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SIMS depth profiling of implanted helium in Al–Mn alloy using CsHe$^+$ molecular ion detection

A K TYAGI, K G M NAIR and K KRISHAN
Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

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Abstract. The use of Cs$^+$ primary ions in conjunction with the detection of CsHe$^+$ molecular ions is proposed for the analysis of helium in metals by secondary ion mass spectrometry (SIMS). Concentration depth profiles of helium implanted at 100 keV in $Al_{60}Mn_{40}$ alloy have been measured. Helium concentrations down to about 100 ppm were measured at moderately low sputtering rate of 0·5 nm/sec. The experimentally determined implantation profile of helium is compared with the theoretical profile obtained using the Monte Carlo Code TRIM.

Keywords. Ion implantation; secondary ion mass spectrometry; depth profiling; sputtering; molecular ions.

1. Introduction

The analysis of inert gases, particularly helium, in metals is of considerable interest (Ullmaier 1983; Donnelly and Evans 1990). Different analytical techniques have been used for the depth profile analysis of helium in solids, the most prominent ones being nuclear reaction analysis (NRA) (Behrisch *et al* 1975; Biersack *et al* 1979), proton backscattering (Blewer 1973, 1976), elastic recoil detection (Ecuyer *et al* 1976; Terreault *et al* 1977) and secondary ion mass spectrometry (SIMS) (Wilson *et al* 1982; Wilson 1984). The first three amongst these are high energy ion beam techniques which need rather larger accelerators and often do not provide high sensitivity, wide dynamic range and high depth resolution inherent to SIMS technique. On the other hand, although SIMS technique, in principle, is applicable to all the elements, the measurement of helium implantation profile was considered very difficult. Helium and other inert gases do not form negative ions and their first ionization potentials are sufficiently high so that positive ion formation is relatively low. Helium has the highest ionization potential in the periodic table (24·58 eV) and is therefore the least sensitive positive atomic ion for measurement by SIMS. Nevertheless, some attempts have been made to measure implantation profiles of helium and other inert gases in solids by SIMS technique. Wilson *et al* (1982) and Wilson (1984) reported depth distributions of (20–300 keV) helium implanted in Si, GaAs, HgCdTe and CdTe measured under high current O_2^+ bombardment in SIMS. Similar results have been reported by Ray *et al* (1988) for 200 keV Ar and Kr implantation profiles in Si, Ge and GaAs measured by SIMS. However, it was proposed (Williams and Streit 1986; Ray *et al* 1988) that in these experiments ionization occurred in inelastic gas phase collisions with the primary beam ions subsequent to the sputter ejection of inert gas neutral atoms. This necessitated the use of very high O_2^+ primary ion current densities (35–40 mA/cm^2) for analysis which in turn resulted in extremely high specimen erosion rates (> 10 nm/sec) and consequently led to the deterioration of depth resolution.

Gnaser and coworkers (1985, 1986, 1987) employed electron impact post-ionization of sputtered helium neutrals to measure concentration depth profiles of helium implanted with energies (0·25–80 keV) in Si and Ni. This technique, known as sputtered neutral mass spectrometry (SNMS), was successful to measure helium concentrations down to 10–100 ppm at erosion rates of 0·1–0·5 nm/sec with a typical depth resolution of about 3·1 nm. Recently, Ray *et al* (1988) described a more convenient SIMS scheme for depth profiling of implanted inert gas atoms in semiconductors. They have measured 200 keV Ar and Kr implantation profiles in Si, Ge and GaAs by monitoring $CsAr^+$ or $CsKr^+$ molecular ions under Cs^+ primary ion bombardment in SIMS. Reasonable detection limits (10–100 ppm) were obtained at low erosion rates ($\sim$ 0·2 nm/sec). There are no reported measurements of helium implantation profiles in metals which in contrast to semiconductors may pose special problems arising due to different electronic transfer properties.

In this paper we report measurement of a helium depth profile in a metallic alloy $Al_{60}Mn_{40}$. The helium implantation was done using 100 keV helium ion beam. The $Al_{60}Mn_{40}$ alloy had a highly ordered stoichiometric bcc structure with twin boundaries. It had very low density of dislocations or other defects which can act as strong trapping sites for helium. In separate irradiation experiments and TEM studies done on this alloy it showed resistance to helium damage till high doses of the order of 5×10^{17} ions/cm^2 (Nair *et al* (to be published)). The alloy was extremely hard (800 VHN) and had very low sputtering rate which made it an attractive candidate for the present investigation.

2. Experimental

The alloy having nominal composition of Al-40 a/o Mn was prepared by melting 99·99% pure aluminium and manganese in an induction furnace under inert gas atmosphere. The alloy was very hard and brittle. It was sliced into 2 mm thick specimens of size 8×8 mm^2 using a diamond wheel. These specimens were then given a fine metallographic polish using diamond abrasive and irradiated with a mass analyzed beam of 100 keV helium ions from a low energy ion accelerator. Irradiations were carried out at room temperature in an irradiation chamber pumped with a turbomolecular pump to a vacuum of 10^{-6} mbar. The ion beam was incident normal to the specimen surface and the beam area was defined by a circular aperture of 5 mm diam. The ion beam current density was kept constant at 2·5 μA/cm^2 during each irradiation. This corresponds to an ion flux of about $1{\cdot}5 \times 10^{13}$ He/cm^2.sec. The beam current and irradiation dose were measured with the help of a current integrator. The secondary electron emission was suppressed to ensure that these did not introduce any error in the ion current and dose measurement.

SIMS analyses were performed in a CAMECA IMS-4f ion microscope-ion microprobe. A 10 keV Cs^+ primary ion beam, with a spot size of about 20 μm, was employed for sputtering. The primary ion beam was raster scanned over a specimen area of $250 \times 250\,\mu m^2$ and positive secondary molecular ions $CsHe^+$ were collected only from the central circular area of 60 μm diam. defined by transfer lens – field aperture couple. This procedure was adopted to avoid crater edge effects (Wilson *et al* 1989). The primary ion beam current was about 100 nA (0·16 mA/cm^2). The instrument was operated at a mass resolution of 300 and with an energy band pass of 130 eV.

3. Results and discussion

Figure 1 shows a typical SIMS depth profile of implanted helium in Al–Mn alloy obtained by monitoring $CsHe^+$ molecular ions. The implantation fluence is $4{\cdot}8 \times 10^{16}$ He/cm^2. The depth scale of the profile was established by measuring sputtered SIMS crater depths using a surface profilometer (Sloan, Dektak). The erosion rate was estimated to be 0·5 nm/sec with an uncertainty of about 10%. Helium concentrations (atoms/cm^3) were determined from the measured secondary ion intensities (c/s) by setting the integral of the measured depth distribution equal to the implanted fluence (Gittins *et al* 1972).

The concentration depth profile of figure 1 demonstrates a dynamic range better than two decades and a detection limit of $< 1 \times 10^{19}$ He atoms/cm^3 (~ 100 ppm). This is quite good considering the very low specimen erosion rate of 0·5 nm/sec employed in present experiments and that the detection of helium as atomic ions is the most difficult situation for SIMS analysis. The depth resolution in present experiments is also expected to be good as the sputtered craters were fairly smooth, erosion rate was very low ($\sim$0·5 nm/sec) and the crater edge effects were avoided by means of optical gating. A lower limit to the depth resolution can be estimated as the penetration depth of primary Cs^+ ions bombarding the specimen with an impact energy of 5·5 keV and at an incidence angle of 42° with respect to the specimen surface normal. This value is about 3·8 nm.

The values of maximum helium concentration (C_m), the depth of maximum

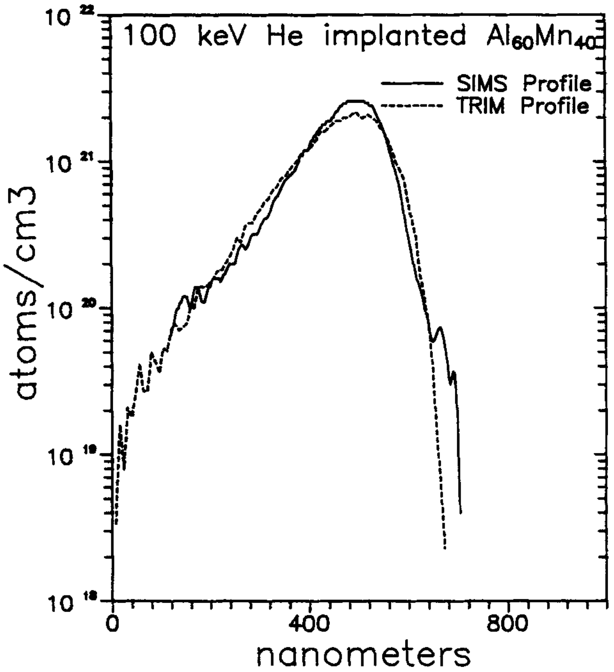

Figure 1. The measured and calculated depth profiles of helium implanted in $Al_{60}Mn_{40}$ alloy at 100 keV to a dose of $4{\cdot}8 \times 10^{16}$ ions/cm^2. The measured profile (solid curve) was obtained by SIMS by monitoring $CsHe^+$ ions. The calculated profile (dashed curve) was obtained using the TRIM code.

concentration (R_m) and the straggling (ΔR_m) can be determined from the measured implantation profile. These values are $C_m \sim 2{\cdot}6 \times 10^{21}$ atoms/cm^3, $R_m \sim 500$ nm and $\Delta R_m \sim 78$ nm for the profile in figure 1. We have also calculated the depth distributions of 100 keV helium ions implanted in an $Al_{60}Mn_{40}$ alloy using the Monte Carlo code TRIM (Biersack and Haggmark 1980). The calculated profile is shown by the dashed line in figure 1. The corresponding values of C_m, R_m and ΔR_m are $2{\cdot}2 \times 10^{21}$ atoms/cm^3, 496 nm and 92 nm, respectively. It is evident that the measured and the calculated depth profiles are in fairly good agreement.

It is interesting to note that monitoring of CsX^+ molecular ions (X designates the element of interest) has provided, in general, a reduction of matrix effects in comparison to the detection of the respective atomic ions (Gao 1988; Magee *et al* 1990). This scheme of cationization is in fact being considered as a more convenient alternative to post-ionization methods for quantitative analysis using SIMS (Migeon and Schuhmacher 1991). Cesium has a very low first ionization potential (3·89 eV) and is therefore emitted from a surface as Cs^+ with almost 100% efficiency. In SIMS, under Cs^+ primary ion bombardment, a steady state is reached when all the cesium bombarding the surface is reemitted as Cs^+. This results in a large flux of Cs^+ leaving the specimen and becoming available to combine with sputtered neutral atoms (X) to form CsX^+ molecular ions at the specimen surface. This mechanism of CsX^+ formation offers decoupling of the sputtering and ionization processes thus making the analysis more quantitative.

To summarize, we have shown that the implanted helium can be depth-profiled by SIMS technique in $Al_{60}Mn_{40}$ by utilizing the detection of $CsHe^+$ secondary molecular ions during sputtering with Cs^+ primary ions. Helium concentrations down to about 1×10^{19} He atoms/cm^3 (~ 100 ppm) were measured at moderately low erosion rate of 0·5 nm/sec. While the present experiments demonstrated the measurement of helium implantation profile in a metallic alloy $Al_{60}Mn_{40}$, the general technique of monitoring CsX^+ molecular ions should be applicable for quantitative in-depth profiling of helium and all other inert gases in metals by means of SIMS technique.

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