Local structures of Co implanted in α-Al₂O₃ single crystal II

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Introduction

Implantation of metal ion brings about the colour of a colourless single crystal oxide, which can be used for the synthesis of new optical materials. Since the structure of the metal species is unclear at moment, two origins for the coloration have been proposed: surface plasmon of the implanted metal particles in dielectric material and electron transitions between valence and conduction orbitals of the metal ionic species. We found the various Co structures implanted in the α -Al₂O₃ depending on the implanted energies (around 20 keV) [1]

We have carried out the structure analysis of cobalt ion implanted in the α -Al₂O₃ which fabricated by high energy (3MeV) ion implantation and post thermal annealing. The colour of the as-implanted Co species is dark grey and it changes to light grey after(during) annealing. The purpose of this study is to unveil the origin of the different colours in two different implantation energies and annealing treatment.

Experiment

A 0.5 mm thick α -Al₂O₃ single crystal was cleaned with acetone. 3×10^{16} atom/cm² of Co⁺ ion was implanted by Ar⁺ plasma assisted ion source(operated at 3MeV). Post annealing was carried out for 1 hour at 1073K, 1273K and 1773K respectively in air. XAFS was measured at BL12C in a fluorescence mode at room temperature in air. The fluorescence X-ray was detected using a 19-elements SSD.

Results and discussion

Fig.1 shows Fourier transform of the k³-weighted EXAFS oscillations. Co-O(0.19nm) peak appears in the Fourier transform of the as-implanted sample, indicating the presence of oxidized Co dispersed in the α -Al₂O₃. This result is different from the case of low energy implantation.

During the annealing process, Co-O peak decreased and disappeared at 1273 K accompanied by the appearance of Co-Co peak. The peak increases with the annealing temperature, indicating the reduction of Co oxide and the creation and growth of the Co metal particles in the α -Al₂O₃. From the curve fitting for the sample annealed at 1773K, coordination number of Co-Co(0.25nm) bond is 9.6, and Co metal particle size is 1.8nm.

However, in low energy implantation, Co species of as implanted sample is metal particle while it is reacted with Al oxide after the annealing to form cobalt aluminates.

The difference of Co behavior against Co beam energy can be explained as follows. The implantation depths for the low (20keV) and high (3 MeV) energy Co beam into α -Al₂O₂ are about 10nm and 1600 nm, respectively calculated from the TRIM code calculation. In the low energy implantation Co species is concentrated at the surface region and Co metal cluster is formed. During the annealing process the Co ions can be reactive with the surface active oxygen and to produce the surface Co aluminate. In the high energy implantation the Co species widely dispersed in the Al₂O₃ lattice which was defected by the high energy ion implantation. During the annealing process, the Al₂O₃ lattice was recovered and Co species was removed from the lattice to create the large Co particles. To the best of our knowledge, this is the first example that clearly shows the annealing effect of coloration by the ion implantation.

References [1] K. Ijima et al., PF activity report(2003)193

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Figure 1 Fourier transforms of the k3-weighted EXAFS oscillations.