

Influence of NO doping on the properties of ZnO thin films on a-plane sapphire grown by catalytic-reaction-assisted chemical vapor deposition

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Zinc oxide (ZnO) is highly useful for various applications. Recently, because of its large bandgap (3.37 eV at RT) and large exciton binding energy (60 meV)¹⁾, its application to optoelectronic devices such as light emitting diodes and laser diodes operating in the ultraviolet region has been intensively investigated²⁻⁷⁾. Despite the advantages of metalorganic chemical vapor deposition (MOCVD) for industrial applications, ZnO film growth by conventional MOCVD requires much electric power to react the source gases and raise the substrate temperature. Therefore, a more efficient means of reacting oxygen and metalorganic source gases is required. We have developed a new CVD method for ZnO film growth using a reaction between an alkylzinc (DMZn) and high-temperature H₂O generated by the Pt-catalyzed exothermic H₂-O₂ reaction⁸⁾. The resulting ZnO films grown on a-plane sapphire (a-Al₂O₃) substrates exhibited excellent electronic property, that is, electron mobility was greater than 180 cm²/Vs. It also became clear that the addition of N₂O gas during the ZnO film growth improved the crystallinity and crystal orientation⁹⁾. Nitrogen oxide gases are expected for nitrogen doping material to the ZnO films. In this study, we have investigated the influence of the NO gas addition on the ZnO film properties.

The structure of the CVD apparatus and the growth procedure used in this study are the same as those shown in a previous paper⁸⁾, except for the addition of NO gas to the reaction zone. The ZnO films were directly grown on a-Al₂O₃ substrates at 773K for 60 min without any buffer layer. The NO gas pressure was varied from 4.4×10^{-3} Pa to 1.6×10^{-1} Pa. The thicknesses of the ZnO films characterized were 4.4–7.3 μm.

By the addition of the NO gas, the full-width at half maximum of ω-rocking curve of ZnO(0002) became large compared with those of undoped ZnO films. Although p-type ZnO films were not obtained, the residual electron concentration decreased from 1.2×10^{17} cm⁻³ to 2.4×10^{16} cm⁻³ by the addition of the NO gas. In the PL spectra of the NO doped ZnO films measured at a low temperature, emission peaks derived from ionized donor bound exciton (D⁺X) and neutral acceptor bound exciton (A⁰X) in addition to those derived from free exciton (FX_A) and neutral donor bound exciton (D⁰X) were observed. By the addition of the NO gas during the ZnO film growth, therefore, it is speculated that a certain amount of nitrogen atoms were incorporated as acceptor impurities in the films.

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