CONF-840760--10

RADIATION-INDUCED SEGREGATION DURING SPUTTERING*

L. E. Rehn, N. Q. Lam and H. Wiedersich
Materials Science and Technology Division
Argonne National Laboratory
Argonne, Illinois 60439

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

CONF-840760--10

DE84 016239

June 1984

FINAL

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Submitted to the International Conference on Ion Beam Modification of Materials to be held in Ithaca, New York, July 16-20, 1984.

*Work supported by the U. S. Department of Energy.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

RADIATION-INDUCED SEGREGATION DURING SPUTTERING*

L. E. Rehn, N. Q. Lam and H. Wiedersich
Materials Science and Technology Division
Argonne National Laboratory
Argonne, Illinois 60439

ABSTRACT

Experimental measurements are reported of the time development of compositional changes which occur deep in a Cu-40 at.% Ni alloy during sputtering at elevated temperatures with 5-keV Ar ions. Large effects are observed due to radiation-induced segregation (RIS), i.e. the preferential transport of nickel atoms in the direction of the defect fluxes. The results are compared with calculated composition profiles obtained using the phenomenological model of Lam and Wiedersich. Qualitative agreement between the model calculations and experimental results is found. Quantitative differences between the model and experiment preclude a reliable estimate of RIS effects in the very near-surface layers. However, the fact that the calculations underestimate the RIS contribution very deep in the specimen while still predicting a substantial RIS contribution in the near-surface region suggests that RIS can play an important role in determining near-surface compositional changes during sputtering at temperatures where defects are mobile.

*Work supported by the U. S. Department of Energy.

Radiation-Induced Segregation During Sputtering*

L. E. Rehn, N. Q. Lam and H. Wiedersich
Materials Science and Technology Division
Argonne National Laboratory
Argonne, Illinois 60439

INTRODUCTION

In general, the composition of the atom flux induced by defects migrating in an alloy is different from that of the bulk. Hence persistent defect fluxes generated during irradiation at elevated temperatures can produce large changes in the local composition of regions which experience a net influx or outflow of defects.^{1,2} In Cu-Ni alloys, this radiation-induced segregation (RIS) is known to cause enrichment of nickel near defect sinks such as the external surface.³ Either interstitial defects preferentially carry nickel in the direction of the defect fluxes, and/or vacancy defects preferentially transport copper atoms in the opposite direction.

During sputtering, large numbers of defects are created in the near-surface region. An estimate of the defect production during sputtering can be obtained by noting that about half as much energy (simple bond-counting argument) is required to remove an atom from the surface as is necessary to displace an atom from a lattice site in the interior of a crystal. Therefore the number of monolayers of defects generated for each monolayer of sputtered atoms is roughly equal to one-half the number of monolayers penetrated by the ion beam. For example, the range of 5-keV Ar ions in a medium atomic number material such as copper is about 10 monolayers (2-3nm). Thus approximately five monolayers of interstitial defects (and five monolayers of vacancies) are generated for each monolayer of sputtered atoms. During sputtering at

*Work supported by the U. S. Department of Energy.

temperatures where the defects are sufficiently mobile relative to the rate of surface recession, large defect fluxes are created which transport alloying components between the peak damage region (located slightly in front of the ion range) and the surface and the interior of the specimen. The large number of mobile defects compared to sputtered atoms provides a significant potential for modifying the distribution of alloying components via RIS.

At least six distinct processes,⁴ ion implantation, Gibbsian adsorption, preferential sputtering, displacement mixing, radiation-enhanced diffusion (RED) and RIS, contribute to compositional changes in the ion implanted region. Because of the large number of competitive processes, it is difficult to separate individual contributions in this region. However, only the two defect-flux driven effects, RED and RIS, can produce compositional changes at depths significantly greater than the implanted ion range. A primary objective of our work is to obtain relevant parameters for RED and RIS by measuring the kinetics of compositional changes well beneath the ion implanted layer, and to utilize these parameters in the phenomenological model of sputter-induced compositional changes developed by Lam and Wiedersich⁴ to assess the contribution from RIS in the implanted layer. A comparison of experimental measurements and preliminary calculations is given in this paper.

EXPERIMENTAL RESULTS

Auger electron spectroscopy (AES) and ion sputtering at room temperature were used to depth-profile subsurface changes produced in a Cu-40 at.% Ni specimen by 5-keV Ar bombardment at elevated temperatures. Details of the experimental procedure can be found elsewhere.⁵ Measurements of the additional nickel found at various depths after sputtering at 500°C for times

of 720,3600 and 7200s with a current density of $180 \mu\text{A}/\text{cm}^2$ are shown in Fig. 1. Here, the difference between the nickel concentration measured after the indicated sputtering time and that measured after sputtering deep into the bulk alloy is plotted on a logarithmic scale as a function of sputtering time at room temperature. The sputtering rate at room temperature (current density again equal to $180 \mu\text{A}/\text{cm}^2$) is calculated to be $\sim 0.55 \text{ nm/s}$. Preferential removal of copper during sputtering of Cu-Ni alloys is well known. This effect increases the near-surface nickel concentration measured after sputtering to $\sim 60 \text{ at.}\%$. However, for the conditions found in the present experiments, i.e. net concentration changes $\leq 15\%$ and no abrupt change in composition with depth, the differences in the nickel concentrations measured at room temperature are essentially equal to the differences which would be obtained if no preferential sputtering occurred. Note that all the data points given in Fig. 1 are for depths ($> 6\text{nm}$) which are significantly greater than the ion range ($\leq 3\text{nm}$).

The results in Fig. 1 reveal two different subsurface regions in which nickel enrichment is observed that decays apparently exponentially with depth. Region I exhibits a relatively steep decay over depths extending to $\sim 100 \text{ nm}$. Region II manifests itself as a considerably shallower concentration gradient penetrating several μm 's into the specimen. Results obtained at 400°C are shown in Fig. 2 (current density $190 \mu\text{A}/\text{cm}^2$ at elevated temperature and during room temperature profiling), and measurements at 400°C with a lower current density ($75 \mu\text{A}/\text{cm}^2$) are given in Fig. 3. All three figures show clearly the two characteristic regions of nickel enrichment, and similar development of the nickel enrichment profiles with increasing sputtering time at elevated temperature.

The exponential decay lengths, δ_I and δ_{II} , of the two Ni-enriched subsurface regions determined from Figs. 1-3 are compiled in Table I. Values of δ_I were obtained by neglecting any contribution from Region II, i.e. directly from the straight lines shown on the figures.

Table I. Experimental values of decay lengths in Regions I and II.

t (s)	500°C; 180 μ A/cm ²		400°C; 190 μ A/cm ²		400°C; 75 μ A/cm ²	
	δ_I (nm)	δ_{II} (nm)	δ_I (nm)	δ_{II} (nm)	δ_I (nm)	δ_{II} (nm)
720	41	1170	--	--	--	--
1200	--	--	24	590	35	660
3600	49	1460	--	--	--	--
7200	63	1600	25	1160	40	900

Several useful observations follow directly from the table: (a) values of δ_{II} are consistently a factor of 20-50 times larger than the corresponding δ_I result; (b) for all three sputtering conditions, the decay lengths of both regions generally increase with increasing sputtering time, but not strongly; (c) at essentially the same sputtering rate, δ_I and δ_{II} are larger at 500°C than at 400°C; (d) reducing the sputtering rate (at 400°C) increases δ_I , but has no strong influence on δ_{II} ; finally, (e) we note from Figs. 1-3 that the magnitude of nickel enrichment at a given depth in Region II increases much more rapidly with increasing sputtering time at elevated temperature than do the characteristic decay lengths.

DISCUSSION

Several authors have shown that the dominant mechanism responsible for nickel enrichment in Region I is RED⁶⁻⁹. The six different effects introduced above combine to produce a highly nickel-enriched region over the ion penetration depth during sputtering of Cu-Ni alloys. At temperatures where sufficient atomic mobility exists, diffusion processes enhanced by the presence of radiation-induced defects extend this nickel enrichment beyond the ion penetration depth. Assuming that the diffusion in the subsurface is enhanced uniformly, the radiation-enhanced diffusion coefficient, D , can be shown to equal the product of the exponential decay length, δ_I , and the surface recession velocity, $\dot{x}$, resulting from sputtering.⁶ Note that this analysis neglects any contribution to Region I from the effect dominant in Region II.

We have previously¹⁰ demonstrated that RIS is responsible for Region II. Nickel is preferentially transported in the direction of the defect fluxes, creating a long tail of nickel enrichment which extends microns deep into the specimen after sputtering at elevated temperatures. As discussed by Okamoto et al.¹¹, the driving force for RIS arises from the gradient in the point defect concentration. Hence the decay length of the nickel enrichment in Region II is proportional to the divergence of the point defect flux. The greater the decay rate of the defect concentration as a function of depth into the specimen, the smaller is the exponential decay length, δ_{II} . The magnitude of nickel enrichment at a given depth in Region II increases with time as the number of defects which have annihilated at that depth increases.

We have used the model of sputter-induced compositional changes developed by Lam and Wiedersich⁴ to calculate changes in composition during sputtering of the Cu-40 at.% Ni alloy at 500°C. We are attempting to "fit" the experimental data by varying the input parameters in a systematic fashion. A comparison of preliminary calculations with the experimental profiles will be given here. The parameters employed in the calculations are the same as in Ref. 4. RIS was included in the calculations by assuming that the copper atoms jump faster via vacancies than nickel atoms do, i.e. the migration enthalpy was set equal to .77 eV and .82 eV for diffusion via vacancies of copper and nickel atoms, respectively. As shown previously,¹⁰ including preferential transport of nickel atoms via interstitials increases the magnitude of nickel enrichment in Region II, but leaves the slope essentially unchanged. Removing all preferential atom transport by defects causes Region II to disappear.

The time dependence of the calculated profiles at 500°C is shown in Fig. 4 for an ion current density of 40 $\mu\text{A}/\text{cm}^2$; steady-state profiles at 500°C for three different ion current densities are given in Fig. 5. Several qualitative features of the experimental profiles are reproduced by this set of calculations. For example, they show a relatively strong and exponential decrease in nickel enrichment over the first several tens of nanometers (Region I), followed by a significantly shallower, but again exponential tail extending very deep into the specimen (Region II). The time development of the calculated profiles (Fig. 4) is also qualitatively similar to that found in Figs. 1-3. The slope of Region I decreases with increasing sputtering time at elevated temperature and the calculated magnitude of nickel enrichment produced by RIS in Region II increases with increasing sputtering time. At a current density of 40 $\mu\text{A}/\text{cm}^2$, sputtering times on the order of a few hours are

predicted to approach steady state conditions. Furthermore, we see that the slope of Region I decreases with decreasing ion current density, as was found experimentally.

Values of δ_I and δ_{II} obtained from the calculations are summarized in Tables II and III.

Table II. Calculated time dependence of δ_I and δ_{II} at 500°C using a 5-keV Ar ion current density of 40 $\mu\text{A}/\text{cm}^2$ and other parameters as in Ref. 4.

	<u>400s</u>	<u>1000s</u>	<u>10^6s</u>
$\delta_I(\text{nm})$	14	18	21
$\delta_{II}(\text{nm})$	310	310	310

Table III. Comparison of calculated and experimental "steady state" values of δ_I and δ_{II} at 500°C for three different current densities of 5-keV Ar.

	<u>Calculated</u>			<u>Experimental</u>
	<u>$4\mu\text{A}/\text{cm}^2$</u>	<u>$40\mu\text{A}/\text{cm}^2$</u>	<u>$400\mu\text{A}/\text{cm}^2$</u>	<u>$180\mu\text{A}/\text{cm}^2$</u>
$\delta_I(\text{nm})$	34	21	18	63
$\delta_{II}(\text{nm})$	460	310	190	1600

Here we see significant quantitative differences between the present set of calculations and the experimental results. First, although the model predicts an exponential tail of nickel enrichment in Region II when RIS is included, the magnitude of the effect calculated with the present set of input parameters is more than an order of magnitude less than that found experimentally. Second, the calculated values of δ_I and δ_{II} are smaller than the experimental values by factors ranging from approximately 3 to 8. Finally, the calculated dependence of δ_I on the sputtering rate, although predicted with the correct sign, is also smaller than that observed experimentally.

We conclude that the model predictions based on the present set of input parameters are qualitatively in agreement with the measurements. However, the large quantitative differences preclude a reliable estimate of the contributions from RIS to sputter-induced compositional changes in the very near-surface layers. In this context, however, it should be noted that the present parameters do predict substantial compositional changes (several atom per cent) from RIS in the very near-surface layers, despite the fact that they yield too small an effect in Region II. The indication, therefore, is that RIS is an important factor in determining near-surface compositional changes during sputtering of Cu-Ni alloys at temperatures where point defects are mobile.

References

1. L. E. Rehn and P. R. Okamoto, in Phase Transformations during Irradiation, F. V. Nolfi, Jr., ed., North Holland, New York (1982) 247.
2. H. Wiedersich and N. Q. Lam, in Ref. 1, p.1.
3. W. Wagner, L. E. Rehn, H. Wiedersich and V. Naundorf, Phys. Rev. 23 (1983) 6780.
4. N. Q. Lam and H. Wiedersich, J. Nucl. Mater. 103 & 104 (1982) 433,
5. L. E. Rehn, V. T. Boccio and H. Wiedersich, Surf. Sci. 128 (1983) 37.
6. P. S. Ho, Surf. Sci. 72, (1978) 253.
7. D. G. Swartzfager, S.B. Ziemecki and M. J. Kelley, J. Vac. Sci. Technol. 19 (1981) 185.
8. R. Webb, G. Carter and R. Collins, Rad. Effects 39 (1978) 129.
9. H. Wiedersich in Surface Modification and Alloying, J. M. Poate and G. Foti, eds., Plenum Press, New York (1983) 261.
10. L. E. Rehn, N. Q. Lam and H. Wiedersich, Mat. Res. Soc. Symp. Proc. (1983), in press.
11. P. R. Okamoto, L. E. Rehn and R. S. Averbach, J. Nucl. Mater. 108 & 109 (1982) 319.

Figure Captions

Fig. 1 Experimental measurements of subsurface nickel enrichment produced by sputtering with a $180\mu\text{A}/\text{cm}^2$ beam of 5-keV Ar ions at 500°C for the indicated times.

Fig. 2 Nickel enrichment profiles measured after sputtering at 400°C with a $190\mu\text{A}/\text{cm}^2$ beam of 5-keV Ar ions for the indicated times.

Fig. 3 Same as Fig. 2, except for an ion current density of $75\mu\text{A}/\text{cm}^2$.

Fig. 4 Calculated time dependence of subsurface nickel enrichment during sputtering at 500°C .

Fig. 5 Steady-state nickel enrichment profiles at 500°C calculated for ion current densities of 4, 40 and $400\mu\text{A}/\text{cm}^2$.