LOW-ENERGY-ION ENHANCED DIFFUSION AT THE SURFACE OF METALS

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Abstract

Radiation enhanced diffusion at the surface of metals has been observed and studied for low-energy nitrogen ions at the surface of copper. The displacement of the target atoms during irradiation creates vacancies and other defects near the surface, thus enhancing the diffusion of implanted materials toward the surface and also into the solid. The mechanism has been studied here by a special method. An overcoat layer has been evaporated on the surface of the thin film sample following the implantation and the defects have been produced in the overcoat layer by another ion. The original implanted ions are observed to diffuse to the new surface through the open channels created by the auxiliary ions. The effect of this diffusion on the range distributions of low-energy ions in copper has also been discussed.

Introduction

Low-energy ion bombardment induces compositional changes in the near surface region which can affect the range and damage distributions of most of the implanted ions in solids [1,2,3]. Atomic transport in irradiated solids has been recently investigated in semiconductors as well as in other solids [2]. Most of the work in this area has been concentrated on high energy ion bombardment, from 60 keV and up [4,5] or intermediate energy [6]. Very little work has been done on low-energy ion bombardment effects [7], i.e. from 50 eV to 5 keV. One of the reasons for the lack of information on enhanced diffusion in this ion energy range is the experimental difficulties involved in carrying out diffusion measurements over narrow layers which occur in this energy range.

Compositional changes in solids can not be accurately described unless we take into account the thermodynamic forces responsible for segregation [8]. In the past, these forces have been ignored because the diffusivity of the target material was thought to be small. However, estimates of the radiation enhanced diffusivity are great and contribute to the quantitative changes in the distributions [9]. For ordinary diffusion in metals the activation energy is typically of the order of 2 eV. Naturally, the diffusion is a transport process and very temperature dependent, such that below room temperature hardly any atomic mobility remains. The atomic mobility is enhanced significantly by radiation [9,10,11]. Therefore, the investigation of such radiation enhanced diffusion is of considerable importance in depth profiling and other kinds of depth studies [12,13]. For example, sputter etching of multi-element targets changes the average surface composition and surface topography due to both preferential sputtering and radiation enhanced diffusion. Similarly, low-energy ion bombardment of substrates and growing films during deposition have been shown to result in dramatic changes in the nucleation characteristics, morphology and defect concentration [14].

The distribution of low-energy ions in metals gives a surface localization as shown in Figure 1 [15,16]. This surface peak contradicts the theoretical Gaussian distribution predicted by well-known theories [17]. In

Keywords: Diffusion; Implantation; Segregation

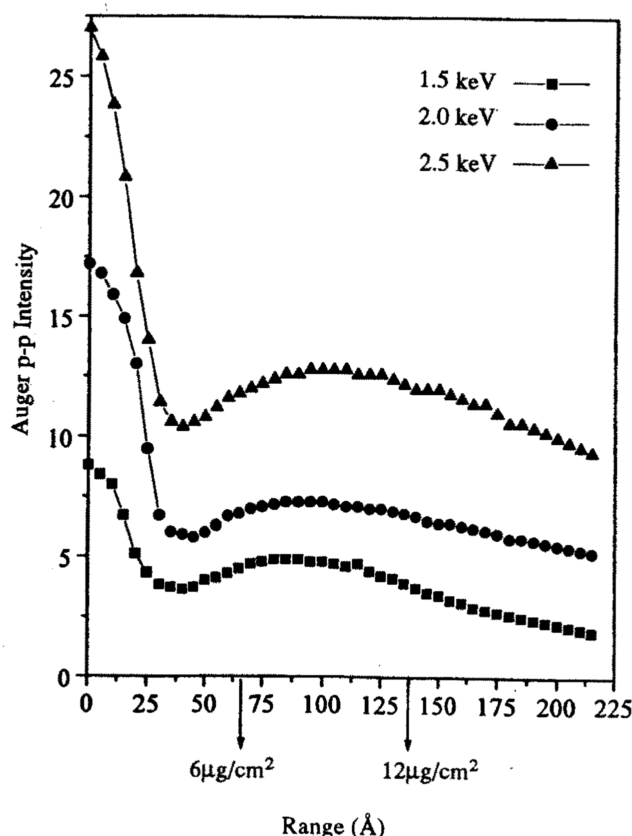


Figure 1. Typical range distributions of low-energy ions in copper

this paper, an experimental technique showing the effects of radiation on diffusion is presented. The surface localized peak and the long tail of the distribution into the sample can be very well explained from the results of the above experiment.

Experimental Procedures

Samples of copper were prepared from high purity (99.95%) rods. The samples were 1/2 inch in diameter and 1/16 inch thick and were polished smooth with 0.05 micrometer polishing paste. After cleaning, the samples were mounted on a vacuum manipulator containing a carousel sample holder. The carousel was able to rotate, which made Auger Electron Spectroscopy (AES) possible following the ion implantation of each sample. AES was performed to monitor the surface contamination as well as the depth profiling of the sample. The carousel was also equipped with a cooling system and each sample was provided with a heating filament such that the temperature of the filament could be varied over a range of -200° to 600°C.

Each sample was cleaned in the chamber by means of heating and sputtering and the contamination at the surface of the sample was monitored by AES. The final Auger spectrum of the clean sample usually noted small peaks of C and O, which equated to less than 5% of a mono-layer contamination. The cleaned sample was then cooled to liquid nitrogen temperature and was kept at this temperature during ion implantation and depth profiling. The cooling of the sample was undertaken to minimize the possible normal diffusion of the implanted materials inside the target.

The ion implantation was performed in an ultra high vacuum (UHV) chamber equipped with an implantation ion gun for sputtering and a cylindrical mirror analyzer (CMA) [18]. The low-energy ion gun used in this experiment was similar to that reported by Shoubert and Tracy [19]. Depth profiling was performed by means of a sputtering gun using argon ions and AES and the atomic composition of the surface was monitored. The base pressure in the chamber was in the range of 10^{-10} torr (mm Hg) which went up to 5×10^{-5} torr during the sputtering of the sample with argon.

Results and Discussion

Typical range distributions of low energy ions (1-5 keV) in copper indicate sharp peaks near the surface of the sample within the first ~15Å (Fig. 1). Along with the surface localized peak, there is a deeper secondary peak and a long tail into the sample [16, 20]. The surface peak in the low-energy nitrogen distribution in copper is not explainable on the theoretical basis of the two major stopping mechanisms, nuclear and electronic, which predict a Gaussian distribution [21]. Normal diffusion of the implanted materials back to the surface was minimized by performing the experiment at liquid nitrogen temperature. However, low-energy ion bombardment can enhance diffusion by introducing a large concentration of point defects, e.g. vacancies and interstitial. Since the threshold energy for atomic displacement in metals and semiconductors is generally on the order of 20-30 eV, then at this low temperature normal diffusion has a minor effect on producing the surface peak. Other mechanisms like chemical reactions between implanted materials and host atoms and also reflections have minor effects on the surface localization as they are present only at low energies. The chemical reaction between nitrogen and copper is very weak as observed by AES and X-Ray Photoelectron Spectroscopy (XPS) [22].

It is believed that the irradiation between vacancies produced during irradiation [10] and the implanted species are mostly responsible for the radiation enhanced diffusion process and consequently for the surface peak. A particular experiment was undertaken to

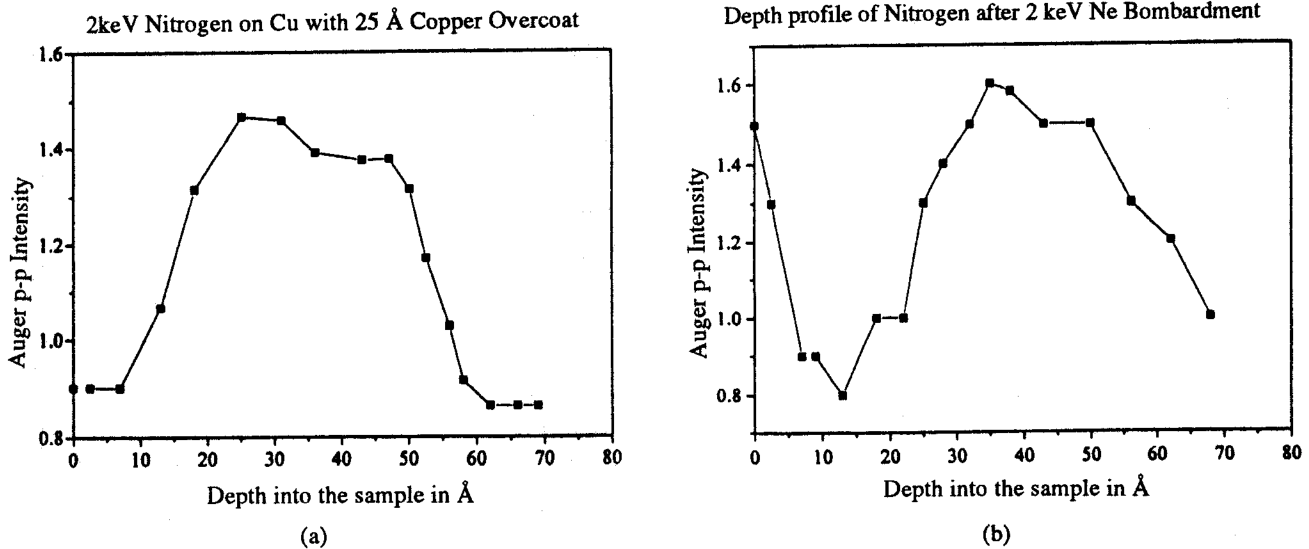


Figure 2. (a): Depth distribution of 2 keV nitrogen ions implanted into a copper sample with 25Å overcoat layer of copper following the implantation. (b): Depth profile of a similar sample as in (a) but later bombarded with 2 keV neon ions. The ordinate in both profiles represents the p-t-p intensity of 389 eV nitrogen Auger signal.

examine this effect. Damage was created in the surface region by an ion different from the ion implanted in the target and the diffusion of the implanted nitrogen ions was monitored. As the first step, nitrogen ions were implanted in a copper sample. The sample was then overcoated with approximately 25 Å copper as determined from a calibrated copper evaporator source. The depth distribution of such a sample is shown in Figure 2a. The overcoated sample was then bombarded by 2 keV neon ions at a dosage of approximately one neon ion per copper atom at the surface. The purpose of choosing such a dosage was to minimize the sputtering effect on the overcoat layer yet to create enough damage in the layer so as to affect the implanted nitrogens.

The role of neon ions is merely to create defects in the overcoat layer, so one can examine the diffusion of nitrogen through such produced defects. The sample was finally depth profiled to obtain the nitrogen distribution after neon bombardment. The results are shown in Figure 2b. The distribution shows surface localization of nitrogen atoms in the overcoat layer. The peak is a result of interaction between the preimplanted nitrogen ions and the later created defects in the overcoat layer by the neon ions, the vacancies produced by the neon ions in the overcoat layer result in open channels to the surface for the nitrogen atoms and a concentration gradient begins to build up toward the surface region of the overcoat layer. The distributions in Figure 2 also show the remaining ions at the original surface of the copper sample before being overcoated.

The results of a similar experiment using 3 keV nitrogen ions implanted in the copper sample are shown in Figure 3. The defects in the overcoat layer are produced by 3 keV neon ions in this case.

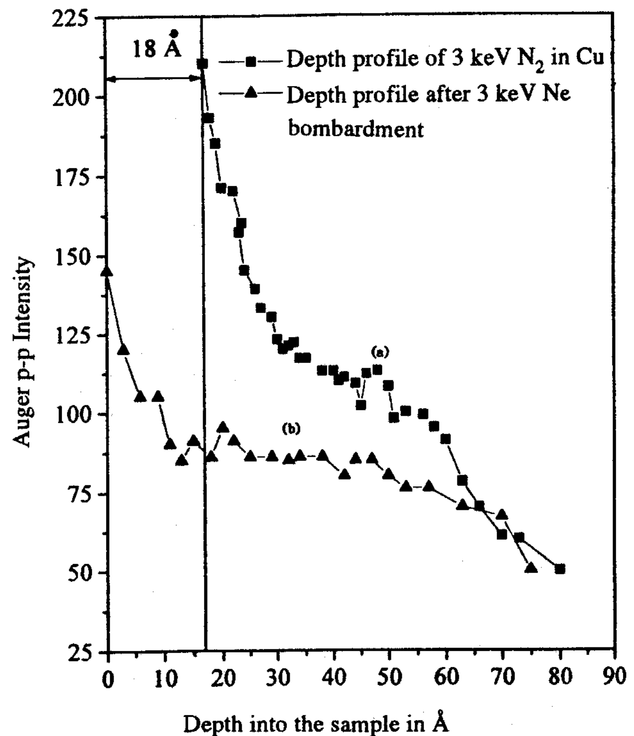
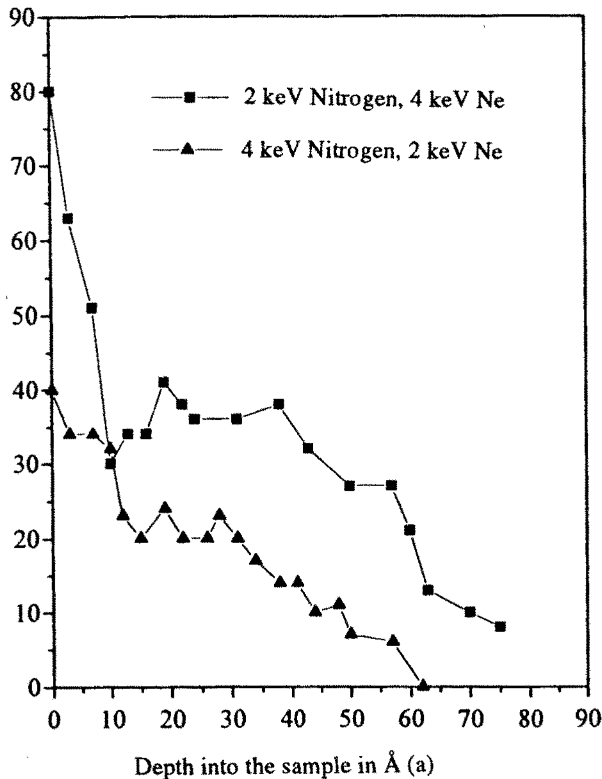


Figure 3. (a): Range distribution of 3 keV nitrogen ions implanted in copper. (b): Depth profile of a similar sample overcoated with approximately 18 Å copper layer and then bombarded with 3 keV neon ions. The vertical line at 18 Å represents the original surface of the sample.

The distortion of the profile upon secondary neon



igure 4. Depth profile of 4 keV nitrogen ions implanted in copper sample which is overcoated with ~20 Å copper ıyer following the ion implantation and then bombarded ·ith 2 keV neon ions. (b): Depth profile of a sample imlanted with 2 keV nitrogen ions and bombarded with 4 keV eon ions in the final step

nplantation depends on how much damage is created n the sample by the neon ions and their projected ange. In fact if the neon ions do not significantly ross the interface of the copper sample and the overoat layer, the resultant distribution should show only ı small diffusion of the original surface localized nirogen to the new surface through the vacancies. Howver, if the neon ions penetrate deep into the distribuion, the whole profile is affected by the produced deects. The results of such experiments are shown in igure 4. It is clear from the two distributions that in he case of the 4 keV nitrogen and 2 keV neon experinent, only the surface localized peak is distorted by RED but, in the case of 2 keV nitrogen and 4 keV neon ions, the whole profile is distorted and none of he peaks in the original distribution is well proounced.

Although in the above experiment the defects were produced by means of an auxiliary ion such as neon, it is believed that similar self-induced defects [10] cause the surface localized peak in the distribution of nitrogen ions in copper. The profile is distorted by the de-

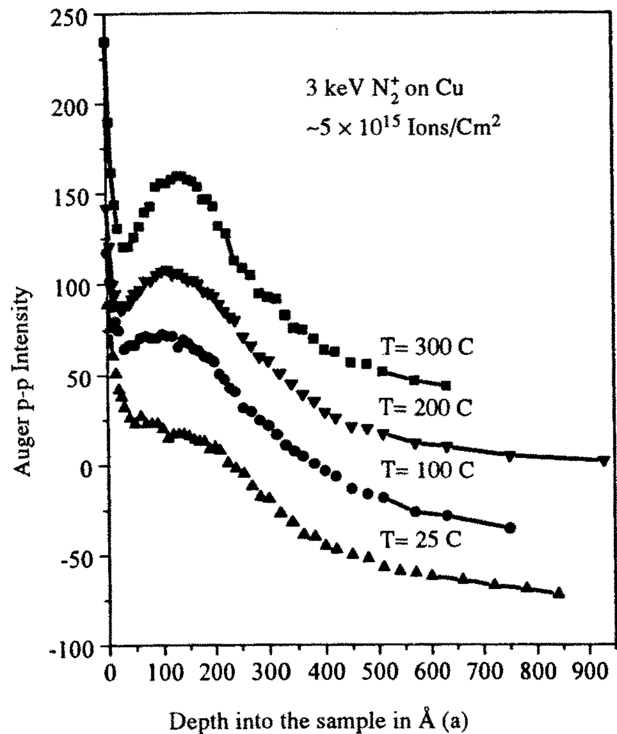


Figure 5. Range distributions of 3 keV nitrogen ions in copper implanted at different temperatures

fects created near the surface during ion implantation and the chemical potential difference at the surface and at the peak of the distribution results in the flow of nitrogen ions toward the surface, creating the surface peak. The fact that the area under the distribution is an indication of the amount of nitrogen ions implanted in the sample, supports the above argument that the original implanted ions flowed to the new surface (Fig. 3).

In another experiment, the same doses of nitrogen ions at the same energy were implanted at different temperatures in a copper sample. The results are shown in Figure 5. When the temperature of the sample is raised, the mobility of the defects increases resulting in a redistribution of the implanted nitrogen atoms [23]. Vacancy migration in one direction will result in mass transport in the opposite direction provided the solute-vacancy interaction is weak [8]. This is in close agreement with the presently observed behavior of the high temperature segregation effect (Fig. 5). Furthermore, these facts all point to the conclusion that vacancy migration is responsible for the observed high temperature segregation effect.

Conclusion

Depth profiles of low energy (1-4 keV) N_2^+ ions

implanted in Cu show a strong surface localized peak and a bulk feature. The enriched surface peak is interpreted as radiation induced segregation of implanted nitrogen ions toward the surface. The mechanism is investigated by creating defects in an overcoat layer on the surface of the sample following the implantation and observing the migration of the initially implanted ions toward the new surface. It is believed that the initial implanted nitrogen ions in copper segregate to the new surface through the open channels created in the overcoat layer by auxiliary ions. The effect of temperature on defect mobility and thus on the range distribution is also investigated.

Acknowledgements

The author wishes to thank Dr. Alex Ignatiev for providing the facilities at the University of Houston which made the performance of the experiments related to this work possible. His moral and financial support is also appreciated. Special thanks are also due to Dr. Sven Touggard for his theoretical and experimental ideas and support. This work was partially supported by the Welch Foundation.

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