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SPUTTER-INDUCED SUBSURFACE SEGREGATION IN A Cu-Ni ALLOY. L. E. Rehn, S. Danyluk, and H. Wiedersich [Phys. Rev. Lett. 43, 1437 (1979)].

As a result of a transposition of manuscript pages, the originally printed version of this Letter was badly garbled. The resulting confusion was such that it could not be rectified by an Erratum of the usual form, and therefore the Letter is reproduced below in its entirety.

Sputter-Induced Subsurface Segregation in a Cu-Ni Alloy

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(Received 30 April 1979)

Measurements of the surface composition of a Cu-Ni alloy using Auger electrons with different average escape depths reveal sputter-induced subsurface compositional changes at elevated temperatures which are larger than those produced directly at the surface by preferential sputtering. The compositional gradients which are produced extend to significantly greater depths than have been considered previously.

Sputtering with low-energy ions is routinely used to produce clean substrates for surface-analysis studies and, in conjunction with many different techniques, to profile the chemical composition of multicomponent alloys beneath an exposed surface.¹ Ion sputtering at elevated temperatures will also play an important role in determining the plasma contaminate level for advanced fusion devices.² An understanding of compositional changes induced by ion sputtering is thus of quite general interest and importance. In this Letter, we report surface and subsurface compositional changes induced in a Cu-Ni (40-at.% Ni) alloy during ion sputtering at temperatures between 50 and 600 °C.

Surface compositional changes during ion sputtering near room temperature have been observed in many alloy systems, an effect which is called preferential sputtering. Sputtering of Cu-Ni alloys at room temperature is known to preferentially remove Cu to a degree which is consistent with the sputtering yield ratios of pure Cu and Ni.^{3,4} However, only very limited information exists on elevated-temperature sputtering effects, and no direct experimental information is available on subsurface changes⁵ at elevated temperatures. In recent models of the sputtering phe-

nomenon developed by Ho⁶ and by Lam, Leaf, and Wiedersich,⁷ subsurface effects are predicted at temperatures where diffusion can promote equilibrium between the altered surface composition and the underlying bulk alloy.

We have used Auger-electron spectroscopy^{1,8} (AES) to monitor near surface compositional changes *in situ*; that is, at temperature during sputtering. A primary electron beam of 3 kV and $\sim 10 \mu\text{A}$ was used to excite the transitions. A $195\text{-}\mu\text{A}/\text{cm}^2$ beam of 5-kV Ar⁺ ions in an Ar atmosphere of 6.5×10^{-3} Pa was used for sputtering. The specimens were resistance heated. The relationship between alloy composition and AES peak-to-peak ratios at appropriate transition energies has been established for Cu-Ni alloys by Goto *et al.*⁹ with use of coevaporation of the pure materials onto liquid-nitrogen-cooled substrates.

Four Auger peaks were monitored, Ni transitions at 102 and 716 eV (double peak) and Cu transitions at 106 and 920 eV. Although the Cu(106 eV) and Ni(102 eV) transitions overlap, ratios of these signals can also be converted into compositions.⁹ The escape depths of Auger electrons vary with energy. Electrons from the low-energy (~ 100 eV) transitions have a mean free path of $\sim 4 \text{ \AA}$, while those from the high-energy transi-

tions (700–1000 eV) have a mean free path of $\sim 15 \text{ \AA}$.¹⁰ The low-energy transitions are therefore more sensitive to the composition of the first few atom layers. The high-energy transitions average the composition over several additional atom layers.

The results of the *in situ* measurements can be summarized as follows. At temperatures below 300 °C, measurements of the low-energy Auger transitions ($\sim 100 \text{ eV}$) show that the Ni concentration in the top few atom layers rises quickly (within 1 minute) to ~ 60 -at.% Ni during sputtering, then remains constant during further sputtering. Above 300 °C, increasingly longer times are required before the Ni concentration becomes constant within experimental error. However, the measurements show that the composition of the top few atom layers eventually approaches ~ 60 -at.% Ni regardless of temperature. Ratios of the peak-to-peak heights of the Ni and Cu low-energy Auger transitions measured during sputtering at 600 °C are shown in Fig. 1 as a function of sputtering time.

Ratios of the Ni(716 eV) to Cu(920 eV) signals measured during sputtering at different elevated temperatures are shown as a function of sputtering time in Fig. 2. Measurements of these high-energy transitions obtained at 50 and 200 °C fall together on a line parallel to and just slightly be-

low (average ratio ~ 0.4) the 300 °C results. The corresponding Ni concentration^{8,9} is shown on the right-hand ordinate. At sputtering temperatures below 300 °C, the concentrations derived from the high- and low-energy transitions are practically identical. The average Ni concentration in the top several atom layers of the Cu-Ni (40 at.%) specimen rises quickly to ~ 60 -at.% Ni, then remains constant within experimental error during further sputtering. Above 300 °C, two additional effects appear. The degree of Ni enrichment determined from the high-energy transitions increases as the sputtering temperature is increased, and a slow, monotonic increase in the Ni concentration is observed for long periods of time as sputtering is contained at a fixed temperature.

The results from the low-energy Auger transitions demonstrate that the Ni concentration in the uppermost atom layers approaches an apparently steady-state value near 60 at.% early in the 2-h sputtering period, and that this value is practically independent of temperature between 50 and 600 °C. The results from the high-energy transitions (Fig. 2) reflect the average composition of a considerably thicker surface layer. They reveal that above 300 °C, the subsurface is enriched in Ni considerably more than the 60 at.% found for the uppermost atom layers, that the subsur-

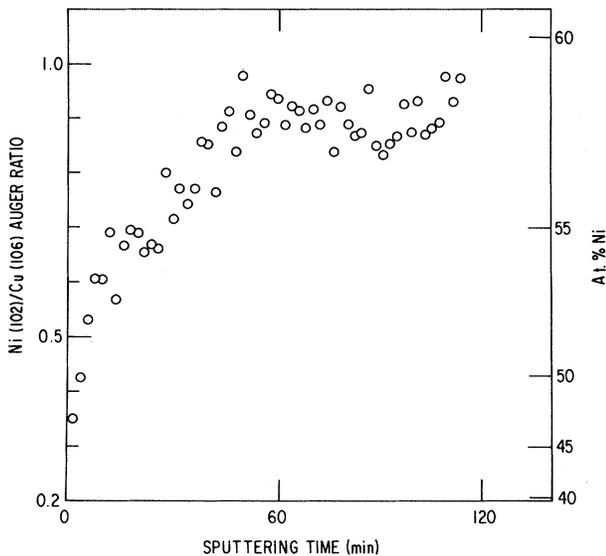


FIG. 1. Peak-to-peak ratios of the lower energy Ni(102 eV) and Cu(106 eV) Auger transitions as a function of time measured during sputtering at 600 °C. The corresponding Ni concentrations, indicated on the right, are in accord with Ref. 8.

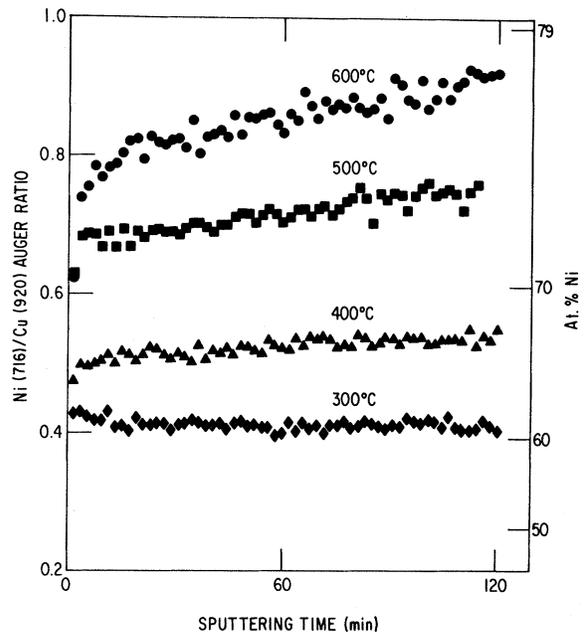


FIG. 2. Peak-to-peak ratios of the higher-energy transitions, Ni(716 eV) and Cu(920 eV), as a function of time during sputtering at different temperatures.

face Ni enrichment is still increasing after 2 h of sputtering, and that the degree of subsurface Ni enrichment increases markedly with temperature. If the sputtering gun is turned off while the specimen is maintained at an elevated temperature, the subsurface effects are observed to anneal out, clearly demonstrating that they are induced by the sputtering. Oxygen signals were below the detection limit ($\lesssim 1$ at.%) during sputtering.

To obtain further information about the extent of subsurface segregation induced by sputtering, the following additional data were taken. The sputtering and heating currents were stopped simultaneously after the 2-h sputtering period. At 600 °C, this produced a drop in specimen temperature to ~ 400 °C after 10 s, to ~ 300 °C after 60 s, and to below 50 °C after 1800 s. The Auger transitions of Cu(920 eV) and Ni(716 eV) were subsequently measured after sputtering the specimen at room temperature for various periods of time. The high-energy transitions were chosen because their larger magnitudes can be measured with greater accuracy. The results of these measurements are shown in Fig. 3. Compositions have not been included on the right-hand side of this figure to emphasize that these curves are not simple composition versus depth profiles. Both preferential sputtering and subsurface mixing occur during the room-temperature sputtering; they alter the concentration gradient induced during elevated-temperature sputtering. However, the depths of temperature-dependent sputter-induced changes can be deduced from the depths to which deviations occur between the curves obtained after sputtering at different elevated temperatures.

A comparison of the Auger ratios measured immediately after cooling to room temperature and at the end of the sputtering period (Fig. 2) shows that the cooling rate was not sufficient to prevent some readjustment of the surface composition during cooling from the higher temperatures. However, the most striking feature of Fig. 3 is the depth to which sputter-induced segregation occurs at the higher temperatures. Deviations from the bulk composition are evident for sputtering times at room temperature of up to $\sim 5 \times 10^3$ s for the specimen which had been sputtered for 2 h at 600 °C, and up to $\sim 1.5 \times 10^3$ s for the specimen which had been sputtered for 2 h at 500 °C. The sputtering rate used to obtain the results in Fig. 3 is ~ 6 Å/s. After 2 h of sputtering at 500 and 600 °C, subsurface Ni enrichment therefore extends to depths of ~ 1 and 3 μm , re-

spectively. These large depths indicate that appreciable diffusion occurs at temperatures above 300 °C due to mobile point defects created by the sputtering process.

These results lead to the following description of compositional changes which occur in the Cu-Ni alloy during sputtering. Both the low- and high-energy Auger transitions, which sample depths of a few and several atom layers, respectively, yield the same degree of Ni enrichment after sputtering for short periods of time at temperatures up to 300 °C. This result has previously been reported for room-temperature sputtering,¹¹ and leads to the conclusion that sputtering below 300 °C quickly produces a steady-state altered layer whose composition is constant over a depth which is greater than the ~ 15 -Å escape depth of the high-energy transitions. Although the surface concentration eventually approaches a value of ~ 60 -at.% Ni regardless of temperature, Ni enrichment in the subsurface region exceeds that of the surface during sputtering above 300 °C. To our knowledge, sputter-induced subsurface segregation in excess of that found at the surface has not been observed or predicted previously. We believe that the subsurface Ni enrichment peak results from Gibbsian segregation of Cu towards the alloy surface.

Substantial surface enrichment of copper is known to occur at equilibrium in Cu-Ni alloys.^{10,12} At temperatures where atomic mobility is sufficient to compete with the rate of surface recession during sputtering, Gibbsian segregation will therefore tend to enrich the outermost atom layer in Cu. At higher temperatures then, excess Cu is driven to the surface via the Gibbsian adsorption driving force. This excess Cu is continually removed by preferential sputtering. Eventually, sufficient Cu depletion (Ni enrichment) occurs in the subsurface region so that the rate at which the additional Cu is supplied to the surface is reduced, and the composition of the outermost layer approaches the same value for all temperatures. At equilibrium, the Gibbsian adsorption layer is extremely narrow,¹² extending only one or two atom layers into the specimen. As Cu depletion occurs in the atomic layers immediately beneath the surface layer, a concentration gradient begins to build toward the interior of the specimen. This gradient provides a long-range driving force for Cu diffusion toward the near-surface, Cu-depleted zone. Sputter-induced point defects enhance the diffusion. The result is a subsurface maximum in the Ni enrichment (Cu

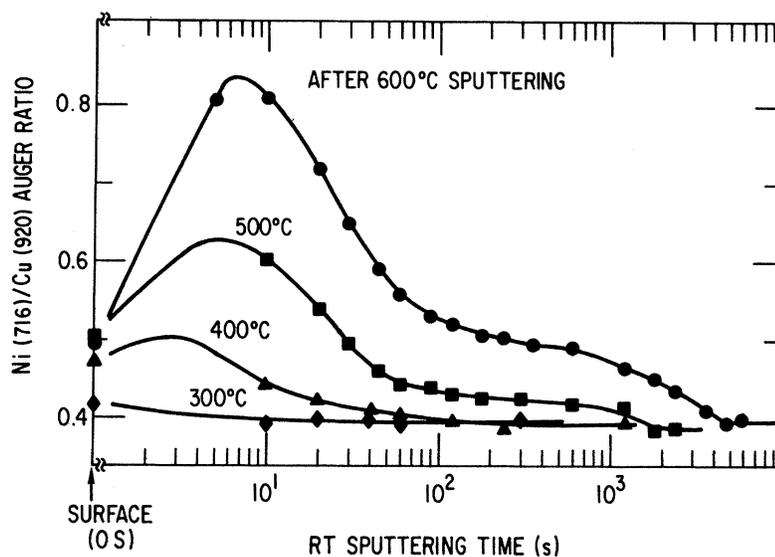


FIG. 3. Peak-to-peak ratios of the higher-energy transitions measured after sputtering for various periods of time at room temperature. Each specimen had previously been sputtered for 2 h at the indicated temperature. Above 300°C, an increase in the sputtering temperature produces an increase in the depth of Ni enhancement.

depletion), followed by a long Ni-enriched (Cu-depleted) tail which penetrates deep into the specimen. Because of the deep penetration of the gradient, long sputtering times are required to reach steady state at the higher temperatures.

This work was supported by the U. S. Department of Energy.

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¹A. Joshi, in *Interfacial Segregation*, edited by W. C. Johnson and J. M. Blakely (American Society for Metals, Metals Park, Ohio, 1979), p. 39.

²W. Bauer, *J. Nucl. Mater.* **76** & **77**, 3 (1978).

³H. Shimizu, M. Ono, and K. Nakayama, *Surf. Sci.*

36, 817 (1973).

⁴P. S. Ho, J. E. Lewis, H. S. Wildman, and J. K. Howard, *Surf. Sci.* **57**, 393 (1976).

⁵Z. L. Liao, J. W. Mayer, W. L. Brown, and J. M. Poate, *J. Appl. Phys.* **49**, 5295 (1978).

⁶P. S. Ho, *Surf. Sci.* **72**, 253 (1978).

⁷Nghi Q. Lam, G. K. Leaf, and H. Wiedersich, to be published.

⁸L. E. Davis, N. C. McDonald, P. W. Palmberg, G. E. Riach, and R. E. Weber, *Handbook of Auger Electron Spectroscopy* (Physical Electronics Industries, Eden Prairie, New Mexico, 1976), 2nd edition.

⁹K. Goto, T. Koshikawa, K. Ishikawa, and R. Shimizu, *J. Vac. Sci. Technol.* **15**, 1695 (1978).

¹⁰C. R. Helms and K. Y. Yu, *J. Vac. Sci. Technol.* **12**, 276 (1975).

¹¹T. Koshikawa, K. Goto, N. Saeki, R. Shimizu, and E. Sugata, *Surf. Sci.* **79**, 461 (1979).

¹²Yee S. Ng, T. T. Tsong, and S. B. McLane, Jr., *Phys. Rev. Lett.* **42**, 588 (1979).