SURFACE SEGREGATION EFFECTS IN AL_2O_3 IMPLANTED WITH HIGH DOSE INDIUM

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(Received November 1989)

ABSTRACT

Implantations of 100 keV In ions to high dose of 6×10^{16} In/cm^2 were performed into a-axis oriented crystals of Al_2O_3 held at a liquid nitrogen temperature. The implantation produced about 80nm thick amorphous surface layer. Isothermal annealing in flowing Ar gas ambient was done at the temperatures of 600, 700, 800, and 900℃. Rutherford backscattering and channeling (RBS-C), scanning electron microscope (SEM) and reflection high energy electron diffraction (RHEED) have been employed to investigate the annealing behaviors.

The indium shows anomalous diffusion in amorphous layer. The migration of indium was composed of two parts: (a) some broadening of In profile corresponding to diffusion within the amorphous layer. (b) segregation of In to surface to form In_2O_3 which appears as islands on the surface. When the ambient is made oxygen free, the segregated In is lost by evaporation at the surface.

Key words: Surface segregation effects Ion implanted Isothermal annealing

Ⅰ.INTRODUCTION

Ion implantation has been used extensively in recent years to create novel mechanical, optical, chemical and electrical properties [1-4]. Implantation parameters such as energy, ion dose, ion species and substrate temperature can be selected to produce surface microstructures which can be crystalline or amorphous[5-8]. Post ion implantation heat treatments produce further changes in microstructure and impurity in implanted layer.

Previous studies[1-8] on ion implantation in Al_2O_3 indicate that (a) lattice damage accumulates to amorphous Al_2O_3. (b) implanted species either undergoes a recrystallization - driven migration outward to surface or do not diffuse appreciably, (c) under certain conditions, a rapid isotropic diffusion of In within the amorphous Al_2O_3 layer is faster than in crystall Al_2O_3 with effective diffusion coefficients up to about 8 orders of magnitude greater.

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In this study, we report our results on the heat treatment of post implantation with high indium dose of 6×10^{16}In/cm^2. The effect of ambient atmosphere during annealing has been studied in detail by employing four different ambients.

II. EXPERIMENTAL

The optically flat, a-axis Al_2O_3 single crystals were used after pre-annealing at 1400°C in an oxygen environment for 5 days, so that these sapphire slices were damage free. In ion implantation was performed at 100 keV energy with the dose of 6×10^{16} In/cm^2 held at about 77K. Ion current density was less than 2 μ A/cm^2 and the chamber vacuum was about 666.6×10^{-7}Pa. The isothermal annealing was performed in flowing high purity Ar gas environment at temperatures of 600, 700, 800 and 900°C. Anneal time was varied from 10 minutes to 24 hours. The role of traces of moisture or oxygen in the gas ambient was studied by performing one hour anneals on identical samples, as follows: (*a*) in flowing dry Ar gas, using liquid nitrogen to dry Ar gas, (*b*) in flowing dry Ar gas with the sample placed on a titanium foil, to getter traces of oxygen, (*c*) in air. The samples were analysed using following techniques: (*a*) 2 MeV helium ion beam RBS-C, (*b*) RHEED using a 100 keV transmission electron microscopy, (*c*) SEM.

III. RESULTS AND DISCUSSION

Indium implantation at liquid nitrogen temperature to high dose of 6×10^{16}In/cm^2 has been studied in detail. The implantation produces amorphous surface layers with thickness about 80 nm. Isothermal annealing in Ar ambient at temperatures of 600, 700, 800, and 900°C show that the amorphous layer undergoes epitaxial regrowth, some indium diffuses within the amorphous layer and some indium diffuses to surface to form In_2O_3 layer on surface.

1.Epitaxial regrowth

The RBS-C spectra Fig.1 to Fig.4 show that the amorphous surface layer undergoes solid phase epitaxial regrowth. At lower temperatures, for example, 600°C and 700°C annealing time up to 24 hours, the amorphous surface layer thickness reduced to 60nm and 28 nm respectively. RHEED patterns confirm that the surface layers are amorphous. However, for higher temperature, for example, 800°C (Fig.3) and 900°C (Fig.4), the regrowth rate is faster than at lower temperatures and the underlying amorphous layer regrows into an imperfect crystal. Perhaps columnar crystallites of α -Al_2O_3 are produced which orient themselves during further annealing.

2. Indium redistribution

Indium redistribution took place during annealing at temperatures of 600, 700, 800 and 900°C. The indium profile is composed of two parts, one is broadened within the amorphous layer, another is segregated at surface (formed In_2O_3)for 600°C, the indium only broadened in amorphous layer and did not segregate to surface, as seen in Fig.1. But for other temperatures, 700, 800 and 900°C(Fig. 2, 3, 4) the indium peak shift to surface. The migration of In gets faster with increasing annealing temperature, since all the observed migration is found to be completed within first short anneal of 15 minutes at 800°C and 10 minutes at 900°C. Indium diffusion within amorphous Al_2O_3 is up to 8 orders of magnitude more rapid than in crystalline Al_2O_3 (10^{-25}cm^2/s). Further annealing up to 24 hours produces no more change in indium profile.

The RHEED patterns (insets Fig. 2, 3, 4) show several rings which all index to In_2O_3 at the surface, showing formation of In_2O_3 at the surface.

3. Origin of oxygen

In order to identify the origin of oxygen picked up during annealing, several identically implanted samples have been annealed at 800°C for one hour with different ambients. The RBS – C spectra (not presented here) indicate that the amorphous phase was formed in implanted layer and indium dose was 5×10^{13}In/cm^2. When we do the annealing, following ambients were used (*a*) in Ar gas, the result was similar with four hours of Fig.3; (*b*) in dry Ar gas, the indium diffuses to surface and about 60% of implanted In is lost from surface; (*c*) in dry Ar gas and the sample was placed on a Ti foil, about 80% of implanted In is lost from surface, and (*d*) in air, the result is quit different from (*b*) and (*c*), the In is not lost during annealing.

Why were the results so different with different ambients? RHEED and SEM were used to study these phenomena. The RHEED results indicate that even when the anneal was done in dry Ar gas still there is a very thin In_2O_3 layer on surface, because we can not reduce oxygen with liquid nitrogen. The RHEED also indicated that the surface is amorphous for (*c*), and no In_2O_3 rings are seen, because the Ti foil can getter the oxygen in dry Ar gas. The oxygen was reduced during annealing so that there is no In_2O_3 formed during annealing. In (*d*) case many In_2O_3 rings are presented because there is plenty of oxygen in air. The SEM picture (not presented here) showed that when the In_2O_3 formed the white spots appeared and EDX measurement indicates that the white spots are rich in indium.

So far we can say the oxygen came from ambient and also explains the In profile after annealing. A tentative model was discussed elsewhere[6]. If the annealing ambient is oxygen free, the most of In will diffuse out to surface, and evaporate from surface. If there is a small amount of oxygen in ambient, some In will form In_2O_3 on surface and some In lost from surface. If the oxygen is rich in anneal ambient, all In diffused to surface will form In_2O_3 layer on surface so that the In profile were composed of two parts, diffusion broadened indium and segregated indium which formed In_2O_3 on surface.

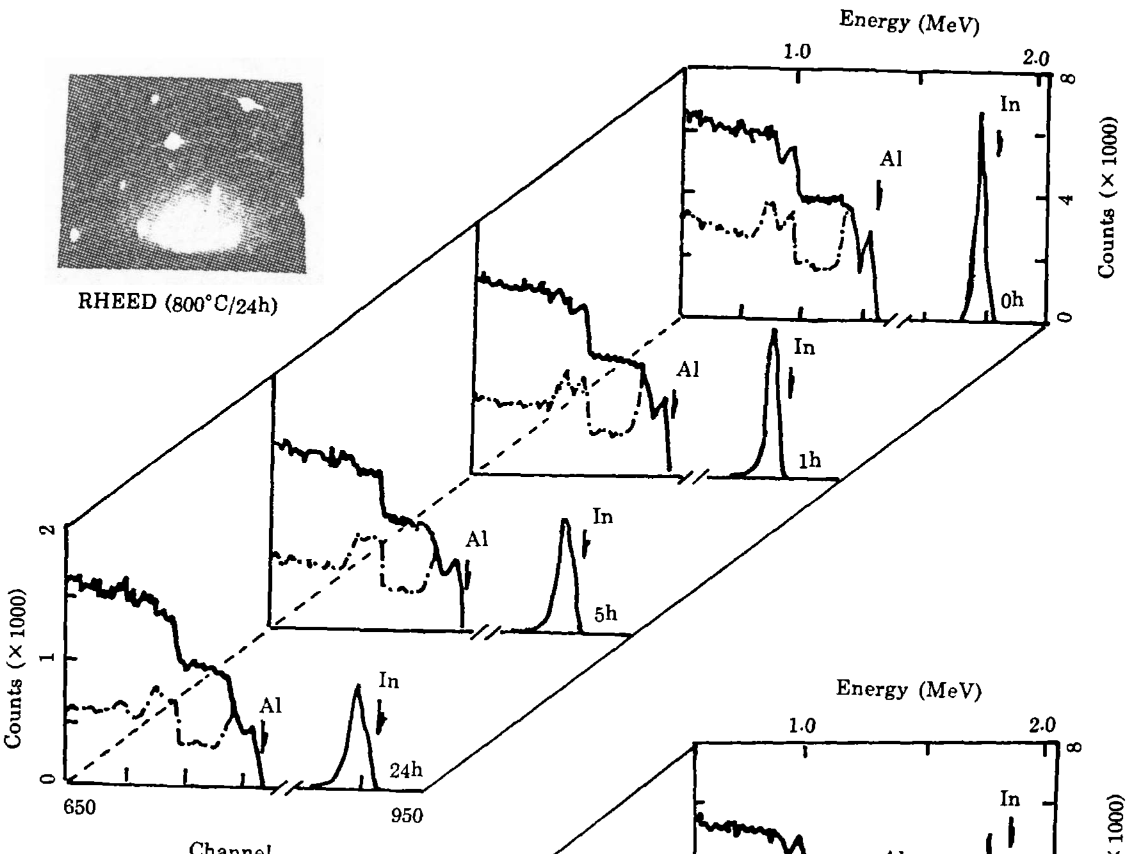

Fig.1 RBS- C spectra of isothermal anneal at 600 °C in flowing Ar gas ambient

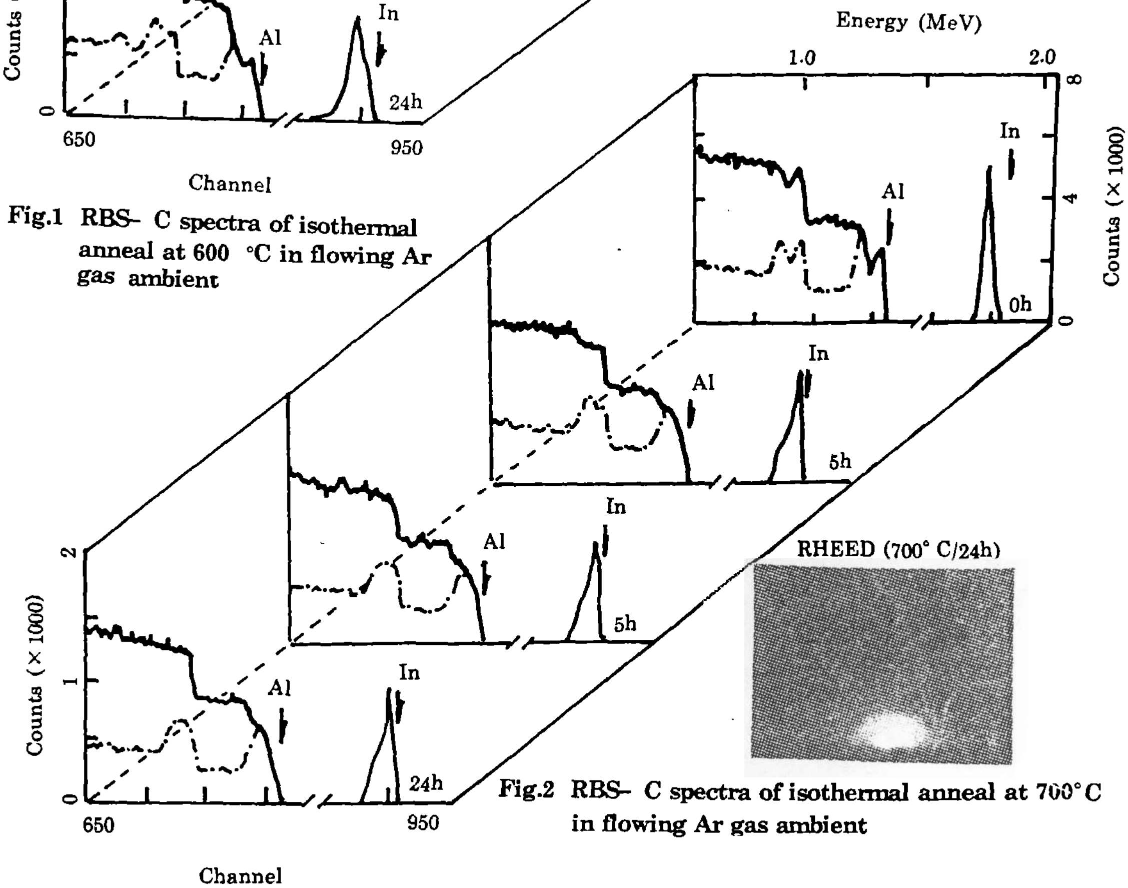

Fig.2 RBS- C spectra of isothermal anneal at 700°C in flowing Ar gas ambient

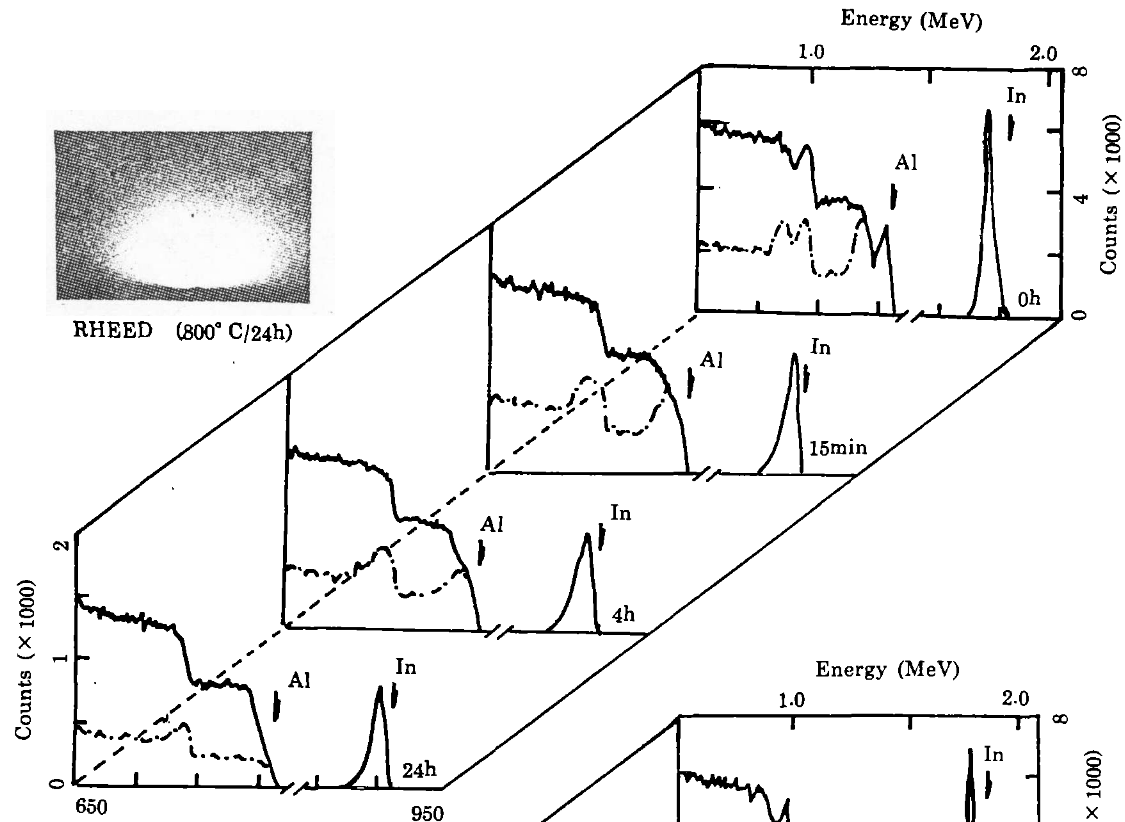

Fig.3 RBS- C spectra of isothermal anneal at 800° C in flowing Ar gas ambient

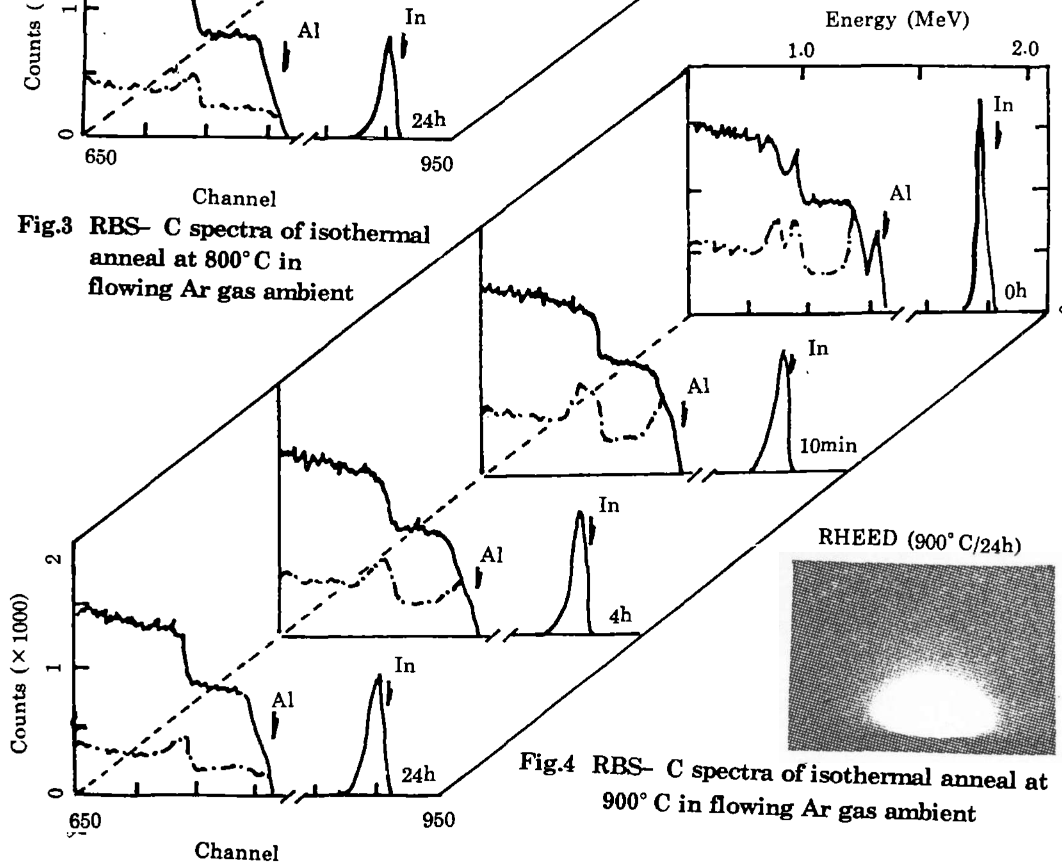

Fig.4 RBS- C spectra of isothermal anneal at 900° C in flowing Ar gas ambient

Ⅳ. SUMMARY

(*a*) High dose (6×10^{16}In/cm^2) indium implantation of a − axis Al_2O_3 at 77K produces amorphous surface layer, the thickness of amorphous layer is 80nm.

(*b*) The amorphous layer undergoes epitaxial regrowth. For further annealing, perhaps columnar crystallites of α − Al_2O_3 are produced at higher temperature (800 and 900°C).

(*c*) In redistribution took place at temperatures of 600, 700, 800 and 900°C. In profile is composed of two parts due to diffusion broadening and surface segregation (which formed In_2O_3 on surface).

(*d*) Indium is very chemically active with oxygen and forms In_2O_3 at the surface. If the anneal ambient is oxygen free, the segregated In evaporates from surface (melting point of In is 159°C).

(*e*) In_2O_3 is very stable at annealing temperature we used.

ACKNOWLEDGEMENTS

The work was sponsored by Australia Research Council. We thank A.P. Pogany for help with RHEED measurements and V. Sood for SEM work.

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