better statistics in the direct elimination method. No special difficulty is expected to improve the accuracy when needed.

There are some difficult unanswered questions about the accuracy of the transformation formulas (5) and (6) themselves. Note that improving them means keeping not only higher-order terms but also more complicated forms of interactions such as next-nearest neighbor and longer-range ones. As a rudimentary check, we solved the four-spin problem defined by (4) with $K_1 = K_2$ exactly and by the elimination process. The agreement is very good if $\frac{1}{2}J \gtrsim K$. One thus expects good answers if $P(K)$ is well spread out for $K \sim J$, i.e., not concentrated near the maximum value. The transformation was applied to a uniform model (i.e., all K_r's are equal) to eliminate two of every three spins. The ground-state energy so obtained was surprisingly good.[6]

In closing, we note that if $P(K)$ is nonsingular, the power-law T dependence (3) is absent for the *classical* model,[1,7] which is defined by replacing the operators $\vec{S}_r$ in (1) by classical unit vectors. The classical susceptibility $\chi_{cl} \sim P(0)\ln(1/T)$ is only weakly divergent for $T \to 0$. [For a singular $P(K) \sim K^{c-1}$, however, $\chi_{cl} \sim T^{c-1}$ (see Ref. 5).] We are aware of the belief in the literature that χ_{cl} should always be an upper bound for the quantum

mechanical χ. This belief is, however, incorrect, as is easily checked by explicitly calculating χ and χ_{cl} for the four-spin system with the Hamiltonian H_{12} in Eq. (4). One finds that when $K_1K_2/2TJ$ and T/J are small, $\chi > \chi_{cl}$. The physical reason is that the quantum mechanical states are discrete. For small T, $\vec{S}_1$ and $\vec{S}_2$ are "frozen" in a singlet state and $\vec{S}_1'$ and $\vec{S}_2'$ become essentially free. This does not happen for the classical case where the excitation energy has a continuous distribution.

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Sputter-Induced Subsurface Segregation in a Cu-Ni Alloy

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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 changes[5] at elevated tempera-

tures. In recent models of the sputtering phe-
nomenon developed by Ho[6] and by Lam, Leaf,
and Wiedersich,[7] subsurface effects are predicted
at temperatures where diffusion can promote
equilibrium between the altered surface composi-
tion 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
~ 10 μA was used to excite the transitions. A 195-
μA/cm^2 beam of 5-kV Ar$^+$ ions in an Ar atmos-
phere of 6.5×10^{-3} Pa was used for sputtering.
The specimens were resistance heated. The re-
lationship between alloy composition and AES
peak-to-peak ratios at appropriate transition en-
ergies 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 transi-
tions at 102 and 716 eV (double peak) and Cu tran-
sitions 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 composi-
tions.[9] The escape depths of Auger electrons
vary with energy. Electrons from the low-energy
(~ 100 eV) transitions have a mean free path of
~ 4 Å, while those from the high-energy transi-
tions (700–1000 eV) have a mean free path of ~ 15
Å.[10] The low-energy transitions are therefore
more sensitive to the composition of the first few
atom layers. The high-energy transitions aver-
age 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 (~ 100 eV) show that the Ni concentra-
tion in the top few atom layers rises quickly
(within 1 minute) to ~ 60-at.% Ni during sputter-
ing, then remains constant during further sputter-
ing. 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 sput-
tering 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
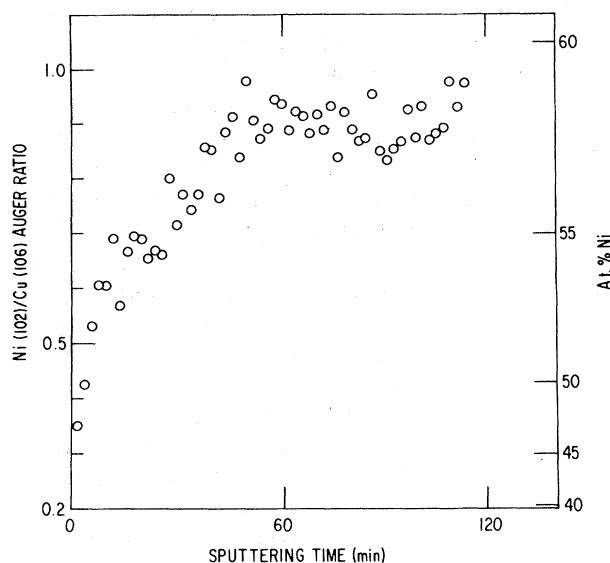temperatures are shown as a function of sputter-

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

ing 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
side of this figure to emphasize that these curves
are not simple composition versus depth profiles.
Both preferential sputtering and subsurface mix-
ing occur during the room-temperature sputter-
ing; they alter the concentration gradient in-
duced 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 ele-
vated 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 compo-
sition during cooling from the higher tempera-
tures. However, the most striking feature of Fig.
3 is the depth to which sputter-induced segrega-
tion occurs at the higher temperatures. Devia-
tions from the bulk composition are evident for
sputtering times at room temperature of up to
~ 5×10^3 s for the specimen which had been sput-
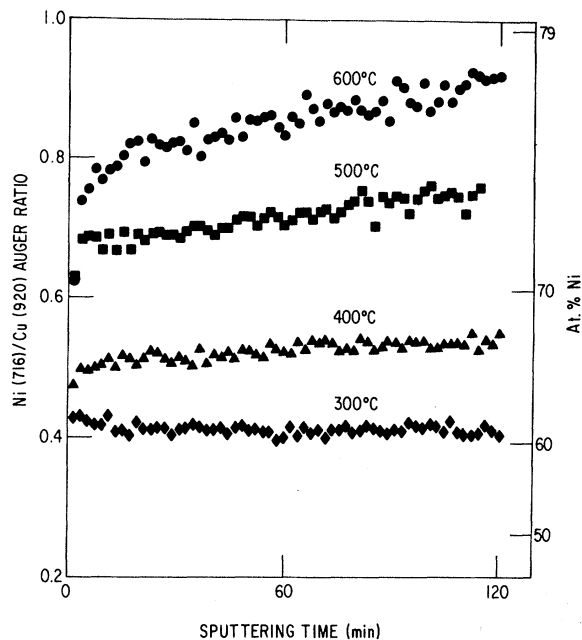tered for 2 h at 600 °C, and up to ~ 1.5×10^3 s for

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.

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, respectively. 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 sub-

surface segregation in excess of that found at 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 subsurface 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 ($\lesssim$ 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 surface has not been observed or predicated pre-
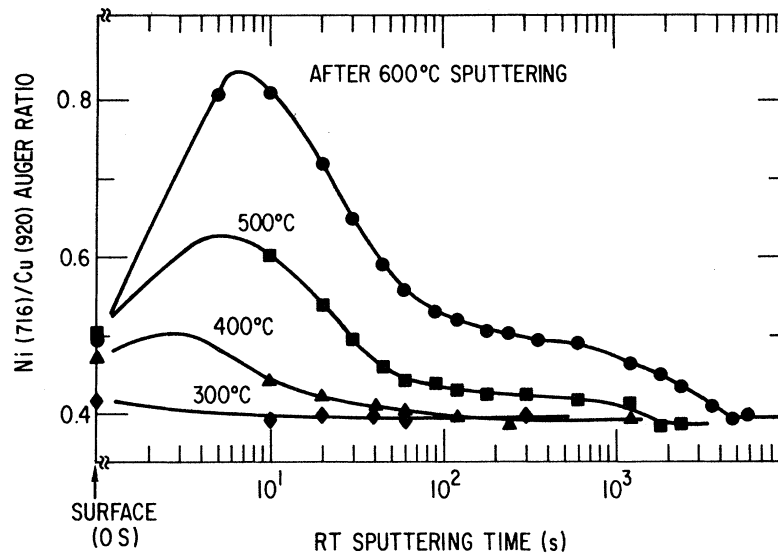
FIG. 3. Peak-to-peak ratios of the higher-energy transitions measured after sputtering for various periods of time at room temperature. Each specimen had previously been sputtered for 2 h at the indicated temperature. Above 300°C, an increase in the sputtering temperature produces an increase in the depth of Ni enhancement.

viously. 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 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.

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