

p-type Zinc Oxide Films Doped with Nitrogen and Aluminum

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Attractive physical properties of zinc oxide make this material very perspective for a series of important applications as transparent conductive oxide, photo-detectors, bio-sensors, piezoelectric devices, solar cells and optoelectronic devices. The main obstacle in many of these applications is a well-known doping asymmetry. The difficulty in formation of p-type ZnO arises from a high background n-type conductivity, self-compensation effects, deep acceptor levels and a low solubility of dopants.

The group V elements such as phosphorus, arsenic and nitrogen are investigated as p-type dopants in zinc oxide. Nitrogen has been regarded as a very good candidate for p-type dopant in zinc oxide, because its atomic radius is very similar to the one of oxygen. Theoretical calculations [1] show that nitrogen in ZnO is a deep donor. Despite this fact a lot of papers report on p-type ZnO obtained as a result of nitrogen doping. However, the p-type conductivity obtained in this way is not stable in time, which is a problem especially when ZnO homojunction is considered. ZnO homojunctions based on the ZnO:N films show rather moderate rectification ratio and low time stability mainly because of nitrogen diffusion across the interface. The aluminum and nitrogen co-doping has been used in order to stabilize p-type conductivity in ZnO. Theoretical calculation [2] show that (Al, N) co-doping lead to formation of (Al-2N) complexes which act as acceptors with ionization energies of 0.17 eV, which is much lower than the ionization energy of the single nitrogen acceptor (0.33 eV).

We report the first results of (N, Al) co-doping of ZnO films grown at low temperature (100 and 130°C) by Atomic Layer Deposition (ALD). The nitrogen was introduced into the ZnO films during the ALD process by changing the oxygen precursor from deionized water to ammonia water. The amount of nitrogen introduced in the ZnO film can be varied between 10^{18} to 10^{21} at cm^{-3} , which depends on the number of ammonia water cycles versus deionized water cycles. Aluminum doping at the level 1-4 atomic % was realized by introducing of the TMA (tri-methyl-aluminum) precursor instead of the diethylzinc precursor in a double exchange chemical reaction with water. The ZnO films doped with nitrogen show up to 3 orders of magnitude lower electron concentration (10^{15} instead of 10^{18} cm^{-3}) as compared with un-doped films. Additional aluminum doping strongly influences conductivity of the films. When amount of introduced Al is at the level of 3% we observe increase of electron concentration to 10^{18} cm^{-3} . When Al concentration is about 1% we observe conversion of the conductivity to the p-type. The p-ZnO (N, Al)/n-ZnO homojunction has been constructed and shows a rectification ratio 10^2 at 3V. Aluminum doping was also used to stabilize the interface of the p-ZnO:N/n-ZnO junction. As a result, the rectification ratio of ZnO homojunction has been enhanced by 3 orders of magnitude and achieved the value of 10^5 at 4V [3].

Acknowledgements. The research was supported by the Polish NCN project DEC-2012/07/B/ST3/03567. The Author RS was financed by the EU 7th Framework Programme under the project REGPOT-CT-2013-316014 (EAgLE).

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