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Deep levels in the MBE ZnO:As/*n*-GaN diodes – Photoluminescence, electrical properties and deep level transient spectroscopy

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In this paper the current understanding of defects in acceptor doped ZnO is briefly reviewed. The results of investigations of ZnO:As/*n*-GaN heterojunctions which have been successfully fabricated by plasma assisted molecular beam epitaxy method are presented. The electrical properties of the junctions, as well as deep levels, have been studied by means of current-voltage (I-V), capacitance-voltage (C-V) characteristics and deep level transient spectroscopy (DLTS). Electrical measurements were supplemented by photoluminescence- (PL) along with secondary ion mass spectrometry (SIMS) and X-ray photoemission spectroscopy (XPS) investigations. The I-V measurements allowed for detailed analysis of current mechanisms, through which the presence of trap states in the investigated junction was confirmed. The C-V results proved that the depletion region of the diode is located within the ZnO:As layer. The DLTS measurements revealed the presence of three hole trap related signals. The activation energies and capture cross sections of these traps were determined and their possible origin has been ascribed. Obtained results allowed for better identification of defects found in the case of the analyzed heterostructure, as well as the studies of its electronic properties.

1. Introduction

Nowadays, zinc oxide (ZnO) is one of the most intensely studied metal oxides. It is a semiconductor that exhibits a wide bandgap of 3.375 eV at room temperature and large exciton binding energy of 61 meV [1] which makes it a promising candidate for future optoelectronic devices operating in the near UV [2]. Because of its transparency to visible light, ZnO has been already used as a transparent conductive oxide in commercial applications, e.g. in solar cells [3]. ZnO is also a piezoelectric material and ZnO-based memory devices together with other applications in spintronics have been proposed [4–6]. The possibility of a self-organized growth of a variety of ZnO-based nanostructures, such as nanowires, quantum-wells, photonic structures etc. [7,8], makes this material interesting for basic solid state physics experiments and single photon light-sources, as it has already been demonstrated for a gallium nitride material system which exhibits similar properties.

Electronic defect states in ZnO are under investigation since the late forties. However, it has to be underlined that there is still little papers about the electrical properties of the *p*-type zinc oxide and deep acceptor-like defects in this material. In contrast, a large number of articles has reported results on deep donor-like defects in the *n*-type ZnO. Conductivity and Hall effect measurements revealed that ZnO is a natural *n*-type semiconductor, thus it is easy to introduce extrinsic donor dopants into it. The electron conductivity in this material is attributed to native defects like the interstitial zinc Zn_i, the oxygen vacancy V_O, the zinc antisite Zn_O and/or impurities like hydrogen [9,10]. All the native defects mentioned above form donor levels in the ZnO energy gap. The most common acceptor levels in the as-grown ZnO sample are the zinc vacancy V_{Zn}, the interstitial oxygen O_i, and the oxygen antisite O_{Zn} [9,11,12]. They become active depending on the technological conditions accepted during the growth of ZnO, namely in the case of the growth under O-rich conditions [9].

Obtaining *p*-type doping in ZnO is still not an easy task due to

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self-compensation and donor levels which effectively prevent achieving hole conductivity in this compound [10,13,14]. Despite the difficulty of *p*-type doping, many papers have reported obtaining *p*-type ZnO. Since the appearance of the first acceptor doping results in literature, there has been widespread discussion which has resulted in a number of theoretical models concerning the way in which acceptor dopants are incorporated into ZnO [15–19]. Among the acceptor dopants, group – V elements are extremely important. Their mode of incorporation into the crystal structure of ZnO is still an open and controversial subject. Therefore, basic research aimed at understanding the nature of acceptor defects is extremely relevant and important. However nowadays, it is well known that *p*-type conductivity in ZnO can be achieved mostly by doping it with group – V elements, using nitrogen (N), phosphorus (P), arsenic (As) or antimony (Sb) [10, 13 and references therein]. Based on the first-principles calculations, for As dopants it was suggested that an $As_{Zn} - 2V_{Zn}$ complex, in which an As atom occupying a Zn site gives a shallow acceptor level by forming a complex with two Zn vacancies, would be the origin of *p*-type conductivity [19,20]. Complicated nature of doping was also predicted as well as observed in the case of Sb dopants [21]. Calculated ionization energy for $As_{Zn} - 2V_{Zn}$ complex, $\varepsilon(0/\text{-}) = 0.15$ eV [19], stays in agreement with other experiments that have been performed on the *p*-type ZnO samples and gave the value of $\varepsilon(0/\text{-})$ from 0.12 to 0.18 eV [14,22].

Although *p*-type conducting ZnO has already been achieved, its stability, reproducibility and control of the hole density are remaining issues. Moreover, the realization of satisfactory *p*-type conductivity requires understanding of the interactions between acceptors and crystal defects, either native or doping-induced. The studies of defects in the space charge region of ZnO layers by means of the capacitance methods were performed mainly on *n*-ZnO Schottky junctions so far [23,24]. It is well known that in the case of a Schottky diode only majority traps can be detected. As for the hole traps they can be traced in *n*-ZnO using space charge spectroscopy if additional optical excitation is employed, in the mode of operation called minority carrier transient spectroscopy (MCTS) [25–27]. This type of experiments is more demanding than thermal admittance spectroscopy (TAS) or deep level transient spectroscopy (DLTS) as it requires an optical setup as well as transparent Schottky contacts.

In our work, defects as well as current transport mechanisms in ZnO:As/*n*-GaN diodes have been studied by means of electrical measurement techniques, such as: current-voltage (I-V), capacitance-voltage (C-V) characteristics and deep level transient spectroscopy. Photoluminescence method has been also applied to study deep levels and emission properties in the case of investigated structures. The presence and uniformity of the As doping was verified by secondary ion mass spectrometry (SIMS), whereas, electronic properties of As in ZnO:As layer were derived from X-ray photoemission spectroscopy (XPS).

The DLTS measurements for the investigated sample revealed the presence of three hole – trap - related signals. The activation energies and capture cross sections of these defects were determined and their possible origin has been ascribed. To the best of our knowledge, there are no reports on the latter result with respect to the MBE grown ZnO:As/*n*-GaN junctions. In order to obtain high quality junctions, control of defects occurring in individual layers of produced structures is very important. Thus, a better understanding of the physical processes in the doped ZnO layers is needed, since it paves the way to their improvement as well as applications. Therefore, we believe that the results obtained in this work can contribute to future fabrication of homojunctions based on ZnO.

2. Experimental details

Epitaxial zinc oxide layers doped with arsenic were grown on commercial *n*-GaN/Al_2O_3 Lumilog substrates by plasma assisted molecular beam epitaxy using a Riber Compact 21 system. The electron concentration, *n*, and Hall mobility, μ, of GaN/Al_2O_3 substrates were measured at room temperature in the van der Pauw configuration. They are as follows: $n = 7 \times 10^{17}$ cm^{-3} and $\mu = 45$ cm^2/V. Proper chemical and temperature pretreatment of GaN substrates before ZnO growth is very important, therefore the substrates were chemically cleaned before the growth process and then out-gassed in a buffer chamber at 700 °C in high vacuum of ~10^{-8} Torr. For GaN substrates a two-step chemical etching procedure was used, based on a H_2SO_4:H_2O_2 (1:1) and a subsequent NH_4F:HF dip. This treatment protects the surface against oxidation and formation of an unintentional Ga_2O_3 oxide layer [28]. Additionally, thin Zn layer was evaporated as a first and in this case ZnO/GaN interface was well defined as well as the crystallographic quality of the ZnO layer as was presented in our previous studies [29]. The ZnO/GaN interface quality is important for preparation of high-performance junctions because defects present at interfaces have a significant impact on the junction's final electrical parameters. The ZnO/GaN interface quality was previously carefully investigated by microscopic techniques [29]. Knudsen cells were used as sources of arsenic (7 N) and zinc (6 N), while rf plasma cell as a source of oxygen. The rf power of the O_2 source was 400 W and 2.3 ml/min flow. The As Knudsen cell thermocouple temperature was 200 °C and the growth temperature measured by a thermocouple on the substrate back side was about 500 °C. The pressure in the growth chamber was ~10^{-5} Torr. The thickness of ZnO:As layers measured "in situ" by a laser reflectometry was ~0.2 μm. Multiple Ti/Al/Ni/Au and Ti/Au contacts have been formed on a GaN and ZnO:As layer by e-beam technique, respectively. After the growth the samples were annealed by rapid thermal annealing (RTA) method in Ar atmosphere for 3 min at 500 °C.

The compositional depth profiles and concentration of atoms were determined by secondary ion mass spectrometry (SIMS) using ion implanted standards as references. The XPS spectra were recorded with a PHI 5000 VersaProbe™ scanning ESCA Microprobe using a monochromatic Al-Kα radiation ($h\nu = 1486.6$ eV) from an X-ray source operating at a 100 μm spot size, a 25 W power and a 15 kV acceleration voltage. Temperature dependent photoluminescence (PL) was measured within 10–300 K range. The 302.5 line of an Ar ion laser was used as the excitation source. Current-voltage (I-V) characteristics were taken with the use of a Keithley 2601A I-V source meter. The capacitance-voltage (C-V) and DLTS studies were performed using a lock-in DLTS system based on a Boonton 7200 capacitance meter and a Janis cryostat with a Lake Shore temperature controller. In all measurements, namely: SIMS, XPS, PL, I-V, C-V and DLTS, the RTA samples were studied. Additionally, an as-grown structure was investigated by XPS as a reference sample.

3. Results and discussion

3.1. SIMS measurements

Control of the uniformity of a dopant distribution in the ZnO layer is important when semiconductor junctions are realized. Uniformity and doping profiles of the intentional dopants in the MBE grown ZnO layers were examined by secondary ion mass spectrometry (SIMS). The studies of the SIMS depth profiles confirmed that the analyzed ZnO sample was successfully doped by arsenic. The concentrations of As atoms in the analyzed structure is about 7×10^{20} at./cm^3 (cf. Fig. 1) and it is constant from the surface