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A — 5 — 2 Electrical Activation and Deep Diffusion of Ion-Implanted Al and Ga in Si

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<u>1. Introduction</u> Diffusion Processes using either aluminum (Al) or gallium (Ga) having high diffusion coefficients are necessary to make deep diffused p-type junctions of silicon (Si). However, in the conventional thermal diffusion process, there have been several disadvantages to consider. These include poor reproducibility, rough diffused-surfaces, complicated masking structures and high manufacturing costs. These problems should be able to be solved by applying an ion implantation process. However, little attention has been paid, so far, to finding a replacement for conventional diffusion by implantation[1]. This is mainly due to the extremely low electrical activity in both Al^+ and Ga^+ implanted Si after annealing[2] (solid solubility $\lesssim 2 \times 10^{19}/cm^3$ for Al and $\lesssim 4 \times 10^{19}/cm^3$ for Ga, respectively). This paper first clarifies the main effects of lowering the activity of Al^+ and Ga^+ implanted Si. Then processes to obtain high electrical activity after annealing at temperatures above 1100°C are proposed. The technique obtained here can be successfully applied to fabrication of devices such as power devices or high voltage IC's to require deep diffused junction structures.

<u>2. General observation results for Al^+ and Ga^+ implanted Si</u> Typical annealing characteristics observed equally for Al^+ and Ga^+ implanted Si are shown in Figs. 1 and 2. Dose dependence of electrically activated Al and Ga concentrations of samples annealed at 800°C for 30 min are shown in Fig. 1. For both Al^+ and Ga^+ implanted samples, electrical activity decreases with the increase of a dose, finally becoming less than 1% at a $1 \times 10^{16}/cm^2$ dose. On the other hand, TEM observations for these samples revealed that high density residual defects existed in all samples in Fig. 1. They also showed that polycrystalline regions remained in layers implanted at doses above $5 \times 10^{15}/cm^2$. From these results, it can be speculated that one cause of the low electrical activity is the interactions between implantation-induced point defects and Al (or Ga) atoms. These are especially strong during annealing stages and the large fraction of Al (or Ga) atoms trapped in residual defects became inactive after annealing. This effect of residual defects on Al (or Ga) atom inactivity is correlated especially for implantation doses above $5 \times 10^{15}/cm^2$ under which conditions polycrystalline regions were formed even after annealing.

The Al and Ga out-diffusion effects evident in high-temperature annealed samples are clearly shown in Fig. 2. Carrier profile results in Fig. 2 were obtained, after a couple of samples, as schematically shown in the figure, were simultaneously annealed in dry N_2 at 1100°C. This indicates Ga out-diffusion is more remarkable than that of Al. In the Al case, the thin native oxide film formed on the implanted surface may act as a barrier to the Al out-diffusion[3]. In connection with this phenomenon, the existence of high concentration Al atoms ($\gtrsim 1 \times 10^{21}$ atoms/cm^3 at a 1×10^{16} ions/cm^2 implantation) was observed in the region close to the surface by SIMS analysis. The above results indicate the following processes are required to improve electrical activity of Al^+ and Ga^+ implanted Si: (1) avoiding generation of the implantation-induced defects in the substrate, (2) protecting the implanted surface with appropriate films to prevent the out-diffusion effect.

<u>3. Ga^+ implantation</u> If implantation into the oxidized substrate surface is carried out and the surface layer is covered with Si_3N_4 films, electrical activity after annealing at temperatures above 1100°C increases to as high as nearly 50%, in strong contrast with several % for usual implantation processes. Ga^+ implantation into the structure of $Si_3N_4 + SiO_2$ films has been reported[1]. However, electrical activity of Ga has not been clarified. A typical example of 1150°C annealing characteristics of Ga atoms implanted into the above structure (800 nm thick SiO_2 and 20 nm thick Si_3N_4) is shown in Fig. 3. The figure indicates annealed layers have high electrical activities and deep diffused junctions in high dose Ga^+ implanted Si. These results

were equally observed under conditions of SiO_2 film thickness below 1 μm and implantation energies below 300 keV. Also, no defects at all were detected in these annealed samples by TEM observations. Comparison of profiles between a carrier profile and a total Ga profile is shown in Fig.4. This figure clearly shows that almost all Ga atoms in the substrate are electrically activated except for the surface region up to a depth of 10 μm. It was also confirmed by chemical analysis that the remaining Ga atoms (about 2 x $10^{15}/cm^2$) almost all remained in Si_3N_4 films.

4. Al^+ implantation   Even if the same structure as for Ga^+ implantation was used for Al^+ implantation, the electrical activity of implanted Al^+ was below 1% after annealing at temperatures above 1100°C. This is considered to be due to the strong interaction between Al and SiO_2 during high temperature heat treatment[3]. Diffusion of Al atoms into the substrate is restricted by this interaction. In this case, higher electrical activation was obtained for the higher energy implanted samples whose surface was coated by CVD SiO_2 films after implantation. Typical examples of deep Al carrier profiles obtained using these processes are shown in Fig. 5.

5. Conclusion   Deep diffused junctions using Al^+ and Ga^+ implantation into Si were realized, keeping high electrical activity, by optimizing ion implantation procedure and by protecting the implanted surface with appropriate films.

References: 1) Y. Koshiro et al: IEEE Trans. Electron Devices, ED-28 1229 (1981). 2) G. Dearnaley et al: Ion Implantation (North-Holland, Amsterdam and London, 1973) p.609. 3) M. Kozawa: National Technical Report, 14 183 (1968). 4) K. Kuga: Bunseki Kagaku, 30 529 (1981).

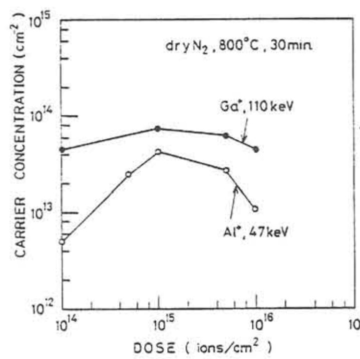

Fig. 1 Dose dependence of electrically activated Al and Ga.

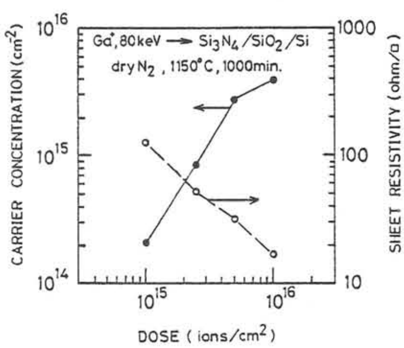

Fig. 3 Annealing characteristics of Ga atoms implanted into an oxidized layer. The oxidized surface was coated with a 20 nm thick Si_3N_4 film after implantation.

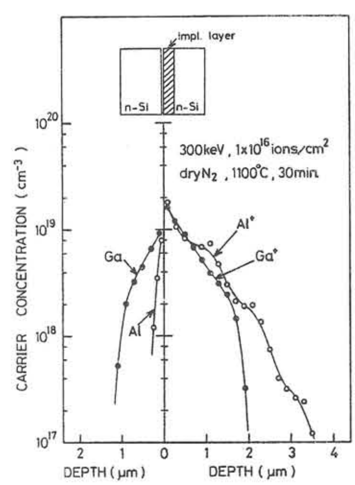

Fig. 2 Carrier profiles showing Al and Ga outdiffusion effects.

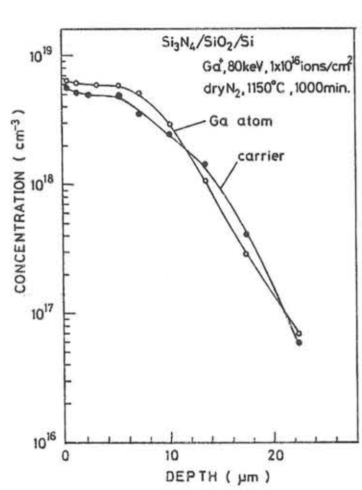

Fig. 4 A carrier profile and a total Ga profile in a Fig.3 sample implanted with a 1 x 10^{16} /cm^2 dose. The total Ga profile was obtained by the flameless atomic absorption method[4].

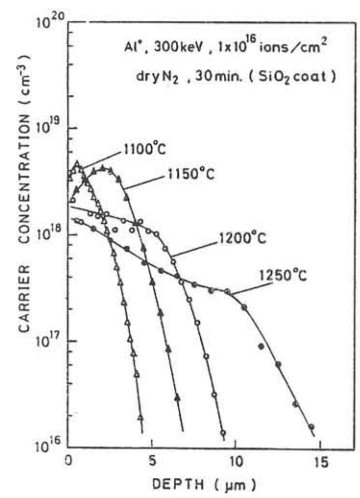

Fig. 5 Al carrier profiles after high temperature annealing. Implanted surfaces were coated with 200 nm thick CVD SiO_2 films after implantation.