PREFERENTIAL SPUTTERING OF $Cu_{76}Ni_{15}Sn_9$*

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ABSTRACT

Using collection film technique combined with Auger electron spectroscopy is analysis, the preferential sputtering of the ternary alloy $Cu_{76}Ni_{15}Sn_9$ bombarded with 27 keV Ar^+ at normal incidence is studied. After bombardment, the target surface is examined with SEM, and the surface composition of different topographical feature areas is measured with electron probe micro-analyser (EPMA). The experiment results show that Cu atoms are preferentially ejected compared with Ni atoms, and Sn atoms come third within the ejection angle range from 0° to 60°. The results are discussed from the viewpoint of sputtering from a very rough surface.

Keywords Auger electron spectroscopy, Topography, Preferential sputtering, $Cu_{76}Ni_{15}Sn_9$

1 INTRODUCTION

A better understanding of preferential sputtering of multicomponent alloys may be important in the fields of film making, surface composition analysis, and the choice of the material facing the plasma for a fusion reactor, and so on. Now, the preferential sputtering of binary alloy and the surface composition change after ion bombardment have been studied by many authors. But, the corresponding study for ternary alloy is very few, especially for its preferential sputtering. The experimental results for Ag-Au-Cu[1], Ag-Au-Pd[2], Fe-Cr-Mo[3] and Si (Fe, W)[4] systems only show the average of composition of the whole material surface, because the diameter of the beam spot of analyzer is larger ($\geq 50\mu m$) than the size of the locally rich field, and the analysed location is also random. Actually, according to our investigation for binary alloy, the sputtered surface not only has the characteristical change of the topography, but also appears the phenomenon that the element locally enriches according to the surface topographical features[5]. So, we can suppose that ternary alloy is possible to appear the same phenomenon after bombarded by ions, thereby, the preferential sputtering is influenced as the binary alloy system[6]. To test the correction of above reasoning, the ternary alloy $Cu_{76}Ni_{15}Sn_9$ is selected, the

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variation of preferential sputtering respective intensity $R_{ij}(\theta)$ (where i and j are the component atoms in sputtered material) with the ejection angle θ (the angle between the direction ejected atom and target surface) under 27 keV Ar^+ ions bombardment using collection film technique combined with AES is analysed, the change of the respective percent concentration of the composition atoms in the topographical feature micro-region using SEM and EPMA (electron probe micro-analyser) is examined. The discussion about the experiment results shows that the variation of $R_{ij}(\theta)$, as a function of θ, has a relationship with the surface topographical features, the structure of sample material and the element "locally rich" phenomenon.

2 EXPERIMENTAL

The sample, $Cu_{76}Ni_{15}Sn_9$ is smelted by the high purity metals according to the ratio of weight. All samples prepared by mechanical polishing are in the form of a disc of 15 mm diameter and 1 mm thickness. The samples (indirectly cooled by liquid nitrogen) are bombarded in the electromagnetic isotope separator with normally incident Ar^+. The sputtered materials are collected on a LN_2-cooled aluminium strip (99.999% purity) mounted around the target on a cylinder with a radius of 2.5 cm.

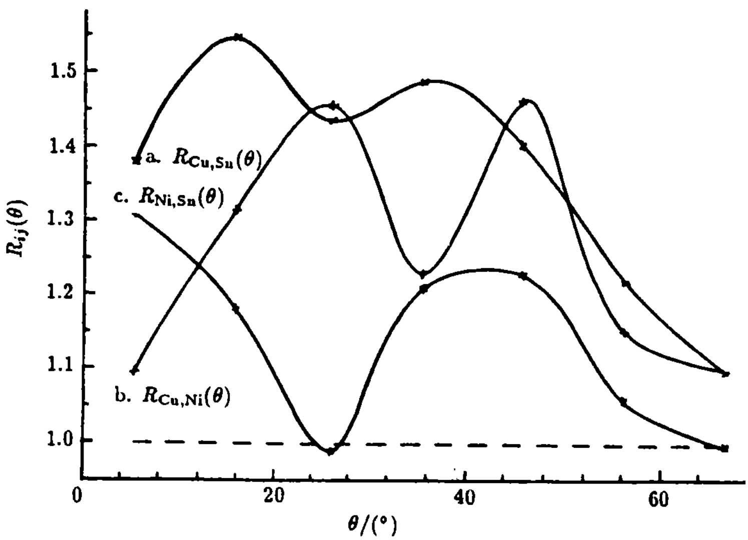


Fig.1 $R_{ij}(\theta) \sim \theta$ curves of $Cu_{76}Ni_{15}Sn_9$ bombarded with 27 keV Ar^+ ions

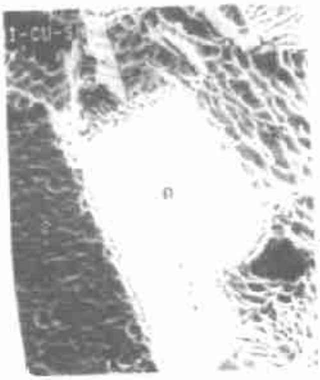
After the sputtering experiment, the collector foils are divided into several sections, the central location of each section is examined by AES to obtain the normalized sputtered composition ratio $R_{ij}(\theta)$ as a function of ejection angle to the surface normal (θ) for a ternary alloy.

$$R_{ij}(\theta) = (N_i/N_j)_{\rm m}/(N_i/N_j)_{\rm b} \quad (1)$$

where N_i, N_j are the counts of i and j component atoms respectively; m, b denote measured and matrix values. It can be seen that when $R_{ij}(\theta) > 1$, the i atom preferentially ejects; $R_{ij}(\theta) < 1$, j does; and $R_{ij}(\theta) = 1$, the ejections of i and j are not preferential. Fig.1 shows the composition ratio $R_{ij}(\theta)$ versus ejection angle for $Cu_{76}Ni_{15}Sn_9$ bombarded with 27 keV Ar^+ ions (dose: 1.4×10^{18} Ar^+/cm^2).

Table 1
Composition of various textured regions on an irradiated surface by EPMA spot analysis

Region	The first			The second			The third		
Composition	Cu	Ni	Sn	Cu	Ni	Sn	Cu	Ni	Sn
Protrusion	77.5	18.6	3.9	79.6	16.4	4.0	80.5	15.8	3.7
Pit	48.0	40.4	11.6	80.5	16	3.5	80.9	15.5	3.6
Respective fraction in alloy matrix	Cu: 78.3		Ni: 16.7		Sn: 5.0				



The irradiated surfaces were examined by SEM. The examination shows that the surface topography is divided into three micro-regions, and their topographic features are different. Fig.2 shows the surface topography of $Cu_{76}Ni_{15}Sn_9$ with 27 keV Ar^+ ions (dose: 1.4×10^{18} Ar^+/cm^2). The results of measurements of the irradiated surface composition in various textured regions by SEM combined with EPMA are showed in Table 1.

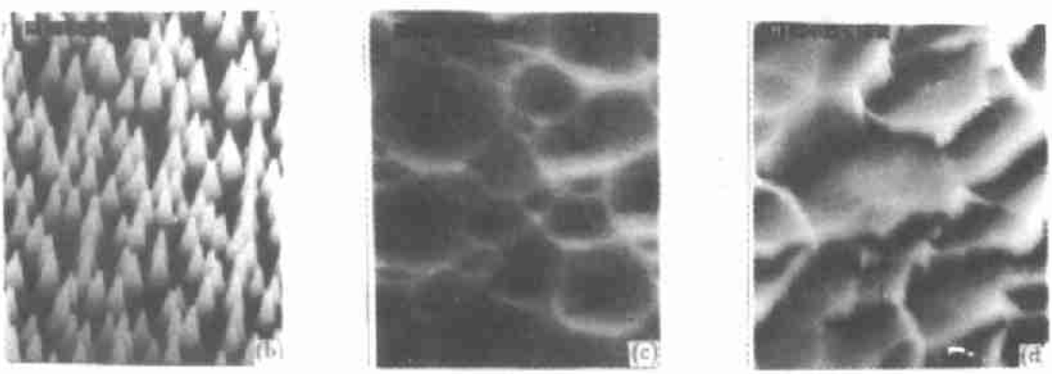


Fig.2 Surface topography of $Cu_{76}Ni_{15}Sn_9$ bombarded with 27 keV Ar^+ ions
(a) Full view of surface topography; (b), (c), (d) are the 1st, 2nd, 3rd typical micro-regions

3 DISCUSSION

3.1 According to the data of $R_{ij}(\theta)$, one can obtain

$$\bar{R}_{ij}(\theta) = \sum^{n} R_{ij}(\theta)/n \tag{2}$$

where n is number of examination, $\bar{R}_{ij}(\theta)$ is the average intensity of preferential sputtering. The results are $\bar{R}_{Cu,Sn}(\theta) = 1.4$, $\bar{R}_{Cu,Ni}(\theta) = 1.2$, and $\bar{R}_{Ni,Sn}(\theta) = 1.1$. So the Cu atoms preferentially eject compared with Sn and Ni atoms, while Sn atoms come third. The meaning is obviously, that when the ternary alloy system $Cu_{76}Ni_{15}Sn_9$ bombarded with 27 keV Ar^+ ions, the first preferential ejection component atoms are Cu, the second is Ni, and the ejection of Sn atoms is restrained.

In the previous studies, the ternary alloy system is considered as binary alloy system of two components in the ternary alloy system[1,7,8]. Our results show that Cu atoms preferentially eject in Cu-Ni binary alloy system ($\bar{R}_{Cu,Ni}(\theta) = 1.2$), it is consist with the results of Betz[8], Shimizu[9] and Lam[10]. The results $\bar{R}_{Cu,Sn}(\theta) = 1.4$, and $\bar{R}_{Ni,Sn}(\theta) = 1.1$ show that Cu atoms and Ni atoms preferentially eject compared with Sn atoms. Up to now, it has not been found that the data of preferentially sputtering of Cu-Sn system and Ni-Sn system can be compared with.

According to Sigmund's theory, the sputtering yield is decided by atom mass and surface bining energy[10]. The previous studies pointed out that for components with medium and heavy atomic weight the partial yield ratios are in qualitative agreement with the sputtering yields of the elements[1]. In our experiment, according to the data given by N. Matsunami[11], $Y_{Cu}/Y_{Sn} \approx 1.5$, $Y_{Cu}/Y_{Ni} \approx 1.5$, $Y_{Ni}/Y_{Sn} \approx 1.2$ obtained consist with above results qualitatively. It seems as that the surface binding energy of atoms is more important than the collision cascade effects. However, the surface binding energy of composition atoms of alloy is generally different from that of pure element[12], therefore, the effect of the surface binding energy in preferential sputtering of alloy will need to be studied further.

3.2 The preferential ejection almost takes place at $0° < \theta < 60°$ and the preferential ejection intensity $R_{ij}(\theta)$ changes with ejection angle θ obviously. These results may be obtained from Fig.1. It is considered that these results may have relationship with the structure of sample material, the topographical features during ions bombardment and the "locally rich element" phenomenon.

3.2.1 $R_{ij}(\theta)$ is enhanced at $0° < \theta < 60°$. It can be seen from the topographical features that the whole target surface is divided into three typical micro-regions (Fig.2a). Fig.2b is partial magnification of the first micro-regions, it can be seen that the surface is covered by many cones with equal apex angles, the "V" concave groove is formed between each cones, and its field angles equal about 45°. So the ejection of the atoms from the concave groove bottom is not blocked in this field angle range. The second region surface scattered cone eroded pits with various sizes and equal field angles about 120° (Fig.2c). The third region's topographical feature is different from the first and the second region's, but all the eroded gullies have the same forms, and the field angle between two inclines also equal about 120° (Fig.2d). In the summary, averagely, the ejection angle range of ejected atoms from the eroded gully, pit and concave groove bottom estimated approximately at $0° \sim +60°$ and $0° \sim -60°$. In addition, considering the shielding effects of surface topography to ejected atoms and local distribution of element according to topographic features, the following results were obtained:

a. $R_{ij}(\theta)$ is enhanced at $0° < \theta < 60°$. The topographical features have shielding effect on the atom ejection, and the maximum ejection angle is $\sim 60°$. At the same time, Cu and Ni elements have been enriched respectively in different regions, it is possible to strengthen the preferential sputtering on the range $0° — 60°$. In addition, the shielding of topography blocked or reduced the ejection atoms sharply at $\theta > 60°$, so that the examination was difficult as in Fig.1.

b. $R_{Cu,Sn}(\theta)$ should change at the ejection angle $0° < \theta < 20°$. According to the element distribution of the three micro-regions (Table 1), in the second and the third regions, Cu element only enriches a little and Sn element is a little poor, but in the first region, Cu element is very poor, especially in the bottom of the concave groove, it shows that the sputtering in the first region is very important. At the valley of the $R_{Cu,Sn}(\theta)$ curve nearby $\theta = 0°$ relates to that Cu element is depletion at the bottom of the "V" groove possibly, because the atoms at the bottom of the groove only eject nearby 0°.

c. $R_{Ni,Sn}(\theta)$ has a peak in the range $0° \sim 20°$. The results examined by EPMA show that Ni element enriches largely at the bottom of "V" groove (see Table 1), this is possibly an important cause that $R_{Ni,Sn}(\theta)$ has a peak value nearby 0°.

d. The variation of $R_{Cu,Ni}(\theta)$ in the range $0° \sim 20°$. In this range, $R_{Cu,Ni}(\theta)$ expends and strengthens in the valley nearby $\theta = 0°$. This feature may be explained qualitatively by the phenomena that Cu element is depletion and Ni element is largely enriched at the bottom of "V" groove in the first region.

3.2.2 The variation on peaks and valley of $R_{ij}(\theta)$ with θ. As indicated above, the surface topographical features of the target can be divided into three micro-regions, (1), (2) and (3) in Fig.2a. Analyses show that each micro-region virtually corresponds to a certain crystal plane, for example, the first micro-region consists of many cones with equal apex angles, that is in agreement with the Whitton's results of the surface topographical feature structures obtained by 10 keV Ar^+ (dose: 1×10^{19} Ar^+/cm^2) bombarding the low index [13, 3, 1] plane of Cu crystal sample[13,14]. The second region having many eroded cone pits on the surface is the same as the Tanovic's results obtained by 40 keV Ar^+ (dose: 10^{20} Ar^+/cm^2) bombarding Cu(111) target. According to Ref.[15], the topographical features of the third micro-region possibly correspond to the (100) crystal plane. For the above discussion, one can consider that $Cu_{76}Ni_{15}Sn_9$ alloy is polycrystal, because different crystal grain has different direction to the target surface, that means the various crystal planes may be exposed on the target surface and the planes can be formed on the surface topography with different structure during ion bombardment. In other words, there are three crystal planes exposed mainly to $Cu_{76}Ni_{15}Sn_9$ surface, (11, 3, 1), (111) and (100). The investigations show that the ions ejected in different direction of crystal plane have different surface binding energy[16], so the differential sputtering yields are also different. Because the direction of crystal axis of polycrystal sample is random, the quantitative determination of the variation of preferential sputtering intensity with angle θ is very difficult. However, qualitatively, the influence of crystal planes on ejected atoms is very important. For example, according to the knowledge of crystallography the angle between the [111] axis and the [100] axis is 55°, between [100] and [211], [100] and [411] is 35° and 19°, and so on. The phenomena that $R_{ij}(\theta)$ changes with θ as peaks or valley maybe are the results that the above factors lead to synthetically.

4 CONCLUSIONS

a. The respective ratios of sputtered atoms of $Cu_{76}Ni_{15}Sn_9$ alloy are measured by AES, and the differential yield ratios $R_{ij}(\theta)$ of two components i and j are obtained, thereby, the experiment results show that the first preferential sputtering atom is Cu and the second Ni in this alloy sputtering.

b. The phenomena of the preferentialy ejection almost takes place at $0° < \theta < 60°$, maybe relate to the surface topographical features, because analyses found that the maximum half field angle of each pit on the target surface for the three micro-regions is just 120°.

c. The phenomena that $R_{ij}(\theta)$ changes with θ as peaks and valley possibly has relationship between the polycrystal structure features of $Cu_{76}Ni_{15}Sn_9$ alloy and the atom's local enrichment (or depletion) according to the different surface topographical features.

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