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Magnetic Resonance Studies of Oxygen and Zinc-Vacancy Native Defects in Bulk ZnO Crystals

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ZnO is currently attracting increasing attention as a key material for a wide variety of electronic and optoelectronic applications. Optical, electrical, and magnetic properties of ZnO are believed to be strongly influenced by native defects. However, unambiguous experimental evidence confirming the formation of these defects in as-grown ZnO as well as evaluations of defect densities is currently sparse. In this talk we shall review our recent results from comprehensive defect characterization of as-grown bulk ZnO. By using electron paramagnetic resonance (EPR) and optically detected magnetic resonance (ODMR) spectroscopies, we show that both oxygen and zinc vacancies are formed in ZnO grown from melt without subjecting to irradiation. Defect concentrations are also determined. Based on spectral dependences of its EPR and ODMR signals, the V_{Zn}^- defect is concluded to act as a deep acceptor responsible for the red emission peaking at around 1.6 eV, but does not participate in the green emission as commonly believed. The energy level position of the V_{Zn} corresponding to the (2-/-) transition is determined to be at E_v+1.0 eV. The center is also shown to exhibit a strong JT distortion with a JT energy of 0.8 eV. On the other hand, oxygen vacancies are probably less important in carrier recombination since they were only detected in EPR but not in ODMR. Annealing properties of both defects were also studied and higher thermal stability of the Zn vacancy was concluded. It was also suggested that annealing of the V_{Zn} centers is facilitated by thermally-activated diffusion of impurity atoms to the V_{Zn} sites. The obtained results are of importance for a better understanding of the defects in ZnO. They also provide useful information on control of electrical properties and defect-reaction induced degradation during device processing and operation, in the material that is commonly used as a substrate for epitaxial growth of layered device structures based on ZnO.