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A Study of the Growth Process of Altered Layer during Ion-bombardment on Clean Surfaces of Cu-Ni Alloys

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Abstract

The growth process of an altered layer was investigated for a Cu-Ni alloy at various temperatures by means of AES measurement in both a lower energy Auger electron spectrum (LEAES) and a higher energy Auger spectrum (HEAES). Surface composition estimated from the LEAES differed in general from that estimated from the HEAES. The LEAES data showed a more rapid decrease in Cu-concentration during argon ion-bombardment than the HEAES data. Based on the difference in the escape depth in the different energy regions, a changing process of the depth profile of the altered layer was postulated. The changing process of the surface composition was found to vary with sample temperatures; namely, the rate of the change decreased with the increase of sample temperature. At sufficiently high temperatures (above 500°C) the surface composition did not change any more from the initially equilibrated value by the ion-bombardment. This fact indicates that the diffusion phenomenon plays an important role in the growth process of the altered layer and that the process is greatly influenced by balancing conditions between the selective sputtering which gives rise to enrichment of Ni-atoms at the surface and the diffusion which gives rise to enrichment of Cu-atoms at the surface.

1. Introduction

It is well known that ion-bombardment of alloy surfaces gives rise to selective sputtering, resulting in changes in surface composition from that of the initial surface within a thickness of several tens of angstroms. Such a layer is designated as "altered layer" in the present study. Concerning this phenomenon, a number of studies have been made experimentally and/or theoretically [1–8]. Werner [2] and Oostrom et al. [3] proposed models for the selective sputtering based on mass balance. In the models, however, the diffusion process was not taken into account in spite of the fact that the enhanced diffusion under ion-bombardment plays an important role for the growth of the altered layer as Pickering pointed out [4]. The present authors [5] and Arita et al. [6] proposed new models for the change of surface composition in alloy surfaces considering competition between the selective sputtering itself and the diffusion, although the

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method of data analysis differed.

The selective sputtering of Cu-Ni alloys has been investigated extensively by Shimizu et al. [7], Ho et al. [1] and Saeki et al. [8], however, they did not take into account the diffusion phenomenon in the data analysis. The present authors [5] investigated the depth profiles of the altered layers of Cu-Ni alloys and found enhanced diffusion at the surface layers. However, the growth process of the altered layer was not investigated in that study.

In the present study, we will describe the change of the surface composition of a clean Cu-Ni alloy under argon ion-bombardment with the aid of the measurements in both the lower energy spectrum (LEAES) and the higher energy spectrum (HEAES), and make clear the growth process of the altered layer. By utilizing the difference in the escape depth of Auger electrons in both energy regions, the change in the depth profile during the ion-bombardment can be presented. In addition, the ion-bombardment at different temperatures makes it clear that the diffusion influences remarkably the growth process and the depth profile of the altered layer at a steady state as well.

2. Experimental

The sample used in the present study was a polycrystalline plate of 48% Cu-52% Ni alloy in bulk composition. The dimension of the sample was $25 \times 7.5 \times 0.15 \, \text{mm}^3$. It was buff-polished, washed in distilled water, xylene and acetone one after another using a supersonic washing device, and mounted onto a sample holder which was made of the same alloy as the sample itself in order to avoid deposition of foreign elements other than copper and/or nickel during the sputtering process.

The sample was spot-welded to the sample holder and could be heated up to 1000°C by passing ac current across it. The base pressure of the system was less than 2×10^{-10} Torr routinely after bake-out of the system for ten hours at 150°C. The clean surface was prepared by simultaneous argon ion-bombardment ($P_{Ar} = 5 \times 10^{-5}$ Torr, 6 μA/cm^2, 700 eV) and annealing at 600°C.

A conventional Auger electron spectroscopic system with a CMA optics was used. An Auger spectrum was observed with a primary electron energy $E_p = 2000$ eV, $I_p = 5 \, \mu$A with a beam diameter of 0.2 mm at the sample surface. Modulation voltage was 2 V for the LEAES and 20 V for the HEAES. The surface composition was determined by the peak-to-peak heights of Cu-$M_1M_{4,5}M_{4,5}$ (106 eV), Ni-$M_1M_{4,5}M_{4,5}$ (101 eV) for the LEAES and Cu-$L_3M_{4,5}M_{4,5}$ (920 eV), Ni-$L_3M_{2,3}M_{2,3}$ (712 eV) for the LEAES.

Before each experimental run, the clean surface was bombarded with argon ions in argon atmosphere ($P_{Ar} = 6 \times 10^{-6}$ Torr, 0.38 μA/cm^2, 700 eV) and annealed at 600°C for one minute, simultaneously. The incident angle of the argon ions was 45° with respect to the surface normal throughout the present study. By the above pretreatment, the initial surface composition was a constant in each experiment. The initial values were estimated to be 83% Cu by the LEAES and 50% Cu by the HEAES. Subsequently, the sample was bombarded under the same conditions as in the pretreatment at a given temperature and the change in the surface composition was measured following the ion-bombardment by both the LEAES and HEAES. The bombardment was carried out at room temperature, 100, 150, 200, 250, 300, 400 and 500°C.

3. Data Analysis

According to the physical mechanism of Auger electron emission [9], the current from the WXY Auger electrons from an element α can be described as

$$I_{\alpha, WXY} = (1/4\pi) \int_{\Omega} \int_{E_w}^{E_p} \int_0^{\infty} I(E, Z) \gamma_{\alpha, WXY} \sigma_{\alpha}(E)$$

$$\exp[-Z/\lambda^{\beta}(E_{\alpha, WXY}) \cos \theta] X_{\alpha} dZ dE d\Omega \qquad (1)$$

where E_p and E_w are the energy of incident electrons and the ionization energy for core level W in the element α, respectively; $I(E, Z)$ is the excitation flux at the depth Z and energy E; $\sigma_{\alpha}(E)$ is the ionization cross section for the core level W of the element α by electrons with energy E; $\gamma_{\alpha, WXY}$ is the probablity that the excited atoms will decay through the WXY Auger transition; $X_{\alpha}(Z)$ is the atomic concentration of the element α at the depth Z; $\lambda^{\beta}(E_{\alpha, WXY})$ is the mean free path of the WXY Auger electrons in a matrix β; and $\exp[-Z/\lambda^{\alpha}(E_{\alpha, WXY}) \cos \theta]$ is the escaping probability for the WXY Auger electrons originating at the depth Z and directed along a path making an angle θ with respect to the surface normal. $I(E, Z)$ is described as

$$I(E, Z) = I_p + I_B(E, Z) \qquad (2)$$

where I_p is the current of the primary electrons and $I_B(E, Z)$ is the current returned to the depth Z by back-scattering. The concentration $X_{\alpha}(Z)$ varies within the sampling depth of Auger electrons in general and hence it will be described as

$$X_{\alpha}(Z) = X_{\alpha}^b + f_{\alpha}(Z) \qquad (3)$$

where X_{α}^b is the bulk concentration of the element α and $f_{\alpha}(Z)$ is the difference in the concentration of the element at the depth Z from the bulk concentration. Substituting eqs. (2) and (3) into (1) and integrating, the Auger current is expressed as

$$I_{\alpha, WXY} = T\gamma_{\alpha, WXY}\sigma_{\alpha}(E_p)[1 + R_{\alpha}(E_p, E_w)]I_p\lambda^{\beta}(E_{\alpha, WXY}) \cos \theta_0 X_{\alpha}^b$$

$$+ \int_0^{\infty} f_{\alpha}(Z) \exp[-Z/\lambda^{\beta}(E_{\alpha, WXY}) \cos \theta_0] dZ \qquad (4)$$

$$R_{\alpha}(E_p, E_w) = 1/\sigma_{\alpha}(E_p)I_p \int_{E_w}^{E_p} I_B(E, Z)\sigma_{\alpha}(E) dE \qquad (5)$$

where T is the transmission coefficient and θ_0 is a constant for CMA optics (42.3°). In case of a binary alloy such as Cu-Ni, the relative peak-to-peak height of Cu-Auger peaks can be described as

$$I_{Cu}/(I_{Cu} + \delta I_{Ni}) = X_{Cu}^b + \int_0^{\infty} f_{Cu}(Z) \exp[-Z/\lambda_{Cu} \cos \theta_0]/\exp[-Z/\lambda_{Cu} \cos \theta_0] dZ \qquad (6)$$

$$\delta = \gamma_{Cu, WXY}\sigma_{Cu}(E_p)[1 + R_{Cu}(E_p, E_w)]/\gamma_{Ni, WXY}\sigma_{Ni}(E_p)[1 + R_{Ni}(E_p, E_w)] \qquad (7)$$

based on the fact that the relative sensitivity δ is independent of the composition of the alloy [10] and λ_{Cu} is equivalent to λ_{Ni} in a given energy region. Namely, eq. (6) indicates that the relative peak-to-peak height of copper is the sum of the bulk concentration and the weighted average of the escaping electrons with angle θ_0 with respect to the surface normal for the depth distribution of the concentration $f_{Cu}(Z)$ in the case of CMA optics.

Since the Auger peak-to-peak height in the derivative spectrum is generally proportional to the Auger current [11], the following relation is valid,

$$I_{Cu}/(I_{Cu} + \delta I_{Ni}) = H_{Cu}/(H_{Cu} + \delta H_{Ni}) \tag{8}$$

where H is the peak-to-peak height of a given Auger current from a given element in the derivative spectrum.

When $f_{Cu}(Z)$ is constant and equivalent to X_0 over the sampling depth of the Auger electrons, the relative peak-to-peak height is written as

$$H_{Cu}/(H_{Cu} + \delta H_{Ni}) = X_{Cu}^b + X_0 = X_{Cu}^s \tag{9}$$

Therefore, the relative peak-to-peak height of copper takes a constant value for a given alloy in both the LEAES and HEAES data. When the in-depth distribution $f_{Cu}(Z)$ varies within the sampling depth, however, it differs between the LEAES and HEAES data depending on the in-depth distribution and the escape depth of the Auger electrons.

4. Results and discussion

Fig. 1 shows the change in the peak-to-peak heights with the ion-bombardment of the sample at room temperature. The peak heights are normalized by the peak height of the elastic electrons of $E = 1000$ eV measured separately. In this figure, it is seen that the surface layer observed by the LEAES reached a steady state after a 20 minute ion-bombardment, while that observed by the HEAES reached a steady state after a 10 minute bombardment. The time lag to attain the steady state in the LEAES data with respect to the HEAES data is considered to be due to the difference in the sampling depth. Namely, the HEAES is relatively insensitive to variation of the surface composition of the outer-most layer in comparison with the LEAES, since the escape depth of the Auger electrons in the HEAES is approximately three times greater than that in the LEAES. Therefore, the time lag indicates that the overall concentration and/or composition of the altered layer becomes almost constant after a 10 minute bombardment, while the concentration near the outermost surface layer still
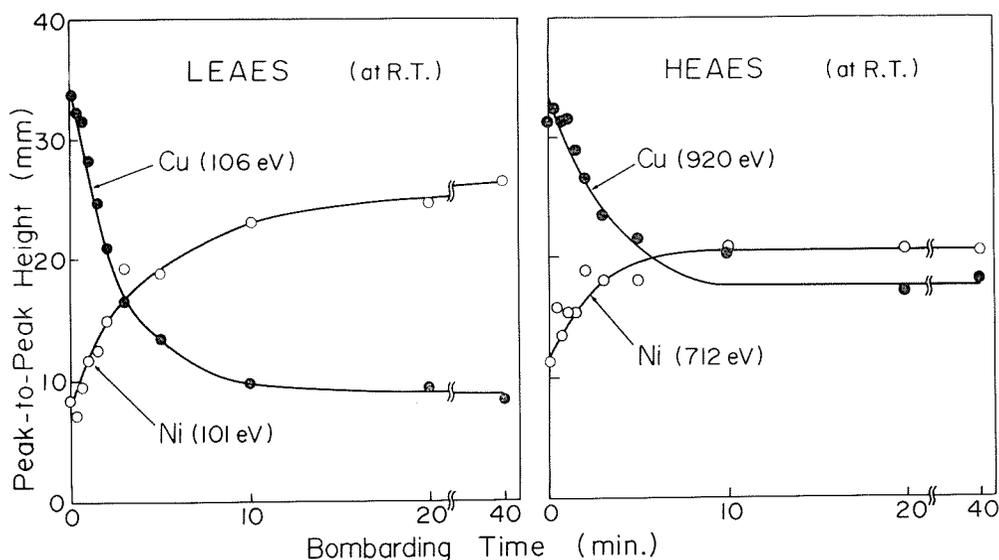

Fig. 1 Changes in AES peak peak heights in the LEAES and HEAES with the argon ion-bombardment at room temperature for 48% Cu–52% Ni alloy
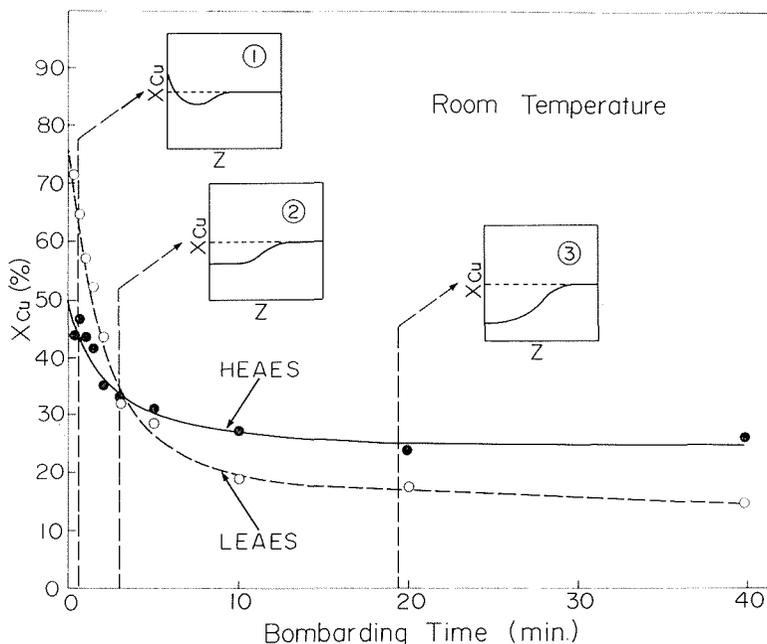
Fig. 2 Changes in surface composition of the Cu-Ni alloy
with the ion-bombardment at room temperature

changes with successive bombardment.

Fig. 2 shows the change in the surface composition with the ion-bombardment at room temperature. As seen in the figure, the initial Cu-rich surface becomes Ni-rich surface with the bombardment. The change in the surface composition in the thinner layer is more marked than in the thicker layer at the beginning of the ion-bombardment and the decay curves cross each other at a 3 minute bombardment. Subsequently they gradually attain a steady state.

Considering the difference in the escape depth of the Auger electrons between the LEAES and HEAES [12], such depth profiles shown in the small figures inserted in Fig. 2 can be proposed. In the state (1), after a 40 second bombardment, the surface composition was estimated as 65% Cu by the LEAES and 45% Cu by the HEAES data, while it is 48% Cu in the bulk. Therefore, the depth profile is considered as the curve (1). In the state (2), after a 3 minute bombardment, the depth profile can be described as the curve (2), since the surface compositions estimated from the LEAES and HEAES are identical. In state (3), after a 19 minute bombardment, such a depth profile as the curve (3) is extracted, since both the LEAES and HEAES data show Ni-rich values with respect to the bulk and the extent of the enrichment is greater in the LEAES than the HEAES data.

The variation of the surface composition with the ion-bombardment at 300°C is shown in Fig. 3. In comparison with the results at room temperature, the rate of decrease of Cu-concentration is slower at 300°C and the steady state is not observed whithin 40 minutes. On the basis of the same consideration as the above, the depth profile is proposed as the curves (4) and (5), for example.

Fig. 4 shows the results observed at 500°C. In case of the ion-bombardment at such high temperature, the surface composition does not change with the ion-
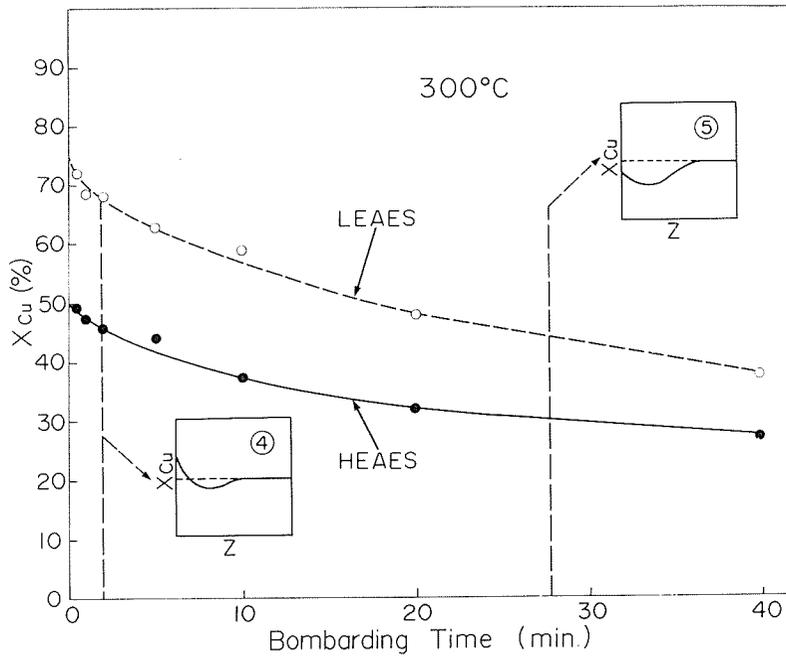
Fig. 3 Changes in surface composition during the ion-bombardment of the Cu-Ni alloy at 300°C
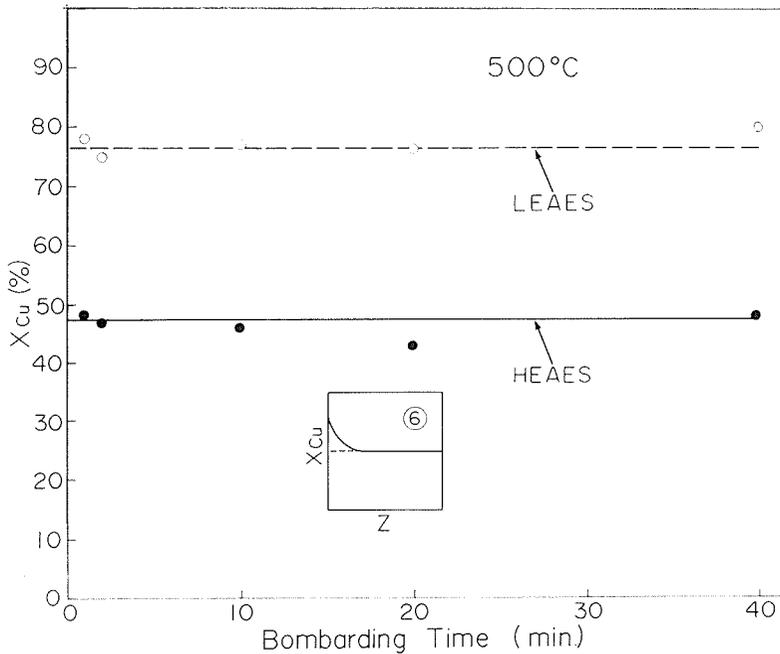

Fig. 4 Changes in surface composition during the ion-bombardment of the Cu-Ni alloy at 500°C

bombardment in both the LEAES and HEAES and is kept constant during the whole period of the bombardment.   Hence the depth profile is considered as the curve ⑥ [10].

Because the temperature dependence of sputtering yield of copper and nickel

are considered to be very small over the entire temperature range adopted in the present study [13], the above temperature dependence can be regarded as the effect caused by diffusion. From this view point, it will be explained as follows: the surface composition and the depth profile during the ion-bombardment at time t and depth z is determined by competition between the sputtering rate of the individual component and the diffusion rate. At lower temperatures around room temperature, the sputtering rate is greater than the diffusion rate and enrichment of nickel takes place in the surface layer as a result of selective sputtering of copper. On the other hand, at sufficiently high temperatures around 500°C, the diffusion rate is greater than the sputtering rate and hence more rapid rearrangement of atoms to keep a thermodynamically more stable surface occurs eventually. In the intermediate temperature range, the sputtering rate is a little larger than the diffusion rate and the difference between the two rates decreases slowly due to the enrichment of nickel in the surface layer. Subsequently, both the rates will balance at a certain surface composition.

As reported previously [14], the depth profile of the equilibrated surface layer is approximated very well with an exponential function of Z. Hence the depth profile of Cu-Ni alloys is considered as shown in Fig. 5 (a) for the annealed surface (600°C, 1hr.). In this state, chemical potential of each layer is balanced. Regarding the altered layer at a steady state formed at room temperature, on the other hand, the depth profile is considered as Fig. 5 (b). The slight difference of the surface compositions between the previous work and the present work is due to the different conditions of the annealing and the ion-bombardment.

Fig. 6 shows the change in the depth profile with the ion-bombardment of the well annealed and equilibrated surface. On bombarding the equilibrated surface ($t=0$) Cu-atoms on the surface are sputtered away selectively and the
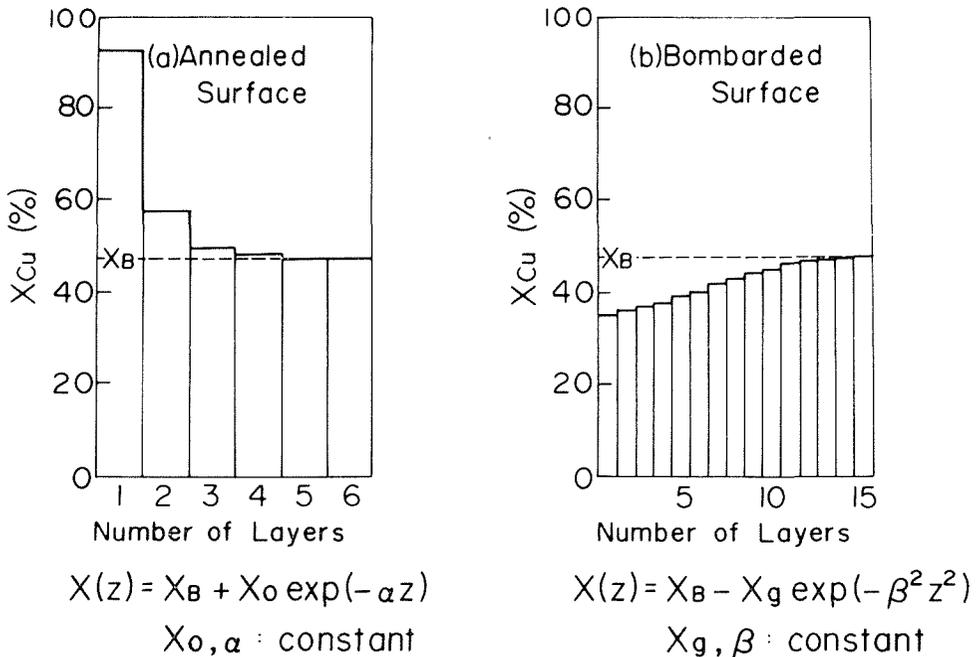

$$X(z) = X_B + X_0 \exp(-\alpha z)$$
$$X_0, \alpha : \text{constant}$$

$$X(z) = X_B - X_g \exp(-\beta^2 z^2)$$
$$X_g, \beta : \text{constant}$$

Fig. 5 Estimated depth profile of the equilibrated surface and
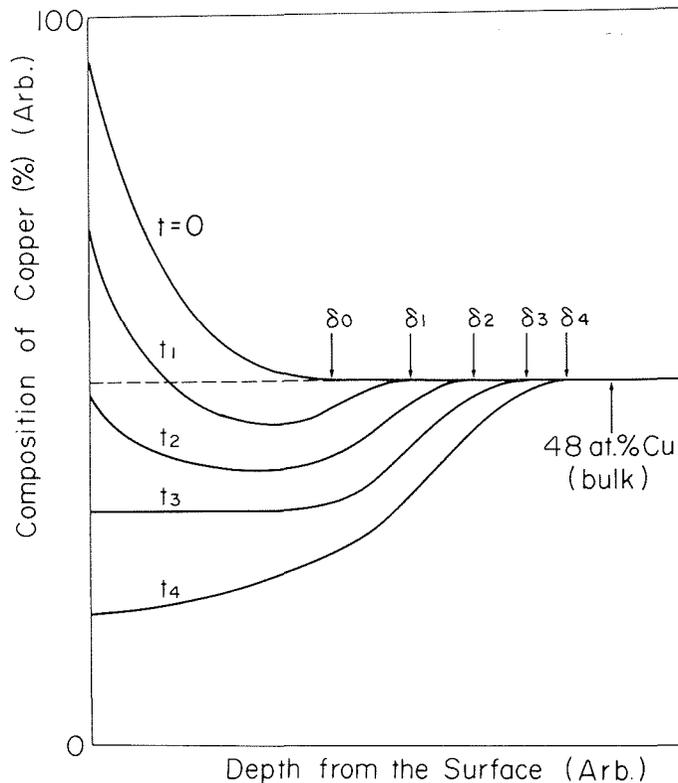altered layer for the Cu-Ni alloy

Fig. 6 Proposed growth process of the altered layer of the Cu-Ni alloy

chemical potential changes accordingly.   Then Cu-atoms will diffuse to the surface from the inner layers.   The rate of diffsion will be enhanced by excess defects introduced into the surface layers by radiation damages.   As the concentration of the defects is considered to decrease with depth, the rate of diffusion will be greater in the outerlayer than in the inner layer.   Therefore, deficiency of copper might arise in the intermediate region in the depth profile $(t=t_1)$. When the sputtering rate of copper is faster than the diffusion rate, the concentration of copper on the surface will decrease gradually $(t=t_2, t_3)$.   However, the amount of Cu-atoms in the inner layer also decreases in the period of the sputtering through the diffusion and/or the knock-on phenomenon.   Simultaneously, the Cu-atoms on the upper surface layer are sputtered out and the surface becomes more Ni-rich.   In this way the rate of the sputtering and diffusion will balance with each other and the depth profile will be kept constant $(t=t_4)$.

Because the rate, v_δ, with which the altered layer is formed is consiered to be a constant during the sputtering in a given material, the altered layer seems to become thicker with the ion-bombardment and reaches a constant thickness at a steady state.   The relation between the rate, v_δ, and the rate, v_s, with which the position of the surface recedes will be as $v_s > v_\delta$ at the beginning of the sputtering.   In the intermediate stage of the sputterig, the rate, v_s, decreases in comparison with its initial value due to the selective sputtering to result in smaller v_s.   At the steady state, on the other hand, both the rate will be equal $(v_s = v_\delta)$ and hence the thickness of the altered layer is kept constant.   The rate v_s depends on the surface composition, while the rate v_δ is considered to be

independent of the surface composition. It might be a function of the composition and/or structure in the bulk and hence the thickness of the altered layer at a steady state depends on the matrix.

5. Conclusion

The growth process of the altered layer and the process of changes in the depth profile due to selective sputtering were postulated for Cu-Ni alloy at various temperatures with the aid of the measurement of the LEAES and the HEAES. The difference in the surface compositions between those estimated from the LEAES and the HEAES data provided us with the depth profile of the surface layers and revealed the growth process of the altered layer. The temperature dependence of the decay curves in both the LEAES and HEAES with the argon ion-bombardment clarified that the surface composition and the depth profile in the altered layer were determined by the balancing conditions between the sputtering rate and the diffusion rate.

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