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Schottky Junctions Based on the ALD-ZnO Thin Films for Electronic Applications

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The ZnO-based Schottky diodes revealing a high rectification ratio may be used in many electronic devices. This paper demonstrates several approaches to obtain a ZnO-based Schottky junction with a high rectification ratio. The authors tested several methods such as: post-growth annealing of the ZnO layer, acceptor (nitrogen) doping, as well as the ZnO surface coating with a properly chosen dielectric material. The influence of these approaches on the diode's rectification ratio together with modeling based on the differential approach and thermionic emission theory are presented.

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1. Introduction

Zinc oxide (ZnO) is presently tested for advanced electronic applications. For example, a ZnO-based junction is considered as a selector in the new generation of 3D memory cells built in the so-called cross-bar architecture [1, 2]. For this application a ZnO-based junction (Schottky or p–n one) should have a sufficiently high rectification ratio. The hybrid structures, in which ZnO plays a role of the n-type partner of organic material or acts as a transparent conductive oxide, are also tested for photovoltaic cells [3–5].

Despite several possible applications, construction of good quality ZnO-based Schottky junctions still remains a challenging issue. This is due to the high n-type conductivity of ZnO obtained by various deposition methods [6–8]. The modeling shows that the electron concentration in ZnO to form a Schottky junction with a good rectification ratio should not be higher than 10^{16}–10^{17} cm^{-3} [9]. This is crucial to achieve a low value of the diode's reverse current. Moreover, a high carrier mobility is desired to get a high forward current. Additional complication stems from a relatively high concentration of surface states in ZnO resulting in the Fermi level pinning. This deteriorates the rectification ratio significantly. Moreover, the Schottky barrier height (SBH) does not follow the difference in work functions of ZnO and metal. In fact, different metals have been tested as the Schottky contacts to ZnO [10] and the reported SBH was often independent of the metal used. It was shown that different surface pre-treatments [11, 12] improve the junction's current–voltage (I–V) characteristics. Till now the best diodes were obtained for ZnO bulk crystals (mainly hydrothermally grown ones) [13, 14] as they have basically low carrier concentration $n \approx 10^{14}$–10^{15} cm^{-3} due to the effective compensation with Li atoms.

In this work we discuss electrical properties of the ZnO-based Schottky junctions with silver as the Schottky metal. We apply several approaches (post-growth annealing, acceptor (nitrogen) doping via the NH_4OH precursor used as an oxygen source, surface coating with a properly chosen dielectric material) to obtain the Schottky diodes with required properties.

2. Experimental

The ZnO films were grown at low temperature (between 60 °C and 200 °C) by the atomic layer deposition (ALD) method using diethylzinc ($Zn(C_2H_5)_2$, DEZ) or dimethylzinc ($Zn(CH_3)_2$, DMZ) and deionized water as precursors. As a nitrogen dopant the aqueous solution of NH_3 (ammonia water) was applied. ZnO films were obtained as the result of one of two alternative double exchange reactions

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$$Zn(C_2H_5)_2 + H_2O \rightarrow ZnO + 2C_2H_6 \tag{1}$$

or

$$Zn(CH_3)_2 + H_2O \rightarrow ZnO + 2CH_4 \,. \tag{2}$$

The junctions with a silver Schottky electrode have been formed using either as grown ZnO layers, after their post-growth annealing, for ZnO doped with nitrogen, or after ZnO surface coating with a thin dielectric film (HfO_2), introduced between ZnO and the Ag Schottky contact. The area of the Schottky contact was about 0.7 mm^2. Coating with a dielectric material was performed in a separate ALD process (at 135 °C) involving a reaction between tetrakis(dimethylamido)hafnium(IV) and H_2O.

The current–voltage characteristics (CVC) were collected using the Keithley 236 source measure unit and then processed according to the differential approach [15–17]. It bases on determination of the differential slope of the CVC curves from Eq. (3) [15]:

$$\alpha(V) = \frac{\mathrm{d}(\lg I)}{\mathrm{d}(\lg V)} = \left(\frac{V}{I}\right)\left(\frac{\mathrm{d}I}{\mathrm{d}V}\right), \tag{3}$$

where V and I stand for the voltage and the current, respectively. For CVC the α value denotes the ratio of the static resistance $R = V/I$ to the differential resistance $\mathrm{d}R = \mathrm{d}V/\mathrm{d}I$, or the ratio of the differential conductivity $\mathrm{d}\sigma = \mathrm{d}I/\mathrm{d}V$ to the conductivity $\sigma = I/V$. The α value also represents the exponent in the power law dependence $I(V) = V^{\alpha}$. Similarly, the γ parameter describing the exponential law in the form of $I(V) = \exp(V^{\gamma})$ can be found as [15]:

$$\gamma(V) = \frac{\mathrm{d}(\lg \alpha)}{\mathrm{d}(\lg V)} = \left(\frac{V}{\alpha}\right)\left(\frac{\mathrm{d}\alpha}{\mathrm{d}V}\right). \tag{4}$$

While processing the experimental dependences $I(V)$ using Eq. (3) one can reveal the regions of $\alpha =$ const. These are the regions where the $I(V)$ dependence is adequately approximated by a power law. Similarly, while analyzing the experimental dependences $I(V)$ using Eq. (4) one will find the regions of $\gamma =$ const. These ones correspond to the exponential behavior of $I(V)$.

In such a case the general analytical expression for the combination of power and exponential functions can be written as

$$I(V) = \beta V^{\alpha} \exp\left(\frac{\gamma}{|\gamma|}\left(\frac{V}{V_0}\right)^{\gamma}\right), \tag{5}$$

where β and V_0 are constant.

According to this definition, the differential approach towards the analysis of experimental data allows one to determine the dominant carrier transport mechanism in the junction, judging from the dimensionless α and γ parameters. The typical values of α and γ for different known transport regimes are listed e.g. in [15].

3. Results and discussion

As already mentioned in Introduction, to construct a good quality ZnO-based Schottky diode one has to overcome the problem of heavy unintentional n-type doping that is frequently reported for this material. Such a behavior has been attributed to a high concentration of donor type defects. Hydrogen atoms located in the interstitial positions [18, 19], zinc interstitials [20] and oxygen vacancies are claimed to be the most important shallow donors in ZnO. These defects are hampering p-type doping in ZnO [21].

The free electron concentration (n) in ZnO must be minimized to obtain a rectification in a metal–semiconductor junction. Therefore, we tested different approaches to decrease n value.

For example, a post-growth annealing of a ZnO film (at 180 °C and 250 °C) results in a drop of n up to three orders of magnitude, as already reported in [22]. The rectifying effect is then observed [23]. Unfortunately, this solution is not applicable for the heterostructures containing temperature-sensitive organic materials, such as e.g. pentacene [24]. Moreover, the low thermal budget restrictions imposed to ZnO by the construction of a new generation of 3D memory cells built in the cross-bar architecture makes the annealing procedure inapplicable in some cases. In the latter case, the so-called back-end-of--line (BEOL) metallization, in which the metal paths are placed not only at the top, but also at the bottom of the junction, was tested by us [1]. For other purposes the "classical" front-end-of-line (FEOL) architecture may be used [25].

Another problem was observed by us when using the silver Schottky contact. When placed at the top of the structure (on the ZnO layer) the Schottky electrode tends to oxidize. This results in the oxygen outdiffusion from ZnO. This leads to the formation of a very thin highly conductive layer under the Ag contact, which destroys the rectifying effect. As shown by us in [1], the effect can be avoided when the Schottky metallization was deposited at the bottom of the structure, primarily to ZnO deposition. The following contact oxidation blocked the oxygen outdiffusion from ZnO. This allowed to obtain a diode with rectification ratio of 10^8 (at ± 2 V) and current density of about 10^4 A cm^{-2}. Such parameters were suitable for a selector application in the cross-bar memories [1]. The obtained diode revealed the ideality factor $\eta \approx 2.06$ and is still competitive with the ones constructed for analogous purposes by industrial companies [26].

In the present work we test the "traditional" architecture (with the top Schottky contact) for the sensing applications of ZnO-based structures [27, 28]. We first tested the applicability of ZnO films doped (compensated) with nitrogen applying the NH_4OH precursor. Nitrogen acts as a p-type dopant in ZnO (with high ionization energy of about 1.3 eV [29]), effectively compensating the free electron concentration [28]. Figure 1 shows that nitrogen is built-in uniformly into the host material. We observed that N-doping results in a substantial drop of n down to the values of about 10^{14} cm^{-3}. We also noticed a decrease of diode reverse current with increasing nitrogen concentration (see Fig. 2). However, if N concentration exceeds 2–3% we observe a decrease of electrons' Hall mobility due to the enhanced scattering processes at ionized impurities. The forward (driving) current is then decreasing (see Fig. 2).

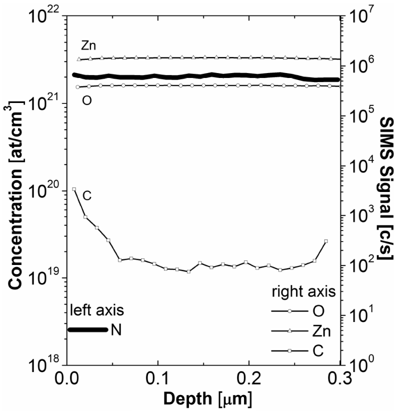

Fig. 1. Secondary ion mass spectroscopy (SIMS) profile of ZnO:N thin film with doping level of about 2.3%. As can be seen, nitrogen is uniformly distributed in the ZnO.

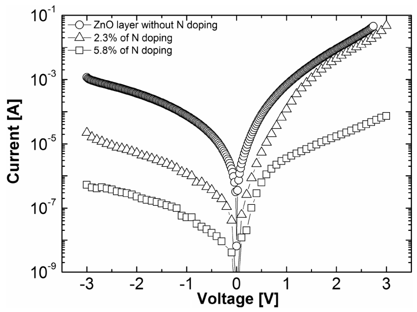

Fig. 2. Current–voltage characteristics of ZnO/Ag junctions for undoped ZnO (circles), ZnO:N with 2.3% of nitrogen (triangles) and ZnO:N with 5.8% of nitrogen (squares).

An "optimally doped" ZnO:N/Ag diode reveals the rectification ratio 2.1×10^3 at ± 3 V and ideality factor $\eta \approx 2.65$ according to the well known thermionic emission theory, defining the thermionic emission current I_{th} as:

$$I_{\mathrm{th}} = I_{\mathrm{s}} \left[\exp\left(\frac{q(V - I_{\mathrm{th}} R_{\mathrm{s}})}{\eta k T} \right) - 1 \right], \quad (6)$$

where R_{s} and I_{s} denote a diode series resistance and a saturation current, respectively. I_{s}, from which a Schottky barrier height φ_{B} can be estimated, is given by

$$I_{\mathrm{s}} = A A^* T^2 \exp\left(\frac{-q\varphi_{\mathrm{B}}}{kT} \right), \quad (7)$$

where A is the contact area (approximately 0.7 mm^2) and A^* denotes the effective Richardson constant (theoretically for ZnO $A^* = 32$ A K^{-2} cm^{-2}). As derived from these formulae, φ_{B} for the ZnO:N-based diode is about 0.7 eV. A similar value of φ_{B} has been reported for the Schottky junctions on bulk ZnO [13, 28].

From the low temperature Hall effect measurements we found that scattering on ionized impurities and grain boundaries are the two dominant (and competitive) scattering mechanisms in ZnO films. The first one is especially efficient in the case of epitaxial films with an electron concentration $n \approx 10^{18}$ cm^{-3} and can be described by the Brooks–Herring theory, according to which the Hall mobility μ and temperature T stay in the relation of $\mu \propto T^{3/2}$ [30]. The second one (applicable probably to the nitrogen-compensated films as well) seems to dominate in polycrystalline films with the grain diameter of about 20–25 nm and low ($n \approx 10^{16}$ cm^{-3}) carrier concentration. Further details will be given elsewhere.

Further increase in the ZnO/Ag junction's rectification ratio (up to 10^4–10^5 at ± 2 V) — see Fig. 3 — is possible for the ZnO film coated with a thin layer of high-k dielectric material, e.g. HfO_2. The investigations presented in [31] proved that the optimal thickness of covering is about 2.5 nm. The main advantage of such an approach is band bending regulation.

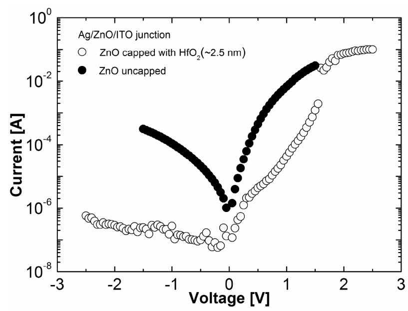

Fig. 3. Influence of HfO_2 capping layer on the I–V characteristics of Ag/ZnO/ITO structure with the top Ag Schottky contact: diode with uncoated ZnO (black circles) and coated with $\approx$ 2.5 nm of HfO_2 (white circles).

Thin film of HfO_2 deposited on the ZnO layer still allows carriers' flow through the junction and does not affect importantly n concentration of the underlying ZnO film. For that reason aluminum oxide (Al_2O_3) should not be used for capping as Al effectively provides free electrons to the host ZnO film [32]. The HfO_2-coated diodes reveal the SBH reaching 0.5–0.7 eV.

After constructing of Schottky diodes we tested their sensing properties. We have done this for the junctions built in the planar architecture, where the current is parallel to the film surface. This allows to functionalize the structure easily. As presented in Fig. 4a–c, the reverse current of the diode evidently increases under the exposition to a droplet of acetone (C_3H_6O). In fact, the effect disappears after C_3H_6O evaporation, which takes about 5 min. Interestingly, the diode-based sensor resets at room temperature (Fig. 4b) without any special treat-

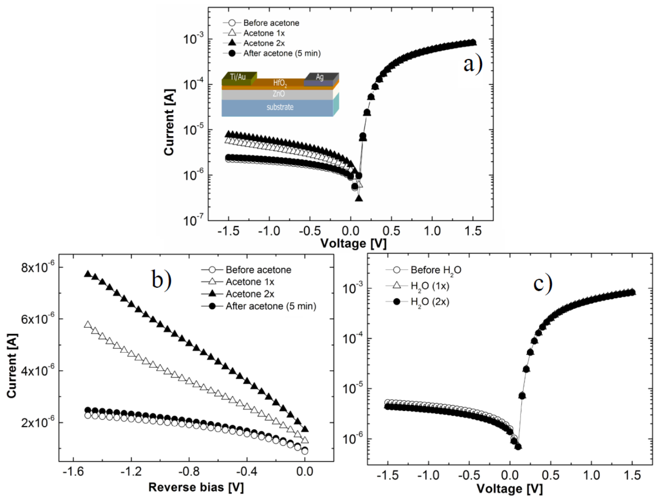

Fig. 4. Sensing properties of a planar ZnO-based Schottky diode: after exposition to acetone (C_3H_6O) in semilogarithmic scale (a), linear scale (b) and after exposition to H_2O in semilogarithmic scale (c). The junction's scheme is presented in the inset to Fig. 4a.

ment and shows almost no response when treated with water (see Fig. 4c).

The junctions' modeling performed according to the differential approach, presented in Fig. 5a–c showed that the differential slope α demonstrates various behaviors under introducing the HfO_2 interlayer (Fig. 5a). In all cases except the one when the thickness of the HfO_2 interlayer (d) is 2.5 nm, there is the restriction of the current imposed by the contact emission at high bias (> 1 V).

The evidence of this is the value of α: in these cases $\alpha \leq 1$ [16]. Only the case with $d = 2.5$ nm shows the values of $\alpha = 1.5$ at high bias, corresponding to the bimolecular recombination when concentration of major (n) and minor (p) charge carriers is almost equal [16, 33, 34]. So, there is the thickness of HfO_2 layer $d = 2.5$ nm, which favors a good injection of both types of charge carriers into the ZnO film.

The differential images of $\alpha(V)$ and $\gamma(V)$ for low bias ($V < 1$ V) are shown in Fig. 5b and c. The initial range of $\alpha(V)$ ($0 < V < 0.1$ V) shows an ideal diode behaviour where $\alpha = kT/\eta eV$ and $\gamma = 1$ [35]. The next ranges of curve have two sections which can be approximated by the reciprocal exponent (0.2 V $< V <$ 0.4 V with $\gamma = 1$) and the reciprocal square root exponent (0.4 V $< V <$ 0.8 V with $\gamma = -0.5$).

4. Summary and conclusions

The properties of ZnO/Ag Schottky junctions have been discussed. Zinc oxide films were grown by the atomic layer deposition method using either diethylzinc or dimethylzinc and deionized water as precursors. The films were deposited at low temperature between 60 °C and 200 °C. We have shown that: post-growth annealing,

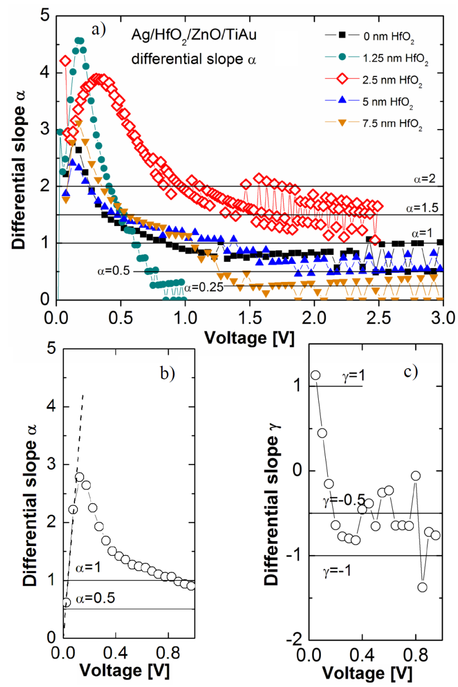

Fig. 5. The differential slope (α) versus voltage for the ZnO/Ag Schottky diodes with different thickness of HfO_2 interlayer (a). The $\alpha(V)$ (b) and $\gamma(V)$ (c) dependences show an ideal diode behavior for the low voltage range ($0 < V < 0.1$ V) according to Eq. (3) and Eq. (4).

ZnO doping with nitrogen and the layers' surface covering with a thin dielectric film (HfO_2) before introducing the silver electrode result in the higher rectification ratio of the Schottky junction.

The best results (the highest rectification ratio) have been achieved in the diode constructed in the "inversed" architecture (with the bottom Schottky electrode). For the FEOL architecture the best results have been obtained for a ZnO surface coated with a thin dielectric layer.

Modeling of the structures, based on the thermionic emission theory and differential approach gives the ideality factors $\eta \approx 2$. The sensing application of the obtained junctions has been demonstrated.

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