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p type doping of zinc oxide by arsenic ion implantation

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p type doping of polycrystalline ZnO thin films, by implantation of arsenic ions, is demonstrated. The approach consisted of carrying out the implantations at liquid-nitrogen temperature (~ -196 °C), followed by a rapid *in situ* heating of the sample, at 560 °C for 10 min, and *ex situ* annealing at 900 °C for 45 min in flowing oxygen. *p* type conductivity with a hole concentration of $2.5 \times 10^{13} \text{ cm}^{-2}$ was obtained using this approach, following implantation of $150 \text{ keV } 5 \times 10^{14} \text{ As/cm}^2$. A conventional room-temperature implantation of $1 \times 10^{15} \text{ As/cm}^2$, followed by the same *ex situ* annealing, resulted in *n* type conductivity with a carrier concentration of $1.7 \times 10^{12} \text{ cm}^{-2}$. © 2005 American Institute of Physics. [DOI: 10.1063/1.2128064]

A significant amount of research activity is directed nowadays toward the formation of *p* type ZnO. This is due to the fact that the generation of *p* type material is one of the last major obstacles hindering the development of ZnO-based electronic and optoelectronic devices.^{1,2} The group V elements: N, P, As, and Sb, are potential acceptors when substituting for O in the ZnO lattice. Indeed, there have been several recent reports claiming successful *p* type doping of ZnO with N,^{3–6} P,^{7,8} and As.^{9–11} In all these cases, the doping was obtained by means of a nonlocalized thin-film deposition process. For device application it would, however, be highly desirable to perform site-selective doping, by ion implantation, for example.^{2,12}

p type doping of ZnO is complicated by the fact that the most stable point defects in ZnO are donors and they dominate the transport properties of this material,^{13,14} hence, most bulk and thin film ZnO is *n* type. Ion implantation is invariably accompanied by radiation damage, thus when ion implantation is performed in ZnO, residual defects may dominate the electrical transport properties of the implanted layers, that will tend to exhibit *n* type characteristics, or very poor *p* type as the potential acceptors will be heavily compensated.

The annealing of implantation-induced lattice disorder, as well as ion implantation doping of ZnO, has been the subject of previous studies. Of particular relevance to this work are the following results. Ion channeling experiments revealed that it is almost impossible to render ZnO amorphous even by liquid-nitrogen temperature implantation, and using very large doses.¹⁵ It was speculated that the sample annealed during warmup, a conjecture that is consistent with more recent electron irradiation studies, which showed that defect annihilation processes are strong at temperatures as low as -143 °C (130 K).¹⁶ A combination of positron annihilation, Raman, and Hall effect measurements,¹⁷ on phosphorus-implanted single crystals of ZnO, suggested that implantations generated vacancy-type defects which coa-

lesced, after annealing at ~ 700 °C, to form large vacancy clusters. These clusters required very high heat treatment temperatures (≥ 1100 °C) to anneal out. However, the P⁺-implanted layers remained *n* type after annealing. Both of these results imply high mobility of defects at room temperature. In particular, interstitials appear to be able to migrate away from the implantation region, thus leaving behind a vacancy-rich zone that leads to the formation of the vacancy clusters observed by positron annihilation. Concomitantly, the imbalance in interstitial and vacancy local concentrations precludes defect recombination and makes the complete removal of implantation-induced lattice disorder very difficult. As indicated earlier, the more stable defects tend to be donors in ZnO, further complicating the chances to produce *p* type material by ion implantation.

Ion implantation has been employed to induce *n* type electrical conductivity in ZnO by implantation of H⁺,¹⁸ Ga⁺, Al⁺, and B⁺ ions,¹⁹ and creation of acceptor centers has been reported upon N⁺ (Ref. 20) and As⁺ (Ref. 21) implantations. These results are very encouraging, and suggest that more work is necessary to elucidate and control the effect of residual defects on the electrical properties of implanted ZnO, in order to achieve *p* type doping by ion implantation.

In this letter, we present results of Hall effect and conductivity measurements, demonstrating successful *p* type doping of ZnO by implantation of As ions. A doping approach that had been successfully applied to the doping of diamond [the so-called cold implantation rapid annealing (CIRA) method],^{22,23} has been employed. This implantation/annealing scheme consists of carrying out the implantations at a temperature low enough to freeze in the interstitials created by the irradiation, and thus avoid the creation of a defect imbalance that precludes the proper annealing of the implantation-induced lattice damage. The low-temperature implantation is followed by a very rapid *in situ* heating of the sample, to induce short range interstitial-vacancy recombination, and substitutional lattice location of the dopants. An *ex situ* annealing is carried out to further anneal any residual lattice defects, and enhance the electrical activation of the dopants.

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TABLE I. Values of sheet resistance, mobility, carrier concentration, and carrier type, determined by Hall effect and conductivity measurements, performed at room temperature, for as-prepared (CIRA implant), and as-prepared and annealed samples. Values for a conventional room-temperature As implantation, as well as the unimplanted samples, are also shown for comparison. The symbol “-” indicates that the experimental determination was not possible, usually due to the high resistivity or low mobility of the particular sample.

Sample	As-prepared				Annealed			
	R_s Ohm/sq	μ cm ² /V s	n_s cm ⁻²	Type	R_s Ohm/sq	μ cm ² /V s	n_s cm ⁻²	Type
Substrate (annealed in O ₂)	$\geq 1 \times 10^7$	...	...	...	1.59 ± 0.03 $\times 10^5$	3.3 ± 0.3	1.2 ± 0.1 $\times 10^{13}$	N
Substrate (annealed in air)	$\geq 1 \times 10^7$	...	...	...	2.11 ± 0.03 $\times 10^5$	4.5 ± 0.5	6.7 ± 0.7 $\times 10^{12}$	N
Implanted (CIRA process)					CIRA implanted and annealed			
Implanted species	R_s Ohm/sq	μ cm ² /V s	n_s cm ⁻²	Type	R_s Ohm/sq	μ cm ² /V s	n_s cm ⁻²	Type
N (annealed in air)	$\geq 1 \times 10^7$	...	...	...	1.87 ± 0.03 $\times 10^5$	2.4 ± 0.3	2.1 ± 0.3 $\times 10^{13}$	N
N (annealed in O ₂)	$\geq 1 \times 10^7$	...	...	...	$\geq 1 \times 10^6$	...	$\leq 1 \times 10^{12}$	...
P (annealed in O ₂)	3.11 ± 0.01 $\times 10^4$	1.5 ± 0.1	1.4 ± 0.1 $\times 10^{14}$	N	3.7 ± 0.1 $\times 10^5$	1.6 ± 0.1	1.0 ± 0.1 $\times 10^{13}$	N
As (annealed in O ₂)	2.17 ± 0.01 $\times 10^5$	0.6 ± 0.1	4.9 ± 0.5 $\times 10^{14}$	N	3.6 ± 0.2 $\times 10^5$	6.9 ± 0.1	2.5 ± 0.3 $\times 10^{13}$	P
Species	Implanted conventional implant				Implanted and annealed			
R_s	μ	n_s	Type	R_s	μ	n_s	Type	
As (annealed in O ₂)	3.63 ± 0.05 $\times 10^6$	0.1 ± 0.1	1.6 ± 0.2 $\times 10^{14}$	N	3.17 ± 0.5 $\times 10^5$	1.4 ± 0.2	1.7 ± 0.2 $\times 10^{12}$	N

Polycrystalline thin films of ZnO were deposited on oxidized silicon (500–1000 nm of SiO₂ on Si) substrates, by radio-frequency magnetron sputtering. The depositions were performed using stoichiometric ZnO targets in an oxygen atmosphere, at pressures of ~ 0.5 – 1.5×10^{-3} Torr, and with the substrates at room temperature. The composition of the films was determined (and the thickness estimated) by Rutherford backscattering spectrometry (RBS) using a 2.25 MeV, He⁺⁺ beam, and a surface barrier detector positioned at a scattering angle of 165°. The program RUMP (Ref. 24) was used to fit the RBS spectra. This analysis revealed that the films were stoichiometric to within the experimental error (Zn:50±2%, O:50±2%), with thickness of about 200 nm (using the density of bulk ZnO: $\rho=5.6$ g/cm³). Implantation energies (calculated with SRIM 2000)²⁵ were chosen such that the projected ranges of the implants were ≤ 100 nm, i.e., well within the ZnO layer. Implantations were performed with the samples held at liquid-nitrogen temperature, followed by an *in situ* rapid heating to 500–560 °C, using the CIRA approach.^{22,23} Subsequent thermal annealing, at 900 °C, for 45 min, was performed in a quartz tube furnace, in flowing oxygen, or in air. The potential acceptor ions, N⁺, P⁺, and As⁺, were implanted using the following conditions (ion, energy, dose): N⁺, 40–50 keV, 1×10^{15} cm⁻², P⁺, 130 keV, 5×10^{14} cm⁻², As⁺, 150 keV, 5×10^{14} cm⁻². Resistivity, mobility, and carrier concentration, and type, were evaluated by Hall effect and conductivity measurements, at

room temperature in van der Pauw four-point probe configuration. AuPd contacts were deposited near the corners of the samples by sputtering at room temperature. No further heating of the contacts was performed. Thin gold wires were attached to the contacts using In as a solder material. This procedure resulted in ohmic contacts for all samples. Only the highly resistive as-prepared samples, showed small deviations from linear behavior in current-voltage curves used to characterize the contacts.

Table I shows the results of the room-temperature Hall effect and conductivity measurements for as-implanted, and as-implanted and annealed samples. Values for the as-prepared, and as-prepared and annealed ZnO/SiO₂/Si implantation substrates, are also presented for comparison. Figure 1 presents in graphical form the sheet carrier concentration of the samples before and after annealing in an oxygen atmosphere. The as-prepared substrate was highly resistive ($R_s \geq 1 \times 10^7$ Ω/square), and the Hall effect was too weak to allow for the determination of the carrier concentration. Upon annealing, either in oxygen or air ambient, the carrier concentration increased somewhat and became measurable (within the capabilities of our instrumentation), being *n* type with a value of $\sim 10^{13}$ cm⁻².

As a control, a conventional room-temperature implantation of As⁺ (100 keV, 1×10^{15} cm⁻²) was performed. This has resulted in an *n* type carrier concentration of $1.6 \pm 0.2 \times 10^{14}$ cm⁻². After annealing in oxygen atmosphere, at

FIG. 1. Sheet carrier concentration of ZnO thin films measured after implantation (except for the sample labeled as unimplanted), and after implantation and annealing in oxygen atmosphere (900 °C for 45 min). The implantations were performed using the CIRA approach except for the one labeled as conventional. Error bars are represented by the marker size.

900 °C, the sample had a rather low carrier concentration of $1.7 \pm 0.2 \times 10^{12} \text{ cm}^{-2}$, still exhibiting *n* type. However, the sample implanted with As^+ , using the CIRA procedure, while still being *n* type with carrier concentration of $4.9 \pm 0.5 \times 10^{14} \text{ cm}^{-2}$ after implantation, turned *p* type upon annealing in oxygen atmosphere, at 900 °C, with a carrier concentration slightly larger than 10^{13} cm^{-2} . The conductivity and carrier concentration of the (unimplanted) zinc oxide thin films used in this work, increased upon heat treatment. As could be expected, the carriers generated by the heat treatment appear to be mostly donors since the films turned *n* type.²⁶ The sample implanted with N^+ , and annealed in oxygen, showed very high resistivity, and may have been highly compensated due to the presence of both acceptors produced by N doping, and donors produced by the heating of the substrate. The sample implanted with P^+ was also *n* type. The mobility of all the implanted and annealed samples was in the single digits, as was the mobility of the annealed (unimplanted) ZnO substrates. Further studies are in progress to investigate these results and to try to optimize these implantation/annealing schemes to also yield *p* type conductivity. The sample implanted with As using the CIRA approach, exhibited a very clear Hall voltage, with polarity corresponding to *p* type doping. However, the carrier concentration was much smaller than the implanted dose, again pointing at the presence of both types of carriers in a highly compensated sample. Interestingly, it has recently been proposed that the doping of ZnO with As is not due to the substitution of the larger radius As for oxygen, but rather to the formation of a complex consisting of As in the Zn site and two Zn vacancies ($\text{As}_{\text{Zn}}-2\text{V}_{\text{Zn}}$).²⁷ The present results may support this proposal.

The successful *p* type doping of ZnO using the CIRA method presented here, suggests that the CIRA approach is indeed effective in preventing diffusion of interstitials during implantation, and inducing short-range interstitial-vacancy recombination during the *in situ* rapid anneal at 500–560 °C, thus facilitating further defect annealing during the subsequent *ex situ* heat treatment at 900 °C, for 45 min, in oxygen. These findings may pave the way for the selective area *p* type doping of zinc oxide, and the development of novel devices based on this material. Furthermore our findings show that CIRA implantation doping is effective not only in diamond, but it is also applicable to achieve doping in compound semiconductors.

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