical composition in the surface layer are shown in Table 1.

Table 1 Variation of chemical composition of W- Mo alloy before and after sputtering(mole fraction, %)

Sputtering time / min	Composition W	Mo	Fe	Analysis method
Before sputtering	56.000	44.000		AES
	11.835	88.165		EDS
5	14.450	81.769	3.781	EDS
10	12.933	83.866	3.201	EDS
30	12.751	71.357	15.892	EDS
180	24.615	71.233	4.152	EDS
600	23.220	72.574	4.206	EDS

The chemical composition analysis in the surface layer before sputtering by Auger energy spectrometry indicates that there exists serious surface segregation, while the chemical composition in this layer determined by X-ray energy dispersive spectrometry is similar to that of the matrix. Because the Auger energy spectrometry can not reflect the real situation after sputtering at high temperature, the chemical composition in the surface layer was determined by X-ray dispersive energy spectrometry. The whole sputtering process demonstrates that the preferential sputtering is strongest at the initial stage, and at this moment the content of W reaches the highest. The sputtering yield of W will increase, followed by the increase of the content of Mo, which will cause another turn of preferential sputtering, and finally forms the cyclic preferential sputtering in a definite range of chemical composition. Fe in the surface layer was introduced by the inverse diffusion of Fe into the source cathode. The chemical composition of the source surface is kept in the range of (70 % ~ 75 %) Mo-(22 % ~ 25 %) W.

3.3 Surface morphological variation

Fig.2 shows the X-ray diffraction patterns of the W- Mo alloy source before and after sputtering. It is thus evident that before sputtering (110) peak is the strongest, and after sputtering (200) peak is the strongest. This is related to the fact that the atoms sputtered from the close-packed direction are the most in the sputtering process. Fig.3 represents the initial surface morphology of the W- Mo alloy before sputtering, in which the pores produced by powder metallurgy can be clearly seen. Fig.4 shows the morphology variation vs time in the sputtering process. It is thus clear that the surface morphology changes from smooth to rough, and there occurs macroscopic roughing after 10 h sputtering. The increase of the roughness is beneficial to increasing

Fig.2 X-ray diffraction patterns of W- Mo alloy source
(a) —Before sputtering; (b) —After sputtering

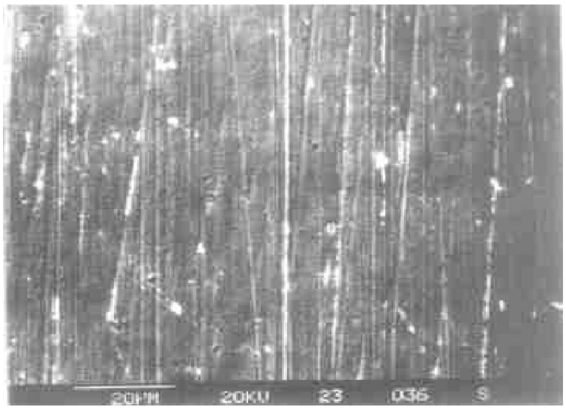

Fig.3 Initial surface morphology of W-Mo alloy source

the total sputtering amount, thus providing enough alloying elements for the surface alloying and maintaining the effective supply in the process of metallic cementation.

3.4 Influence factors of sputtering

The above analyses about morphology and composition of the surface layer of the W-Mo alloy source indicates that the sputtering behavior has two characteristics in the process of ion bombardment: 1) There is a transitional period before the stable state is reached, 2) There occurs obvious surface morphology variation. As regards to the source target material, the main factors which affect sputtering are: a) the difference between the atomic masses, b) the difference between the binding energies and c) the segregation of the alloying elements in the surface layer. In the process of double-glow discharge plasma metallic cementation, the macroscopic technological parameters, gas pressure and source voltage are important factors which affect sputtering. They affects the sputtering yield by changing the energy of ion bombardment and the emission of secondary electrons in the source surface. Wang *et al*[13] pointed out that the surface morphology formed in the sputtering process is

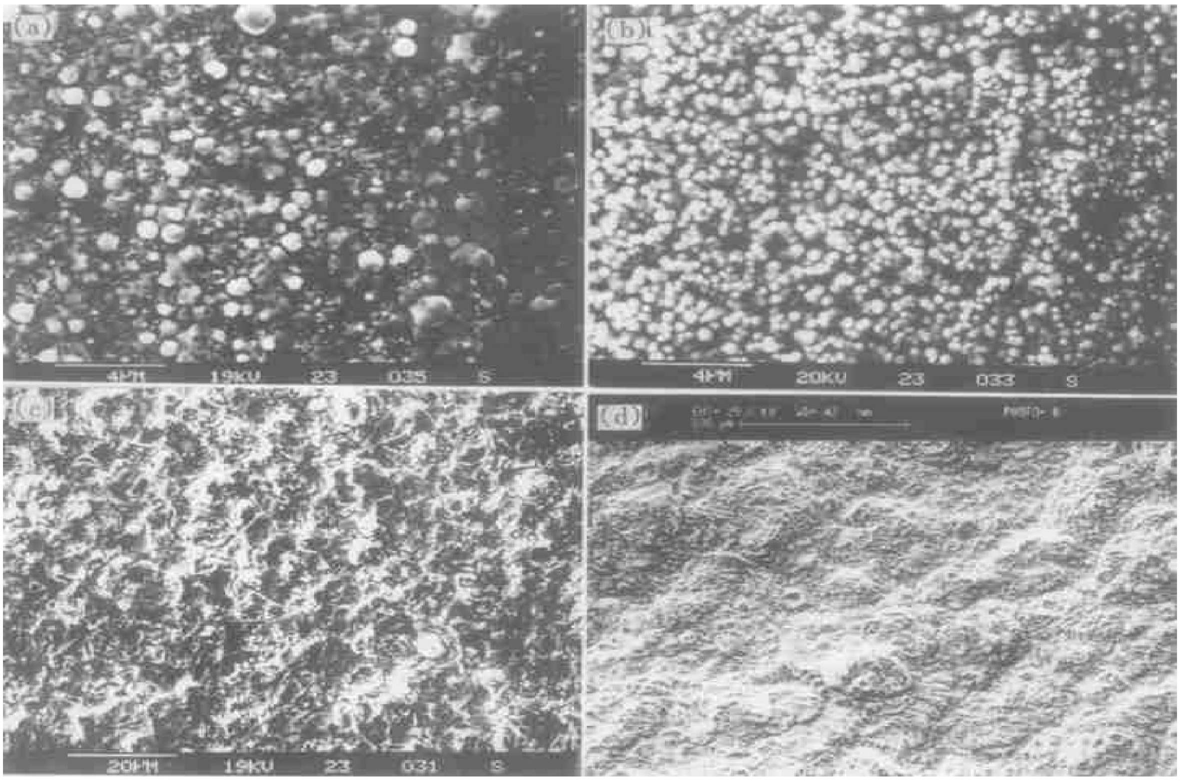

Fig.4 Morphological variation of W-Mo alloy source with sputtering time

(a) —5 min; (b) —10 min; (c) —30 min; (d) —600 min also an important factor which affects the preferential sputtering, it evidently affects the incidence angle of ion bombardment. Yamamura[14] proposed that the relation between sputtering yield $Y(0)$ and incidence angle θ can be described by the semi-empirical formula as follows:

$$Y(\theta)/Y(0) = x^f \exp[-m(x-1)] \quad (1)$$

where $Y(\theta)$ is the sputtering yield at an incidence angle of θ, $Y(0)$ is the normalized sputtering yield, $x = (\cos\theta)^{-1}$, and f and m are two constants. By simulation and experiment[15], it is found that Y_{max} occurs at $\theta \approx 75°$. In the process of double-glow metallic cementation, the sputtering at the sides is the strongest, the width of the source reduces by approximately 1 mm after 100 h sputtering.

Less attentions have been paid to the effect of temperature on sputtering yield. Generally speaking, in a certain range of temperature in which the sputtering yield can be considered to be closely related with the heat of sublimation, the sputtering yield almost does not vary with temperature. Above the critical temperature, the sputtering yield tends to increase. Under the experimental conditions of this work, the surface temperature is 1180 ℃ measured by infrared temperature gauge. Because the source is made of high melting point metals by powder metallurgy, it can be believed that the sputtering yield does not vary with temperature in the temperature range of metallic cementation.

In the metallic cementation by double-glow discharge plasma alloying, the main macroscopic technological parameters which affect the sputtering of the W-Mo alloy source are source voltage and gas pressure. Their influence law needs to be further studied.

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