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Dominant shallow donors in zinc oxide layers obtained by low-temperature atomic layer deposition: Electrical and optical investigations

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Abstract

This work is focused on the electrical and optical analyses used to estimate the activation energy of the dominant shallow donor in thin ZnO films obtained at low temperature by the atomic layer deposition process. These two approaches, based on the temperature-dependent classical Hall effect and photoluminescence investigations, yielded a donor activation energy E_D in the range of 30–40 meV, including the estimated error margins. This value, as confirmed by layer composition studies, is attributed to the presence of zinc atoms in the interstitial positions of the ZnO lattice.

Keywords: Zinc oxide; Thin films; Atomic layer deposition; Defects; Electrical conductivity (*n*-type)

1. Introduction

Zinc oxide (ZnO) has been studied as a semiconducting material since the 1930s [1]. The research is motivated by its possible applications in modern electronic and optoelectronic devices. ZnO is currently being tested, for example, as a channel in transparent thin film transistors [2,3], a semiconducting partner in the new generation of memory devices [4–7] and a transparent electrode in solar cells [8–10], where it is predicted to be a cheaper equivalent of indium–tin oxide (ITO) [11]. From this point of view, a thorough insight into the electrical properties of ZnO is crucial.

However, in spite of enormous efforts, controlling the electrical parameters of zinc oxide still remains a scientific problem. In this material, obtained by a number of methods, the Fermi level is located near the conduction band minimum, meaning that ZnO strongly prefers *n*-type conductivity. Therefore, a high electron concentration can be easily achieved, even without intentional doping [10]. This fact is also commonly related to the presence of native defects, among which zinc interstitials [12,13] and oxygen vacancies [14,15] are regarded as the most important. Besides these intrinsic defects, hydrogen as an unintentional dopant significantly influences ZnO electrical properties as well [16,17]. Hence, in the "typical" as-grown ZnO the observed electron concentration (n) is from 11 to 15 orders of magnitude higher than the intrinsic n level ($\sim 10^6\ cm^{-3}$) derived directly from its bandgap width ($\sim$3.3 eV at 300 K). To obtain zinc oxide that is suitable for some of the above-mentioned applications (excluding the "ITO analogue" material, where low resistivity is desired),

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numerous efforts have focused on the *n*-type doping reduction. For this to be successful, its conductivity mechanisms must be understand. Importantly, it is also necessary to obtain a stable *p*-type ZnO material. The approaches towards this purpose include mainly post-growth annealing [18,19] or doping with different acceptors, e.g. group I [19,20] and V [21,22] ones.

Reaching a decreased electron concentration in ZnO thin films appears to be more difficult than in the case of the single crystals of this material, which are often fairly well compensated (like those obtained from a hydrothermal method) due to the specific growth conditions [23]. The present work is devoted to the identification of the dominant shallow donor in ZnO films obtained by the low-temperature atomic layer deposition (ALD) process. This deposition method has recently attracted increased attention mainly because it is the best solution for growing high-*k* dielectrics in highly integrated circuits; however, the possibilities of its applications are much broader. It is successfully used for zinc oxide growth under a low-temperature regime [7], which becomes a more and more important issue for such modern applications as hybrid organic/inorganic electronics or three-dimensional non-volatile memories.

2. Experimental details

2.1. Growth technique and measurements' methodology

ZnO layers were grown at low temperature (LT) by the ALD process in the Cambridge NanoTech Savannah 100 and Microchemistry F-120 reactors using double exchange reactions between the organic zinc precursors (diethylzinc (DEZn) or dimethylzinc (DMZn)) and deionized water. The chemical reactions were as follows:

$$Zn(C_2H_5)_2 + H_2O \rightarrow ZnO + 2C_2H_6 \quad (1)$$

$$Zn(CH_3)_2 + H_2O \rightarrow ZnO + 2CH_4 \quad (2)$$

The advantage of used reactive zinc precursors stems from their high vapor pressure (>10 torr at 300 K), allowing the growth temperature to be decreased to 100 °C. This enables films to be obtained with low electron concentration ($n \sim 10^{16}$ cm^{-3}), as shown in Ref. [24]. Further details of the growth technique can be found in the recent review paper by Miikkulainen et al. [25].

The key electrical data were acquired across a wide temperature range based on the classical Hall effect in the six-probe configuration. A system equipped with an electromagnet producing a magnetic field $B = 0.7$ T and a liquid helium cryostat were used to perform the temperature-dependent investigations between 4 and 450 K. For comparison, the electron concentration at 300 K was also determined separately, using the setup working in the Van der Pauw configuration ($B = 0.426$ T). In both cases the ohmic contacts (Ti/Au bilayer of 100 Å/400 Å thickness) were evaporated in a vacuum.

The low-temperature photoluminescence (LT PL) spectra (measured at $T \geqslant 15$ K) were collected in the wavelength range of 340–450 nm using a setup including a He–Cd laser as an excitation source ($\lambda = 325$ nm, $P = 0.02$ W).

The topography of the ZnO layers was analyzed with a scanning electron microscope (SEM). This equipment also enabled composition analysis to be performed by the electron dispersive X-ray (EDX) technique. The unintentional hydrogen contamination of the obtained ZnO layers was examined by secondary ion mass spectroscopy (SIMS).

2.2. ZnO films

The preliminary (room-temperature) data were collected on polycrystalline ZnO films deposited on three different types of substrates: Si (used for morphological investigations), quartz and glass (for optical and electrical measurements). The examined layers were grown at temperatures T_g between 100 and 200 °C and divided into two groups according to their thickness, regulated by the number of the ALD cycles used (see below):

- group 1: 1000 ALD cycles was applied, which resulted in a film thickness of ~100–200 nm (in these cases 100 °C $\leqslant T_g \leqslant$ 200 °C);
- group 2: 2500 ALD cycles was applied; the obtained layers were between 300 and 450 nm thick (deposited within the temperature range of 100 °C $\leqslant T_g \leqslant$ 200 °C).

For the advanced temperature-dependent optical and electrical studies, ZnO films exhibiting high crystalline quality, obtained from DEZn (DMZn) and H_2O at slightly elevated temperatures (250–320 °C), were necessary. They had a thickness of between 0.5 and 2 μm (3000–10,000 ALD cycles). An example of the growth optimization procedure resulting in the highly crystalline ZnO layers from DEZn and H_2O precursors is described elsewhere [26].

3. Results

3.1. Polycrystalline ZnO layers: influence of unintentional contaminations

Considering the undoped polycrystalline ZnO layers grown by the low-temperature ALD technique, two reasons for their high conductivity have to be taken into account: unintentional contaminations and possible non-stoichiometry in the Zn-to-O ratio. Due to the presence of hydrogen and carbon atoms in the growth precursors ($Zn(CH_3)_2$, $Zn(C_2H_5)_2$, H_2O), one can expect their influence on the observed electron concentration in the as-grown ZnO films. However, the corresponding SIMS investigations performed on the samples from the two above-mentioned groups revealed the decreasing contribution of hydrogen to the overall composition of the ZnO