PRECIPITATION OF Kr AFTER IMPLANTATION INTO Al*

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ABSTRACT

Transmission electron microscopy (TEM) was used to perform a systematic study of the microstructural evolution in Al as a function of the fluence received during 65 keV Kr^+ ion implantation at room temperature. At the lower fluences ($2 \cdot 10^{16}$ to $2 \cdot 10^{19} \text{ Kr}^+ \text{m}^{-2}$), isolated dislocation loops and the evolution of a dislocation network was observed by TEM. Above fluences of $10^{19} \text{ Kr}^+ \text{m}^{-2}$, the microstructure is dominated by a high density of Kr bubbles whose average size increases with dose. The appearance of additional electron diffraction reflections indicates that the majority of the bubbles contain solid fcc Kr that is epitaxially aligned with the fcc Al matrix. Above fluences of $2 \cdot 10^{20} \text{ Kr}^+ \text{m}^{-2}$ an increasing fraction of the Kr is in a liquid or gas-like phase. The thermal stability of the microstructure, characteristic of the different fluence regimes, was investigated up to 640 °C by in situ TEM annealing experiments.

INTRODUCTION

Interest in the precipitation of noble gases in metals has been stimulated by observations of extremely high atom densities and solid phases of the noble gas atoms contained within small bubbles at room temperature /1-8/. Such bubbles and the microstructural changes associated with their production are important to the complete understanding of the ion beam mixing or material modifications produced by energetic noble gas atoms. As an extension of this previous work, a systematic study of the precipitation of Kr implanted into Al at room temperature was performed with the emphasis on the role of Kr in the microstructural evolution. Also the thermal stability of the microstructure and the Kr precipitates was investigated in several TEM in situ annealing experiments up to 640 °C.

EXPERIMENTAL

Thin polycrystalline Al films (~ 70 nm thick) with grains several μm in diameter were prepared by evaporation of high purity Al in a vacuum of $5 \cdot 10^{-9}$ Torr onto cleaved NaCl. Specimens were then floated in water onto Cu TEM grids and were implanted with 65 keV Kr^+ ions at room temperature at a flux of about $2.5 \cdot 10^{16} \text{ Kr}^+ \text{m}^{-2} \text{sec}^{-1}$ to fluences between $2 \cdot 10^{16} \text{ Kr}^+ \text{m}^{-2}$ and $2 \cdot 10^{20} \text{ Kr}^+ \text{m}^{-2}$. Simulations with the TRIM computer code /9/

indicate that the Kr depth profile within the Al film peaks near the center of the film at this implantation energy. TEM observations were performed with a Philips EM-400T at an operating voltage of 120 kV and at magnifications up to 100000. Thus, image details of diameters $\gtrsim 1$ nm are detectable. Dislocation structures present at lower fluences, ϕ , were imaged under kinematical imaging conditions by their diffraction contrast, whereas Kr bubbles (Fig. 1,2) were imaged under defocus contrast. The lattice constant of the solid fcc Kr was determined from {111} Kr reflections in the electron diffraction pattern. The averaged amount of Kr, C_{Kr} , retained in the films was determined for three different ϕ by Rutherford backscattering of 1.6 MeV He ions (from the IFF Tandetron accelerator). A linear increase of C_{Kr} with ϕ is observed up to $4 \cdot 10^{20} \text{ Kr}^+ \text{m}^{-2}$ (corresponding to $C_{Kr} = 0.12$) indicating a very efficient trapping of Kr in these films. Changes in the microstructure during annealing up to 640°C were investigated in TEM in situ experiments using stepwise temperature increases of about 20 minutes duration.

RESULTS

The microstructural evolution during implantation - as observable by TEM - may be categorized on the basis of the Kr implantation fluence. In the low fluence regime ($\lesssim 10^{17} \text{ Kr}^+ \text{m}^{-2}$) the implantation produces isolated dislocation loops. The loops increase in size as the Kr fluence is increased until

($\phi \gtrsim 10^{18} \text{ Kr}^+ \text{m}^{-2}$) their interaction results in the formation of a dislocation network. At Kr fluences above $10^{19} \text{ Kr}^+ \text{m}^{-2}$, the microstructure is dominated by the appearance of cavities produced by the clustering of vacancies (Fig. 1). The cavities display typical TEM contrast behavior under defocus imaging conditions. At a fluence of $1 \cdot 10^{20} \text{ Kr}^+ \text{m}^{-2}$, a high density of small cavities ($2 \cdot 10^{24} \text{ m}^{-3}$, $2r \sim 1.7 \text{ nm}$) is observed within the single-crystal Al grains (Fig. 1a). The grain boundaries are decorated by considerably larger cavities ($2r \sim 6 \text{ nm}$). The average cavity size within the grains increases with ϕ until at $6 \cdot 10^{20} \text{ Kr}^+ \text{m}^{-2}$ the size distribution contain cavities as large as 40 nm.

At fluences greater than $6 \cdot 10^{19} \text{ Kr}^+ \text{m}^{-2}$ Kr precipitates as a solid within cavities. This is indicated by additional reflections in the electron diffraction pattern identifiable as due to solid Kr (Fig. 1a). Dark field imaging using these reflections establishes that the locations of the Kr precipitates coincide with the cavities. The symmetries of Kr diffraction patterns observed for different orientations of the Al matrix shows that the Kr precipitates in these cavities are epitaxially aligned with the Al matrix as solid fcc Kr. At a fluence of $1.3 \cdot 10^{20} \text{ Kr}^+ \text{m}^{-2}$ the average Kr density deduced from the Kr lattice parameter is $2.64 \cdot 10^{28} \text{ Kr m}^{-3}$ corresponding to a Kr pressure of about 22 Kbar /10/. At $2.2 \cdot 10^{20} \text{ Kr}^+ \text{m}^{-2}$ the density is $2.52 \cdot 10^{28} \text{ Kr m}^{-3}$ corresponding to a pressure of about 16 Kbar. This is of the order of the estimated equilibrium

pressure $p = 2\gamma/r \sim 20$ Kbar (free surface energy $\gamma = 1 \text{ Nm}^{-1}$ for Al [11/ average radius $r = 0.85 \text{ nm}$) of such cavities. This indicates that the cavities contain Kr under high pressure but that they are not highly overpressurized in contrast to the case of small He bubbles formed during low energy He implantation of Al [3/]. The comparably higher number of radiation induced vacancies expected from cascades produced by energetic Kr^+ implantation may explain this observation.

As the fluence is increased and the cavity size increases, the Kr density decreases. At fluences above $2 \cdot 10^{20} \text{ Kr}^+ \text{m}^{-2}$, when larger cavities are present, an additional diffuse ring of diffraction intensity, superimposed on the diffraction spot pattern (Fig. 1b) indicates that an increasing amount of the Kr is in a liquid or gas-like state. This observation suggests that cavity growth during implantation is accompanied by a phase transformation of the Kr from the solid into a liquid or gas-like state.

The thermal stability of the room temperature implanted specimens was studied for both low and high Kr fluences. Annealing of the dislocation structures was investigated for two low-fluence specimens that initially contained isolated dislocation loops ($2 \cdot 10^{17} \text{ Kr}^+ \text{m}^{-2}$) and dislocation loops intermingled with dislocation tangles ($2 \cdot 10^{18} \text{ Kr}^+ \text{m}^{-2}$). For the lowest fluence the dislocation loops were completely annealed away above 200°C , and the specimen regained the appearance of unirradiated ma-

terial. For the higher fluence, annealing up to 550 °C did not result in any observable Kr precipitation. The specimen showed only minor differences to the first: at 170 °C the smaller loops had disappeared by dissolving or coalescing into the larger loops or tangles, and at 230 °C most of the dislocations had disappeared. The thermal stability of the Kr bubbles was investigated by annealing a specimen implanted at room temperature with $1.1 \cdot 10^{20} \text{ Kr}^+ \text{ m}^{-2}$. This specimen contained in the unannealed state a dislocation network and bubbles ($2r \sim 1.7 \text{ nm}$), and its electron diffraction pattern contained the extra spots associated with solid Kr. During annealing up to 300 °C there were only minor changes in the bubble and dislocation structures. The Kr in the bubbles remained solid. Above 300 °C the bubbles began to coarsen to form larger bubbles, the bubble density decreases and the diffraction spots due to the Kr decreased in intensity while a diffuse ring became visible. At 420 °C the average bubble size had approximately doubled and the extra diffraction spots were barely detectable. The grain boundary bubble size had become very large (projected size $< 20 \text{ nm}$). At 540 °C the bubbles began to form facets. At 640 °C the microstructure consisted of large bubbles ($2r < 20 \text{ nm}$) and a dislocation network that had considerably coarsened. The large grain-boundary bubbles had coalesced and some holes were formed in the specimen. Observation at room temperature showed all the remaining bubbles to be faceted (Fig. 2).

Although the electron diffraction pattern at 420 °C indicated that almost none of the Kr was solid, the pattern taken upon cooling to room temperature contained both the solid Kr diffraction spots and the liquid gas-like diffraction ring. This is additional indication that thermally induced phase changes in some of the bubbles may occur. This growth can be achieved by either bubble coalescence or Ostwald ripening process. The bubble coarsening continued as the temperature was increased, and after annealing at 540 °C the extra electron diffraction from the solid Kr was undetectable at room temperature. The Kr density, determined from the Kr lattice parameter measured at room temperature, showed a monotonic decrease with annealing temperature. The Kr lattice diffraction disappeared as the average Kr density decreased to about the value of solid Kr at its one atmosphere melting point /12/.

CONCLUSIONS

The precipitation of Kr in Al was investigated with TEM and RBS, both during room temperature Kr implantation (fluences $< 6 \cdot 10^{20} \text{ Kr}^+ \text{m}^{-2}$) and during subsequent annealing at higher temperatures (annealing temperatures $T_a < 640 \text{ }^\circ\text{C}$). The results may be interpreted as follows:

During room temperature implantation the Kr becomes efficiently trapped and forms a high density of small Kr pre-

cipitates or bubbles. With increasing ϕ these bubbles grow and coarsen due to absorption of Kr and radiation-induced vacancies. Electron diffraction reveals that epitaxial alignment of solid Kr dominates in small bubbles and indicates bubble pressures of the order of the equilibrium bubble pressure. An increasing fraction of the Kr transforms into a liquid or gas-like phase as the bubbles grow during further implantation.

During annealing bubbles coarsen with increasing T_a , probably under vacancy absorption at high temperatures as result of thermal vacancy absorption. Consequently an increasing fraction of Kr also transforms from a solid state into a liquid or gas-like state during annealing.

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REFERENCES

- /1/ W. Jäger and J. Roth, J. Nucl. Mater. 93&94 (1980) 756.
- /2/ J.C. Rife, S.E. Donnelly, A.A. Lucas, J.M. Gilles and J.J. Ritsko, Phys. Rev. Lett. 46 (1981) 1220.
- /3/ W. Jäger, R. Manzke, H. Trinkaus, R. Zeller, J. Fink and G. Crecelius, Rad. Effects 78 (1983) 315.
- /4/ J.H. Evans and D.J. Mazey, J. Phys. F: Met. Phys. 15 (1985) L1.
- /5/ M. Eldrup and J.H. Evans, J. Phys. F: Met. Phys. 12 (1982) 1265.
- /6/ A. vom Felde, J. Fink, Th. Müller-Heinzerling, J. Pflüger, B. Scheerer, G. Linker and D. Kaletta, Phys. Rev. Lett. 53 (1984) 922.
- /7/ C. Templier, C. Jaouen, J.-P. Rivière and J. Grilhé, C.R. Acad. Sci., Paris 299 (1984) 613.
- /8/ R.C. Birtcher and W. Jäger, J. Nucl. Mater, to be published.
- /9/ J. Biersack and L.G. Haggmark, Nucl. Instr. and Meth. 174 (1980) 257.

/10/ C. Ronchi, J. Nucl. Mater. 96 (1981) 314.

/11/ L.E. Murr, Interfacial Phenomena in Metals and Alloys
(Addison-Wesley, Reading, MA. 1975).

/12/ D.L. Losee and R.O. Simmons, Phys. Rev. 172 (1968)
944.

FIGURE CAPTIONS

Fig. 1: TEM defocus contrast of Kr-filled cavities produced by 65 keV Kr^+ -implantation into Al and corresponding $\langle 110 \rangle$ electron diffraction patterns from the same area. Note Kr diffraction spots in epitaxial relation to and of the same symmetry as the Al diffraction spots. Additional spots occur due to double diffraction.
(A) $\phi = 1.1 \cdot 10^{20} \text{ Kr}^+ \text{m}^{-2}$
(B) $\phi = 5.5 \cdot 10^{20} \text{ Kr}^+ \text{m}^{-2}$.
Diffraction contrast from dislocations is superimposed in (A).

Fig. 2: TEM defocus contrast of faceted cavities produced by 65 KeV Kr^+ -implantation into Al ($\phi = 1.1 \cdot 10^{20} \text{ Kr}^+ \text{m}^{-2}$) after annealing to 640°C .

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