BOMBARDMENT-INDUCED SEGREGATION AND REDISTRIBUTION*

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ABSTRACT

During ion bombardment, a number of processes can alter the compositional distribution and microstructure in near-surface regions of alloys. The relative importance of each process depends principally on the target composition, temperature, and ion characteristics. In addition to displacement mixing leading to a randomization of atomic locations, and preferential loss of alloying elements by sputtering, which are dominant at relatively low temperatures, several thermally-activated processes, including radiation-enhanced diffusion, radiation-induced segregation and Gibbsian adsorption, also play important roles. At elevated temperatures, nonequilibrium point defects induced by ion impacts become mobile and tend to anneal out by recombination and diffusion to extended sinks, such as dislocations, grain boundaries and free surfaces. The high defect concentrations, far exceeding the thermodynamic equilibrium values, can enhance diffusion-controlled processes, while persistent defect fluxes, originating from the spatial non-uniformity in defect production and annihilation, give rise to local redistribution of alloy constituents because of radiation-induced segregation. Moreover, when the alloy is maintained at high temperature, Gibbsian adsorption, driven by the reduction in free energy of the system, occurs even without irradiation; it involves a compositional perturbation in a few atom layers near the alloy surface. The combination of these processes leads to the complex development of a compositionally-modified layer in the subsurface region. Considerable progress has been made recently in identifying and understanding the relative contributions from the individual processes under various irradiation conditions. In the present paper, selected examples of these different phenomena and their synergistic effects on the evolution of the near-surface compositions of alloys during sputtering and ion implantation at elevated temperatures are discussed.

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1. Introduction

The effect of ion bombardment on the near-surface composition of alloys has created considerable excitement in recent years and become the subject of many detailed investigations. The current interest in surface compositional modifications by energetic particles was motivated by the importance of this phenomenon in many areas of materials science. These include routine application of ion sputtering to depth-profile the composition of multicomponent materials, increasing use of ion-beam mixing and ion implantation to tailor new materials with improved hardness, wear, corrosion resistance, catalysis, adhesion and/or reflectance, and concern about plasma contamination in fusion devices by sputtered particles from walls and limiters.

Surface composition alterations by preferential sputtering and displacement mixing near room temperature have been observed in many alloy systems. Experimental measurements and understanding of this phenomenon have been reviewed in detail by Andersen [1], Betz [2], Kelly [3,4], and Betz and Wehner [5]. At high temperatures where additional thermally-activated processes are important, the problem of ion bombardment-induced alloy composition changes becomes more complex [1,6-14]. For example, during elevated-temperature bombardment, nonequilibrium point defects induced by ion impacts are mobile and interact among themselves, with solute elements and

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with extended sinks, such as dislocations, grain boundaries and free surfaces. The high defect concentrations can enhance diffusion-controlled processes, while persistent defect fluxes, resulting from the spatial nonuniformity in defect production and annihilation, can induce significant redistribution of alloying elements because of radiation-induced segregation. Furthermore, when the alloy is heated to a sufficiently high temperature, Gibbsian adsorption (i.e. thermal segregation of alloy constituents to surfaces and interfaces, driven by the reduction in free energy of the system) occurs even without irradiation. Gibbsian adsorption can be strong and achieves equilibrium more rapidly at higher temperature since diffusion is required. This segregation gives rise to a perturbation in the alloy composition in the outermost atom layers near the surface, and thus affects the boundary conditions of the bombardment-induced surface modification problem. The combination of these processes leads to the complex development of a compositionally-modified layer, whose thickness and composition depend on bombardment time, the type of alloy, the target temperature, and the species, energy and flux of the incoming ions. Significant progress has been made over the past five years in identifying and understanding their synergistic effects. The predictions of current models of bombardment-induced surface composition changes are qualitatively in agreement with existing experimental data. Quantitative predictions are still rather uncertain because many of the physical parameters required for the calculations are not well known.

In the present paper, a simple description of the kinetics of the processes involved is given, and selected examples of recent important progress are reviewed. The discussion will be limited to elevated-temperature bombardments of metallic alloys, with primary emphasis placed on

phenomenological modeling and direct measurements of surface and subsurface compositional changes.

2. Basic processes

In order to discuss intelligently the complex interplay of the diverse physical processes in changing alloy subsurface compositions during ion bombardment, elucidated by recent phenomenological model studies and experimental investigations, a brief characterization of the individual processes is presented in this section. We will proceed from the predominantly athermal processes, namely preferential sputtering and displacement mixing, to the thermally-activated processes, including radiation-enhanced diffusion, radiation-induced segregation, and Gibbsian adsorption. Each of these processes has been investigated both experimentally and theoretically with various degrees of sophistication in the past (see, for example, [1,5,10] and references therein). A good physical understanding of them already exists, even though only a limited number of studies has specifically addressed the phenomenon of bombardment-induced surface modifications.

2.1 Preferential sputtering (PS)

At frequently used ion energies, i.e., between ~ 0.5 and 500 keV, the slowing-down of the incident ions in the target material generates displacement cascades and nonequilibrium point defects (interstitials and vacancies). The cascades are the physical origin of sputtering, when they take place in the vicinity of the surface, imparting to near-surface atoms sufficient energy and momentum in the outward direction to overcome their surface binding energy [14,15]. There are strong reasons to expect sputtering to be preferential in most alloy systems, on the basis of mass and surface

binding effects. The former effect results from differences in momentum transfers to atoms of unequal masses. The latter effect arises because the various alloy components, in general, have different surface binding energies, and, hence, require different amounts of energy to escape from the surface. The resulting preferential loss of certain alloying elements by sputtering leads to compositional changes, the spatial extent of which depends on the diffusional processes. Initially, as a consequence of PS, the compositions of the flux of atoms sputtered from the alloy surface and of the bulk are generally quite different. However, after long bombardment times, the steady-state composition of the sputtered-atom flux becomes equal to that of the bulk of a thick target, as dictated by the matter-conservation law. An extensive review of PS effects has been given recently by Betz and Wehner [5].

Using the phenomenological description of PS, we define the total number of k-atoms ejected from an alloy target per incident ion, Y_k , as follows:

$$Y_k = \sum_{n=1}^{\infty} P_k^{(n)} C_k^{(n)} \quad (1)$$

where $P_k^{(n)}$ is the effective yield of k-atoms per unit concentration per ion, and $C_k^{(n)}$ is the atomic fraction of k-atoms in the nth layer. The distinction between "true" PS or primary effects and secondary effects in alloy sputtering is made explicit in this definition. The factor $P_k^{(n)}$ contains all the physical variables that are directly related to the individual sputtering events (i.e., the type and energy of the incident ion, the type of sputtered atom and its surface binding energy), whereas secondary effects arising from, e.g., Gibbsian adsorption and radiation-induced segregation influence Y_k because they affect the alloy composition in the near-surface region, $C_k^{(n)}$. Hence, PS is said to occur whenever $P_k^{(n)} \neq P_l^{(n)}$ in any nth layer.

From a practical point of view, the sputtered atoms come predominantly from a rather shallow layer, as shown by Sigmund [14] and in more detail by Falcone and Sigmund [16]. For low-energy sputtering, the contributions decrease approximately exponentially with depth, with a decay length on the order of two atomic layers. Thus, eq. (1) can be replaced by a good approximation:

$$Y_k = P_k^{(1)} C_k^{(1)} + P_k^{(2)} C_k^{(2)} . \quad (2)$$

If we define γ as the probability for atoms in the second layer to contribute to the sputtered-atom flux, then eq. (2) can be rewritten as

$$Y_k = S_k [(1-\gamma)C_k^{(1)} + \gamma C_k^{(2)}] \quad (3)$$

with S_k being the sputtering coefficient of the k-component, i.e. the number of k-atoms sputtered per incident ion per unit concentration. S_k is not necessarily the coefficient for the pure element and many depend on the alloy composition.

Now, considering a binary alloy AB bombarded by a flux of ions ϕ (ions/cm²s), the total rate at which atoms of both components are removed per unit area is

$$\begin{aligned} dN/dt &= \phi (Y_A + Y_B) \\ &= \phi \left\{ S_A [(1-\gamma)C_A^{(1)} + \gamma C_A^{(2)}] + S_B [(1-\gamma)C_B^{(1)} + \gamma C_B^{(2)}] \right\} \end{aligned} \quad (4)$$

Consequently, the alloy surface recedes at a velocity or sputtering rate

$$\dot{\delta} \equiv d\delta/dt = \Omega dN/dt \quad (5)$$

where Ω is the average atomic volume and δ is the total surface displacement, i.e., the thickness of the surface layer removed by sputtering. Note that $\dot{\delta}$ is time dependent because PS, Gibbsian adsorption and radiation-induced segregation make $C_A^{(n)}$ and, hence, $C_B^{(n)} \equiv 1 - C_A^{(n)}$ time dependent. Therefore, from a theoretical point of view, $\dot{\delta}$ and $C_A^{(n)}$ must be calculated in a mutually consistent fashion.

2.2 Displacement mixing (DM)

In addition to sputtering atoms from the surface, the displacement cascades also give rise to DM, which comprises recoil implantation and cascade mixing. Recoil implantation occurs when the lighter atoms are preferentially transported in the beam direction due to preferential momentum transfer, whereas cascade mixing is a random-walk process resulting from the movement of higher-order recoils [17-21]. Both recoil implantation and cascade mixing have been observed in recent investigations of marker-layer shift and broadening during ion bombardment. Generally, the effect of cascade mixing has been found to be much larger than that of recoil implantation [18,19,22]. To a good approximation, DM can be assumed to be temperature independent, since the energies involved in the cascades are substantially greater than thermal energies. The basic aspects of DM have been reviewed recently by Averback [23].

To the degree that the mixing process can be considered as a random walk of atoms, a simplified quantification of DM can be formulated within a diffusion model [17,20,21]. The displacement-induced diffusion coefficient can be expressed in the well-known form

$$D_k^* = \langle R^2 \rangle / 6t \quad (6)$$

where $\langle R^2 \rangle$ is the mean square distance an atom has traveled in a time interval t , during which it has made N uncorrelated jumps. If we define $\langle r^2 \rangle$ as the mean square length of the individual jumps, then the coefficient D_k^* becomes

$$D_k^* = \langle r^2 \rangle \nu / 6 \quad (7)$$

with $\nu \equiv N/t$ being the site-exchange frequency. Using a semi-empirical approach, this frequency is related to the defect-production rate K (displacements per atom per second, dpa/s) by $\nu = \epsilon K$, where ϵ is the total number of site replacements per displacement (i.e. per Frenkel pair, created). Recent molecular-dynamics calculations indicate that $\epsilon \approx 35$ for low primary recoil energies in Cu [25]. In general, the larger the recoil energy, the higher the value of ϵ , because the displacement cascades are larger. On the other hand, the mean square jump distance $\langle r^2 \rangle$ should be a few times the nearest-neighbor distance λ^2 , because a fraction of the atoms will be relocated by more than a nearest-neighbor distance for larger recoil momenta in off-close-packed directions. Thus, we can write D_k^* in an approximate form

$$D_k^* \approx \lambda^2 \eta K / 6 \quad (8)$$

where η should be on the order of 10^2 - 10^3 . Values of η within this range have been derived from experimental measurements of ion beam mixing [23] and of disordering rates in ordered alloys [26,27] at low temperatures. The net flux of A-atoms across a fixed lattice plane can then be calculated by

$$\Omega J_A^* = -D_A^* \nabla C_A \quad (9)$$

It is noted that the product ηK and, hence, the effective diffusion coefficient D_k^* are assumed to be temperature independent, and that replacement collisions are always expected to randomize the alloy system. However, events that take place after the collisional phase of the cascade (i.e., at $\sim 10^{-12}$ s), such as induced defect migration and/or induced recombination are affected by thermodynamic forces. These induced "quasi-thermal" diffusion processes within the cascades may give rise to the frequently observed "chemical" effects in ion-beam mixing, where the chemical affinity and/or heat of mixing can influence the rate of intermixing [28-31].

2.3 Radiation-enhanced diffusion (RED)

As mentioned above, DM of alloying elements is the dominant atom-transport mechanism during bombardment at low temperatures where vacancies are immobile. At elevated temperatures, however, the thermally-activated diffusional process becomes dominant. Generally, between ~ 0.2 and $\sim 0.6 T_m$ (where T_m is the absolute melting point) radiation-induced point defects are mobile, and their concentrations can easily exceed the thermodynamic-equilibrium values by several orders of magnitude. Since the total local diffusion coefficients of A and B atoms in the alloy are proportional to the concentrations of vacancies (v) and interstitials (i), C_v and C_i , i.e., [32,33]

$$D_A = d_{Av} C_v + d_{Ai} C_i$$

and

$$D_B = d_{Bv} C_v + d_{Bi} C_i,$$

(10)

diffusion of the alloying elements is strongly enhanced by irradiation. Here, in describing the enhancement of diffusion in a form that can conveniently be extended to the treatment of radiation-induced segregation in the next section, we introduce the diffusivity coefficients d_{Av} , d_{Bv} , d_{Ai} and d_{Bi} , which contain the kinetic characteristics for diffusion of the elements A and B via vacancies and interstitials, respectively. The coefficients d_{kj} are defined as

$$d_{kj} = \lambda_j^2 Z_j \nu_{kj} / 6 \quad (11)$$

where $k = A$ or B , $j = i$ or v , λ_j and Z_j are the elementary jump distance and the coordination number of defect j , respectively, and ν_{kj} is the effective exchange jump frequency of a k - j pair. It is noted that, even though the diffusivity coefficients are assumed to be spatially independent, the total diffusion coefficients, given by eqs. (10), depend on spatial coordinates via the concentrations of atoms and defects.

At higher temperatures (above $\sim 0.6 T_m$), the concentration of equilibrium vacancies becomes larger than that of radiation-induced defects and the normal thermal diffusion via vacancy mechanism dominates the atom transport process. Several detailed reviews of the existing theories and experimental measurements of RED have been published over the past decade [34-37].

2.4 Radiation-induced segregation (RIS)

Concurrently with RED, RIS takes place in the alloy during irradiation, because the same defects that are responsible for RED can also induce segregation of alloying elements. The physical origin for RIS is as follows. At sufficiently high temperatures, those mobile point defects that escape mutual recombination anneal out by diffusion to extended sinks. Since

the defect fluxes are always associated with fluxes of atoms, any preferential association of defects with a particular alloy component and/or preferential participation of a component in defect diffusion will couple a net flux of the alloying element to the defect fluxes. This preferential defect-solute flux coupling will lead to a spatial redistribution of the alloy composition during irradiation. Thus, RIS can produce concentration gradients in initially homogeneous alloys even in the absence of PS and/or Gibbsian adsorption. Model descriptions of RIS in dilute alloys [38], concentrated binary [32] and ternary [39] alloys are available, and extensive reviews of RIS and its effects on alloy microstructure have been published recently [33,40,41].

A simple treatment of RIS, proposed by Wiedersich et al. [32], is based on the concept of partitioning the defect fluxes into those occurring by exchange with the various alloy components, and the atom fluxes into those taking place via vacancies and interstitials. In a binary alloy AB, for example, the fluxes of atoms and defects with respect to a coordinate system fixed on the crystal lattice can thus be expressed in terms of concentration gradients, and partial and total diffusion coefficients of all the species present:

$$\Omega J_V = (d_{AV} - d_{BV})C_V \alpha \nabla C_A - D_V \nabla C_V, \quad (12a)$$

$$\Omega J_I = -(d_{AI} - d_{BI})C_I \alpha \nabla C_A - D_I \nabla C_I, \quad (12b)$$

$$\Omega J_A = -D_A \alpha \nabla C_A - C_A(d_{AI} \nabla C_I - d_{AV} \nabla C_V), \quad (12c)$$

and

$$\Omega J_B = -D_B \alpha \nabla C_B - C_B(d_{BI} \nabla C_I - d_{BV} \nabla C_V), \quad (12d)$$

Here, α is the thermodynamic factor which is related to the activity coefficients of the alloy components and differs from unity when the alloy is no longer ideal, and D_V , D_I , and D_A and D_B (already defined in eqs. (10)) are

the total diffusion coefficients of the defects and alloy constituents, respectively, which can be described in the general form

$$D_j = \sum_k d_{kj} C_k \quad (j = i, v \text{ and } k = A, B)$$

and

$$D_k = \sum_j d_{kj} C_j ,$$
(13)

with d_{kj} being given by eq. (11). These coefficients are spatially dependent. As expressed in eqs. (12), the defect fluxes are driven by the A- and B-atom concentration gradients as well as by their own concentration gradients. Similarly, the atom fluxes are induced by both the defect concentration gradients and the atom chemical-potential gradients. The first terms on the right-hand side of eqs. (12a) and (12b) represent the Kirkendall effects from the vacancy and interstitial diffusion mechanisms, respectively. These terms have opposite signs simply because the interstitial flux induces an atom flux in the same direction, whereas the vacancy flux generates a flux of atoms in the opposite direction.

Some predictions can be derived from the flux equations, eqs. (12), for the segregation trends, by assuming that quasi-steady state with respect to the defect buildup has been achieved. At quasi-steady state, $J_v = J_i$, the total flux of A atoms is given by [33]

$$J_A = -\bar{D} \nabla C_A - \hat{D} \left(\frac{d_{Ai}}{d_{Bi}} - \frac{d_{Av}}{d_{Bv}} \right) \nabla C_d \quad (14)$$

where the subscript "d" denotes either vacancy or interstitial,

$\bar{D} = (d_{Av} C_A D_B + d_{Bv} C_B D_A) / (d_{Av} C_A + d_{Bv} C_B)$, and $\hat{D} = (d_{Bv} d_{Bi} C_A D_B) / (d_{Av} C_A + d_{Bv} C_B)$.

At short irradiation times, the concentration gradient ∇C_A in an initially

homogeneous alloy is rather small; therefore, the direction and magnitude of J_A are controlled by the last term in eq. (14). For example, the net flux of A atoms will be in the same direction as the defect fluxes if $d_{Ai}/d_{Bi} > d_{Av}/d_{Bv}$ or $v_{Ai}/v_{Bi} > v_{Av}/v_{Bv}$ via eq. (11). In this case, the A component will be enriched in any region where there is an influx of defects. On the contrary, if $v_{Ai}/v_{Bi} < v_{Av}/v_{Bv}$, the net A-atom flux will occur in the direction opposite to the defect fluxes, and the element A will be depleted in regions where an influx of defects exists. It is noted that the magnitude of J_A will be maximum when A atoms migrate exclusively via an interstitial mechanism and B atoms via vacancies.

If the defects - either vacancies or interstitials - interact strongly with a particular alloy component, say A atoms, to form tightly-bound, but mobile, atom-defect complexes, then the net flux of A atoms and the defect fluxes will also be in the same direction. Any preferential participation of A atoms in the interstitial population can be accounted for by incorporating into the diffusivity coefficients d_{Ai} and d_{Bi} [eq. (11)] factors that represent the nonrandom occupation of interstitials by A and B atoms:

$$C_{iA} = C_i C_A \exp(H_{iA}^b/kT) / [C_A \exp(H_{iA}^b/kT) + C_B]$$

and

(15)

$$C_{iB} = C_i C_B / [C_A \exp(H_{iA}^b/kT) + C_B],$$

where k is the Boltzmann constant, T is the absolute temperature, and H_{iA}^b is the effective A-interstitial binding energy.

On the other hand, in order to account for atom transport by tightly-bound, mobile A atom-vacancy (vA) complexes in dilute alloys, additional terms derived from the contribution of the complex flux $J_{vA} = -D_{vA} \nabla C_{vA}$ must be

included in eqs. (12a, c and d) for J_v , J_A and J_B :

$$\begin{aligned}\Omega J_v &= [(d_{Av} - d_{Bv})\alpha - K_{vA} D_{vA}] C_v \nabla C_A \\ &\quad - (D_v + K_{vA} D_{vA} C_A) \nabla C_v \\ \Omega J_A &= - [\alpha D_A + (1-2C_A) K_{vA} D_{vA} C_v] \nabla C_A \\ &\quad - d_{Ai} C_A \nabla C_i + C_A [d_{Av} - (1-2C_A) K_{vA} D_{vA}] \nabla C_v\end{aligned}\quad (16)$$

and

$$\begin{aligned}\Omega J_B &= -[\alpha D_B + 2C_B K_{vA} D_{vA} C_v] \nabla C_B \\ &\quad - d_{Bi} C_B \nabla C_i + C_B [d_{Bv} + 2C_B K_{vA} D_{vA}] \nabla C_v,\end{aligned}$$

where D_{vA} is the diffusion coefficient of the vA complex, $D_{vA} = \lambda^2 \nu_{vA}/6$ (ν_{vA} being the complex jump frequency), and K_{vA} is the rate constant for the formation of vA complexes in equilibrium, $K_{vA} = 12 \exp(R_{vA}^b/kT)$ (R_{vA}^b is the complex binding energy). It should be pointed out that for concentrated alloys, atom transport by tightly-bound vacancy-solute complexes is unimportant, and eqs. (12) are applicable.

2.5 Gibbsian adsorption (GA)

When the alloy system evolves towards equilibrium, a thermodynamic driving force gives rise to either enrichment or depletion of the A component at the surface, depending on whether the heat of absorption for the element A is negative or positive [42]. This thermal-segregation phenomenon is known as GA, which tends to minimize the surface free energy. In the absence of sputtering, GA achieves equilibrium after a certain time which is mainly controlled by the temperature. The higher the temperature, the shorter this time is. At equilibrium, the atom fractions of A and B in the "surface phase" (assumed to be confined to the outermost atom layer), $C_A^{(1)}$ and $C_B^{(1)}$, are related to the respective atom fractions in the "bulk phase", C_A^b and C_B^b , by

the relationship [42]

$$C_A^{(1)}/C_B^{(1)} = (C_A^b/C_B^b) \exp(-\Delta G_a/kT) \quad (17)$$

where $\Delta G_a = \Delta H_a - T\Delta S_a$ is the GA free energy, with ΔS_a and ΔH_a being the entropy and enthalpy (or heat) of adsorption for the A component, respectively.

During the concentration buildup towards equilibrium, the net flux of A atoms into the surface atomic plane, j_A , is calculated by

$$j_A = (v_A^{b(1)} C_A^b C_B^{(1)} - v_A^{(1)b} C_A^{(1)} C_B^b) \xi \quad (18)$$

where ξ is the atomic layer thickness, and the surface-to-bulk jump frequency $v_A^{(1)b}$ is related to the bulk-to-surface jump frequency $v_A^{b(1)}$ by the following equation derived from the condition of equilibrium ($j_A = 0$)

$$v_A^{(1)b} = v_A^{b(1)} \exp(\Delta G_a/kT) . \quad (19)$$

Since $v_A^{b(1)}$ is a function of jump frequencies and "bulk" concentrations of defects,

$$v_A^{b(1)} = v_{Av} C_v^b + v_{Ai} C_i^b , \quad (20)$$

GA can be strongly enhanced by irradiation at temperatures below $\sim 0.6 T_m$. Furthermore, since GA involves a perturbation of the alloy composition in one or two atomic layers near the surface, i.e. to a depth comparable to the sputter depth [16], the extraction of information about PS from measurements

of surface compositional changes requires a good understanding of the interplay of these GA and PS processes.

Equation (17) indicates that the plot of $\ln[C_A^{(1)}/C_B^{(1)}]$ versus $1/T$ is a straight line, whose slope and intercept are related to ΔH_a and ΔS_a . The temperature dependence of GA has been measured recently on a number of alloys [11,12,43,44] using ion scattering spectroscopy (ISS), which is a technique extremely sensitive to the first surface atom layer. Some typical results are presented in fig. 1 for Ni-Cu and Ni-Au alloys [11,12]. The values of ΔH_a and ΔS_a deduced are tabulated in table 1, together with the data obtained recently for a Ni-9.5 at.% Si alloy [44]. The ISS technique was first employed to demonstrate GA of Cu in the Ni-Cu system by Brongersma et al. [45,46]. Other analytical techniques such as Auger electron spectroscopy (AES) [47-50] and time-of-flight atom-probe field-ion microscope (FIM) [51-53] were also used to study GA. Unfortunately, owing to the finite escape depth of the Auger electrons, AES cannot yield definitive information on the composition in the outermost atom layer. The FIM technique, on the other hand, provides information about the first surface layer composition; however, FIM measurements can easily be affected by thermal segregation of interstitial impurities, such as S and P, since it is difficult to subject the field emission tip of the alloy specimens used to "cleaning" treatments by intermittent sputterings at high temperatures [54].

3. Compositional redistribution in alloys during inert-gas ion sputtering

3.1 Theoretical modeling

Taking into account the effects of all the processes described above, we can cast the bombardment-induced composition modification phenomenon into a phenomenological model by formulating the following set of coupled partial

differential equations describing the temporal and spatial evolution of defect and atom concentrations

$$\partial C_V / \partial t = -\nabla \cdot J_V + K - R \quad (21a)$$

$$\partial C_I / \partial t = -\nabla \cdot J_I + K - R \quad (21b)$$

and

$$\partial C_A / \partial t = -\nabla \cdot (J_A + J_A^*) \quad (21c)$$

where R is the total local rate of defect losses by recombination and annihilation at internal sinks. The equation for the B component is not needed because $C_B \approx 1 - C_A$. The accumulation of incident chemically-inactive ions is neglected.

The time-dependent defect and atom distributions can be determined by solving eqs. (21) numerically for appropriate initial and boundary conditions. For the semi-infinite geometry with a moving boundary, the sputtered surface can be mathematically immobilized by the transformation $z = 1 - \exp[-\beta(x-\delta)]$ of the physical space $\delta \leq x < \infty$ to a reduced space $0 \leq z < 1$ [6,55], with β being a scaling factor. The inclusion of GA in the model requires, however, that the first two atomic layers be treated in a discrete fashion [9]. Below the second layer, the evolution of concentrations in time and space are calculated using a continuum formalism [6,55].

Model calculations have been carried out to predict the dependence of surface and subsurface compositions of bombarded alloys on several material and irradiation variables, as well as to fit and interpret experimental measurements. Although the effects of each individual process or of a combination of processes on the compositional modification in model alloys can be studied in detail [8,9,56], because the present phenomenological approach

permits straightforward variation of the primary physical parameters, a quantitative comparison of theoretical calculations with experiments is difficult at present, since many of these parameters are still virtually unknown, especially for alloys [11,12,44,57,58]. For this reason, in order to fit the experimental measurements, a large number of calculations must be performed using various combinations of physical parameters. Semi-quantitative modeling of bombardment-induced compositional redistributions in Ni-Cu [11], Ni-Au [12] and Ni-Si [44] alloys undergoing 3-keV Ne⁺ sputtering has been undertaken recently. Some selected examples are shown in the following for a Ni-40 at.% Cu alloy. In the calculations, the energies of vacancy migration via Ni and Cu atoms were taken to be within the ranges $H_{Ni-v}^m = 0.95-1.0$ eV and $H_{Cu-v}^m = 0.93-0.99$ eV, respectively, consistent with the estimate for the effective vacancy migration energy in a Ni-40 at.% Cu alloy (~ 0.96 eV) obtained by linear interpolation of the energies for pure Ni and Cu. Here, H_{Cu-v}^m was assumed to be smaller than H_{Ni-v}^m (by ~ 0.02 eV), based on the previous observation that Cu solutes are depleted at (i.e., they segregate away from) the irradiated surface [40]. The interstitial migration energy was taken to be 0.15 eV, the same for both alloying elements. Point defects were allowed to annihilate at internal sinks, which were assumed to be radiation-induced dislocations whose spatial distribution was identical to that of the damage rate K . The peak density was allowed to build up linearly with time, reaching a saturation level $\rho^{\max}$ at a time t^* :

$$\rho(\text{at damage peak}) = \begin{cases} \rho_0 + (\rho^{\max} - \rho_0)t/t^* & \text{for } t < t^* \\ \rho^{\max} & \text{for } t > t^* \end{cases} \quad (22)$$

where ρ_0 is the density of intrinsic dislocations, taken to be 10^7 dislocations/cm². The density $\rho^{\max}$ and time t^* were assumed to be 10^{10} dislocations/cm² and 10^2 s, respectively. The GA entropy and enthalpy for Cu were measured experimentally (listed in table 1).

The calculated spatial distribution of Cu atoms during 3-keV Ne⁺ sputtering at 500°C is illustrated in fig. 2 for a number of sputtering times. The spatially-dependent damage rate K , normalized to its maximum value, is shown by the dashed curve in the top illustration ($t = 0$). The effective rate K was deduced from the theoretical damage rate K_0 , calculated using the TRIM code [59] with a displacement energy of 30 eV, by $K = \epsilon K_0$. Here, the defect-production efficiency ϵ was estimated to be ~ 0.4 [60]. The peak damage occurs at ~ 1 nm and the total range is ~ 7 nm. With an ion flux of 3.75×10^{13} ions/cm²s used in the calculations and experiment (see section 3.2), the calculated peak-damage rate was $K_0^{\max} = 3.5 \times 10^{-2}$ dpa/s. Because a logarithmic scale is used for the distance axis to illustrate rapid compositional variations near the surface and moderate ones at greater depths, the composition of the first atomic layer, 0.206 nm thick, is shown in step-like form. The thickness of the surface layer removed by sputtering is indicated for various times. Since the initial starting conditions correspond to the thermodynamic equilibrium state of the alloy, with an equilibrated Cu enrichment (due to GA) at the surface, the Cu surface concentration, $C_{\text{Cu}}^{(1)}$ is very high initially, then decreases with sputtering time, and finally attains a steady-state value after $\sim 10^4$ s. The thickness of the compositionally-altered layer at 500°C is already noticeably larger than the damage range.

The temperature dependence of the bombardment-induced compositional changes, as reflected by both the time evolution of $C_{\text{Cu}}^{(1)}$ and steady-state concentration profiles, is shown in fig. 3. Two sets of initial conditions

were used: (i) thermodynamic equilibrium state of the alloy, with Cu GA at the surface, and (ii) uniform composition of the alloy up to the surface (i.e., it was assumed that the alloy was brought to temperature and sputtered instantaneously). However, regardless of the initial starting conditions, the steady-state surface and subsurface compositions are unique for a given temperature. As seen in fig. 3A, at short sputtering times, $t \lesssim 10$ s, GA controls the magnitude of $C_{Cu}^{(1)}$; when starting from the equilibrium state, $C_{Cu}^{(1)}$ is nearly 100 at.%. With increasing time, however, PS and RIS lead to a gradual decrease in $C_{Cu}^{(1)}$ towards a steady-state value given by

$$\frac{S_{Cu} [(1-\gamma)C_{Cu}^{(1)} + \gamma C_{Cu}^{(2)}]}{S_{Ni} [(1-\gamma)C_{Ni}^{(1)} + \gamma C_{Ni}^{(2)}]} = \frac{C_{Cu}^b}{C_{Ni}^b} \quad (22)$$

At steady state, the surface alloy composition, $C_{Cu}^{(1)}/C_{Ni}^{(1)}$, is thus determined by the partial sputtering coefficients, the contribution of the second layer to the sputtered-atom flux, γ , and the bulk composition, in such a way that the compositions of the sputtered-atom flux and the bulk alloy become equal. The temperature dependence of steady-state $C_{Cu}^{(1)}$ is connected with the magnitude of γ [11]. The results plotted in fig. 3A were obtained for $\gamma = 0.35$. We will discuss further the effect of γ in the next section, in conjunction with the interpretation of experimental measurements.

Figure 3B shows the steady-state concentration profiles in the subsurface region calculated for various temperatures. The values of $C_{Cu}^{(1)}$ and $C_{Cu}^{(2)}$ are clearly indicated, using a logarithmic scale for the depth. Near room temperature, where point-defect mobility is limited, PS and DM are the main processes that govern the development of the alloy composition in the altered layer, which extends to a depth approximately equal to the damage range. The

additional effect of GA, which is quite small at this temperature, is reflected by the noticeable difference between $C_{\text{Cu}}^{(1)}$ and $C_{\text{Cu}}^{(2)}$. Above $\sim 100^\circ\text{C}$, GA, RED and RIS become significant, and effectively determine the extend of, and the composition in, the altered layer. The higher the temperature, the thicker the altered layer. At 700°C , for example, the thickness of this layer is $\sim 2\text{ }\mu\text{m}$, which is ~ 300 times larger than the damage range. Compositional changes at such large depths suggest that the effects of RED and RIS are profound at elevated temperatures. The long times which are necessary to achieve steady state at high temperatures derive from the extension of the concentration gradient to such depths.

3.2 Experimental observations

The first study of high-temperature ion bombardment-induced surface composition changes was carried out ten years ago by H. Shimizu et al. [61] on Ni-Cu alloys using AES. They observed a strong effect of sputtering temperature on the near-surface composition in the temperature range from 100 to 600°C . However, since the compositional changes were not measured in situ during sputtering, the interpretation of their results was complicated by secondary effects noticed during cooling of the sputtered specimen to the temperature where AES was performed. Their observations have, nevertheless, indicated the importance of thermally-activated processes in sputter-induced composition alterations.

In situ AES measurements of near-surface compositional changes in a Cu-40 at.% Ni alloy during 5-keV Ar^+ sputtering at elevated temperatures were made by Rehn et al. [7,62]. Two pairs of Auger transitions were used: Ni transitions at 102 and 716 eV, and Cu transitions at 106 and 320 eV. The low-energy Auger electrons are more sensitive to near-surface composition changes (in the first two atom layers), whereas the higher-energy electrons contain

information about the composition further below the surface (within a depth of ~ 1.3 nm). These measurements revealed that the Cu depletion in the deeper subsurface region, which increased steadily with temperature from 300 through 600°C, significantly exceeded that in the first two surface layers. This was explained in terms of strong GA of Cu playing an important role in the formation of the altered layer. The time required to achieve steady state in the near-surface region was found to increase rapidly with increasing temperature. Steady-state concentration profiles were also measured after rapid specimen cooling to room temperature. They indicated that deviations from the bulk composition occurred up to depths of ~ 1 and $3 \mu\text{m}$ in the specimens sputtered at 500 and 600°C, respectively.

Swartzfager et al. [63] performed a similar study on Cu-Ni, Ag-Au and Au-Pd alloys using ISS, which is a surface layer-sensitive technique. The alloys were sputtered with 2-keV Ne^+ ions at temperatures between 200 and 550°C, and the compositional changes in the outermost atom layer were probed in situ with the same ions. Steady-state concentration profiles were measured after sample quenching to ambient temperature. Similar to AES studies, it was found that the altered-layer thickness increased rapidly with temperature above $\sim 400^\circ\text{C}$. With the aid of a theoretical model formulated by Ho [64], which includes only PS and RED, the steady-state concentration profiles were analyzed in order to obtain information about RED in the bombarded alloy. The RED coefficients were found to be between 10^{-16} and $10^{-15} \text{ cm}^2/\text{s}$, virtually independent of temperature below $\sim 400^\circ\text{C}$, indicating that in this regime the defects annihilate predominantly at fixed sinks. The time evolution of the alloy composition in the first atom layer during bombardment was unfortunately not measured.

A systematic ISS study of low-energy ion bombardment-induced composition modifications in Ni-Cu alloys was carried out by Lam et al. [11]. Both the compositional changes in the outermost atom layer during sputtering and steady-state concentration profiles were measured. Their results are shown in figs. 4 and 5, where the evolution of the Cu/Ni ISS ratio measured on a Ni-40 at.% Cu alloy during 3-keV Ne^+ sputtering (with a flux of 3.75×10^{13} ions/cm²s) at temperatures and during depth-profiling at room temperature is plotted. Longer times were required to reach steady state at higher temperatures because of the rapidly-increasing thicknesses of the altered layers. These measurements were in good agreement with other studies discussed above, and could be semi-quantitatively fitted by the results of theoretical modeling described in section 3.1. However, Lam et al. observed that the steady-state $C_{\text{Cu}}^{(1)}$ was noticeably temperature dependent during sputtering above $\sim 400^\circ\text{C}$. This was in contrast to previous theoretical predictions, which were based on the assumption that sputtered atoms originated entirely from the first atomic layer [6,8,9]. The observed gradual increase of the steady state $C_{\text{Cu}}^{(1)}$ (larger than C_{Cu}^b) with temperature cannot be explained in terms of the temperature dependence of the sputtering coefficients in a reasonable way, because it would require that (i) the partial sputtering coefficients be strongly temperature dependent, and (ii) Ni atoms become preferentially sputtered at high temperatures. It is unlikely that these requirements can be fulfilled because both the sputtering coefficients and sputtering preference in alloys should not be significantly temperature dependent below $\sim 0.7 T_m$ in view of the temperature-independent coefficients found for pure metals sputtered by chemically-inactive ions at these temperatures [65]. In addition, the sputtering coefficients have also been found to be composition independent for Ni-Cu alloys [66]. These

arguments led Lam et al. to interpret the temperature dependence of $C_{\text{Cu}}^{(1)}$ in terms of significant contributions to the sputtered-atom flux from subsurface layers, predominantly from the second layer. GA tends to increase the Cu concentration in the first atomic layer relative to that in the subsurface layers, as the rate of atom exchange between these layers increases with increasing temperature. The steady-state condition [eq. (22)] can be met with an increased $C_{\text{Cu}}^{(1)}$, if this increase is balanced by a corresponding decrease in $C_{\text{Cu}}^{(2)}$. That is, a sufficient fraction of the sputtered-atom flux originates from the second layer. By comparing detailed model calculations (discussed in section 3.1) with experimental observations, Lam et al. suggested that this fraction was $\gamma \approx 0.35$ [11]. This value of γ is, even though on the high side, consistent with recent estimates of the characteristic depth of sputtering by Kelly and Oliva [67]. Substantial Cu depletion in the second and deeper layers in Ni-Cu alloys bombarded at elevated temperatures has been found in both theoretical calculations [8,9,11] and experiments (see fig. 5, as well as [7,63]). Similar steep concentration gradients have also been observed by Andersen et al. [68], who used measurements of the temperature dependence of the angular distribution of material sputtered from a Pt-Cu alloy to show that during ion bombardment the outermost atom layer is enriched with Cu, a component that is known to Gibbsian-adsorb.

Lam et al. have also deduced the RED coefficients from the measured concentration profiles, using Ho's equation describing the alloy composition in the altered layer at steady state [64]. Their results were in good agreement with ISS data of Swartzfager et al. [63] and consistent with AES measurements of Shimizu et al. [69] and Rehn et al. [57]. These RED studies clearly demonstrate that point defects produced in the near-surface region during ion sputtering at elevated temperatures migrate well into the sample

interior. Since the same defects which are responsible for RED can also produce RIS, some contribution of RIS to compositional changes in the deeper region far from the surface is expected. Such contribution was measured recently [57].

4. Implant redistribution in metals during ion implantation

The same processes that are operative during inert-gas ion sputtering of alloys also occur during ion implantation of metals. However, in the implantation case, the incoming ions are incorporated into the host metal matrix to create a new alloy; the solute (or implant) concentration is thus time dependent. Once becoming a new component of the alloy system, the implant is subjected to sputtering and redistribution caused by the operation of the processes described above.

A kinetic model has been developed recently by Lam and Leaf [55] to investigate the synergistic effects of these processes on the spatial redistribution of implanted atoms during implantation. The effects of spatially-nonuniform rates of damage and ion deposition, as well as the movement of the bombarded surface as a result of sputtering and introduction of foreign atoms into the system, were taken into account. The evolution of implant concentration profile in time and space was calculated for various temperatures, ion energies, and ion-target combinations. The results of this work are useful in elucidating the essential physics of the elevated-temperature ion implantation process.

We consider a metal substrate B into which A atoms are implanted at a flux ϕ . A number of A atoms will end up in interstitial sites, and the rest in substitutional sites of the host lattice. The respective rates of implantation into these sites are $f_i \phi$ and $f_s \phi$ (atom fraction/s). During

implantation, point defects are created by ion impact at a rate K (dpa/s). Since the interstitial defects are distinguishable by atom species (in contrast to vacancies), the rate of interstitial production is partitioned into KC_A and $KC_B \equiv K(1-C_A)$ for A- and B-interstitials, respectively, with C_A and C_B being the respective local concentrations of A and B atoms in substitution. The interstitials and vacancies annihilate by mutual recombination and/or diffusion to defect sinks. In addition, vacancies and B-interstitials can interact with free solute atoms, giving rise to the formation of vacancy-solute complexes and conversion of B-interstitials to A-interstitials, respectively.

The local concentrations of vacancies (v), B-interstitials (iB), A-interstitials (iA), A-vacancy complexes (vA) and free substitutional solutes (A) change with implantation time according to the following system of kinetic equations:

$$\begin{aligned}
 \partial C_v / \partial t &= - \nabla \cdot J_v & + K & & - f_s \phi & + F_v \\
 \partial C_{iB} / \partial t &= - \nabla \cdot J_{iB} & + K(1-C_A) & & & + F_{iB} \\
 \partial C_{iA} / \partial t &= - \nabla \cdot J_{iA} & + KC_A & + f_i \phi & + F_{iA} \\
 \partial C_{vA} / \partial t &= - \nabla \cdot J_{vA} & & & + F_{vA} \\
 \partial C_A / \partial t &= - \nabla \cdot J_A & - KC_A & + f_s \phi & + F_A
 \end{aligned} \tag{23}$$

where the F 's denote the local rates of creation and loss of species by chemical-type reactions (i.e. formation and dissociation of defect-solute complexes, and defect recombination and annihilation), and the J 's are the fluxes of the mobile species, defined as [38]:

$$\begin{aligned}
 J_v &= - (1 + \sigma_v C_A) D_v \nabla C_v \\
 J_{iB} &= - (1 + \sigma_i C_A) D_{iB} \nabla C_{iB} \\
 J_{iA} &= - D_{iA} \nabla C_{iA} \\
 J_{vA} &= - D_{vA} \nabla C_{vA} \\
 J_A &= - \sigma_i C_A D_{iB} \nabla C_{iB} + \sigma_v C_A D_v \nabla C_v .
 \end{aligned} \tag{24}$$

Here, D_v , D_{iB} , D_{iA} and D_{vA} are the diffusion coefficients of defects and defect-solute complexes. The constants α_v and α_i are the capture factors for vacancy-solute and interstitial-solute encounters. For strong defect-solute binding, $\alpha_v = 6$ and $\alpha_i = 6$, and for repulsion or no interaction, $\alpha_v = 2$ and $\alpha_i = 0$ [38,70]. The free solute flux arises from the coupling of A atoms with free B-interstitial and vacancy fluxes.

Concurrently with the buildup of solute concentration in the host matrix, the surface is subjected to displacements, due to the introduction of foreign atoms into the system and sputtering. The former gives rise to surface relaxation in the $-x$ direction, at a rate $\dot{\delta}_-$, whereas the latter causes surface recession in the $+x$ direction, at a rate $\dot{\delta}_+$. The rate $\dot{\delta}_-$ can be calculated from the net atom flux towards the surface:

$$\dot{\delta}_- = J_{iA} + J_{iB} - J_v - J_{vA}, \quad (25)$$

while the rate $\dot{\delta}_+$ is determined by the ion flux, the partial sputtering coefficients, S_A and S_B , and the surface concentrations of A and B atoms:

$$\dot{\delta}_+ = \phi \Omega [S_A C_A^{(1)} + S_B (1 - C_A^{(1)})], \quad (26)$$

where the concentration of the second layer to the sputtered-atom flux is neglected. The net surface displacement rate,

$$\dot{\delta} \equiv d\delta/dt = \dot{\delta}_- + \dot{\delta}_+, \quad (27)$$

is therefore controlled by the competition between the rates of ion collection and sputtering.

Detailed information on the temporal and spatial evolution of the surface and subsurface alloy composition can be obtained by solving eqs. (23) and (27) numerically for a semi-infinite medium, starting from the thermodynamic equilibrium conditions. The moving boundary was accommodated for by the same transformation as that used in section 3.1. The first two atom layers were treated discretely in order to include the effect of GA [71]. Sample calculations were performed for low- and high-energy Si^+ and Al^+ implantations into Ni [55]. It has been known from previous studies that in irradiated Ni, Si atoms segregate in the same direction as the defect fluxes, whereas Al solutes migrate in the opposite direction [40]. Thus, the effects of different segregation mechanisms could be examined with the present model.

Redistributions of Al and Si solutes in Ni during 50-keV implantation at 500°C are presented in figs. 6 and 7, respectively. The normalized rates of defect production and ion deposition, calculated with the TRIM code [59], are included in the top portions. The most-probable damage and ion ranges for Al^+ and Si^+ ions are $R_d \approx 13$ and 12 nm, and $R_i \approx 27$ and 24 nm, respectively. For the ion flux used, 6.25×10^{13} ions/cm²s (i.e., 10 $\mu\text{A}/\text{cm}^2$), the calculated peak-damage rates were $K_o^{\text{max}} = 7.92 \times 10^{-2}$ and 8.63×10^{-2} dpa/s for the respective Al^+ and Si^+ bombardments of Ni. The effective defect-production rate K was estimated by multiplying the calculated rate by a defect-production efficiency of 0.3 [60]. The sputtering coefficients for the host and solute atoms, S_B ($B = \text{Ni}$) and S_A , in Ni-Al and Ni-Si alloys were taken to be 3.5 and 2.0 atoms/ion, and 3.5 and 1.0 atoms/ion, respectively [72]. Here, S_A and S_B were assumed to be equal to the coefficients for the pure A and B elements. Since sputtering is significant at 50 keV, the bombarded surface recedes into the sample

with time. The surface displacements δ are indicated in the figures. In the Al-implantation case (fig. 6), $C_{Al}^{(1)}$ increases with time to a steady-state value of ~ 50 at.%, which is governed by the partial sputtering coefficient of the implant, S_{Al} . This value is substantially larger than that obtained in very high-energy implantation, where sputtering is negligible and $C_{Al}^{(1)}$ is controlled by RIS. However, the total implant concentration remaining in the sample is significantly smaller because of sputtering. Furthermore, the shape of the steady-state implant profile is dictated by PS, RED and RIS.

The evolution of the Si profile (fig. 7) is rather different from that of Al, because of the different RIS behaviors. After a short implantation time, Si enrichment occurs at the surface because of RIS, and the Si distribution peak starts moving into the sample interior. With increasing time, $C_{Si}^{(1)}$ increases monotonically, attaining a steady-state value of ~ 100 at.% at $t \gtrsim 2 \times 10^4$ s. This value is predicted because $S_{Si} = 1$ atom/ion. Unlike the Al case, the Si profile shows a significant shift of the implant distribution into the beyond-range region. At steady state, the peak of the distribution is at 90 nm from the surface, i.e., about four times the ion most-probable range. In addition, high-level tails extending deep into the sample can be observed behind the distribution peak for long implantations. The predicted translation of the Si-distribution peak into the sample interior was consistent with recent experimental measurements by Mayer et al. [73] in Si-implanted Ni at elevated temperatures. The propagation of the implant concentration peak into the bulk was also reported by Watkins [74] for 60-keV Cu^+ implantation into Ti.

5. Summary and conclusion

The complex interplay of various processes, including preferential sputtering, displacement mixing, radiation-enhanced diffusion, radiation-induced segregation and Gibbsian adsorption, in altering the subsurface alloy composition during elevated temperature bombardment has been reviewed. In general, considerable progress has been made, both theoretically and experimentally, during the recent years in identifying the relative importance of the individual processes under various irradiation conditions. The phenomenon of bombardment-induced compositional redistribution is simplest at low temperatures where only the athermal processes, i.e. preferential sputtering and displacement mixing, are dominant. The thickness of the resulting compositionally-altered layer is approximately equal to the ion range. As temperature is increased, the radiation-induced point defects become increasingly mobile, and radiation-enhanced diffusion, radiation-induced segregation and Gibbsian adsorption affect the extent of, and the composition in, the altered layer. The depth of this layer can become orders of magnitude larger than the range of the sputter ions, because point defects can migrate deep into the undamaged microstructure well beyond the defect production region. The increased altered-layer thickness causes a corresponding increase in transient time necessary to reach steady state. In the case of inert-gas ion sputtering of alloys, the steady-state composition at the sputtered surface is always determined by preferential sputtering (which includes the partial sputtering coefficients and the contribution from beneath the first atom layer to the sputtered-atom flux) and the bulk composition of the alloy. On the other hand, for the case of ion implantation of metals, the steady-state surface composition is predominantly controlled by the partial

sputtering coefficient of the implanted solute; the shape of the implant profile is dictated by preferential sputtering, in addition to radiation-enhanced diffusion and radiation-induced segregation.

The multitude of processes that affect surface layer composition during ion bombardment can provide a good flexibility in modifying alloy surfaces. It is now evident that a wide variety of microstructures, and phase and composition distributions can be produced in near-surface regions of alloys by appropriate choices of energy, type and flux of the bombarding ions, the irradiation temperature, and the initial structure and composition of the target. This flexibility is also extremely beneficial for future experimentation to further our understanding of the complex phenomenon of bombardment-induced compositional segregation and redistribution.

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Table 1: ISS measurements of ΔS_a and ΔH_a for Ni-Au [12], Ni-Cu [11] and Ni-Si [44] alloys.

	Ni-6 at.% Au	Ni-40 at.% Cu	Ni-9.5 at.% Si
$\Delta S_a/k$	-1.09	-2.60	0.26
$\Delta H_a(\text{eV})$	-0.45	-0.42	-0.054

FIGURE CAPTIONS

- Fig. 1. Temperature dependence of the ISS intensity ratio measured on Ni-40 at.% Cu and Ni-6 at.% Au alloys maintained at thermal equilibrium.
- Fig. 2. Calculated time evolution of Cu concentration profiles in a Ni-40 at.% Cu alloy sputtered with 3-keV Ne^+ ions at 500°C. The profile of the damage rate K is shown by the dashed curve in the top portion, and the thickness of the surface layer removed by sputtering is indicated. The energies for vacancy migration via Cu and Ni atoms were taken to be 0.95 and 0.97 eV, respectively.
- Fig. 3. (A) Calculated time evolution of the composition in the outermost atom layer of a Ni-40 at.% Cu alloy during 3-keV Ne^+ sputtering at various temperatures. Two sets of initial conditions were used: the thermodynamic equilibrium state of the alloy (solid curves), and the nonequilibrium uniform alloy composition (dotted curves). (B) The corresponding compositional profiles at steady state. The vertical line indicates the boundary between the first and second atomic layers. The migration energies of vacancies and interstitial via Cu and Ni atoms are tabulated. The symbols are used simply to label the curves for different temperatures.
- Fig. 4. Time evolution of the Cu/Ni ISS intensity ratio measured during 3-keV Ne^+ sputtering of a Ni-40 at.% Cu alloy at various temperatures [11].
- Fig. 5. Steady-state concentration profiles of the altered layers in a Ni-40 at.% Cu alloy after sputtering with 3-keV Ne^+ ions at various temperatures. The dashed vertical line indicates the boundary between the first and second atom layers [11].

Fig. 6. Development of the Al profiles during 50-keV implantation at 500°C. The normalized damage (K_O) and ion-deposition ($P_{\Delta x}$) rates are shown in the top portion, and the surface displacements δ resulting from sputtering are indicated. Note that the concentration scales are multiplied by factors shown in each plot [55].

Fig. 7. Time evolution of the Si profiles during 50-keV implantation at 500°C. The normalized damage and ion-deposition rates are shown in the top portion. Surface displacements δ resulting from sputtering are indicated. Note that the depth scales in plots for $t = 0.1$ s and $t > 10$ s differ by a factor of 5 and the concentration scales are multiplied by factors shown near the curves [55].

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7