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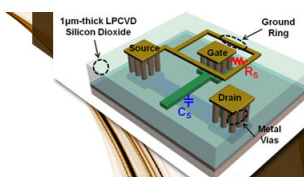
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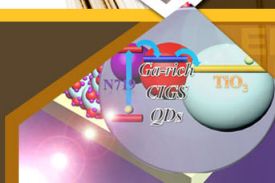
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Electrical characteristics of Al-implanted ZnSe

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Aluminum was implanted in ZnSe at 90 keV to a dose of 10^{15} ions/cm² at room temperature. Hall-effect and sheet-resistivity measurements were made on the samples for various annealing conditions. The implanted layer is found to be degenerate *n*-type having a sheet resistivity of $\sim 10^3 \Omega/\square$, after annealing at 900 °C for 4 h.

The production of low-resistivity layers is an important goal of ion implantation efforts in semiconductors. Factors which affect the conductivity, such as radiation damage and compensation, can often be conveniently studied by Hall-effect measurements. Most of the early work in the II-VI compounds, including ZnSe, has been concerned with the formation of *p-n* junctions,¹⁻⁵ and consequently the implanted layers have in general been of high resistivity (due to self-compensation), making Hall measurements difficult. Thus, it is of interest to create a low-resistivity layer in ZnSe and we have done this by implanting high-resistivity *n*-type material with a known shallow donor, Al.^{6,7} In this way, we have produced degenerate electrical behavior (for the first time, we believe, in an ion-implanted II-VI compound) and have been able to show that the Al is almost uncompensated.

The substrate used was a melt-grown cubic single crystal of undoped high-resistivity ($\sim 10^8 \Omega\text{cm}$) *n*-type ZnSe. The use of a high-resistivity substrate makes it possible to confine the resulting electrical characteristics to the lower-resistivity implanted-layer region. The crystal was mechanically polished and chemically etched at 90 °C for 1 min in a mixture of 2 parts H₂SO₄ and 3 parts saturated aqueous solutions of K₂Cr₂O₇, followed by a 20-sec rinse in a boiling 25% solution of NaOH. Aluminum was then implanted⁸ at 90 keV to a dose of 10^{15} ions/cm² at room temperature. A projected ion range of 920 Å was calculated from the theory of Lindhard, Scharff, and Schiøtt⁹ with an assumed Gaussian profile. Implanted samples were annealed up to 1050 °C in evacuated quartz ampoules of $\sim 10^{-6}$ Torr for times up to 4 h. Each sample was removed from its ampoule following a water quench to room temperature. Samples were cut into small rectangular parallelepipeds having typical dimensions of 1.0 × 0.5 × 0.1 cm and

Ohmic contacts were attached using an ultrasonic soldering gun and pure In solder. The dc Hall-effect and sheet-resistivity measurements were made over the temperature range 5.5–300 °K, in a magnetic field of 18 kG. A conventional five-lead configuration was used to minimize the problem of contact resistance.

Samples were annealed for 30 min at 600, 750, 900, and 1050 °C and additionally for times of 1 and 4 h at 900 °C. Precise Hall measurements were possible only for the 900 °C annealed samples and indicated *n*-type conductivity. The results of room-temperature electrical measurements are given in Table I. The sample annealed for 4 h at 900 °C was further investigated over the temperature range 7–300 °K, and these data are presented in Fig. 1. The quantities ρ' and n' are the so-called sheet-resistivity and effective sheet carrier concentration, respectively. For a uniform implantation, $n' = nz$ and $\rho' = \rho/z$, where n and ρ are the normally defined carrier concentration and resistivity, respectively, and z is the layer thickness. Because of the near degeneracy of the data at 900 °C, as demonstrated in Fig. 1, n' and μ , the effective mobility, are calculated assum-

TABLE I. Room-temperature electrical properties of Al-implanted ZnSe as a function of annealing time and temperature.

Temperature (°C)	Time	Sheet resistivity ρ' (Ω/\square)	Concentration n'	Mobility μ (cm ² /V sec)
25	days	$\sim 10^9$		
600	30 min	1.0×10^8		
750	30 min	4.0×10^4		
900	30 min	2.0×10^4	1.5×10^{15}	0.20
	1 h	7.5×10^3	1.0×10^{15}	0.85
	4 h	2.0×10^3	0.85×10^{15}	3.90
1050	30 min	$\sim 10^9$		

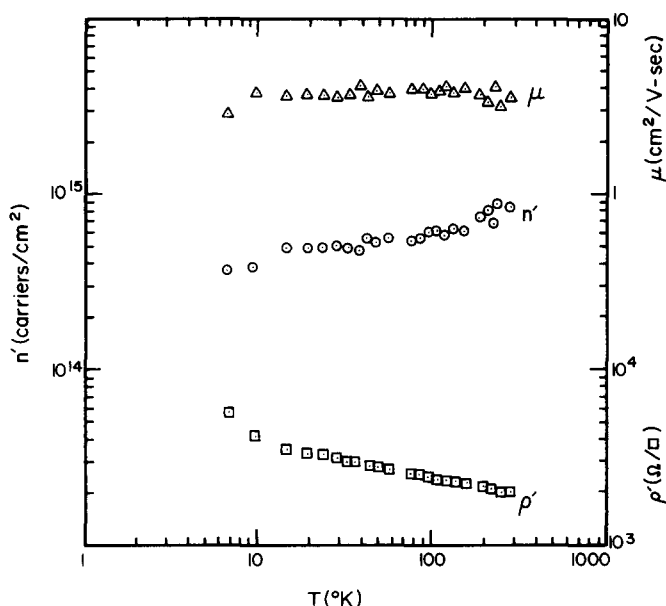


FIG. 1. Temperature dependence of Hall-effect and sheet-resistivity measurements for Al-implanted ZnSe. The sample was annealed at 900 °C for 4 h in vacuum.

ing a Hall factor of unity. In Table I it is seen that the resistivity decreases with increasing annealing time and temperature except that at 1050 °C it increases again to near the substrate value. This latter fact is probably due to thermal etching of the implanted layer during annealing, as evidenced by a yellowish deposit on the wall of the evacuated ampoule. Also, it should be mentioned that the samples annealed for 1 and 4 h at 900 °C were implanted in the dark, while the other samples were illuminated with high-intensity light in an attempt to reduce space-charge effects. This fact could account for the 50% difference observed in n' at 900 °C.

From Fig. 1 and Table I several observations can be made. (i) The quantities ρ' , μ , and n' are almost independent of temperature, implying nearly degenerate carriers (the Mott criterion for ZnSe is $n > N_c \approx 7 \times 10^{17} \text{ cm}^{-3}$). This lack of temperature dependence also suggests that profile effects are not too important.¹⁰ (ii) For the 900 °C data, $n' \approx 10^{15} \text{ cm}^{-2}$, almost the same as the implanted Al dose. This implies that most of the Al are uncompensated donors. Since the magnitude of n' changes little with annealing time, the Al must become electrically active in less than 30 min. (iii) The mobilities are very low compared to pure ZnSe. An explanation of this fact is difficult because we do not as yet know the densities of either the Al ions or the damage

centers. Often a mobility as low as 0.2 cm²/V sec is indicative of high disorder in the solid.¹¹

It is useful to compare Al implantation with conventional Al doping. A melt-grown ZnSe sample doped with about 100 ppm Al exhibits high resistivity ($\sim 10^7 \text{ } \Omega \text{ cm}$), evidently due to compensating centers formed by Zn vacancies and Al.¹² Heat treating the sample in molten Zn for 24 h at 900 °C reduces the resistivity to 0.01 $\Omega \text{ cm}$. In Al-implanted ZnSe, low resistivity is achieved by annealing in vacuum at 900 °C for a short period of time, suggesting that such compensating centers are not present.

In conclusion, it has been demonstrated here that implantation of high-resistivity n -type ZnSe by Al ions can create a degenerate n -type layer with a relatively low sheet resistivity and that the Al donors are nearly uncompensated. However, much work remains to be done, for example, on the investigation of profiles and annealing processes, but it is clear that Al may be an important implant species in II-VI compounds.

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