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HIGH-TEMPERATURE Au IMPLANTATION INTO Ni-Be AND Ni-Si ALLOYS*

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HIGH-TEMPERATURE Au IMPLANTATION INTO Ni-Be AND Ni-Si ALLOYS

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ABSTRACT

The effects of implantation temperature and target composition on the depth distribution of the implanted species were systematically investigated in the present work. Au⁺ ions were implanted at 300 keV into polycrystalline Ni-Be and Ni-Si alloys at temperatures between 25 and 700 °C to a dose of 10¹⁶ cm⁻². The depth distributions of Au were analyzed with RBS using He⁺ at both 1.7 and 3.0 MeV, and those of the other alloying elements by SIMS. Theoretical modeling of compositional redistribution during implantation at elevated temperatures was also carried out with the aid of a comprehensive kinetic model. The analysis indicated that below ~250 °C, the primary controlling processes were preferential sputtering and displacement mixing, while between 250 and 600 °C radiation-induced segregation was dominant. Above 600 °C, thermal-diffusion effects were most important. A systematic fitting of model calculations to experimental measurements provided values for various defect migration and formation parameters.

INTRODUCTION

In the present work, an investigation of the effect of temperature on the near surface alloy composition during ion implantation was conducted.

The athermal processes affecting alloy composition in the near-surface region include preferential sputtering (PS), displacement mixing (DM) and ion implantation. A thermally-activated process that can also affect the distribution of alloy components is Gibbsian Segregation (GS). The driving force for GS is the minimization of the free energy. The compositional perturbation caused by GS is confined to the first few atom layers of the alloy surface. Two additional thermally-activated processes that occur during ion implantation at elevated temperatures are radiation-enhanced diffusion (RED) and radiation-induced segregation (RIS). These both arise from the migration of point defects created by irradiation. The exact nature of the changes produced by these mechanisms depends greatly on the temperature as well as on the interactions between the defects and solute atoms in the matrix [1].

Spatial redistributions of Au and other solutes during Au implantation into Ni-Si and Ni-Be alloys were analyzed with RBS and SIMS. The experimental results were compared with the results of model calculations [2].

EXPERIMENTAL PROCEDURE

The materials used in this investigation were rectangular samples (16x6x1 mm³) of Ni-12.7 at. % Si and Ni-1.0 at. % Be alloys, annealed at 1100 °C and polished to a mirror finish. The implantations were performed with 300 keV Au⁺ ions at a flux of 4.2x10¹² cm⁻² s⁻¹ for Ni-Si and 5.6x10¹² cm⁻² s⁻¹ for Ni-Be and at temperatures between 25 and 700 °C.

For analysis, the implanted specimens were first profiled with RBS using 1.7 MeV He⁺. For specimens where the solute had diffused very deep into the matrix (i.e. for high-temperature implantations), it was necessary to complement the analysis with 3.0 MeV He⁺ RBS. The Au profiles were obtained by comparing the acquired RBS spectra those generated by the RSVP computer code [4] and successively altering the code input until a reasonable fit was achieved [3].

To measure the Si and Be distributions, the implanted areas were sputter depth-profiled with SIMS, using 17.5 keV Cs⁺ ions and 17.5 keV O₂⁺ ions, respectively.

RESULTS

The profiles of Au implanted in Ni-Si and Ni-Be are given in Figs.1 and 3, respectively. For all curves, the Au profiles, as determined by the RBS and SIMS, are given by the indicated symbols, while theoretical calculations are presented as dashed-dotted lines. For each system, the spatial distribution of damage (K) and ion-deposition (I) rates as determined by TRIM [5] are given in the upper-left figure. These rates have been normalized to their respective maximum values. The peak values for each system are $K_{\max}(\text{dpa/s}) = 0.057$ and $I_{\max}(\text{atom frac/2nm}) = 0.076$ for Ni-Si and $K_{\max}(\text{dpa/s}) = 0.068$ and $I_{\max}(\text{atom frac/2nm}) = 0.072$ for Ni-Be.

The profiles of the Au implant show similar trends in both alloys. At temperatures below ~250 °C, the thermally activated processes are unimportant due to the low mobility of vacancies, and the implant profile is primarily determined by PS and DM. The profiles in this temperature range are practically insensitive to temperature. They are slightly broader, and the concentration peak is closer to the surface, than the TRIM-calculated implantation profile. At temperatures above 250 °C, the concentration in the peak decreased, and the penetration tail extended deeper into the sample. No appreciable change in peak position was observed up to ~500 °C. This behavior is interpreted, through model calculations, to be due to significant RIS between ~250 and 600 °C. The ion implantation establishes persistent fluxes of defects toward the surface and out of the peak damage region, leading to preferential transport of Au away from the surface and into the peak damage region [6-8]. In fact, comparison of theoretical modeling with measurements shows that $H_{\text{Au-v}}^{\text{m}} < H_{\text{Ni-v}}^{\text{m}}$ and $H_{\text{Au-i}}^{\text{m}} > H_{\text{Ni-i}}^{\text{m}}$, i.e. Au atoms diffuse faster (slower) than the Ni by exchange with vacancies (interstitials). This implies that the Au peak will always appear in the peak damage region. At 700 °C or above, RIS becomes ineffective, and the Au profile is controlled mostly by thermal diffusion. The Au profiles show that the peak moves deeper into the sample, and the concentration tail extends far beyond the projected range of the ions.

The concentration profiles of the major solutes in the implanted Ni-Si and Ni-Be alloys were analyzed with SIMS. The Si profiles are shown in Fig. 2. The temperature dependence of the Si redistribution is the same as that for the Au implant. Below ~250 °C, the curves for the Si are essentially flat, only PS and DM contribute significantly to the component migration. Above 250 °C, there is evidence of RIS, as the Si solute has migrated out of the peak damage region, towards the surface and into the bulk. This redistribution occurs because of preferential binding of Si with interstitials [9]. When the interstitial-solute complexes become mobile, they migrate to extended sinks, and away from the peak damage region toward the surface and the bulk. And at 700 °C, there is only a slight depletion extending approximately 200 nm in depth, beyond which the Si concentration returns to the bulk value. This indicates that back-diffusion has become significant as the number of thermal vacancies present begins to compare with the level of radiation-induced defects.

Fig. 1. Depth-profiles of Au atoms implanted at 300 keV into Ni-Si at 35, 250, 500 and 700 °C. Measurements were made with RBS and SIMS as indicated. The results of model calculations are also shown for comparison.

Fig. 2. Depth-profiles of Si atoms in Ni-12.7% Si alloy implanted with 300 keV Au ions at 35, 250, 500 and 700 °C. Measurements were made with SIMS. The results of model calculations are also shown for comparison.

Fig. 3. Depth-profiles of Au atoms implanted at 300 keV into Ni-Be at 35, 200, 550 and 700 °C. Measurements were made with RBS and SIMS as indicated. The results of model calculations are also shown for comparison.

Fig. 4. Depth-profiles of Be atoms in Ni-1% Be alloy implanted with 300 keV Au ions at 35, 200, 550 and 700 °C. Measurements were made with SIMS. The results of model calculations are also shown for comparison.

The redistributions of the Be solute show very much the same trends as the Si (Fig.4). It appears, however, that the depths of Be depletion are significantly greater than for the Si, and the Be is also more depleted in the peak-damage region. This effect is also reproduced in the theoretical modeling.

It is important at this point to comment on the SIMS results for the Si and Be in the near surface region. Examination of the results reveals the appearance of depletion near the surface, which is in contrast to the expected results, namely enrichment of solutes at the surface. These observations can be explained as artifacts from the nature of the SIMS sampling process. In order to insure that sufficient numbers of ionized particles are sputtered from the surface, a reactive species is used in the sampling. This means that until the reactive species reaches an equilibrium value in the sampling region, the counts received are not proportional to the true composition in the alloy [10]. Therefore, the SIMS values for the first 10-20 nm should not be considered representative of the actual concentrations.

THEORETICAL MODELING

The theoretical model used in the present work includes the synergistic effects of solute implantation, PS, DM, GS, RED and RIS [2]. It is essentially an extended version of the code used for studying bombardment-induced modification of alloy surface composition [1,11]. This model updates the host matrix with the bombarding ions, thus making the alloy composition time-dependent. It takes input from TRIM code [5] for the spatial distributions of damage rate and ion-deposition rate. The defects interact with updated alloy solutes, and the preferential coupling of defect fluxes with the solutes contributes to the compositional redistribution. All of the processes summarized can be cast together into a system of coupled partial differential equations which phenomenologically describe the changes in defect and atom concentrations in time and space [11,12]. This set of equations is then solved numerically with the LSODE package of subroutines [13].

The observations were interpreted by fitting the model calculations to the experimental results under the same irradiation conditions. It was necessary to vary the defect parameters as inputs to the model to achieve reasonable fits and some compromise was necessary to fit the results at all temperatures. The values of these parameters are summarized in Table 1.

Table 1. Defect parameters used in model calculations

Parameter	Notation	Au into Ni-Si	Au into Ni-Be
Eff. vac. formation enthalpy	H_v^f	1.5 eV	1.5 eV
Vac. migr. enthalpy via Ni	H_{Ni-v}^m	1.10 eV	1.00 eV
Vac. migr. enthalpy via Au	H_{Au-v}^m	1.05 eV	0.95 eV
Vac. migr. enthalpy via solute	H_{C-v}^m	1.20 eV	1.10 eV
Int. migr. enthalpy via Ni	H_{Ni-i}^m	0.15 eV	0.15 eV
Int. migr. enthalpy via Au	H_{Au-i}^m	0.19 eV	0.19 eV
Int. migr. enthalpy via solute	H_{C-i}^m	0.60 eV	0.60 eV
Int. solute binding enthalpy	H_{C-i}^b	0.90 eV	0.90 eV

SUMMARY

1. The implant profiles and solute redistributions during 300 keV Au⁺ implantation into Ni-Si and Ni-Be alloys at different temperatures were measured using RBS and SIMS. The results indicated a specific range of temperatures where significant solute segregation was observed. This segregation was into the peak-damage region for the implanted Au and out of the peak-damage region for the Si and Be solutes.

2. Model calculations were performed to fit the experimental results. A general approximation of the solute profiles was achieved using various defect parameters summarized in Table 1. The redistribution of the solute atoms can be explained by preferential sputtering and diffusion mixing at low temperatures, radiation-induced segregation between ~250 and 600 °C, and thermal diffusion above 700 °C

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