Pergamon

Vacuum/volume 51/number 3/pages 413 to 416/1998

0042–207X/98 $19.00+.00

PII: S0042–207X(98)00184–5

Calculation of sputtering yields under high-fluence bombardment of a Cu_xNi_{1-x} alloy

Li-Ping Zheng,[a,b,c,*] Ri-Sheng Li,[b,c] and Ming-Yao Li,[a] [a] *Shanghai Institute of Nuclear Research, Academia Sinica, P.O. Box 800–204, Shanghai 201800, China;* [b] *Laboratory of Atomic Imaging of Solids, Institute of Metal Research, Academia Sinica, Shenyang 110015, China;* [c] *International Center for Materials Physics, Academia Sinica, Shenyang 110015, China*

received for publication 7 May 1998

Under 2 keV Ar ion bombardment of a Cu_xNi_{1-x} alloy, at high fluence and at low temperature, Cu and Ni sputtering yields, the total sputtering yield (Cu+Ni yields), and the sputtering yields from the first surface layer and from beneath this layer for Cu and Ni, have been separately calculated by an improved kinetic BIGS (bombardment-induced Gibbsian segregation) model. Calculations indicate that these sputtering yields are strongly dependant on the Cu (segregating species) bulk composition. A cause of the possible correlation between sputtering angular distribution and bulk composition of the segregating species is also analysed for the segregating system. © 1998 Elsevier Science Ltd. All rights reserved

Under high-fluence low or room temperature bombardment, the influence of Gibbsian segregation on the surface composition change of alloy is now clearly known.[1–6] Thus, besides the extreme composition feature, induced by bombardment, the segregating species should be enriched at the outermost surface (forming a surface spike) and depleted beneath it, thus forming a reverse compositional spike between the first surface layer and the subsurface; BIGS (bombardment-induced Gibbsian segregation) is now recognized to exhibit the intermediate feature, that the depletion of the segregating species at the second surface layer is slight when the bulk composition of the segregating species is low or high, but this depletion becomes considerable when the bulk composition is intermediate.[1–4,6]

Bombarded Cu—Ni alloys are ideal segregating systems, because they should not show strong preferential collisional behavior due to their near identical masses and comparable surface binding energies. The bulk-dependent total sputtering yield (Cu + Ni yields) has been measured.[7] Besides the total one, calculations of bulk-dependent Cu and Ni sputtering yields, particularly the calculations of bulk-dependent sputtering yields from the first surface layer and from beneath this layer for Cu and Ni, respectively, may be available both for practical applications and for the physical understanding of the BIGS features. This is one goal of the present work.

In 1989, Kelly obtained an important rate equation for bombardment-induced composition change of alloy surface.[2] In 1995, our improved kinetic BIGS model gave a similar rate equation (eqn (3a) of Ref. [6]). Segregation is always strong. In our model, during a bombardment but not afterwards, the jump rate, W_{21} (i), of the segregating species at the instantaneous (i.e. not steady) state, i, from the second surface layer 2 into the first surface layer 1 is related to N_1 (i), C_1 (i) and C_2 (i) by (eq (3b) of Ref. [6])

$$W_{21}(i) = KN_1(i)[1-C_1(i)]C_2(i) \tag{1}$$

Here, K is the constant for jumps favorable to BIGS, which is similar to the k_+ of eqn (5) of Ref. [2], N_1 (i) is the instantaneous concentration of vacancies in the first layer, and C_1 and C_2 (i) are instantaneous concentrations (or composition) of the segregating species in the first and the second layer, respectively. It is suggested that eqn (1) is valid during the bombardment but not afterwards. Note that N_1 (i), C_1 (i) and C_2 (i) have the same physical units. Also note that since the lattice sites conservation is exactly adopted in the simulation, $[1-C_1$ (i)] in eqn (1) should be replaced by $[1-C_1$ (i)$-N_1$ (i)]. However, under low current conditions, we have N_1 (i) $\ll 1$, so for simplicity we may still employ $[1-C_1$ (i)] instead of $[1-C_1$ (i)$-N_1$ (i)].

It is found that eqn (1) can exhibit a strong matrix effect of BIGS for a bombarded A_xB_{1-x} alloy, where A and B stand for the segregating and nonsegregating species, respectively. For example, at the low fluence limit, i.e. $i \rightarrow 0$, the instantaneous jump factor of $[1-C_1$ (i)]C_2(i) approaches a maximum value (0.25) when x (the bulk composition of A) equals 0.5; it tends to 0 when x tends to 0 or 1. Thus, W_{21} (i) maximizes when x equals 0.5 and tends to zero when x tends to 0 or 1, provided that K and N_1 (i) have only a weak dependence on the bulk composition.[6]

Systems presently being studied are a series of Cu_xNi_{1-x} alloys (x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9) bombarded with 2 keV Ar ions at normal incidence, which is the same as used in

* To whom all correspondence should be addressed.

the Betz's measurements.[7] The constant K for BIGS equals 3.9 and each layer is chosen to be 2.5 Å (about a mean atomic spacings).[6]

For the bombarded Cu_xNi_{1-x} alloy, the measured total sputtering yield increases from 2.9 atoms/ion (the sputtering yield of pure Ni) to 4.8 atoms/ion (that of pure Cu) when x (the Cu bulk composition) increases from 0 to 1 (Fig. 13 of Ref. [7]). The simulated total sputtering yield, Y_{total}, increases from 3.0 atoms/ion to 4.7 atoms/ion when x increases from 0.1 to 0.9 (Fig. 1(c)). Our results are in good agreement with the experimental sputtering data of Betz.[7] For example, the measured data equal 3.0, 3.7 and 4.6 atoms/ion while the simulated ones equal 3.0, 3.9 and 4.7 atoms/ion, for x equal 0.1, 0.5 and 0.9, respectively.

Also for the bombarded Cu_xNi_{1-x} alloy, as x increases from 0.1 to 0.9, the simulated sputtering yield of Cu, Y_{Cu}, increases from 0.3 atoms/ion to 4.3 atoms/ion (Fig. 1(a)), while that of Ni, Y_{Ni}, decreases from 2.7 atoms/ion to 0.4 atoms/ion (Fig. 1(b)). In addition, the simulated normalized sputtering yield ratio, $Y_{Cu}/Y_{Ni}/(x/(1-x))$, varies only between 0.95 and 1.05, i.e. it approximates 1 for any bombarded Cu_xNi_{1-x} alloy. This indicates that our calculations may obey the partical conservation law, at high fluence, i.e. at the steady-state.

In our recent work on the bombardment-steady-state of Cu_x-Ni_{1-x}, a correlation between the simulated surface composition gradient and the bulk composition (x) of Cu (segregating species) exhibits an intermediate feature of BIGS (Fig. 1 of Ref. [6]), i.e., the gradient of Cu maximizes when x equals 0.5 (the intermediate value). Corresponding to this, it might be shown that the simulated sputtering yield ratio, Y_1/Y_2 (1 stands for the first surface layer and 2 stands for all layers except the first one) for Cu maximizes, but Y_1/Y_2 for Ni minimizes, when x equals 0.5 (Fig. 2). In other words, the correlation between Y_1/Y_2 and x also shows an intermediate feature of BIGS.

Measured sputtering angular distributions of binary alloys[9,10] have shown that at high fluence, i.e. at the steady-state, the distribution of the non-segregating species is more forward-peaked than that of the segregating species. The above phenomenon is caused by the surface composition gradient.[11,12] It also seems clear that if the nonstoichiometric sputtering is insignificant, the sputtered atom from beneath the first surface layer

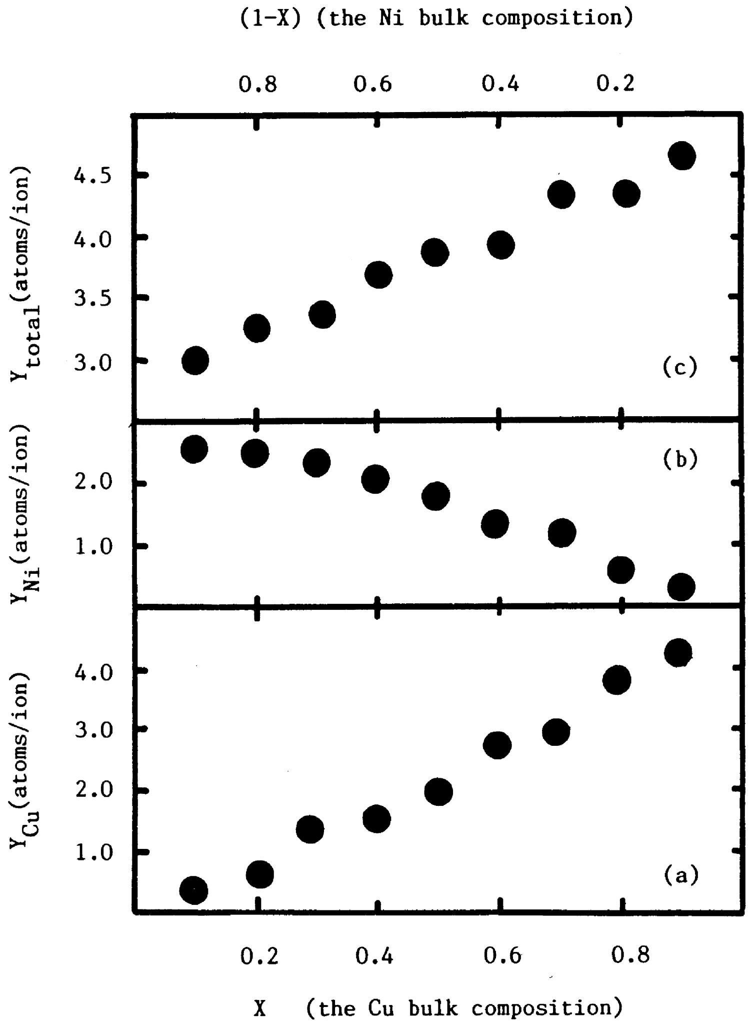

Figure 1. The simulated sputtering yield of Cu, Y_{Cu}, that of Ni, Y_{Ni}, and the simulated total sputtering yield, Y_{total}($Y_{total} = Y_{Cu} + Y_{Ni}$), vs x (the Cu bulk composition) at the steady-state of Cu—Ni alloys bombarded with 2 keV Ar ions.

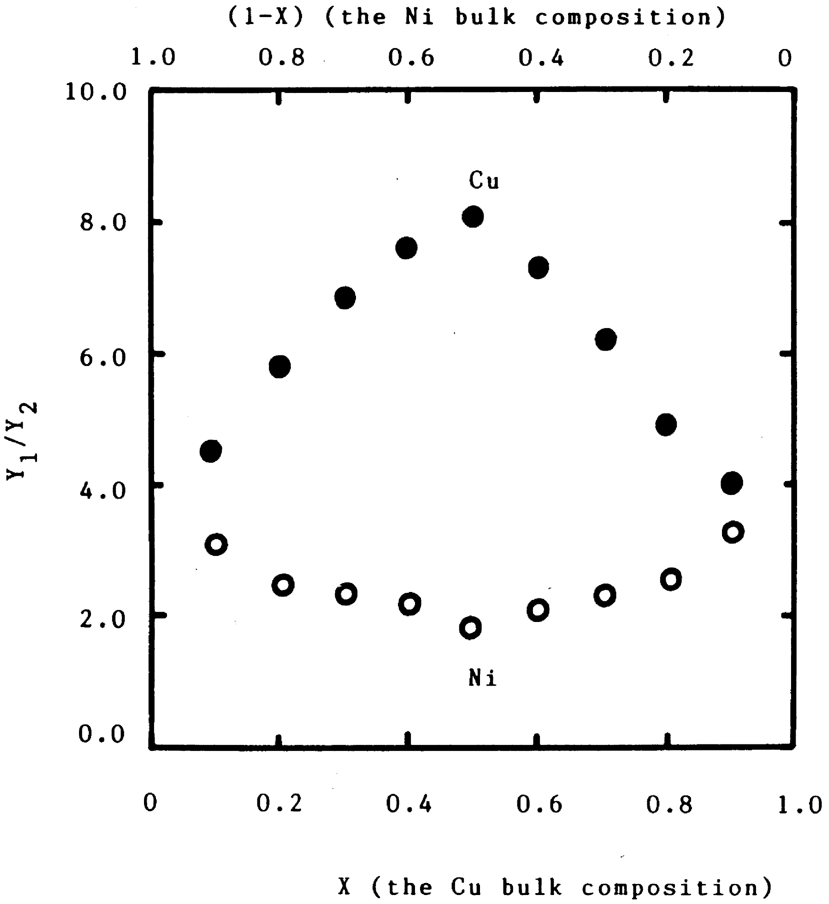

Figure 2. For Cu and Ni, simulated sputtering yield ratios, Y_1/Y_2 (from the first surface layer/from beneath this layer), vs x (the Cu bulk composition), at the steady-state of Cu—Ni alloys bombarded with 2 keV Ar ions. Here, Y_1 and Y_2 stand for sputtering yields of Cu (or Ni) from the first surface layer and from beneath this layer, separately, i.e. $Y_1 + Y_2 = Y_{Cu}$ (or Y_{Ni}).

is ejected normally (i.e. normal to the surface), but that from the first surface layer is ejected without any preference, being ideally proportional to $\cos\theta$ (where θ is the polar ejection angle). Thus, for individual elements of the binary alloy, knowledge of both their sputtering yields from the first surface layer, Y_1, and those from beneath this layer, Y_2, is helpful for better understanding of the above angular effect. For a segregating system (the bombarded $Cu_{0.5}Ni_{0.5}$ alloy), Y_1/Y_2 for the segregating species (Cu) is much larger than that for the non-segregating species (Ni) (Fig. 2), so it is possible that the distribution of the non-segregating species (Ni) is more forward-peaked than that of the segregating species (Cu).

A substantial amount of work has been done by Dumke *et al.* in 1983,[13] Hubbard *et al.* in 1989,[14] and by Shapiro *et al.* in 1995,[15] on bombarded In-Ga eutectic alloys (typically, a $In_{0.12}Ga_{0.88}$, i.e. $x = 0.12$), in which Gibbsian segregation occurs at room temperature. MD (Molecular Dynamics) simulations[15] have shown that the n-value (obtained by the fitting function $\propto \cos^n(\theta)$ to the sputtering polar angle distribution) equals 1.71 for pure Ga (i.e. $x = 0$), 2.44 for pure In (i.e. $x = 1$), and 2.66 for Ga of In-Ga eutectic (i.e. $x = 0.12$), but 1.9 for In of In-Ga eutectic (i.e. $x = 0.12$) at 3 keV bombarding energy (Table 5 of Ref. [15]). The MD simulations[15] are in good agreement with the measurements.[13,14] These results[13–15] may imply that the n-value minimizes for In but maximizes for Ga when x (the In bulk composition) equals an intermediate value, during the bombardment of a In_xGa_{1-x} eutectic alloy. It is our contention that for the segregating system (the bombarded Cu_xNi_{1-x} alloy), Y_1/Y_2 for the segregating species (Cu) maximizes but Y_1/Y_2 for the non-segregating species (Ni) minimizes when x equals an intermediate value (Fig. 2).

In conclusion, according to the above discussion, the intermediate feature of BIGS may be exhibited not only in the surface composition profile but also in the sputtering for the bombarded segregating alloy.

Acknowledgements

Supported by the National Natural Science Foundation of China.

References

1. Kelly, R. *Surf. Interface Anal.* 1985, **7**, 1.
2. Kelly, R. *Nucl. Instr. and Meth.* 1989, **B39**, 43.
3. Li, R. S., Koshikawa, T. and Goto, K. *Surf. Sci.* 1982, **121**, L561.
4. Li, R. S., Li, J. H., and Hu, T. Z. *Surf. Sci.* 1992, **260**, 209.
5. Zheng, L. P., Li, R. S., Li, M. Y., Chen, M., and Xia, X. Q. *Nucl. Instr. and Meth.* 1992, **B71**, 39.
6. Zheng, L. P., Li, P. S., Xia, X. Q., Li, M. Q., and Li, M. Y. *J. Vac. Sci. Technol.*, 1995, **A13**, 1826.
7. Betz, G. *Surf. Sci.*, 1980, **92**, 283.

8. Cui, F. Z., Li, H. D., and Zhang, J. P. *Nucl. Instr. and Meth.* 1987, **B21** 478.
9. Andersen, H. H., Stenum, B., Sorensen, T., and Whitlow, H. J. *Nucl. Instr. and Meth.* 1983, **209/210**, 487.
10. Ichimura, S., Shimizu, H., Murakami, H., and Ishida, Y. *J. Nucl. Mat.* 1984, **128/129**, 601.
11. Sigmund, P., Oliva, A., and Falcone, G. *Nucl. Instr. and Meth.* 1982, **194**, 541.
12. Kelly, R., and Oliva, A. *Nucl. Instr. and Meth.* 1986, **B13**, 283.
13. Dumke, M. F., Tombrello, T. A., Weller, R. A., Housley, R. M., and Cirlin, E. H. *Surf. Sci.* 1983, **124**, 407.
14. Hubbard, K. M., Weller, R. A., Weathers, D. L., and Tombrello, T. A. *Nucl. Instr. and Meth.* 1989, **B36** 395.
15. Shapiro, M. H., Bengtson, K. R., and Tombrello, T. A. *Nucl. Instr. and Meth.* 1995, **B103**, 123.