Schottky contact to ALD-ZnO: transport mechanisms and H_2O_2 effects

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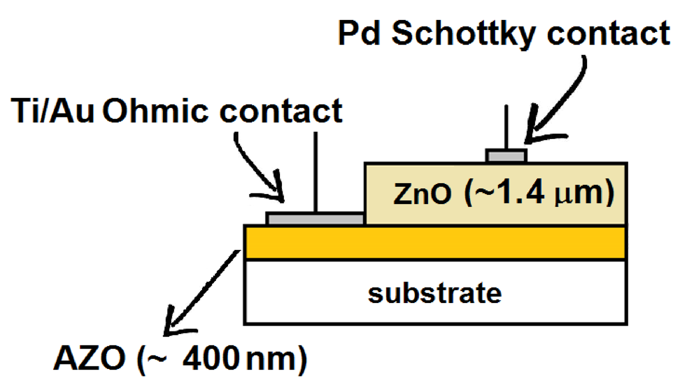
Motivation

Vertical structures based on Pd Schottky contacts (SCs) to a ZnO/AZO bilayer have been realized and electrically characterized. Following a preliminary annealing study on the separated ZnO and AZO layers the ZnO/AZO bilayer has been first annealed at 450℃ for 30 min to reduce the carrier concentration and then functionalized with a H_2O_2 dip prior to Pd deposition. On the basis of Transmission electron Microscopy and Capacitance vs Voltage measurements it has been found that the H_2O_2 treatment lowers the surface roughness and creates a ~200 nm thick layer formed by ZnO crystallites with grain size ~10 nm embedded into an amorphous matrix with reduced carrier concentration. However, contrary to what previously reported no formation of ZnO_2 has been observed. The obtained SCs showed a rectification ratio ~10^2 at -2V/+2V with a detailed analysis based on the differential approach pointing to field enhanced emission from defective channels as the main leaking mechanisms.

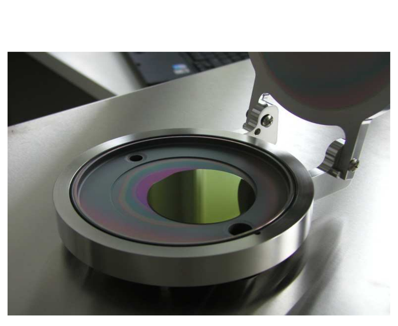
ZnO-based Schottky diodes – basic preparation details

- *c*-sapphire substrates (10×7 mm) and a control wafer were cleaned in acetone, isopropanol and deionized water (DI);
- Polycrystalline bottom AZO films were grown at 200℃ using diethylzinc (DEZn), DI, trimethylaluminum (TMA) and nitrogen as zinc, oxygen and aluminium precursors and purging gas, respectively;
- To counterbalance the anticipated RMS increase while lowering the growth temperature, the deposition of top ZnO layer was performed at 120℃ instead of 100℃ with the total number of cycles chosen to deposit a ~1.4 µm thick layer;
- Part of the AZO/ZnO structures were annealed at 450℃ for 30 min. in N_2 flow and subsequently cleaned in an ultrasonic bath with acetone and isopropanol for 10 min each and dipped in a 30% H_2O_2 solution for 15 minutes[(1-3)];
- Then, the circular Pd contacts with a diameter of 0.8, 0.6, 0.4 and 0.15 mm (with an 10% overall error) and a nominal thickness of ~70 nm were evaporated;
- Finally, a 1h hot plate annealing at 200℃ in air was performed, after which the ZnO layer covering the Ti/Au Ohmic contact has been etched using an HCl based solution.



ZnO growth:

$$C_2H_5–Zn–C_2H_5 + H_2O \rightarrow ZnO + 2C_2H_6$$



Savannah100 ALD reactor

Beneq TFS 200 ALD reactor

(1) R. Schifano, E. V. Monakhov, U. Grossner, B. G. Svensson, *Appl. Phys. Lett.* **91**, 193507 (2007);

(2) Q. L. Gu, C. C. Ling, X. D. Chen, C. K. Cheng, A. M. C. Ng, C. D. Beling, S. Fung, A. B. Djurisic, L. W. Lu, G. Brauer, H. C. Ong, *Appl. Phys. Lett.* **90**, 122101 (2007);

(3) S. Kim, H. Kim, T. Seong, *Appl. Phys. Lett.* **86**, 112101 (2004).

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Results

1. Electrical and structural studies of the AZO and ZnO films and resulting the Schottky structure

RT Hall data (VdP conf.)

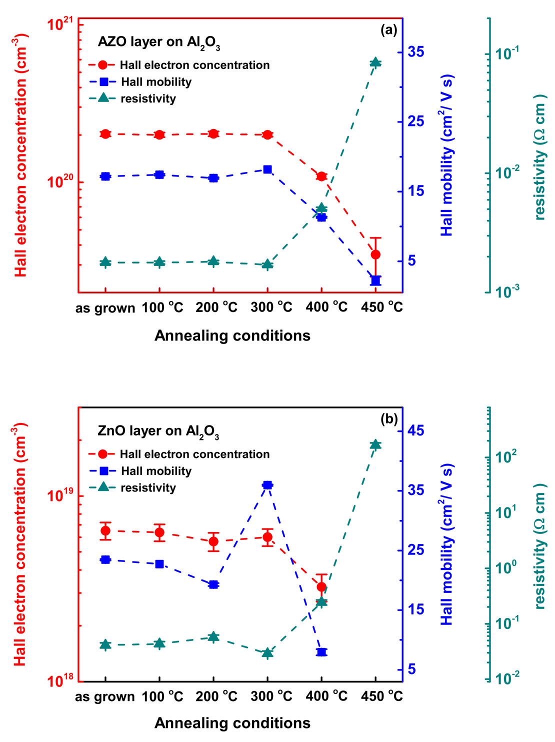

FIG. 1. Dependence of the Hall carrier concentration, Hall mobility and resistivity on the annealing temperature (subsequent isochronal annealing of 30 min in N_2 flow) for the separate (a) AZO and (b) ZnO layers grown on *c*-sapphire.

As grown ZnO ALD layers present a carrier concentration too high for SCs realization, i.e. an annealing at 450℃ for 30 min. in N_2 flow is required.

TEM / HRTEM studies

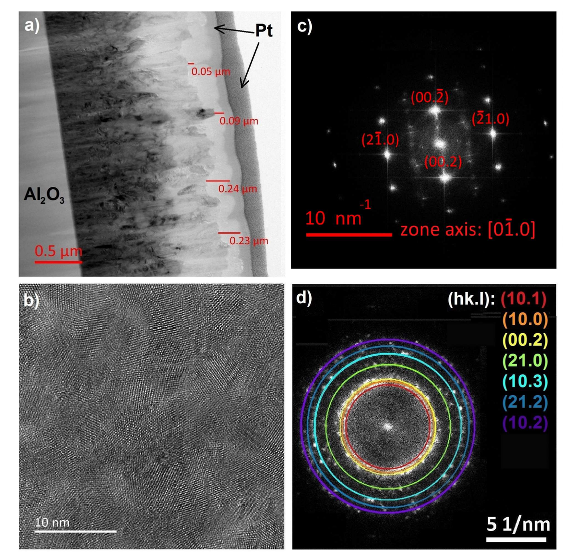

FIG. 2. (a) Cross sectional TEM image of the overall AZO/ZnO structure. The thickness of the topmost part of the ZnO film (H_2O_2 affected) is also indicated in few points. (b) An HRTEM image of the H_2O_2 modified layer. (c) FFT corresponding to a HRTEM image of a ZnO unaffected region. (d) FFT obtained from the HRTEM of the H_2O_2 affected region of ZnO shown in (b). Both the (c) spot and (d) ring pattern can be indexed according to the ZnO reflections reported.

As consequence of the H_2O_2 treatment the affected layer turns into an oxygen rich amorphous matrix with embedded crystallites of size .~10 nm.

SCs electrical characteristics

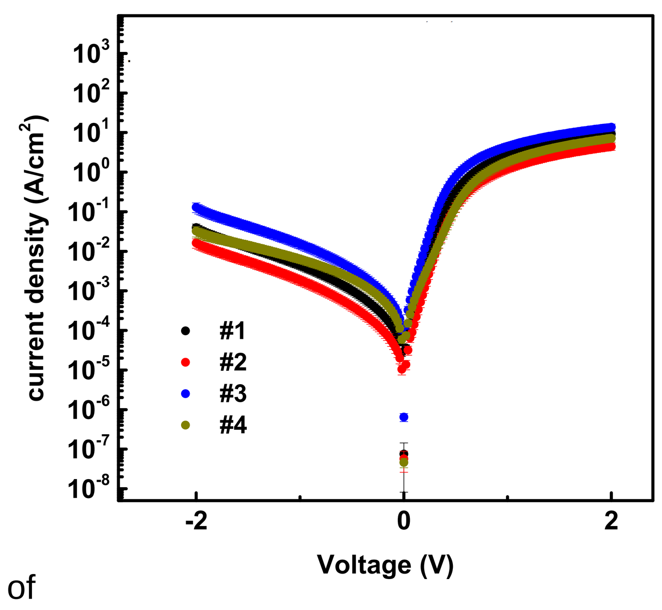

FIG. 3. *I–V* characteristics of four selected SCs. A rectification ratio of ~10^2 at -2V/+2V has been achieved. The SCs have been found to be stable after 7 months' storage at room temperature in air.

SIMS measurements have been performed (not shown) to verify the limited Al diffusion through fast diffusion channels following the annealing step.

2. SCs electrical investigations

To perform a quantitative analysis of the devices' electrical characteristics a thermionic regime has been assumed for the SCs, while leakage mechanisms have been investigated using a differential approach:

$$I = A J_0 \exp\left[\frac{q(V - IR_s)}{\eta kT}\right]\left\{1 - \exp\left[\frac{-q(V - IR_s)}{kT}\right]\right\} + \frac{V - IR_S}{R_P}$$

J_0 – reverse saturation current density for an ideal Schottky contact;
R_s – diode series resistance;
k – Boltzmann constant;
A – Schottky contact size;
η - diode ideality factor;
R_P – is modeling the leakage current (not necessarily Ohmic).

$$\left\{\begin{array}{l} \alpha(V) = \frac{V}{I}\frac{dI}{dV} \\ I \propto V^a \exp(bV^c) \end{array}\right\} \Rightarrow \alpha(V) = a + bcV^c$$

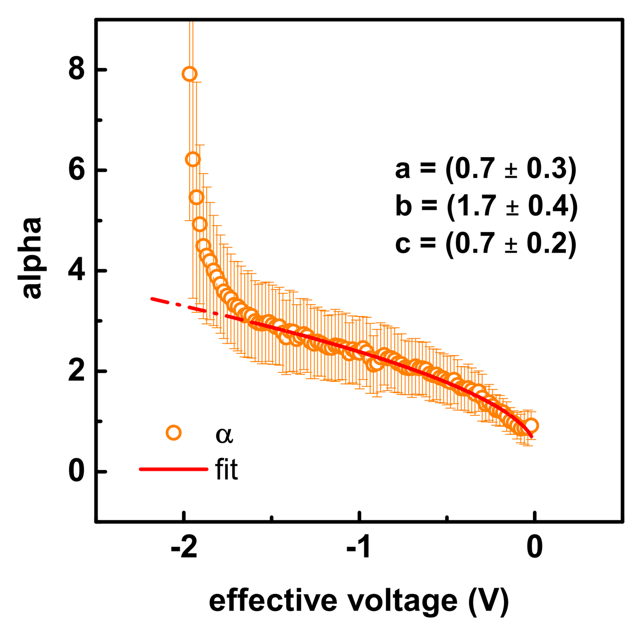

FIG. 4. α vs reverse bias as derived from the differential approach (circles).The fitted curve and the extracted a, b and c values are also shown.

Parameter	Value
η	3 – 4
R_S [Ω]	60 – 160
a	0.6 – 0.7
b	1.2 – 1.9
c	0.6 – 0.7

- Due to the vertical structure used a low series resistance is achieved (R_S ~ 60-160 Ω),
- The sublinear dependence of the current on the voltage both in the power law and the exponential term (a and c) points to field enhanced emission from defective *channels* as the main leaking mechanisms,
- Electrical experimental evidence for a near surface decreased carrier concentration consistent with the TEM results indicating oxygen excess in the H_2O_2 affected layer .

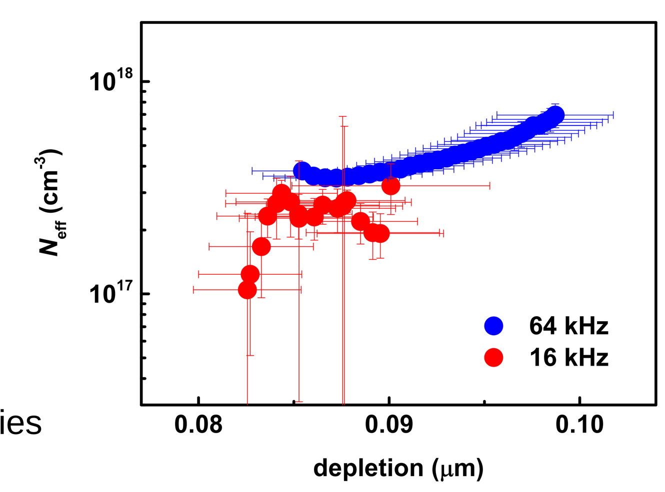

FIG. 5. Effective carrier concentration (N_{eff}) versus depleted region depth obtained with probing frequencies of 16 kHz and 64 kHz. The x–axis zero refers to the Pd/ZnO interface.

Conclusions

- Vertical structures based on Pd Schottky contacts deposited on a ALD grown ZnO/AZO bilayer have been realized by using Ti/Au to the AZO as Ohmic back contact and H_2O_2 functionalization of the ZnO surface;
- The devices exhibited promising characteristics: they have been found to be stable after 7 months' storage at room temperature in air and exhibit **rectification ratio $I_{ON}/I_{OFF} \geq 10^2$ at -2V/+2V** with ideality factors in the 3-4 range;
- Thanks to the chosen device structure and presence of the AZO layer the series resistance has been reduced to 60-160 Ω, which is up to 1 order of magnitude lower than what previously reported for Schottky contacts to ALD grown ZnO layers of similar thickness but using a planar configuration;
- Differential approach analysis indicates highly defective channels placed in parallel to the Schottky contacts as the main leakage source for the reverse biased devices. Cross sectional TEM analysis of the ZnO/AZO bilayer shows a **~50-320 nm thick oxygen rich layer formed by ~10 nm crystallites embedded into an amorphous matrix**. This results from the H_2O_2 functionalization prior to the Pd Schottky contacts application.