Electrical characteristics of Au and Ag Schottky contacts on *n*-ZnO

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Au and Ag Schottky contacts on the epiready (0001)Zn surface of bulk *n*-ZnO crystals show Schottky barrier heights of 0.65–0.70 eV from capacitance–voltage measurements, activation energies for reverse saturation currents of 0.3–0.4 eV and saturation current densities ranging from 10^{-5} A cm^{-2} on surfaces etched in HCl to 8×10^{-7} A cm^{-2} on solvent cleaned samples. The diode ideality factors were in the range 1.6–1.8 under all conditions. The properties of both the Au and the Ag Schottky diodes were degraded by heating in vacuum to temperatures even as low as 365 K. The degradation mechanisms during annealing were different in each case, with the Au showing reaction with the ZnO surface and the Ag contacts showing localized delamination. Mechanical polishing of the ZnO surface prior to contact deposition produced a high-resistivity damaged layer with prominent deep level defects present with activation energies of 0.55 and 0.65 eV. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1604173]

ZnO is attracting attention for use in piezoelectric transducers, gas sensors, varistors, light emitting and light detecting devices operating in the blue-UV wavelength region.[1–20] The availability of large size bulk crystals and good lattice match to GaN make it a potential substrate material for the GaN epitaxy.[2] High quality Schottky diodes are necessary for some of these applications. It has been found that low-reactive metals such as Au, Ag, and Pd form relatively high Schottky barriers of 0.6–0.8 eV with *n*-ZnO[21–27] but the barrier heights do not seem to follow the difference in the work function values, indicating the non-negligible impact of the interface defect states. The thermal stability of the Schottky diodes on *n*-ZnO has not been extensively studied but many authors indicate that for Au serious problems arise for temperatures higher than 330 K.[23,24,26] At least one study has shown the thermal stability of the Ag/*n*-ZnO Schottky diodes to be higher than that of Au Schottky diodes.[23] The effect of various surface treatments on the values of reverse currents and of the ideality factor of the forward current characteristics has also not been systematically studied. Neville and Mead[22] reported ideality factors very close to unity ($n=1.05$) after depositing Au and Pd on the *n*-ZnO surface etched for 15 min in concentrated phosphoric acid, followed by 5 min etch in concentrated HCl and rinsed in organic solvents. However, similar surface treatments used in other reports led to unacceptably high leakage for Au diodes. Low ideality factors of 1.19 and excellent reverse currents of 1 nA at -1 V were obtained for the Au/*n*-ZnO Schottky diodes prepared on the O surface of undoped bulk crystals boiled in organic solvents and given a short etch in concentrated HCl.[26] Some authors have reported good electrical performance of the Schottky diodes after etching in concentrated nitric acid.[23] However, it should be noted that in the majority of articles the ideality factors of the ZnO Schottky diodes are considerably higher than unity which has been explained by the prevalence of tunneling, the impact of interface states or the influence of deep recombination centers. In this letter we present the results of electrical measurements performed on Au and Ag Schottky diodes prepared on undoped bulk *n*-ZnO, comparing the barrier heights and the thermal stability of these contacts.

The samples were the (0001) undoped grade I quality bulk ZnO crystals from Eagle-Picher. The samples were epiready one-side-Zn-face polished by the manufacturer. The room temperature electron concentration and mobility from van der Pauw measurements were 9×10^{16} cm^{-3} and 190 cm^2/V s, respectively. Au or Ag Schottky diodes were prepared by vacuum deposition through shadow masks. The barriers were 0.75×0.75 mm^2 rectangles in the case of Au and 1 mm in diameter circles in the case of Ag. The ohmic contacts were made by In. Prior to the metals deposition the samples were cleaned in organic solvents [acetone, trichlorethane (TCE) and methanol], rinsed in de-ionized (DI) water and blown dry with nitrogen. Some of the samples were then etched in concentrated HCl or HNO_3. Contact properties were examined by capacitance–voltage $C-V$ measurements using the low frequency admittance analyzer HP4192A, the current–voltage $I-V$ measurements using the HP4140B picoamperemeter, deep level transient spectroscopy (DLTS) measurements using the 4280A C-t meter with external pulse generator HP8112A in the temperature range 85–400 K.[28,29] We also studied the effects of polishing with diamond slurry combined with subsequent etching.

Figure 1 compares the 293 K $I-V$ characteristics of the Au Schottky diodes deposited on our *n*-ZnO crystals with the surface subjected to three different treatments. Curve 1 is for the surface given a standard organic solvents cleaning by boiling for 3 min consecutively in acetone, in TCE and methanol with DI water rinse and blowing dry with nitrogen (treatment I). Curve 2 was obtained for the Schottky diodes

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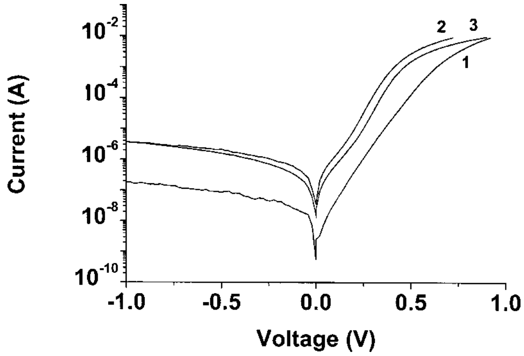

FIG. 1. Room temperature $I-V$ characteristics for Au Schottky diodes prepared on n-ZnO with only organic solvents cleaning (curve 1), with organic solvents cleaning and etching in HCl for 3 min. (curve 2), with organic solvents cleaning and etching in HNO3 for 3 min. (curve 3).

TABLE I. Ideality factor n, reverse current at -0.5 V I_r, saturation current density J_s, the activation energy for the saturation current E_a and the cutoff voltage V_c in $C-V$ for various Au/ZnO and Ag/ZnO Schottky diodes measured at room temperature.

Metal	Surface treatment	I_r(A)	n	J_s(A/cm^2)	E_a(eV)	V_c(V)
Au	Organic solvents	8.6×10^{-8}	1.8	8.4×10^{-7}	0.35	0.65
Au	HCl	2.1×10^{-6}	1.6	8×10^{-6}	0.4	0.64
Au	HNO_3	1.6×10^{-6}	1.8	4.8×10^{-6}	0.29	0.65
Ag	HCl	2.5×10^{-6}	1.6	1×10^{-5}	0.3	0.69
Ag	HNO_3	2×10^{-6}	1.8	6×10^{-6}	0.35	0.68

additionally etched in concentrated HCl for 3 minutes and given a rinse in DI water (treatment II). Curve 3 corresponds to the organic cleaning of the surface and additional etching for 3 min in concentrated HNO_3 (treatment III). Capacitance–voltage ($C-V$) measurements yielded cutoff voltages of 0.65 V in each case, in good agreement with the reported 0.65 eV values of the Schottky barrier heights of Au on the (0001) ZnO surface.[22,24,28] The $I-V$ characteristics of all studied samples showed the ideality factor n close to 2 (see Table I) and almost the same in all cases. This is commonly observed for the n-ZnO Schottky diodes and is often ascribed to the prevalence of tunneling.[30] The temperature dependence of the saturation current showed activation energies much lower than expected from the barrier height obtained from the $C-V$ plots. Thus tunneling seems to be an important factor in determining the current flow mechanism in our diodes. DLTS spectra measured on all these diodes showed similar spectra (Fig. 2), with the presence of two electron traps with activation energies close to 0.2 and 0.3 eV and low concentration of about 10^{14} cm^{-3} often observed in undoped n-ZnO.[23,24,26] Thus the diodes prepared on epiready (0001)Zn surface of undoped bulk n-ZnO crystals without etching show a considerably lower reverse current while having virtually the same ideality factor, $C-V$ characteristics, and DLTS spectra as the diodes with etched surfaces. Anneal temperatures near 370 K were sufficient to produce surface reactions involving Au, leading to the formation of the near surface layer with reduced electron concentration and a high density of deep level defects.

Ag Schottky diodes prepared with similar surface treatments showed no meaningful differences with the Au contacts in terms of $I-V$ characteristics, $C-V$ characteristics, DLTS spectra, or thermal stability. Once again, solvent cleaning produced the lowest reverse currents.

To examine the effect of polish damage, we used a diamond slurry to remove approximately 10 μm of material. The resulting surface was smooth and shiny, showing no scratches. This surface was first cleaned in organic solvents and etched for 3 min in concentrated HCl. After that Ag Schottky diodes were deposited; the room temperature $I-V$ characteristic of this diode is shown in Fig. 3. The diode exhibited a high series resistance which also manifested itself in a strong capacitance dependence on frequency as shown in Fig. 4. The capacitance strongly decreases with frequency, the roll-off frequency being as low as about 100 Hz. Clearly, the surface polishing introduces a damaged high-resistivity layer at the surface of n-ZnO and this damaged layer cannot be effectively removed by HCl etching for 3 min. We further etched this sample in concentrated HNO_3 for 3 min and remade the Schottky diode. The resultant $I-V$ characteristic showed a much lower series resistance and so did the capacitence frequency ($C-f$) characteristic (Figs. 3 and 4). The electron concentration deduced from $C-V$ measurements gave the value of 6×10^{16} cm^{-3} close to that in the control

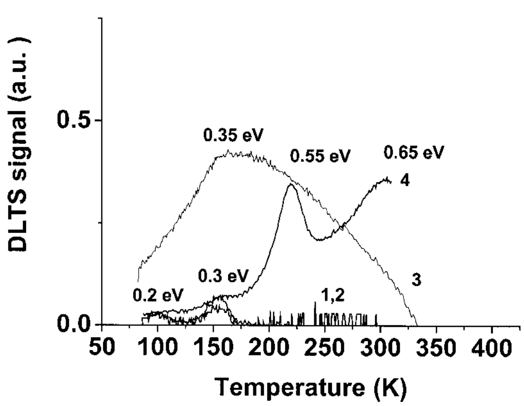

FIG. 2. DLTS spectra measured with time windows $t_1=100$ ms, $t_2=1000$ ms, reverse bias of -1 V, forward bias pulse of 0 V (100 ms long) on various ZnO Schottky diodes; curve 1 is for the organic solvent cleaned Au/n-ZnO; curve 2 is for the HNO_3 etched Au/n-ZnO; curve 3 is for the organic solvents cleaned Au diode after the first DLTS measurement; curve 4 is for the Ag diode prepared on mechanically polished and etched in HNO_3 (3 min.) surface.

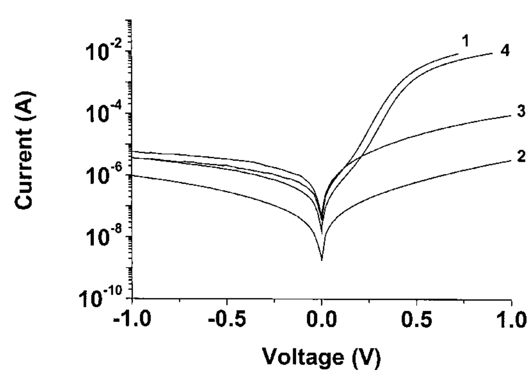

FIG. 3. Room temperature $I-V$ curves measured on the HNO_3 etched Ag diode with epiready surface (curve 1), on the Ag Schottky diode with the surface polished and etched in HCl for 3 min. (curve 2), on Ag Schottky diode with the surface prepared by the subsequent 3 min. etching of the polished and HCl treated surface in HNO_3 (curve 3), on the surface given one more etch in HNO_3 for 6 min. (curve 4).

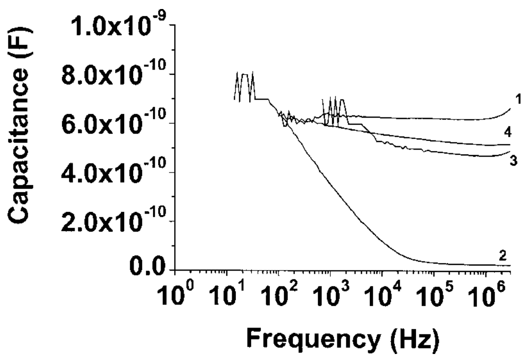

FIG. 4. Room temperature capacitance–frequency $C-f$ characteristics measured on the HNO_3 etched Ag diode with epiready surface (curve 1), on the Ag Schottky diode with the surface polished and etched in HCl for 3 min. (curve 2), on Ag Schottky diode with the surface prepared by the subsequent 3 min. etching of the polished and HCl treated surface in HNO_3 (curve 3), on the surface given one more etch in HNO_3 for 6 min. (curve 4).

material. DLTS spectra showed that, in addition to the 0.2 and 0.3 eV electron traps, polishing introduces a high density of 0.55 and 0.65 eV electron traps whose signatures are similar to the defects created in n-ZnO by proton implantation.[26] Additional HNO_3 etching for 6 min resulted in $I-V$ characteristic close to that observed on the diode prepared on epiready surface with HNO_3 etching as described in the previous section (see Fig. 3). The electron concentration measured on this diode was close to 10^{17} cm^{-3}. The $C-f$ characteristic also almost returned to its ''epiready'' position and the concentration of the 0.55 and 0.65 eV traps in DLTS was decreased by about an order of magnitude. Thus we conclude that at least 9 min etch in HNO_3 is needed to remove the surface damage introduced by mechanical polishing which is in agreement with the results reported in Ref. 6.

In summary, for Au and Ag Schottky contacts on the epiready (0001)Zn surface of the undoped n-ZnO samples the best result in terms of the lowest reverse current values was given by simple cleaning of the surface in organic solvents. Mechanical polishing introduces to the surface of n-ZnO a high-resistivity damaged layer with greatly increased concentration of deep traps with activation energies of 0.55 and 0.65 eV. At least 9 min etching in concentrated HNO_3 is necessary to remove the effects of this damaged layer.

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