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# A comparative study of the electrical properties of Pd/ZnO Schottky contacts fabricated using electron beam deposition and resistive/thermal evaporation techniques

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A systematic investigation to check the quality of Pd Schottky contacts deposited on ZnO has been performed on electron beam (e-beam) deposited and resistively/thermally evaporated samples using current-voltage, IV, and conventional deep level transient spectroscopy (DLTS) measurements. Room temperature IV measurements reveal the dominance of pure thermionic emission on the resistively evaporated contacts, while the e-beam deposited contacts show the dominance of generation recombination at low voltages, $<0.30$ V, and the dominance of pure thermionic emission at high voltages, greater than 0.30 V. The resistively evaporated contacts have very low reverse currents of the order of $10^{-10}$ A at a reverse voltage of 1.0 V whereas the e-beam deposited contacts have reverse currents of the order of $10^{-6}$ A at 1.0 V. Average ideality factors have been determined as $(1.43 \pm 0.01)$ and $(1.66 \pm 0.02)$ for the resistively evaporated contacts and e-beam deposited contacts, respectively. The IV barrier heights have been calculated as $(0.721 \pm 0.002)$ eV and $(0.624 \pm 0.005)$ eV for the resistively evaporated and e-beam deposited contacts, respectively. Conventional DLTS measurements reveal the presence of three prominent defects in both the resistive and e-beam contacts. Two extra peaks with energy levels of 0.60 and 0.81 eV below the conduction band minimum have been observed in the e-beam deposited contacts. These have been explained as contributing to the generation recombination current that dominates at low voltages and high leakage currents. Based on the reverse current at 1.0 V, the degree of rectification, the dominant current transport mechanism and the observed defects, we conclude that the resistive evaporation technique yields better quality Schottky contacts for use in solar cells and ultraviolet detectors compared to the e-beam deposition technique. The 0.60 eV has been identified as possibly related to the unoccupied level for the doubly charged oxygen vacancy, $V_o^{2+}$. [doi:10.1063/1.3658027]

## INTRODUCTION

ZnO, a wurtzitic semiconductor with a wide bandgap and high excitonic binding energy at room temperature is presently used in many diverse applications. Of importance and relevance to this article is its use in electronic and optoelectronic applications. With its wide experimental bandgap of 3.4 eV, it finds applications in the realization of blue and ultraviolet (UV) light emitting devices such as light emitting diodes and lasers and also daylight-blind UV detectors. It also finds important applications in the photovoltaic industry in its use as transparent conducting films and fabrication of solar cells. However, the fabrication of good quality and reliable Schottky contacts on ZnO remains a challenge[1] as it depends on the cleaning procedure used and the type of metals used for the contact. Good quality contacts, i.e., with low series resistance, low leakage current, and high barrier heights are essential for the electrical characterization of devices using DLTS. Since DLTS is a capacitance based technique, it is a requirement that the device should have a very low leakage current so as not to short circuit the device. Reports on the effect of leakage current on DLTS measurements have been published.[2–4] To be able to fabricate high quality optoelectronic devices such as ultraviolet detectors, high quality Schottky contacts are required. It is important and ideal that good quality Schottky contacts should have minimal defects as defects often affect device operation and at times determine the efficiency of devices, e.g., in solar cells where the efficiency depends on the carrier lifetime of the majority charge carriers. Another issue of concern is the effect of deposition techniques on the quality of contacts produced. Reports on the fabrication of contacts on ZnO using metals with low melting points, Pd, Au, among others have been published,[5–8] in which the resistive evaporation technique has been used. A challenge comes when one needs to use metals with high melting points, Pt, Ir, Ru, etc., as a Schottky contact where different techniques have to be employed, e.g., the sputter deposition and e-beam deposition technique. In this article, we have singled out the electron-beam deposition technique for the deposition of Schottky contacts using high melting point materials and used Pd (since it can also be resistively evaporated) to check the difference in the quality of the contacts produced in comparison with the resistive evaporation technique. It is expected that the two deposition techniques should produce contacts with

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TABLE I. A summary of contacts deposited on ZnO using the resistive and e-beam deposition techniques to check the degree of rectification of contacts.

| Growth technique | Metal | Deposition technique | Reverse current at 1 V (A) | Forward current at 1 V (A) | Degree of rectification | Measurement temperature (K) |
|---|---|---|---|---|---|---|
| RF sputter | Ir | e-beam | $10^{-9}$ | $10^{-7}$ | 2 | Ref. 9 |
|  | Pt | e-beam | $10^{-8}$ | $10^{-5}$ | 3 | RT (Ref. 10) |
| MOCVD | Au | e-beam | $10^{-6}$ | $10^{-4}$ | 2 | (Ref. 11) |
| DRMS | Au | e-beam | $10^{-8}$ | $10^{-6}$ | 2 | 293 (Ref. 12) |
| Hydrothermal | Ag | e-beam | $10^{-6}$ | $10^{-2}$ | 4 | 300 (Ref. 13) |
| Hydrothermal | Pd | e-beam | $10^{-7}$ | $10^{-2}$ | 5 | RT (Ref. 14) |
| MOCVD | Pd | Thermal | $10^{-7}$ | $10^{-3}$ | 4 | (Ref. 5) |
| PLD | Pd | Thermal | $10^{-6}$ | 1 | 6 | 290 (Ref. 6) |
| Magnetron sputtered | Au | Thermal | $10^{-7}$ | $10^{-3}$ | 4 | RT (Ref. 7) |
| Melt | Pd | Thermal | $10^{-10}$ | $10^{-2}$ | 8 | 298 (Ref. 15) |

different qualities. Table I shows a summary of some of the findings from the fabrication of Schottky contacts using the thermal/resistive evaporation and e-beam technique. There is a difference in the quality, i.e., the degree of rectification (in this case, defined as the ratio of the forward current to the reverse current at 1.0 V) and reverse current at 1.0 V for the references used in this article.[9–15] On average, the resistively/thermally deposited contacts show a higher degree of rectification compared to the e-beam deposited contacts. In using the resistive evaporation technique, one uses the thermal resistance of the material to evaporate it unlike in the electron beam deposition technique where an electron beam is used to heat and evaporate the source material. In the latter technique, since electrons are accelerated by a high voltage and bent by the magnetic field toward the material to be evaporated, chances are, some other material is ionized and will not be effectively bent by the magnetic field. This ionized material might impinge on the surface of the sample hence affecting the quality of the contact produced which is unlikely with the resistive evaporation technique. We have systematically studied the effects of the deposition techniques on the quality of the Pd contacts on ZnO using current voltage, IV, and conventional DLTS measurements.

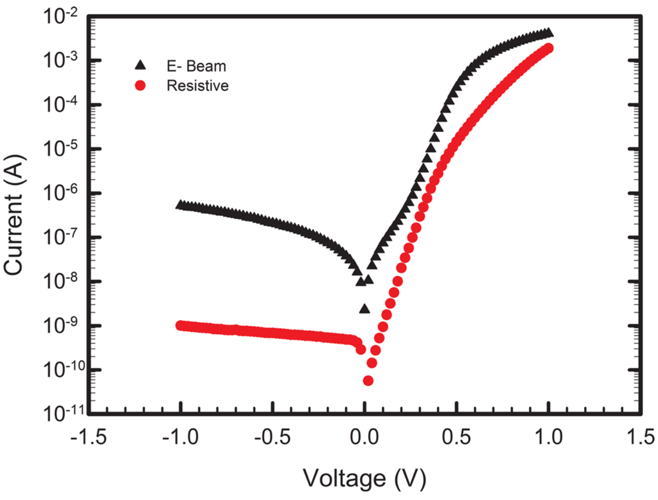

FIG. 1. (Color online) A semi-logarithmic IV characteristics of resistively and e-beam deposited Pd Schottky contacts measured at 298 K. The red circles represent the resistively evaporated contacts and the dark triangles represent the e-beam deposited sample.

## EXPERIMENT

The samples used in this study were melt grown obtained from Cermet, Inc. with carrier concentration of about $8.0 \times 10^{16}$ cm$^{-3}$ as from Hall effect measurements.[16] Sample cleaning was performed as described by Ref. 8. Ohmic contacts with a composition of Ti/Al/Pt/Au and relative thicknesses of 20/2080/40/80 nm were e-beam evaporated onto the O-polar face for both samples. Sample annealing at 200 °C was performed under an Ar flow for 30 mins. Pd Schottky contacts of thicknesses 100 nm and diameter 0.6 mm were thermally evaporated on the Zn-polar (0001) face for the first sample and e-beam deposited on the second sample. Room temperature IV measurements were then performed in the dark. Finally, conventional DLTS was carried out in the 30–350 K temperature range at a quiescent reverse bias of $-1.0$ V and a filling pulse $V_p = 0.30$ V.

## RESULTS AND DISCUSSIONS

Figure 1 shows the semi-logarithmic IV plot for the resistively/thermally evaporated and e-beam evaporated Pd Schottky contacts. Thermally evaporated contacts indicate the dominance of pure thermionic emission in the voltage range examined, while the e-beam deposited contacts indicate the dominance of generation recombination current[17] at low voltages, i.e., 0.30 V and the dominance of pure thermionic emission at voltages greater than 0.30 V. It can be observed that the upper part, i.e., the high voltage regions of the curves is affected by series resistance effects.[18] The IV characteristics have been analyzed by using the usual thermionic emission model for both the resistively evaporated and the e-beam deposited contacts. For the e-beam deposited contacts, the region that resembles pure thermionic emission $0.3 < V < 0.5$ has been used. The reverse current for the

TABLE II. Values of Schottky barrier height (SBH), ideality factor, series resistance $R_s$, and current at 1.0 V for the resistively and e-beam deposited contacts.

| Deposition technique | SBH (eV) | Ideality factor | $R_s$ (Ω) | I (at $-1$ V) (A) |
|---|---|---|---|---|
| Thermal/resistive | $0.721 \pm 0.002$ | $1.43 \pm 0.01$ | 190 | $7.92 \times 10^{-10}$ |
| e-beam | $0.624 \pm 0.005$ | $1.66 \pm 0.02$ | 110 | $5.68 \times 10^{-7}$ |

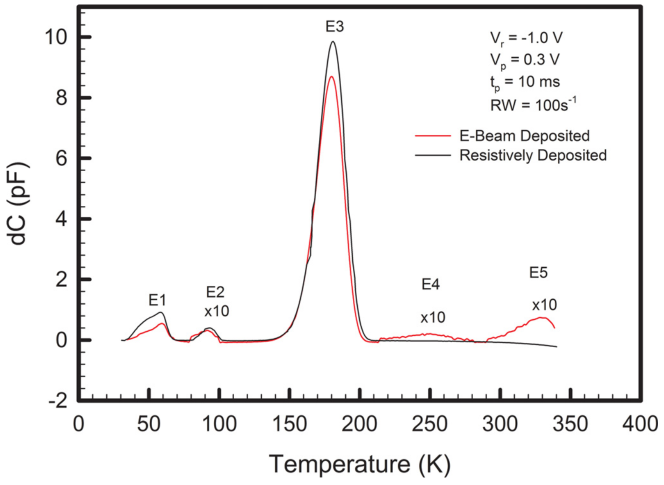

FIG. 2. (Color online) DLTS spectra for the resistively and e-beam deposited samples measured at a quiescent reverse bias of $-1.0$ V, a filling pulse height, $Vp = 0.30$ V, filling pulse width of 10 ms and rate window of 100 $s^{-1}$ in the 30–350 K temperature range.

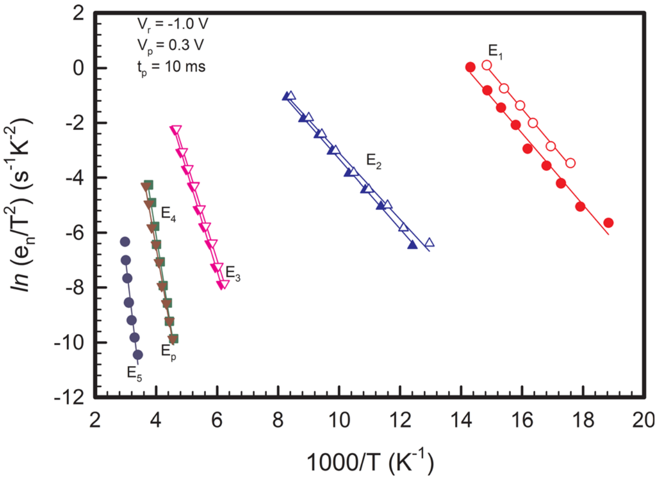

FIG. 3. (Color online) Arrhenius plots for the resistively and e-beam deposited Schottky contacts. Open symbols are for resistively deposited contacts, while closed symbols represent the e-beam deposited contacts. Dark red triangles show the defect observed after proton irradiation.

resistively evaporated contacts is almost constant with increase in reverse bias while that for the e-beam deposited contacts shows a dramatic change with bias. Table II shows the parameters that were extracted from the IV characteristics of the contacts. There is a clear distinction between the thermally evaporated and e-beam deposited contact parameters. High barrier heights have been observed on the thermally evaporated contacts together with very low reverse currents and ideality factors.

To try and explain the observed difference in the IV characteristics, conventional DLTS measurements have been performed. Figure 2 shows the DLTS spectra obtained from the resistively evaporated and e-beam deposited contacts. It can be clearly observed that the resistively evaporated contacts have three peaks while the e-beam deposited contacts have five peaks.

The activation energies together with the apparent capture cross sections of the observed defects have been extracted from the Arrhenius plots presented in Fig. 3.The results are presented in Table III.

Defects labeled E1, E2, and E3 have been observed in both samples. Defect E1 with activation energy ($0.111 \pm 0.001$) eV below the minimum of the conduction band can be the same defect that was observed by Auret *et al.*[1] in ZnO grown by the vapor phase technique and melt growth technique[19] with energy level 0.12 eV and Grundmann *et al.*[6] with energy level 0.10 eV. The slight difference in energy level could be due to the fact that it is observed close to the freeze out region hence an accurate determination of its energy level can be difficult as the capacitance drops sharply within a small change in temperature, as illustrated in Fig. 4. The decrease in capacitance at high temperature for the e-beam contacts is due to the nature of the E4 defect.

Another setback for the accurate determination of E1 is its electric field dependence as has been reported by Refs. 1, 20. The asymmetry of the peak in Fig. 2 which was also observed and reported by Ref. 1 also contributes to the limitation in the accurate determination of E1. The E3 defect with activation energy ($0.32 \pm 0.01$) eV below the conduction band is possibly the same defect that was observed by Polyakov *et al.*[21] on samples obtained from Eagle-Pitcher, Grundmann *et al.*[6] in pulsed laser deposited ZnO, and Auret *et al.*[19] in melt grown ZnO. Its identity has been attributed to intrinsic defects, either interstitial zinc or the oxygen vacancy $V_o$.[22] The third defect labeled as E2 common to both the thermally evaporated and e-beam deposited contacts, with energy level ($0.107 \pm 0.003$) eV has also been observed by Auret *et al.*[1] in ZnO grown by the vapor phase technique. Since E1 and E3 have been observed in ZnO grown by different techniques,[1,6,19,21] they can be native defects, common to n-type single crystal ZnO. The E2 defect has been observed in both the e-beam deposited and resistively deposited contacts hence it is not responsible for the generation recombination effects observed in the e-beam contacts.

TABLE III. Values of energy levels and apparent capture cross-sections obtained on the resistively and e-beam deposited Pd/ZnO Schottky contacts.

| | E1 | | E2 | | E3 | | E4 | | E5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Deposition technique | Level (eV) | Capture cross section $\times 10^{-12}$ cm$^2$ | Level (eV) | Capture cross section $\times 10^{-16}$ cm$^2$ | Level (eV) | Capture cross section $\times 10^{-14}$ cm$^2$ | Level (eV) | Capture cross section $\times 10^{-11}$ cm$^2$ | Level (eV) | Capture cross section $\times 10^{-11}$ cm$^2$ |
| Resistive | 0.111 | 5.16 | 0.110 | 1.23 | 0.31 | 2.71 | | | | |
| e-beam | 0.112 | 1.48 | 0.106 | 1.85 | 0.32 | 3.79 | 0.60 | 3.64 | 0.81 | 2.24 |

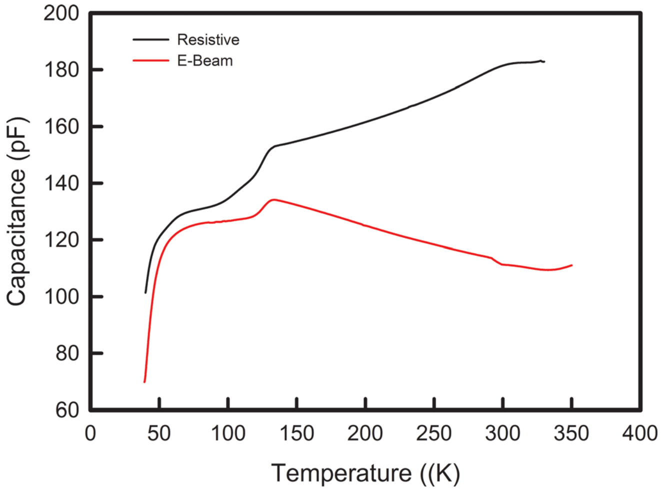

FIG. 4. (Color online) A Capacitance temperature graph for the e-beam and resistively deposited Pd Schottky contacts measured at a reverse bias of −1.0 V.

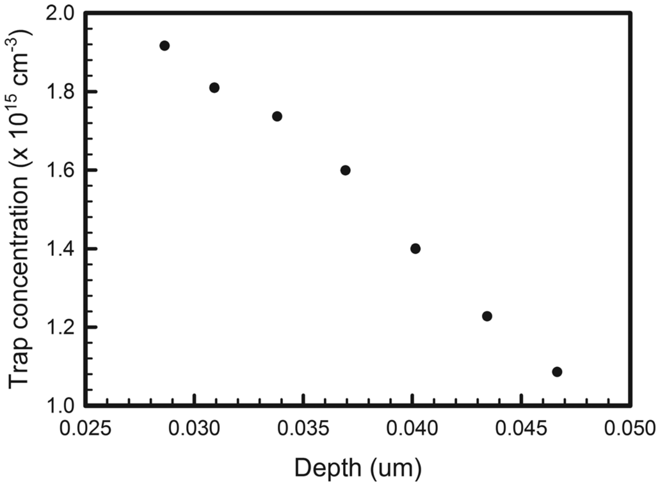

FIG. 5. The depth profile of the E4 peak measured at a constant reverse bias of 1.0 V in 0.05 V increase in pulse.

The E4 and E5 defects which have been introduced by e-beam damage on the surface of ZnO may act as generation/recombination centers. The two defects E4 and E5 with energy levels 0.60 and 0.81 eV below the conduction band and apparent capture cross-sections of $3.64 \times 10^{-11}$ cm$^2$ and $2.24 \times 10^{-11}$ cm$^2$, respectively have not been experimentally observed and reported before. Auret *et al.*[1] observed a defect with an energy level of 0.59 eV, almost the same energy as E4 after proton bombardment on vapor phase grown ZnO with energy of 1.8 MeV. Mtangi *et al.*[23] also observed a defect $E_p$ (shown in the Arrhenius plots of Fig. 3) with energy level 0.54 eV below the minimum of the conduction band after 1.6 MeV proton bombardment of melt grown ZnO. This indicates that E4 and E5 are a result of high energy particle bombardment on ZnO.

During e-beam deposition, the filament used is not a true point source of electrons.[24] Stray electrons that originate at the filament and are not focused onto the metal impinge onto the sample, causing damage. Also some other negatively charged ionized gas particles originating from and close to the filament area can be accelerated toward the sample causing damage to the sample. A defect with the same energy level as E4 has been reported by Patterson *et al.*[25] from theory and has been explained as the unoccupied level for the doubly charged oxygen vacancy, $V_o{}^{2+}$. Since the identity of E3 is not clear as yet, there is a possibility that E3 is interstitial Zn related. However, von Wenckestern *et al.*[22] argue that the E3 is not necessarily connected to intrinsic defects such as zinc interstitials or oxygen vacancies, suggesting that the origins of E3 are possibly transition metal ions. If this is the case, then E4 might be related to the doubly charged oxygen vacancy in ZnO. These defects may also be the cause of high leakage currents as they promote the movement of carriers under high electric field environments through tunneling resulting in the poor quality of devices.

Figure 5 shows the depth profile of the E4 peak examined at a constant reverse bias of 1.0 V and increasing the pulse in steps of 0.05 V. We managed to probe a region up to a depth of 46.2 nm below the interface. The concentration of E4 decreases from $1.91 \times 10^{15}$cm$^{-3}$ at 28.8 nm to $1.08 \times 10^{15}$cm$^{-3}$ at 46.2 nm. The decrease in concentration with depth is a clear indication that this defect is due to high energy particles impinging onto the sample which lose their energy as they go deeper into the bulk of ZnO. The depth profile for E5 could not be accurately determined because of the negative going capacitance transient at high temperatures as shown in Fig. 4.

## CONCLUSIONS

We have successfully investigated the effects of different deposition techniques on Schottky contact quality. The thermal/resistive evaporation technique has yielded contacts with a very low reverse current. Pure thermionic emission has proved to be the dominant current transport mechanism in the voltage range examined. The e-beam deposition technique has produced contacts with high leakage currents. Generation recombination has proved to be the dominant current transport mechanism at low voltages. Conventional DLTS measurements have revealed the existence of three defects with energy levels 0.111, 0.107, and 0.31 eV below the minimum of the conduction in both samples which have been attributed to native defects in ZnO. Two extra peaks with energy levels 0.60 and 0.81 eV below the conduction band have been observed in the e-beam deposited contacts and have been explained as the cause of generation recombination effects and high leakage currents observed in the e-beam deposited samples. The 0.60 eV level has been explained as possibly related to an unoccupied level for the doubly charged oxygen vacancy, $V_o{}^{2+}$, that is only if the E3 defect is interstitial Zn related or transition metal ions related. For the fabrication of solar cells and ultraviolet detectors on ZnO, the resistive/thermal evaporation technique yields better devices with low reverse currents and minimal defects compared to the e-beam technique.

## ACKNOWLEDGMENTS

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