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Schottky Junctions with Silver Based on Zinc Oxide Grown by Atomic Layer Deposition

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This work reports on the Schottky junctions based on zinc oxide layers (grown by Atomic Layer Deposition from dimethylzinc ($Zn(CH_3)_2$) or diethylzinc ($Zn(C_2H_5)_2$) and water precursors). If the strict electrical requirements (electron concentration not higher than 10^{17} cm^{-3} and mobility above 10 $cm^2V^{-1}s^{-1}$) for ZnO are fulfilled, the rectification ratio of ZnO/Ag Schottky junction as high as 10^3 for low forward bias (2 – 3 V) can be achieved. The ideality factor of about $h \approx 2.65$ was calculated basing on the pure thermionic emission theory.

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Introduction

Zinc oxide (ZnO) has recently gathered a lot of attention due to its possible application as a semiconducting partner for ZnO-based Schottky junctions. Many papers have already been published concerning the different classes of Schottky diodes that can be used for various purposes, including ultraviolet photodetectors (involving ZnO epitaxial films grown by the Metalorganic Chemical Vapor Deposition (MOCVD) technique [1]) or hydrogen sensors, fabricated using the same method in the form of Pd/ZnO Schottky contact [2].

Another up-to-date area, to which ZnO-based Schottky junctions are being rapidly introduced is the new generation of 3-D memories built in the cross-bar architecture [3], where the Schottky diode based on ZnO acts as a selecting element [4 - 6]. In this kind of application ZnO-based junction competes with other solutions, such as polycrystalline Si that has typically lower electron mobility and usually does not fulfill a low temperature regime restriction.

The latter application imposes strong limitations on the junction processing as well as on the electrical properties of ZnO. Here, because of the so-called Back-End-Of-Line (BEOL) architecture, in which the metal paths are placed both: below the diode, and at the top of it [7], a low thermal budget during the diode preparation is required, which means that the ZnO growth temperature must be well below 200 °C. This is what differs the BEOL approach from the commonly used Front-End-Of-Line (FEOL) technology, where far higher processing temperatures (even about 1000 °C) are applied.

The ZnO films grown under rigorous temperature restrictions mentioned above also have to fulfill severe electrical requirements. For Schottky diode application ZnO layer should have both: low level of *n* concentration ($n \leq 10^{17}$ cm^{-3}) and a sufficient electron mobility ($m \geq$ 10 $cm^2V^{-1}s^{-1}$) as in this way one can obtain low reverse current in combination with a high forward one [8]. Another challenging problem is the application of good quality Schottky contacts to ZnO, as well as obtaining the satisfying value of electron mobility in this material. There are many papers and reviews containing suggestions on metal that should be chosen for the Schottky junction with ZnO [9, 10] and on additional post-growing treatment that should then be applied to improve its rectification ratio [11]. In some cases the contact deposition temperature plays an important role [12].

In terms of electrical parameters of ZnO in general, one should pay attention to the balanced stoichiometry of ZnO films (Zn-to-O ratio) in order to minimize defects concentration, which are (together with the grain boundaries) active scattering centers for electrons

[13, 14]. Besides, the role of the unintentional dopants (such as carbon and hydrogen atoms) cannot be omitted as well, as they can also act as active donors increasing the electron concentration in ZnO layer, what is undesired for Schottky junction [15, 16]

This paper presents the various approaches towards the problem of good quality of ZnO/Ag Schottky junctions, prepared according to the low temperature regime. We analyzed the influence of growth conditions as well as post-growth annealing in air on the junctions' rectifying characteristics. The dependences between structural, optical and electrical parameters of obtained ZnO thin films will be also discussed.

I. Experimental details

The ZnO films discussed in this paper were grown from organic zinc precursors either dimethylzinc ($Zn(CH_3)_2$ (DMZn) or diethylzinc ($Zn(C_2H_5)_2$, (DEZn) and deionized water by a double exchange reaction in the low-temperature Atomic Layer Deposition (ALD) process. The key advantage of this growth method, widely described e.g. in [17], is its sequentiality, i.e. the precursors meet each other only at the substrate's surface. As the reaction in a volume of the growth chamber is avoided, even very reactive chemical compounds can be applied as precursors. In the discussed case, the reaction leading to the ZnO layer runs as follows:

$$Zn\left(CH_3\right)_2 + H_2O \rightarrow ZnO + 2CH_4 . \quad (1)$$

if dimethylzinc is used as a zinc precursor or:

$$Zn\left(C_2H_5\right)_2 + H_2O \rightarrow ZnO + 2C_2H_6 , \quad (2)$$

when diethylzinc is applied. Additionally, high vapor pressure of zinc precursors allows to decrease the growth temperature far below 200 °C, what is particularly important when so-deposited ZnO thin film is dedicated to the hybrid structures with the temperature-sensitive organic materials [18, 19].

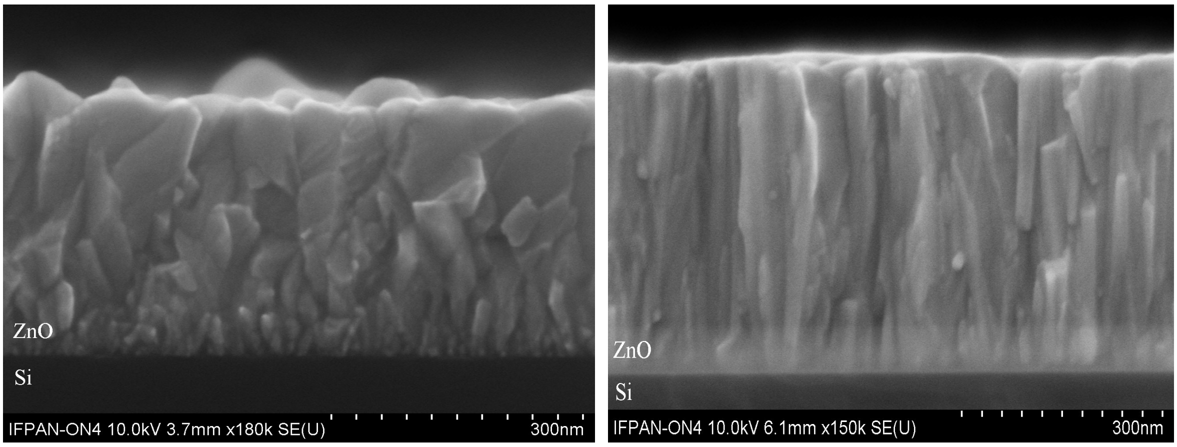
The room temperature photoluminescence (RTPL) spectra were collected in the spectral range between 340 nm and 820 nm with the CM2203 spectrometer equipped with the Xe lamp as an excitation source, whereas the composition analysis was made with the Electron Dispersive X-ray Spectroscopy (EDX) technique, using Scanning Electron Microscope (Hitachi SU-70).

The electrical parameters of ZnO layers were determined on 1cm × 1cm ZnO/glass samples using Hall effect measurements in B = 0.426 T (provided by RH2035 PhysTech GmbH system equipped with a permanent magnet) in van der Pauw configuration. A sputtered Ti/Au bi-layer with mechanically pressed indium at the top was used as an ohmic contact to the ZnO film.

The current-voltage characteristics were collected with the Keithley 236 Source Measurement Unit and subsequently theoretically analysed basing on thermionic emission theory described in Refs. [20, 21].

II. Results and discussion

All the growth substrates (Si, glass and indium-tin oxide (ITO)) were uniformly covered with fairly flat ZnO layers. The RMS parameter (indicating their surface roughness), as measured by the Atomic Force Microscopy (AFM), never exceeded the value of 10 nm. The obtained ZnO samples grew in a columnar structure as shown in Figure 1.



a) b)

Fig. 1. The cross-sectional view of the240 nm thick as-grown ZnO layer deposited at 130°C on the Si substrate. Irrespectively to a kind of zinc precursors: dimethylzinc (a) and diethylzinc (b) ZnO layers grown at low temperature exhibit a columnar microstructure. In both parts of the Figure the plain interfaces between ZnO and Si are clearly seen.

As deduced from the EDX measurements, for both zinc precursors the free carrier concentration in as-grown ZnO samples scales down with the intensity of the defect-related luminescence bands (emission below 2.0 eV) observed in their RTPL spectra as well as with Zn-to-O ratio, as shown in Figure 2 and Table 1.

Table 1

The dependence between electrical parameters and composition analysis of as-grown ZnO films. With balanced Zn-to-O ratio the stoichiometry of the films improves, thus the free carriers' concentration decreases and their

Zn precursor/ ZnO growth temperature	Zn-to-O ratio	Electron concentration n [cm^{-3}]	Mobility m [cm^{2}V^{-1}s^{-1}]
DMZn/100°C	1.15	1.40×10^{18}	0.5
DMZn/100°C	1.11	1.00×10^{17}	3.6
DMZn/100°C	1.10	3.70×10^{16}	13.0

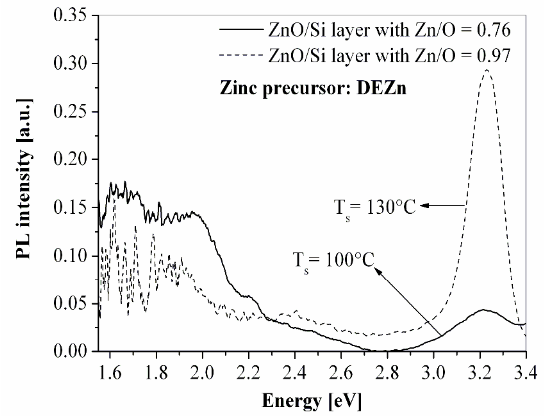


Fig. 2. RTPL spectra acquired from as-grown ZnO/Si films with different Zn-to-O ratio. For the balanced composition (better stoichiometry) of ZnO film the lower free electron concentration is observed (see Table 1). The layers were deposited at 100°C (solid line) and 130°C (dashed).

As it can be noticed from Table 1, when DMZn was applied, the obtained as grown ZnO layers were oxygen deficient ones, giving the maximum of defect emission in the green spectral range, which is assumed to be a result of the presence of oxygen vacancies [22, 23]. The PL spectra of these samples are not shown here. As in some cases of samples from Table 1 the electron concentration was high (n ~ 10^{18} cm^{-3}) we observed no rectification effect on the Schottky junctions constructed on these ZnO layers. The possible explanation of this behavior was given in [24] – the oxygen vacancies are supposed to pin the ZnO Fermi level close to the V_O defect level at approximately 0.7 eV below the minimum of the its conduction band and in consequence the Schottky contact is destroyed.

Importantly, for the ZnO layers discussed in the present work we did not observe any evident correlation between the presence of unintentional doping atoms (carbon, hydrogen) and the films' electrical properties.

A post-growth annealing is one of a very effective ways of the reduction of high electron concentration in ZnO layers dedicated to Schottky junctions. In such a way n can be reduced up to four orders of magnitude as already demonstrated in [25]. However, this approach is inappropriate when ZnO is applied to heterostructures containing organic materials, such as pentacene [18]. We observed that the annealing process results in a remarkable decrease of the defect-related luminescence band (peaked at 1.8 eV) as it is presented in Figure 3. The high intensity of these bands corresponds to a high n concentration in the examined ZnO films. As the n concentration decreases, the reverse current on the Schottky junction becomes lower and the rectifying effect appears [8]. This observation is confirmed to be a general one as this effect was observed for all examined junctions. The *I-V* characteristics of ZnO/Ag Schottky before and after annealing in air at 250 °C for 30 min. are shown in Figure 4a, b.

Regarding the possible applications of ZnO-based Schottky junctions e.g. as a selector in the new generation of 3-D memories built in a cross-bar architecture we decided to perform a low temperature ZnO growth (the ZnO layers were deposited well below 200 °C) as our previous investigations proved that the free electron concentration in the films scales down with a decreasing deposition temperature [26]. Figure 5 shows the dependence of the rectification ratio on the electron concentration in the ZnO film for the corresponding ZnO/Ag junction.

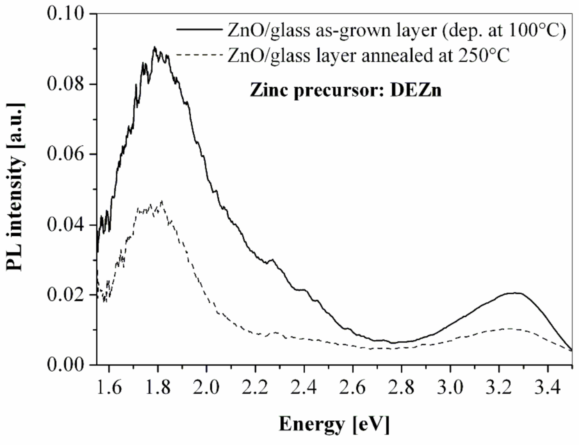


Fig. 3. ZnO/glass PL spectra before (solid line) and after annealing at 250°C for 30 min in air (dashed). After the annealing process the decreased intensity of defect-related bands (peaked at 1.8eV) is observed.

The rectifying properties of the discussed ZnO-based

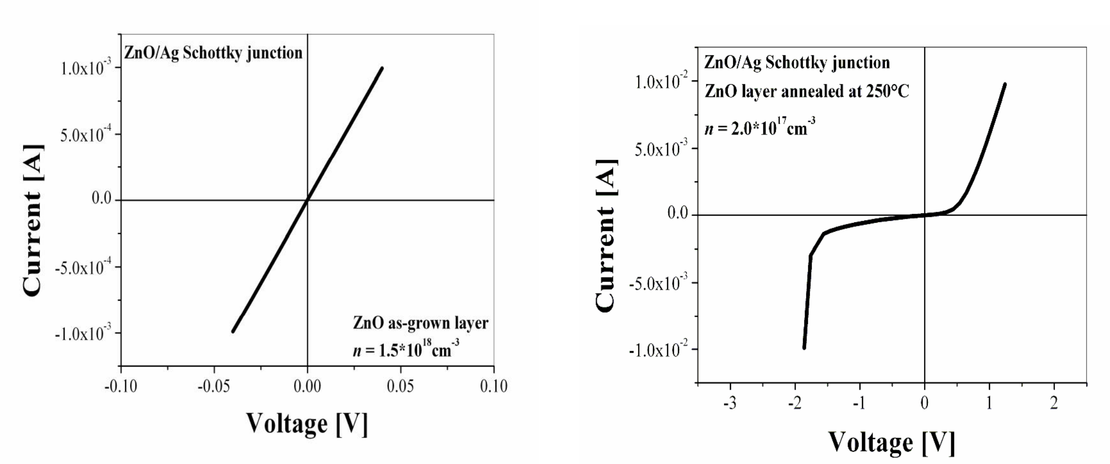


Fig. 4. The rectifying behaviour of ZnO/Ag Schottky diode occurs as a result of a decreased free electron concentration (number of defects) in ZnO thin film after annealing at 250 °C for 30 min.

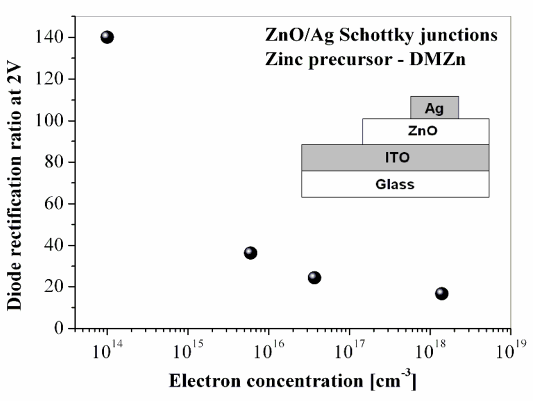


Fig. 5. The dependence of the rectification ratio on the electron concentration for the typical ZnO/Ag Schottky diode. The inset shows a schematic view of the examined structure.

Schottky diode can be improved by doping ZnO layer with nitrogen. We introduced nitrogen to the grown ZnO film by replacing H_2O, serving as an oxygen precursor with ammonia water – 25% of NH_3/H_2O solution. The appropriate Secondary Ion Mass Spectroscopy (SIMS) profiles show that the nitrogen atoms are uniformly distributed in the ZnO layer (see Figure 6).

The RT Hall effect measurements performed on these samples have shown a substantial decrease of electron concentration (n ~ 10^{14} cm^{-3}) and the Hall mobility around $10cm^2V^{-1}s^{-1}$. Such electrical parameters are probably a result of effective N_2 doping (the samples contain about 2.3 –5.8 % of nitrogen, as deduced from SIMS measurements), causing the compensation effects in ZnO as nitrogen is regarded to be a possible candidate for *p*-type doping in this material [27, 28]. For the Schottky diode with nitrogen-doped ZnO we obtained the rectification ratio (I_{ON}/I_{OFF} at ±3V), which is 2 orders of magnitude higher (2.1×10^3) than the one determined for the junction with non-doped ZnO film (1.4×10^1).

The two most evident examples of improved current–voltage dependences measured on ZnO/Ag Schottky junctions containing nitrogen are given in Fig. 7. The diode parameters were extracted assuming the pure thermionic emission theory over the barrier [20], according to which a thermionic emission current I_{th} is described with Eq. 3:

$$I_{th} = I_s\left\{\exp\left[\frac{q(V - I_{th}R_s)}{nkT}\right] - 1\right\}, \qquad (3)$$

where n is the diode ideality factor and R_s, I_s stand for a diode series resistance and saturation current, respectively. I_s, from which a Schottky barrier height j_B can be estimated, is given by:

$$I_s = AA^*T^2\exp\left(\frac{-qj_B}{kT}\right), \qquad (4)$$

where A is the contact area (approximately $0.5mm^2$) and A^* denotes the effective Richardson constant (theoretically for ZnO A^* = 32 $AK^{-2}cm^{-2}$, although the deviations of this value are also possible as an effect of the barrier inhomogeneity between the metal and semiconductor [29]).

As calculated from the thermionic emission theory, junctions presented in Fig. 7 have similar electrical characteristics. The Schottky barrier height j_{B1} was determined to be approximately 0.77 eV for the case of junction containing 5.8 % nitrogen (see Fig. 7a) and j_{B2} ≈ 0.67 eV for the junction with 2.3 % N_2 (see Fig. 7b). The ideality factors were respectively equal to $h_1 \approx 4.30$ and $h_2 \approx 2.65$. Additionally, the value of breakdown voltage was checked for both junctions to be about $U_r = 4$ V.

Taking into account the simplicity of the growth process, the method of doping and the calculation procedure, results are very promising as good quality ZnO-based Schottky diode still remains a vital experimental problem.

Summary

In the present work we demonstrated three possible approaches towards the problem of decreasing the electron concentration in the ZnO thin films grown by ALD technique, what is essential for constructing a good

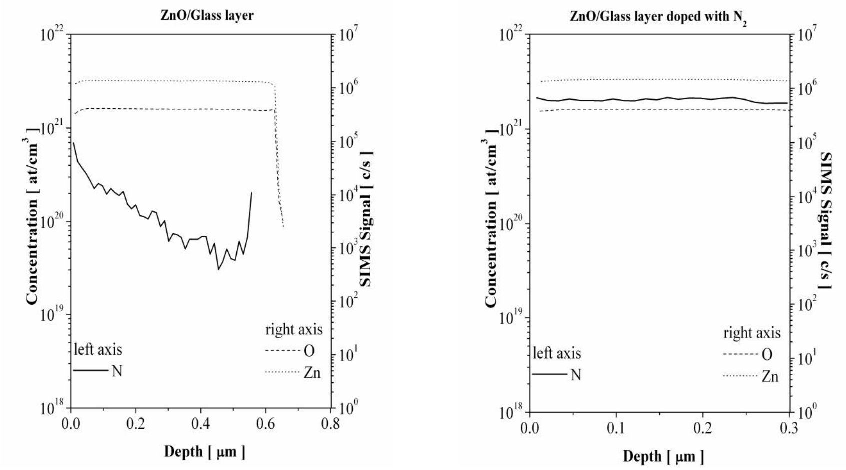
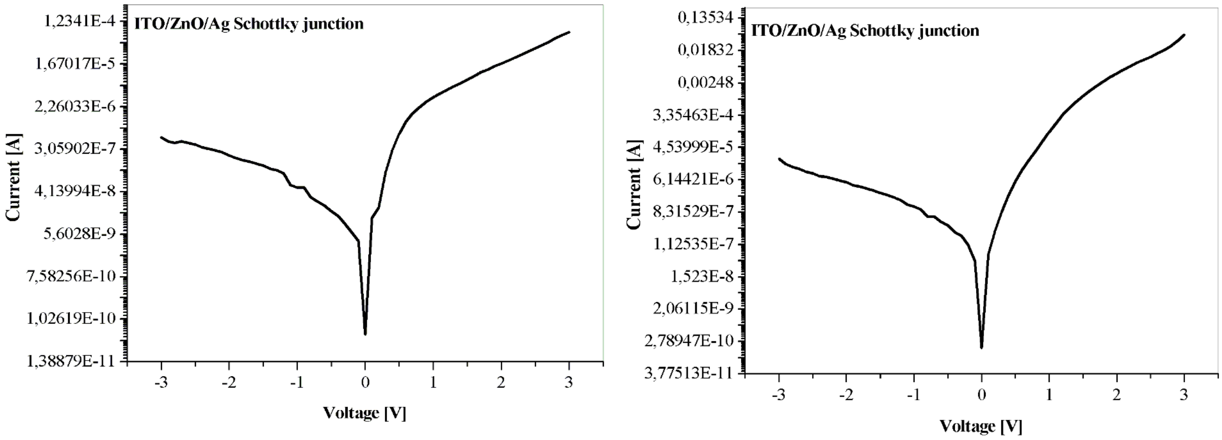


Fig. 6. SIMS depth profiles of ZnO layers: undoped (a) and intentionally doped with nitrogen from NH_3/H_2O precursor (b). In the second case an uniform profile of doping with nitrogen (solid line) can be easily seen. The rectification ratio (I_{ON}/I_{OFF} at ± 3V) of the "doped" diode was about 2 orders of magnitude higher (2.1×10^3) than the one obtained for the "undoped" ZnO/Ag junction (1.4×10^1).



a) Rectification ratio: 1.4×10^2 (at $U = 3$ V)
$n \sim 10^{14}$ cm^{-3}, $\mu \sim 10$ cm^{2}V^{-1}s^{-1}

b) Rectification ratio: 2.1×10^3 (at $U = 3$ V)
$n \sim 10^{14}$ cm^{-3}, $\mu \sim 10$ cm^{2}V^{-1}s^{-1}

Fig. 7. The current – voltage semi-logarythmic plots of nitrogen-doped ZnO/Ag Schottky junctions: with 5.8 % nitrogen (a) and 2.3 % nitrogen (b).

quality Schottky junction based on zinc oxide. One of them is the post-growth annealing, which causes the reduction of electron concentration up to 4 orders of magnitude.

Another approach rely on applying very low deposition temperature, as in polycrystalline ZnO-ALD films free carrier concentration scales with temperature. To ensure the effective compensation processes, the H_2O precursor (oxygen source) can additionally be replaced with the ammonia water (25% of NH_3/H_2O solution) as the nitrogen acts here as a *p*-type dopant. The latter solution allowed us to decrease *n* concentration down to the value of 10^{14} cm^{-3}, which was crucial for constructing the good quality ZnO/Ag Schottky junctions with the Schottky barrier height determined at the level of $j_B \approx 0.7$ eV and ideality factor $h \approx 2.6$ for the best case. Their rectification ratio (I_{ON}/I_{OFF}) was found to be as high as 2.1×10^3 for the bias of ±3 V. For the junctions without intentional nitrogen doping this parameter was about two orders of magnitude smaller (1.4×10^1).

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[1] S. Liang, H. Sheng, Y. Liu, Z. Huo, Y. Lu, H. Shen // *J. Cryst. Growth*, **225**, 110 (2001).
[2] C. Weichsel, O. Pagni, A. W. R. Leitc // *Semicond Sci. Technol.*, **20**, 840 (2005).
[3] M. Godlewski, E. Guziewicz, J. Szade, A. Wojcik-Glodowska, L. Wachnicki, T. Krajewski,

Kopalko, R. Jakiela, S. Yatsunenko, E. Przezdziecka, P. Kruszewski, N. Huby, G. Tallarida, S. Ferrari // *Microel. Eng.* **85**, 2434 (2008).

[4] Y. Sasago, M. Kinoshita, T. Morikawa, K. Kurotsuchi, S. Hanzawa, T. Mine, A. Shima, Y. Fujisaki, H. Kume, H. Moriya, N. Takaura, K. Torii, Hitachi // *Symposium on VLSI Technology,* (2009).

[5] M.-J. Lee, C.B. Lee, S. Kim, H. Yin, J. Park, S.E. Ahn, B.S. Kang, K.H. Kim, G. Stefanovich, I. Song, S.W. Kim, J.H. Lee, S.J. Chung, Y.H. Kim, C.S. Lee, J.B. Park, I.G. Baek, C.J. Kim, Y. Park // *International Electron Devices Meeting,* (2008).

[6] M. Godlewski, E. Guziewicz, S. Gieraltowska, G. Luka, T. Krajewski, L. Wachnicki K. Kopalko // *Acta Phys. Pol. A* **116**, p. 19 (2009).

[7] K. Ishimaru, *Solid-State Electronics* **52**, 1266 (2008).

[8] M. Pra, G. Csaba, C. Erlen, P. Lugli // *J. Comput. Electron.* **7**, 146 (2008).

[9] K. Ip, G. T. Thaler, H. Yang, S. Y. Han, Y. Li, D. P. Norton, S. J. Pearton, S. Jang, F. Ren // *J. Cryst. Growth* **287**, 149 (2006).

[10] M. W. Allen, S. M. Durbin, J. B. Metson // *Appl. Phys. Lett.* **91**, 053512 (2007).

[11] K.Ip, B.P. Gila, A.H. Onstine, E.S. Lambers, Y.W. Heo, K.H. Baik, D.P. Norton, S.J. Pearton, S. Kim, J.R. LaRoche, F. Ren // *Appl. Phys. Lett.* **84** (25), 5133 (2004).

[12] J.S. Wright, R. Khanna, L. F. Voss, L. Stafford, B. P. Gila, D. P. Norton, S. J. Pearton, H.- T. Wang, S. Jang, T. Anderson, J. J. Chen, B. S. Kang, F. Ren, H. Shen, J. R. LaRoche, K. Ip, // *Applied Surf. Science,* **253**, 3766 (2007).

[13] S. Jeon, S. Bang, S. Lee, S. Kwon, W. Jeong, H. Jeon, H. J. Chang, H. -H. Park // *J. Electrochem. Soc.,* **155 (**10), H738 (2008).

[14] K.T. Roro, G.H. Kassier, J.K. Dangbegnon, S. Sivaraya, J.E. Westraadt, J.H. Neethling, A.W.R. Leitch, J.R. Botha, Semicond. Sci. Technol. **23,** 055021 **(**2008).

[15] H. Huang, Z.W. Deng, D.C. Li, E. Barbir, W.Y. Jiang, M.X. Chen, K.L. Kavanagh, P.M. Mooney, S.P. Watkins, *Semicond. Sci. Technol.* **25,** 045023 (2010).

[16] C.G. Van de Walle // *Phys. Rev. Lett.* **85** (5), 1012 (2000).

[17] T. Suntola, *Handbook of Crystal Growth*, Chapter 3b, p. 605, D.T.J Hurle, Elsevier, Amsterdam, Lausanne, New York, (1994).

[18] G. Luka, T. Krajewski, L. Wachnicki, A. Szczepanik, J. D. Fidelus, A. Szczerbakow, E. Lusakowska, K. Kopalko, E. Guziewicz, M. Godlewski // *Acta Phys. Pol. A* **114** (5), 1229 (2008).

[19] E. Katsia, N. Huby, G. Tallarida, B. Kutrzeba-Kotowska, M. Perego, S. Ferrari, F. C. Krebs, E. Guziewicz, M. Godlewski, V. Osinniy, G. Luka // *Appl. Phys. Lett.* **94**, 143501 (2009).

[20] [20] R. F. Pierret, *Semiconductor device fundamentals*, Chapter 14, p. 483, Addison Wesley Longman Publishing Company Inc. (1996).

[21] J. Racko, A. Grmanová, J. Parízek, J. Breza // *Czech. J. Phys.* **47** (6), 649 (1997).

[22] X.L. Wu, G.G. Siu, C.L. Fu, H.C. Ong //*Appl. Phys. Lett*. **78**, 2285 (2001).

[23] A. Dijken, E.A. Meulenkamp, D. Vanmaekelbergh, A. Meijerink, *J. Phys. Chem. B* **104**, 1715 (2000).

[24] M. W. Allen, S. M. Durbin // *Appl. Phys. Lett.* **92**, 122110 (2008).

[25] T. Krajewski, E. Guziewicz, M. Godlewski, L. Wachnicki, I.A. Kowalik, A. Wojcik-Glodowska, M. Lukasiewicz, K. Kopalko, V. Osinniy, M. Guziewicz // *Microelectron. J.* **40**, 293 (2009).

[26] E. Guziewicz, I. A. Kowalik, M. Godlewski, K. Kopalko, V. Osinniy, A. Wojcik, S. Yatsunenko, E. Lusakowska, W. Paszkowicz, M. Guziewicz // *J. Appl. Phys.* **103**, 033515 (2008).

[27] E. Gür, S. Tüzemen, S. Doğan // *Phys. Scr.* **79**, 035701 (2009).

[28] C. Lee, S. Y. Park, J. Lim, H. W. Kim // *Materials Lett.* **61**, 2495 (2007).

[29] W. Mtangi, F. D. Auret, C. Nyamhere, P. J. Janse van Rensburg, M. Diale, A. Chawanda // *Physica B* **404**, 1092 (2009).