Local structures of Co implanted in α-Al₂O₃ single crystal

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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 have carried out the structure analysis of cobalt ion implanted in the α -Al₂O₃. The colour of the as-implanted Co species is dark grey and it changes its colour, depending on annealing temperatures during the post annealing processes. When the sample was annealed at 1000 °C, the colour turned light blue.[1] The purpose of this study is to find the origin of the colour change.

Experiment

A 0.5 mm thick α -Al₂O₃ single crystal was cleaned with acetone. 10¹⁷atom/cm² of Co⁺ ion was implanted by Ar⁺ plasma assisted ion source(operated at 20keV, 1µA). Post annealing was carried out for 3 hour at 1273K in air. XAFS was measured at BL12C in a fluorescence mode at room temperature in air. The fluorescence X-ray was detected by a 19-elements SSD.

Results and discussion

Only Co-Co (0.25nm) peak appears in the Fourier transform of the implanted sample, indicating the presence of Co metal particles dispersed in the α -Al₂O₃. During the implantation, the neutralization of Co ion occurs. However, after the thermal treatment at 1273 K, the Co species are highly dispersed. Figure 1 shows the Fourier transforms of the EXAFS oscillations for the implanted Co species in α -Al₂O₃, followed by 1273 K thermal treatment(solid line). There are two main peaks. The 1st and 2nd peaks are due to the Co-O bond and the Co-Al bond, respectively. Figure 1 shows Fourier transform of the powder Co₃O₄ (broken line) for reference. The 1st shell in the Fourier transform of the Co₃O₄ spinel is Co-O bond (0.19nm). The 2^{nd} and 3^{rd} peaks arise from the Co-Co interaction between the two 16b-site (0.29nm) and from the Co-Co bonds between 16b-site and 8asite(0.34nm) and those between 8a and 8a sites(0.35 nm). The 2nd shell peak in the Co-implanted sample appears at the same position as that of the 3rd shell peak in the

powder Co_3O_4 . The peak of 0.28nm is missing in the Coimplanted sample indicating the Co is located only in the 8a site.

There are several morphologies in Al₂O₃ besides the α -Al₂O₃. γ -phase is another typical morphology which is a defect spinel structure and crystallized at low temperature. Thus the implantation of Co has made α -Al₂O₃ to be a amorphous structure. During the thermal process the γ -Al₂O₃ phase may be first crystallized in which the implanted Co was involved to form the spinel type structure. The other possibility is formation of the binary oxide CoAl₂O₄ which also has a spinel structure with the Co located at the 8a-site. In this case the 2nd peak is composed of Co-Co at 8a sites and Co-Al. Thus we are now analysing the 2nd peak by a curve fitting method to clarify the presence of Co-Co interaction in addition to the Co-Al.

References

[1] Y. Saito et al., Nucl. Inst. and Methods in Phys. Research B59/60,1173 (1991).



Figure 1 Fourier transforms of the k3-weighted EXAFS oscillations. Co-implanted sample (solid line). Powder Co_3O_4 (broken line).

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