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Effect of uniaxial stress on substitutional Ni in ZnO

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The influence of uniaxial stress on the electronic $^3T_1(F)\rightarrow{}^3T_2(F)$ transitions of Ni^{2+} (d^8) in ZnO at 4216, 4240, and 4247 cm^{-1} is studied. It is shown that the split pattern and polarized properties of IR absorption lines are consistent with a dynamic Jahn–Teller effect in the $^3T_2(F)$ state of the defect.

1. Introduction

ZnO is a wide band gap (3.3 eV at 300 K) semiconductor which regained much attention in the last decade due to many potential applications such as: a material for blue and UV light-emitting diodes, radiation hard material, or a transparent highly conducting oxide [1]. Because of theoretically predicted high Curie temperature, there is also considerable interest in the development of transition metal (Co, Mn, Fe, and Ni) doped ZnO-based diluted magnetic semiconductors [2–6].

Nickel is a common impurity in ZnO, which is often unintentionally introduced into the material during the process of crystal growth. In photoluminescence (PL) and IR absorption, Ni results in a number of features. In particular, the $^4T_2(F)\rightarrow{}^4A_2(F)$ transitions of the Ni^{3+} (d^7) ion can be seen in PL spectra at 6090.5 and 6096.2 cm^{-1} [7]. The $^3T_1(F)\rightarrow{}^3T_2(F)$ transitions of Ni^{2+} (d^8) are observed in IR absorption at 4216, 4240, and 4247 cm^{-1} [7,8], whereas the 8340 cm^{-1} line was associated with the $^3T_1(F)\rightarrow{}^3A_2(F)$ transition [8]. Recently, it was shown that this band reveals a substructure associated with the main ^{58}Ni, ^{60}Ni, and ^{62}Ni isotopes, thus confirming the microscopic origin of the defect [9].

Piezospectroscopy provides defect symmetries and yields values for stress shift rates including hydrostatic shift rates [10–12]. In ZnO, piezospectroscopic studies have been recently applied to study numerous hydrogen- and copper-related defects [13–15].

Here we report the results of a uniaxial stress study of Ni performed on the $^3T_1(F)\rightarrow{}^3T_2(F)$ transitions at 4216, 4240, and 4247 cm^{-1}.

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2. Experimental details

ZnO samples used for uniaxial stress measurements in the present study were hydrothermally grown *n*-type substrates supplied by CrysTec GmbH. The dimensions of the samples unintentionally doped with Ni were around $6\times2\times1$ mm^3. The uniaxial stress was applied along the longest side of the samples, which were cut parallel to *c*, [1$\bar{2}$10], or [10$\bar{1}$0]. Intentional doping with Ni was performed on ZnO grown from the vapor phase at the Institute for Applied Physics, University of Erlangen (Germany) [16].

Measurements were performed up to around 0.3 GPa at 8–10 K with a home-built stress rig that was mounted in a He gas flow cryostat equipped with ZnSe windows. The stress was supplied to samples by a pneumatic cylinder and transferred via a push rod. Polarized spectra were obtained using a wire-grid polarizer with a KRS-5 substrate.

Infrared absorption spectra were recorded with a Bomem DA3.01 Fourier transform spectrometer equipped with a globar light source, a CaF_2 beam splitter, and a liquid-nitrogen-cooled InSb detector. The spectral resolution was 0.25 cm^{-1}.

Photoluminescence measurements were carried out at 4.2 K with samples immersed into liquid helium in an Oxford cryostat. Excitation was performed by the 325 nm line of a HeCd laser with an excitation power of around 2 mW.

3. Results and discussion

3.1. Doping of ZnO with Ni

In the literature, a number of IR absorption and PL lines have been attributed to different transition metals embedded in ZnO [7,8,17–19]. Recently, Vlasenko et al. have shown that the sharp