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<td><strong>Author(s)</strong></td>
<td>Gu, QL; Ling, CC; Chen, XD; Cheng, CK; Ng, AMC; Beling, CD; Fung, S; Djuriši, AB; Lu, LW; Brauer, G; Ong, HC</td>
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Hydrogen peroxide treatment induced rectifying behavior of Au/n-ZnO contact


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Conversion of the Au/n-ZnO contact from Ohmic to rectifying with H2O2 pretreatment was studied systematically using I-V measurements, x-ray photoemission spectroscopy, positron annihilation spectroscopy, and deep level transient spectroscopy. H2O2 treatment did not affect the carbon surface contamination or the EC−0.31 eV deep level, but it resulted in a significant decrease of the surface OH contamination and the formation of vacancy-type defects (Zn vacancy or vacancy cluster) close to the surface. The formation of a rectifying contact can be attributed to the reduced conductivity of the surface region due to the removal of OH and the formation of vacancy-type defects. © 2007 American Institute of Physics. [DOI: 10.1063/1.2715025]

Zinc oxide is a wide band gap semiconductor which has recently attracted extensive attention because of its potential for a wide variety of applications, such as optoelectronic, high frequency, gas sensing, piezoelectric and transparent devices, etc.1–4 Fabricating high quality metal contact to ZnO is an important step for successful device fabrication because a metal-semiconductor structure is one of the essential structures for many devices. However, reports of successful rectifying metal/n-ZnO contact have been scarce. The metals used include Au,2–9 Ag,6,10 Pt,11–13 and Pd.2,3,14,15 It has also been shown that surface treatments such as H2O2,12 sulfide,13 ozone,11 and plasma can improve the rectifying contact quality (increase the barrier height, decrease the reverse bias leakage current, and achieve an ideality factor approaching unity). While several explanations, such as good surface morphology, removal of C and OH contamination, and reduction in surface conductivity, have been proposed, the mechanisms behind contact quality improvements are still controversial and not well understood.

We have systematically studied the influence of the H2O2 pretreatment duration and temperature on the properties of Au/n-ZnO contacts. As the observed phenomenon may involve more than one physical process, x-ray photoemission spectroscopy (XPS), scanning electron microscopy (SEM), positron annihilation spectroscopy (PAS), and deep level transient spectroscopy (DLTTS) were used to investigate the influence of contamination, morphology, and defects on the electrical properties of the fabricated Au/ZnO contacts. The ZnO sample used was melt-grown undoped n-type ZnO obtained from the Cermet Inc., U.S. The carrier concentration of the as-received material was found to be 5 × 1016 cm−3. Au contacts having a diameter of 0.5 mm and a thickness of 50 nm were fabricated by thermal evaporation under a vacuum of 10−6 Torr. The time and temperature of the H2O2 pretreatment were systematically varied in the ranges of 1–30 min and from room temperature to the boiling temperature of H2O2, respectively.

The I-V data of the Au/n-ZnO contacts without H2O2 pretreatment shown in Fig. 1 clearly showed the nonrectifying property of the contact. On the other hand, all the samples with H2O2 pretreatment became rectifying, but the ideality factor n, the Schottky barrier height φB, and the leakage current Ileak were dependent on the pretreatment temperature and time, having values in the ranges of n = 1.15–2.89, φB = 0.35–0.65 eV, and Ileak = 10−9–10−4 A (as the reverse bias VR = −1 V). The best performing diode (I-V curve shown in Fig. 1) was obtained by preetching the sample in H2O2 at 100 °C for 3 min. Its ideality factor, Schottky barrier height, and leakage current at −1 V were

![](untreated.jpg) 30min boiling 3 minute 100°C

**FIG. 1.** (Color online) I-V data of the Au/n-ZnO samples with different H2O2 pretreatments.
found to be 1.15, 0.63 eV and 4.2 \times 10^{-9} \text{ A}, respectively. The SEM images (not included) showed that the as-grown ZnO sample had a smooth surface, and the 3 min 100 °C \text{H}_2\text{O}_2 treatment increased the surface roughness and induced appearance of submicron grains on the surface. The worst performing diode was the one pretreated with the longest time period (i.e., 30 min) and the highest temperature (i.e., boiling \text{H}_2\text{O}_2), which had \( n=2.89, \phi_\Sigma = 0.53 \text{ eV}, \) and leakage current equal to 7.8 \times 10^{-8} \text{ A} (at −1 V). The SEM image showed that the surface was damaged after the 30 min boiling \text{H}_2\text{O}_2 treatment.

XPS data revealed that all the samples contained carbon impurities. The C 1s (285.36 keV) signal, which disappeared after Ar sputtering, corresponded to a thickness of about 50 Å implying that the detected C impurity resided at the sample surface. As shown in Table I, the carbon concentration could not be removed with the \text{H}_2\text{O}_2 treatments. The surface carbon contamination therefore does not seem to have any significant adverse influence on the formation of Au Schottky contact. The O 1s signal was well fitted by a two-peak fit having binding energies of 531.25 and 532.76 eV, which corresponded to oxygen bound to the lattice and oxygen in the OH impurity.\(^4\) 3 min \text{H}_2\text{O}_2 treatment results in a significant reduction of the OH intensity from 26.1% to 1.3%, as well as the loss of Zn and the reduction of the Zn:O ratio from 1.85 to 0.40. OH leads to the formation of a high conductivity accumulation layer on both the polar faces of \text{ZnO}.\(^5\) The correlation between the OH removal and the improvement of the metal-\text{ZnO} Schottky contacts has also been observed by Coppa et al.\(^6\) and Mosbacher et al.\(^9\)

PAS was employed to study the vacancy-type defects close to the surface.\(^{16,17}\) Monoenergetic positrons were implanted into the sample with variable positron energy (up to \( \sim 30 \text{ keV} \)), hence varying the positron implantation depth. The implanted positrons will then be thermalized, undergo diffusion, possibly be trapped by vacancy-type defects, and finally annihilate with an electron emitting two gamma photons with energies of \( \sim 511 \text{ keV}, \) providing information about the electronic environment at which the positron annihilates. The Doppler broadening of the annihilation radiation was parametrized by the \( S \) parameter, defined as the ratio of the central region count (i.e., \( A_C \) in Fig. 2) to the total count and is thus associated with the fraction of positrons annihilating with the valance electrons. The \( W \) parameter (wing parameter) is defined as the ratio of a fixed pair of high energy windows (i.e., \( A_{W1} \) and \( A_{W2} \) in Fig. 2) to the total counts, and is thus related to fraction annihilating core electrons. As a positron trapped in the vacancy state has less probability to annihilate with the core electrons having higher momentum relative to the valance electrons, annihilation events originated from the vacancy state would be less Doppler broadened and would thus contribute a larger \( S \) parameter (smaller \( W \) parameter) compared to the bulk state.

The \( S \) parameter as a function of the positron implanting energy of three \text{ZnO} is shown in Fig. 2. The \( S(E) \) data were fitted by the source code VEPFIT,\(^{18}\) where the dynamics of the implanted positrons were described by the diffusion-trapping-annihilation equation considering positron implantation, positron diffusion, positron trapping into vacancy, and subsequent annihilation at different states. The resultant \( S \) parameter measured at different implanting energy is given by \( S(E) = \Sigma f_i S_i, \) where \( f_i \) and \( S_i \) are the fraction and the characteristic \( S \) parameter of positron annihilating at site \( i. \)

For the untreated sample, a single layer model was found to give a good fitting to the data. The positron diffusion length \( L_{\text{eff}} \) was found to be 72±2 nm. The \( S(E) \) data of the 3 min 100 °C and the 30 min boiling treated samples in Fig. 2 clearly show shoulders implying the existence of at least one defective layer corresponding to the high value of the \( S \) parameter. Finally, the SE curves of these two samples were well fitted by the three layer model with the results shown in Table II.

### Table I. Intensities of XPS signals (in atomic ratio) found in the nontreated and the 3 min 100 °C \text{H}_2\text{O}_2 treated \( n \)-type \text{ZnO} samples.

<table>
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<tr>
<th></th>
<th>C (%)</th>
<th>O (%)</th>
<th>OH (%)</th>
<th>Zn (%)</th>
<th>Zn:O ratio on surface</th>
</tr>
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<tbody>
<tr>
<td>Nontreated</td>
<td>14.2</td>
<td>20.9</td>
<td>26.1</td>
<td>38.8</td>
<td>1.86</td>
</tr>
<tr>
<td>100 °C, 3 min</td>
<td>14.2</td>
<td>55.2</td>
<td>1.3</td>
<td>22</td>
<td>0.40</td>
</tr>
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</table>

![FIG. 2. Color online] S(E) data of the untreated (circle), the 3 min 100 °C H\(_2\)O\(_2\) treated (triangle), and the 30 min boiling H\(_2\)O\(_2\) treated \( n \)-ZnO samples. The inset illustrates the definition of the \( S \) parameter and the \( W \) parameter. The solid lines are the fitted curves.
implies that the vacancies created in the H$_2$O$_2$ treatment irrespective of time and temperature were of the identical type.\cite{16} Since O vacancy has low binding energy and thus does not trap positrons at room temperature,\cite{19,20-23} the vacancy defects created by H$_2$O$_2$ treatment are Zn-vacancy-related defects and vacancy clusters, although the Doppler technique used in the present study cannot offer an unambiguous distinction between the two possibilities. XPS data (in Table I) showed that after the H$_2$O$_2$ treatment, the Zn:O ratio significantly reduced to a Zn insufficient value of 0.40. It is thus speculated that the vacancy-type defects formed are Zn vacancy or Zn-vacancy cluster. As Zn vacancy is known to be an acceptor, the H$_2$O$_2$ etching would thus possibly have the effect of forming a defective layer having a relatively low conductivity.

In the DLTS measurements, a deep level having the activation energy of $E_A=0.31$ eV was identified in all of the diodes tested. This defect was also found in some other $n$-type ZnO structure not pretreated by H$_2$O$_2$.\cite{24,25} The deep level concentrations found in the 3 min 100 °C, the 30 min 100 °C, the 3 min 185 °C, and the 30 min 185 °C H$_2$O$_2$ pretreated samples were observed to be independent of the reverse bias applied during the DLTS measurement, the treatment temperature, or the treatment duration (with values of $8.8\times10^{15}$, $1.0\times10^{15}$, $1.2\times10^{15}$, and $8.6\times10^{15}$ cm$^{-3}$, respectively). This implies that the deep level is (1) a uniformly distributed bulk defect, (2) not associated with the vacancy-type defect as detected by PAS, and (3) thus not related to the H$_2$O$_2$ treatment.

In conclusion, Ohmic to rectifying conversion was observed on the Au/$n$-ZnO contact with the pretreatment of H$_2$O$_2$. A good quality Schottky contact was obtained with $n=1.15$, $\phi_S=0.63$ eV, and $I_{load}(V_R=-1$ V$)=4.2\times10^{-9}$ A. The good performance of a Au Schottky contact was associated with the removal of OH surface contamination and creation of a defective surface region, containing zinc vacancy or vacancy cluster. Both of these effects result in the overall reduction of the conductivity of the surface layer. A deep level with $E_A=0.31$ eV was observed in all the samples but was suggested to be unrelated to the H$_2$O$_2$ treatment.

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\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
 & Surface & First layer & Second layer & Bulk \\
\hline
Untreated & $S_2=0.5373$ & NA & NA & $S_2=0.5109$ \\
\hline
3 min & $S_3=0.5453$ & $S_1=0.5224$ & $S_2=0.5212$ & $S_B=0.5092$ \\
100 °C & $L_1=35$ nm & $L_2=48$ nm & $L_B=70$ nm \\
& $X_1=56$ nm & $X_2=393$ nm & \\
\hline
30 min & $S_3=0.5465$ & $S_1=0.5401$ & $S_2=0.5202$ & $S_B=0.5086$ \\
185 °C & $L_1=29$ nm & $L_2=37$ nm & $L_B=72$ nm \\
& $X_1=223$ nm & $X_2=422$ nm & \\
\hline
\end{tabular}
\caption{Fitted results of the $S(E)$ data shown in Fig. 2. The indices $S$, 1, 2, and $B$ in the $S$ parameter and the diffusion length $L$ denote the surface, the first layer, the second layer and the bulk, respectively, while $X_1$ and $X_2$ are the boundary positions of the first and the second layers, respectively.}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{(Color online) S(E) plot of the data obtained from the 3 min 100 °C, the 30 min 100 °C, and the 30 min boiling H$_2$O$_2$ treated $n$-ZnO samples.}
\end{figure}

\begin{thebibliography}{99}
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