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**ION BEAM MODIFICATIONS OF NEAR-SURFACE COMPOSITIONS  
IN TERNARY ALLOYS\***

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ABSTRACT

Changes in the surface and subsurface compositions of ternary alloys during elevated-temperature sputtering with inert-gas ions were investigated. Theoretically, a comprehensive kinetic model which includes all the basic processes, such as preferential sputtering, displacement mixing, Gibbsian segregation, radiation-enhanced diffusion and radiation-induced segregation, was developed. This phenomenological approach enabled to predict the effects of each individual process or of a combination of processes on the compositional modification in model alloys. Experimentally, measurements of compositional changes at the surface of a Ag-40at%Au-20at%Cu alloy during 3-keV Ne<sup>+</sup> bombardment at various temperatures were made, using ion scattering spectroscopy. These measurements were interpreted on the basis of the results of theoretical modeling.

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## 1. Introduction

Changes in the near-surface composition during ion bombardment have been observed in many alloy systems. The phenomenon is simplest at low temperatures where only the athermal processes, i.e. preferential sputtering and displacement mixing, are important. As the temperature is increased, however, the radiation-generated point defects become increasingly mobile, and the thermally-activated processes, such as Gibbsian segregation, radiation-enhanced diffusion and radiation-induced segregation, play dominant roles. Because of the large number of competitive processes, the temporal and spatial development of the near-surface alloy composition in an irradiation environment can be very complex. Numerous investigations of compositional changes in binary alloys during elevated-temperature sputtering were carried out in recent years (see, e.g., [1]); however, only a limited number of studies on ternary systems has been reported [2-5].

The present work concentrates on the mechanisms and kinetics of ion bombardment-induced modifications of the near-surface composition in ternary alloys. Changes in the surface and subsurface compositions of a Ag-40at%Au-20at%Cu alloy during 3-keV Ne<sup>+</sup> sputtering in the temperature range from 30 to 600 °C were measured using ion scattering spectroscopy (ISS). Phenomenological modeling of the process was performed with the aid of a kinetic model developed recently [4]. The experimental results were interpreted in light of the trends and patterns predicted theoretically.

## 2. Near-surface Composition Modifications

### 2.1 Kinetic Processes and Model

A detailed description of the five basic processes mentioned above has been given elsewhere [4]. For the sake of clarity, some physical concepts are summarized here.

*Preferential sputtering* (PS) occurs in most alloy systems because of differences in surface-binding energy and in energy transfer to component atoms of different masses during the slowing-down of incident ions.

*Displacement mixing* (DM) of alloying elements is induced by displacement cascades generated in the alloy by the bombarding particles. As a first approximation, this process can be described by a diffusion model.

*Gibbsian segregation* (GS) is a thermally-activated segregation of the alloying elements to surfaces and interfaces, which reduces the free energy of the alloy system. At equilibrium, such segregation affects the alloy composition only in one or two outermost atom layers.

*Radiation-enhanced diffusion* (RED) is caused by the thermal motion of nonequilibrium point defects produced by the bombarding ions within the solid. Below  $\sim 0.6$  of the melting temperature, the concentrations of these defects can exceed their thermodynamic-equilibrium values by several orders of magnitude. Since the average diffusion coefficients of atoms in the alloy are proportional to the concentrations of point defects, diffusion of the alloying elements is strongly enhanced by irradiation at temperatures where point defects are mobile.

*Radiation-induced segregation* (RIS) is a result of point-defect fluxes. At sufficiently high temperatures, mobile defects escape mutual recombination and anneal out by diffusion to extended sinks. Any preferential association of defects with a particular alloying element and/or preferential participation of a component in defect diffusion will couple a net flux of that alloying element to the defect fluxes. This coupling leads to a compositional redistribution in irradiated alloys.

These basic processes can be cast together into a kinetic model, represented by a system of four coupled partial differential equations [4], which phenomenologically describes the alloy composition modification by ion beam. Numerical solutions of this equation system for appropriate initial and boundary conditions provide detailed information about the evolution of the near-surface alloy composition in time and space.

## 2.2 Experimental measurements

The Ag-40at%Au-20at%Cu alloy used in the present work was prepared by arc melting and subsequent homogenization. Rectangular specimens (0.5x1.5x0.05 cm<sup>3</sup>) cut from rolled material were metallographically polished and then solution annealed in a vacuum better than 10<sup>-6</sup> Pa at 700 °C for 5 h. The sample heating, sputtering and data collection were carried out in the same way as in our previous experiment [5,6]. With a flux of 3.75x10<sup>13</sup> 3-keV Ne<sup>+</sup> ions/cm<sup>2</sup> used, the peak damage rate was estimated to be ~3.3x10<sup>-2</sup> dpa/s.

In order to estimate the surface concentrations from Cu/Ag and Au/Ag ISS intensity ratios, the surfaces of a series of specimens of known compositions were abraded under UHV conditions with a rotating diamond-coated mandrel, and ISS spectra of these *fresh* surfaces were taken. Linear relationships between ISS intensity and bulk concentration ratios were obtained:

$$I_{\text{Cu}}/I_{\text{Ag}} = 0.07 (C_{\text{Cu}}^{\text{b}} / C_{\text{Ag}}^{\text{b}}) \quad (1)$$

$$I_{\text{Au}}/I_{\text{Ag}} = 1.10 (C_{\text{Au}}^{\text{b}} / C_{\text{Ag}}^{\text{b}}). \quad (2)$$

This calibration is drastically different from the one reported in our previous work [5] in which sputter-cleaned surfaces were employed for calibration, but is in good agreement with that obtained by Betz et al. [7] who used AES on *in situ* fractured or

scribed surfaces. A comparison of the above eqs. (1) and (2) with eqs. (1) and (2) of ref. [5] reveals that Ag was preferentially sputtered from the alloy, in contrast to the previous findings [5]. The present calibration procedure eliminates the interference of PS during surface sputter-cleaning in the ISS determination of the true bulk composition.

When the alloy was heated to elevated temperatures, GS occurred. To determine the entropies and enthalpies of segregation ( $\Delta S$ 's and  $\Delta H$ 's), the ISS intensity ratios  $I_{Cu}/I_{Ag}$  and  $I_{Au}/I_{Ag}$  were measured as a function of temperature (from 500 to 750 °C). The effects of PS on these measurements were practically avoided by using a 3-keV He<sup>+</sup> beam. From the intercepts and slopes of the Arrhenius plots of these ratios and using a He<sup>+</sup> ISS ratio vs. composition calibration, we obtained  $\Delta S_{Cu} = 0.26k$ ,  $\Delta S_{Au} = -0.39k$ ,  $\Delta H_{Cu} = 0.13$  eV and  $\Delta H_{Au} = 0.06$  eV for Cu and Au, respectively. The segregation enthalpies are the same as those reported previously [5]; however, the entropies are quite different because the surface concentrations of the alloying elements were not significantly altered by PS during short analyses with He<sup>+</sup> ions.

Two aspects of ion beam-induced composition modification were investigated: (i) temporal evolution of the surface composition during sputtering, and (ii) extent of compositional alteration in the subsurface region. First, the ratios  $I_{Cu}/I_{Ag}$  and  $I_{Au}/I_{Ag}$  were measured during 3-keV Ne<sup>+</sup> sputtering at various temperatures. The results are shown as data points in fig. 1. Then, when steady state had been reached, the specimen was rapidly cooled to room temperature, and  $I_{Cu}/I_{Ag}$  and  $I_{Au}/I_{Ag}$  were subsequently taken as a function of sputtering time. This procedure yields the concentration profiles of Cu and Au below the surface; the data are shown in fig. 2.

### 2.3 Interpretation of Experimental Results

To facilitate the interpretation of the experimental results, theoretical modeling of beam-induced surface and subsurface composition modifications was also carried out for the same alloy under the same irradiation conditions, using the kinetic model briefly described above. However, since the inclusion of the five basic processes in the model introduces a large number of physical parameters into the calculations, a detailed fitting of theoretical calculations to the experimental data is quite involved and is still in progress at present. Therefore, we chose here to only show some results of a qualitative fitting, which can be helpful for the understanding of the experimental observations. All the defect parameters used in these calculations were derived from a previous fitting [5]. The component sputtering yield for 3-keV  $\text{Ne}^+$  on Ag was taken to be  $S_{\text{Ag}} = 3.0$  atoms/ion [8]. With the information obtained regarding PS in this alloy system, we estimated the component sputtering yields for Au and Cu as:  $S_{\text{Au}} = 1.35$  and  $S_{\text{Cu}} = 1.0$  atoms/ion. The calculated time evolution of the surface composition during sputtering at various temperatures and the corresponding steady-state subsurface concentration profiles are shown by the numbered curves in figs. 1 and 2, respectively. Compared with the previous fitting [5], the agreement between the experimental measurements and the present calculations which take into account the pronounced effects of PS appears less than satisfactory. A systematic fitting will thus be needed in order to derive better values for the physical parameters involved. The general trends and patterns observed can, however, be interpreted with the aid of the present modeling.

As seen in fig. 1, since the specimen was maintained at temperature for at least 1 h prior to sputtering, the low values of the surface concentrations of Cu and Au, observed at short sputtering times were caused by GS. With increasing time, these concentrations increased as a result of effective RIS and PS to steady-state values. The higher the temperature, the longer the time required to attain steady

state. For example, this time increased from  $\sim 10^3$  s at 200 °C to  $\sim 10^6$  s at 600 °C.

The spatial development of the subsurface concentration profiles (fig. 2), on the other hand, can be understood as follows. During sputtering at elevated temperatures, GS causes a Ag enrichment in the surface layer [5], which in turn gives rise to a transient PS of Ag. The synergistic effects of GS and PS eventually lead to a substantial depletion of Ag and, hence, enrichment Au and Cu in the near-surface region. Simultaneously, RED and RIS extend the compositionally-altered layer deep into the sample interior. The steady-state altered-layer thickness is determined by the depth at which the Ag transport from the bulk into the depleted zone is equal to the Ag loss from the surface by sputtering. Since this transport is a diffusional process, the higher the sputtering temperature, the thicker the altered layer. At 600 °C, for example, the thickness of this layer was  $\sim 10$   $\mu\text{m}$ , which was  $\sim 1000$  times larger than the total range of damage produced by 3-keV  $\text{Ne}^+$  ions. It is the extension of the concentration gradient to such large depths that requires the very long time to achieve steady state during high-temperature sputtering.

### 3. Summary

Changes in the surface and subsurface compositions induced by heating and by 3-keV  $\text{Ne}^+$  sputtering at elevated temperatures in a Ag-40at%Au-20at%Cu alloy were measured using ISS and compared with theoretical modeling. Several observations have been made:

- (a) By comparing the ISS-intensity/bulk-composition calibrations obtained using fresh alloy surfaces prepared by abrasion under UHV conditions and sputter-cleaned surfaces, PS of Ag was found to occur, in agreement with previous AES data [7].



- (b) During heating prior to sputtering, Cu and Au segregate away from the surface. The segregation enthalpies and entropies were measured to be 0.13 eV and 0.26k for Cu, and 0.06 eV and -0.39k for Au, respectively.
- (c) During elevated-temperature sputtering, the surface concentrations of both Cu and Au increased from low values brought about by GS to higher steady-state limits, as a result of PS of Ag and RIS. Depth-profiling of the steady-state altered layer showed that, owing to PS of Ag and the operation of the thermally-activated processes, enrichment of Cu and Au occurred over a large depth, the value of which depends on sputtering temperature.

### References

- [1] N.Q. Lam and H. Wiedersich, Nucl. Instr. and Meth. **B18** (1987) 471.
- [2] G. Betz and G.K. Wehner, in: Sputtering by Particle Bombardment II, ed., R. Behrisch (Springer, Berlin, 1983) p.11.
- [3] B. Schiffman and M. Polak, Surf. Interface Anal. **9** (1986) 151.
- [4] A.M. Yacout, N.Q. Lam and J.F. Stubbins, Nucl. Instr. and Meth. **B42** (1989) 49.
- [5] S. Tang, N.Q. Lam and A. Yacout, Surf. Sci. **231** (1990) 253.
- [6] N.Q. Lam and H. Hoff, Surf. Sci. **193** (1988) 353.
- [7] G. Betz, M. Arias and P. Braun, Instr. and Meth. **170** (1980) 347.
- [8] H.H. Andersen and H.L. Bay, in: Sputtering by Particle Bombardment I, ed., R. Behrisch (Springer, Heidelberg, 1981) p. 145.

**FIGURE CAPTIONS**

Fig. 1: Time evolution of the surface composition of a Ag-40%Au-20at%Cu alloy during 3-keV Ne<sup>+</sup> sputtering at various temperatures. The experimental measurements are shown by different symbols, and the results of theoretical modeling are indicated by the numbered curves.

Fig. 2: Steady-state depth profiles of Cu and Au in the alloy after sputtering with 3-keV Ne<sup>+</sup> at various temperatures. The different symbols represent the experimental measurements, and the numbered curves indicate the modeling results.

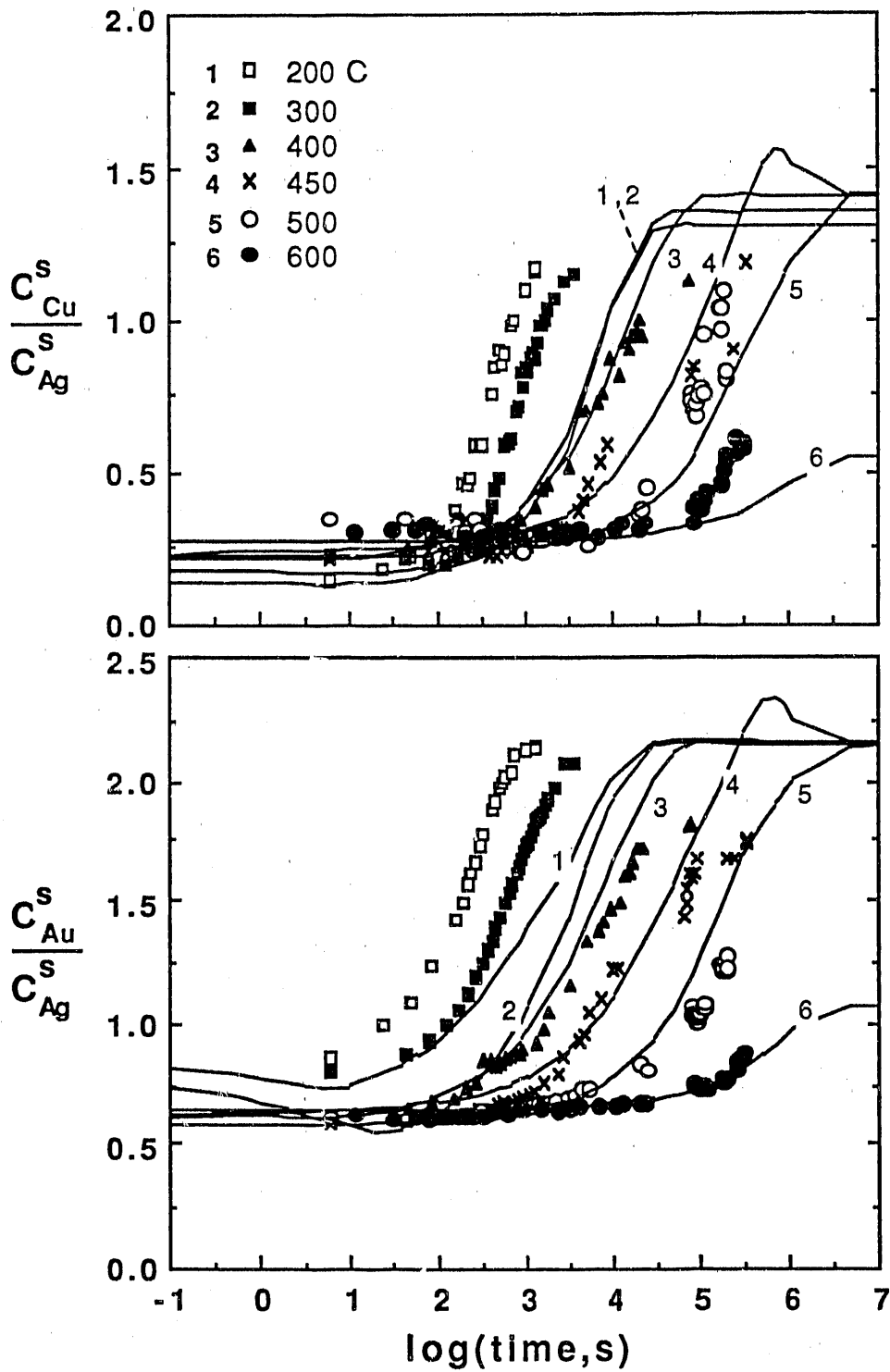


Fig. 1 N.Q. LAM et al. (Paper FP-59)

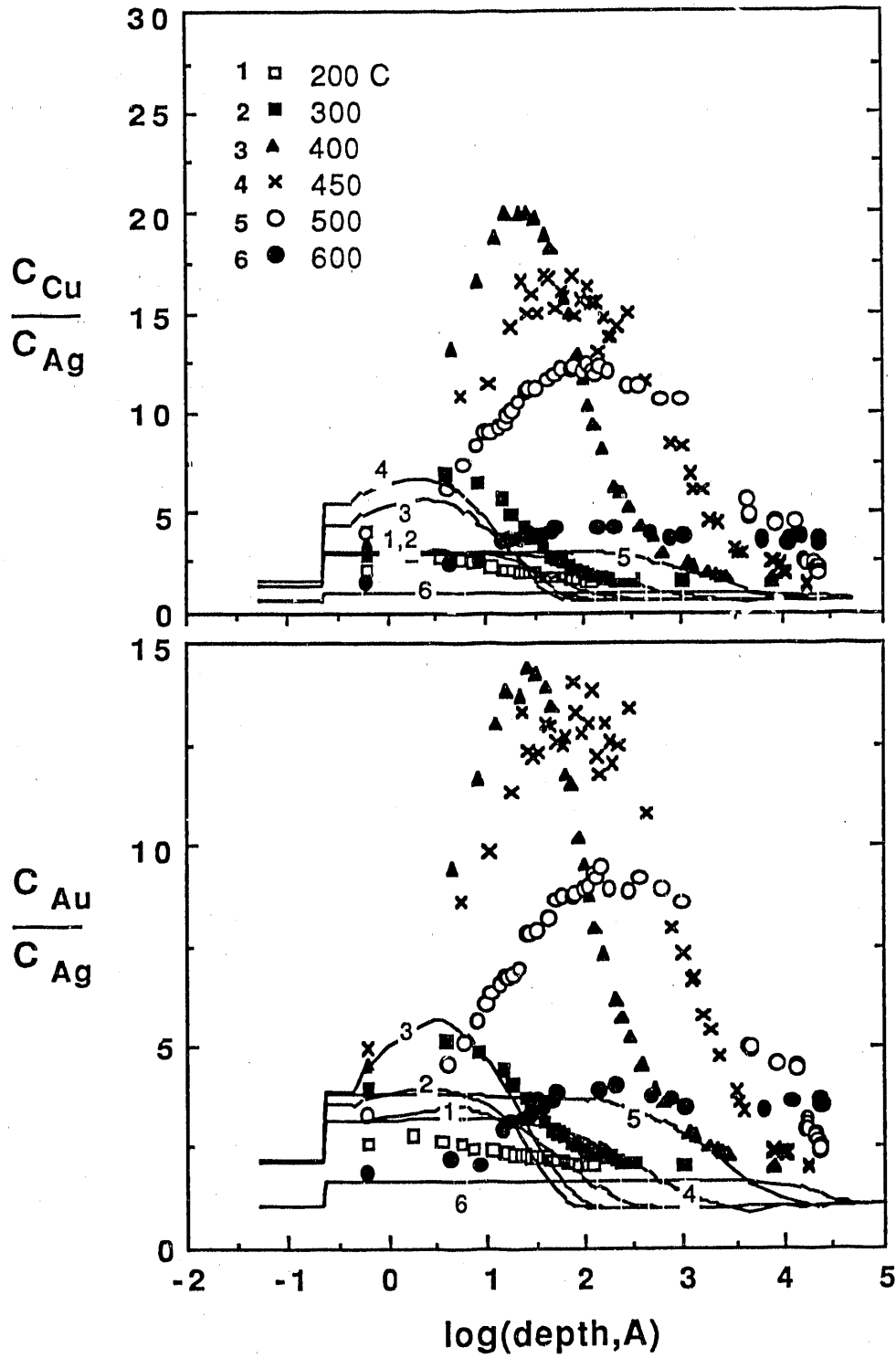


Fig. 2 N.Q. LAM et al.

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