Schottky Diodes on ZnO Thin Films Grown by Plasma-Enhanced Atomic Layer Deposition

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***Abstract*—Enhancement of the properties of zinc oxide (ZnO) based Schottky diodes has been explored using a combination of plasma-enhanced atomic layer deposition (PE-ALD) ZnO thin films and silver oxide Schottky contacts deposited by reactive radio frequency sputtering. The electrical properties of the ZnO thin films were systematically tuned by varying the deposition temperature and oxygen plasma time during PE-ALD to optimize the performance of the diode. Low temperature (80 °C) coupled with relatively long oxygen plasma time (> 30 s) PE-ALD is the key to produce ZnO films with net doping concentration lower than 10^{17} cm^{-3}. Under the optimal deposition conditions identified, the diode shows an ideality factor of 1.33, an effective barrier height of 0.80 eV, and an On/Off ratio of 3.11×10^{5}.**

***Index Terms*—Zinc oxide (ZnO), plasma-enhanced atomic layer deposition (PE-ALD), Schottky diodes.**

I. Introduction

ZINC oxide (ZnO) has drawn significant interest from within the semiconductor industry due to its wide bandgap, low cost, high electron mobility, transparency and low temperature processing capability [1]. ZnO naturally exhibits *n*-type conductivity [1] where the electrical properties can be controlled by suitable impurity doping [2]–[5], annealing [6], and changing deposition temperature [7]. Schottky contacts on ZnO are useful in a wide range of applications, including gas sensors, metal semiconductor field-effect transistors, and ultraviolet photodetectors [8]–[11]. The deposition of high quality Schottky contacts on ZnO still remains a challenge, as the performance depends on factors such as the presence of interface defect states at the metal/ZnO interface, and ZnO electrical properties [12], [13]. Oxidized metal Schottky contacts such as silver oxide (Ag_xO) have been reported as a method for reducing interface defect states between ZnO and Schottky contacts to achieve good rectification properties [9], [10], [14], [15]. ZnO with low carrier concentration (< 10^{17} cm^{-3}) and high mobility is a prerequisite for obtaining a high quality Schottky contact, as this allows for low reverse and high drive current [16].

Atomic layer deposition (ALD) is a promising deposition technique for ZnO films using an organometallic zinc precursor, such as diethylzinc (DEZn) with an oxidizing reagent. Thermal-ALD, using water vapour as a reagent, is widely used for ZnO deposition, however, it is difficult to obtain films with low carrier concentration and high mobility [17]. Recently, plasma-enhanced atomic layer deposition (PE-ALD) has proven to be an effective method to deposit high quality ZnO films with low carrier concentration and relatively high mobility [17]–[19]. However, there is limited literature on the realization of Schottky contacts on ZnO thin films prepared from PE-ALD [20], and further refinement is feasible to optimize the deposition conditions. In this work, the electrical properties of the ZnO thin films were systematically tuned by varying the deposition temperature and plasma time to optimize the performance of the PE-ALD ZnO based diodes.

II. Experiments

The schematic diagram of the device is shown in the inset of Fig. 1(a). A 70 nm thick Ti layer was deposited as the ohmic contact on the SiO_2/Si substrate by radio frequency (rf) sputtering at 73 W, with pure Ar at a chamber pressure of 3.5×10^{-3} mbar. The samples were then loaded into an Oxford Instruments Plasma OPAL reactor to deposit PE-ALD ZnO thin films. In the PE-ALD process, DEZn and an Ar/O_2 plasma were used as the Zn precursor and oxidizing reagent. DEZn was used at room temperature with an Ar carrier gas flow rate of 100 sccm. The Ar and O_2 gas flow rates for the O_2 plasma were 10 and 60 sccm respectively with an rf power of 300 W. DEZn and O_2 plasma were introduced sequentially into the reaction chamber, each followed by an Ar purge to ensure the self-limiting reaction on the surface occurred. The influence of different deposition temperatures (80, 100, and 120 °C) and O_2 plasma times (5, 30, 50, and 70 s) were investigated to optimize the diode performance. The film thickness for all the ZnO films was 40 nm.

After ZnO deposition, the films were etched with 1 % acetic acid to expose the bottom Ti contact and define the device active area. After etching, Ag_xO (60 nm)/Ag (10 nm) top contacts were defined by sputtering via a shadow mask. The Ag_xO was deposited by reactive rf sputtering in Ar/O_2 with a flow rate of 1 sccm/1 sccm using the Ag target (99.999%) and

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rf power of 50 W. Subsequently, an additional Ag capping layer was deposited on Ag_xO by rf sputtering. The diameter of the Schottky contact is 100 µm.

The current-voltage (*I-V*) and capacitance-voltage (*C-V*) characteristics were measured using a semiconductor parameter analyzer (Agilent B1500) and an impedance analyzer (Agilent E4980A) at 10 kHz, respectively. The voltage range was kept within ±1 V in order to avoid damaging the Schottky diodes, as they have breakdown voltage around ±3 V. X-ray photoelectron spectroscopy (XPS) was used to determine the compositions of selected ZnO films and correlate this with the device performance. The surface roughness of selected ZnO films and metal contacts was then measured by atomic force microscope (AFM).

III. Results and Discussions

The current transport through a Schottky diode can be described by a thermionic emission model:

$$I = I_s\left\{\exp\left[\frac{q(V-IR_s)}{nkT}\right]-1\right\} \quad (1)$$

$$I_s = AA^*T^2\exp\left(-\frac{q\phi_{B.IV}}{kT}\right) \quad (2)$$

where I_s is the saturation current, q is the electron charge, R_s is the series resistance, n is the ideality factor, A is the Schottky contact area of the diode, A^* is the effective Richardson constant with a theoretical value of 32 $cm^{-2}K^{-2}$ [21], k is the Boltzmann constant, T is the absolute temperature, and $\phi_{B.IV}$ is the effective barrier height. By fitting the forward *I-V* characteristics with (1) and (2), n and $\phi_{B.IV}$ can be extracted. It should be noted that ideal behavior predicts an ideality factor very close to unity but a number of factors can cause significant deviations as described below.

The net doping density, N_{dep} can be determined from A^2/C^2 vs V plots using

$$\frac{A^2}{C^2} = \left(\frac{2}{\varepsilon_0\varepsilon_s N_{dep}}\right)\left(V_{bi} - \frac{kT}{q} - V\right) \quad (3)$$

Where V_{bi} is the built-in potential of the junction, ε_0 is the permittivity of free space and ε_s is the dielectric constant of the semiconductor (8.5 for ZnO), which was confirmed by *C-V* measurements and is in agreement with values in the literature [22].

We first tested the influence of ZnO deposition temperature on diode performance. For ZnO deposition, the O_2 plasma time was fixed at 5 s and deposition temperatures of 80, 100 and 120 °C were used. The *I-V* characteristics of the Schottky diode with different ZnO deposition temperatures are shown in Fig. 1(a). It can be seen that by decreasing the deposition temperature, both the reverse and forward current decreases, which suggests a reduction of carrier concentration [16]. Schottky diode device parameters for different ZnO deposition conditions are summarized in Table I. There is a clear reduction of N_{dep} when the deposition temperature is reduced. Also it can be seen that $\phi_{B.IV}$ increases and n decreases when the temperature is reduced.

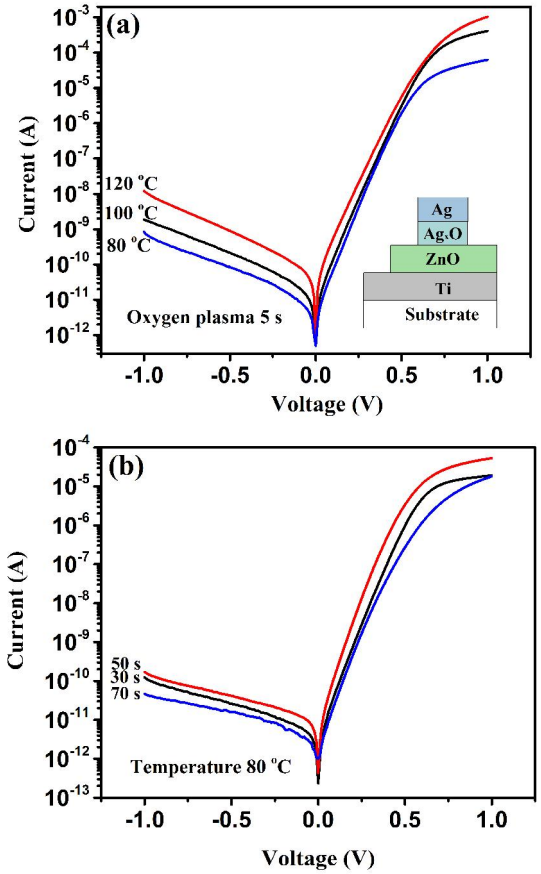

Fig. 1. *I-V* characteristics of Schottky diodes with different PE-ALD ZnO deposition conditions: (a) the O_2 plasma time 5 s and deposition temperatures of 80, 100 and 120 °C, (b) the ZnO deposition temperature at 80 °C and O_2 plasma times of 30, 50, and 70 s. The inset of (a) shows a schematic of the fabricated Schottky diode.

TABLE I. Characteristics of Schottky Diodes from Electrical Measurements

Diode number	ZnO deposition condition	n	$\phi_{B.IV}$ (eV)	*On/Off* ±1V	N_{dep} (cm^{-3})
1	120 °C, O_2 plasma 5 s	1.59	0.76	8.67×10^4	5.23×10^{17}
2	100 °C, O_2 plasma 5 s	1.47	0.80	2.22×10^5	2.19×10^{17}
3	80 °C, O_2 plasma 5 s	1.42	0.82	7.47×10^4	1.84×10^{17}
4	80 °C, O_2 plasma 30 s	1.46	0.82	1.55×10^5	5.89×10^{16}
5	80 °C, O_2 plasma 50 s	1.33	0.80	3.11×10^5	6.84×10^{16}
6	80 °C, O_2 plasma 70 s	1.47	0.83	4.09×10^5	3.89×10^{16}

To further optimize the ZnO thin films for Schottky diodes, the influence of O_2 plasma time on the diode performance was investigated. The ZnO deposition temperature was fixed at 80 °C and O_2 plasma times of 30, 50, and 70 s were used. The *I-V* characteristics of the Schottky diodes with different O_2 plasma times are shown in Fig. 1(b). Excellent rectifying characteristics are obtained with On/Off ratios all above 10^5 at a bias voltage of ±1 V and large $\phi_{B.IV}$ varying from 0.80 to 0.83 eV. Table I shows that low temperature (80 °C) with relatively

long O_2 plasma time (> 30 s) PE-ALD is the key to produce ZnO films with net doping concentration lower than 10^{17} cm^{-3}. The O_2 plasma time also plays an important role in optimizing n. When the plasma time is increased from 30 to 50 s, n is seen to reduce. However, as the plasma time is further increased from 50 to 70 s, n increases, as shown in Table I. It is important to achieve a large $\phi_{B.IV}$ and a high On/Off ratio for a Schottky diode; in addition, n should be close to unity. Hence, the optimal diode is obtained for the ZnO film processed at 80 °C with 50 s O_2 plasma time, which has n = 1.33, $\phi_{B.IV}$ = 0.80 eV, and an On/off ratio of 3.11×10^5. Despite the improvement, n is still larger than unity, this may be due to interface defect states and contact inhomogeneity [23].

A wide range of the effective barrier heights have been observed for an Ag_xO on ZnO [13], [22]. Some of the reported values are higher than our work. This wide range of variation is likely due to the different oxidation state of the Ag which causes effective work function differences, the different crystal orientation at the ZnO surface, and the various ZnO growth methods [13], [14], [22]. Pure metal Ag was also tested for the top electrode. As expected, Ag/ZnO/Ti structures resulted in a lower Schottky barrier due to Fermi level pinning caused by surface states [10], [15]. This confirms the necessity for the use of an oxidation-resistant material like Ag_xO as the Schottky contact, which prevents interfacial reactions in the contact region [13]. Moreover, the reactive rf sputtering of Ag_xO may help to passivate intrinsic vacancies near the Schottky interface [15].

The A^2/C^2 vs V plots for the Schottky diode with different ZnO deposition conditions are shown in Fig. 2. At negative biases, the A^2/C^2 remains almost constant, suggesting that the ZnO film is fully depleted for each of the diodes. We also extracted $\phi_{B.IV}$ and n from five devices under each ZnO deposition conditions and the results are shown in Fig. 3. These five devices showed quite similar performance with small standard deviations for n and $\phi_{B.IV}$, demonstrating good device reproducibility and film uniformity. Some devices were also fabricated on Corning 7059 glass substrates. They all showed similar electrical characteristics to the devices on SiO_2/Si substrates. Hence the results are relevant to possible applications on glass substrates.

In general, longer O_2 plasma time allows complete oxidation of Zn which produces a more stoichiometric film; the reduction of oxygen vacancies and interstitial Zn results in reduction of the carrier concentration of the ZnO film [17], [19]. It is evident from Table I that increasing the O_2 plasma time causes a reducing trend for N_{dep}. However, contrary to this general trend, the diode processed at 80 °C with 50 s O_2 plasma time shows a slight increase of N_{dep}. This slight increase of N_{dep} is confirmed from the I-V characteristics in Fig. 1(b), which shows a corresponding increase of both reverse and forward current for the diode processed at 80 °C with a 50 s O_2 plasma time.

XPS was used to determine the compositions of the ZnO films processed at 80 °C with different O_2 plasma times (30, 50, and 70 s) to correlate composition with device performance. XPS analysis of the O 1s peak for selected ZnO films is shown in Fig. 4. The O 1s spectrum shows a clear shoulder on the higher binding energy side, separated from the main peak by 1.6 eV. Such a peak typically corresponds to the presence of O-H bonds [24]–[26]. Similar results have been obtained for both thermal-ALD ZnO films [7] and PE-ALD ZnO films [27]. Previous work [7], [18] has shown that the carrier concentration of ALD ZnO films, is inversely related to the O-H concentration, and can explain the formation of trap sites due to interstitial O-H [7].

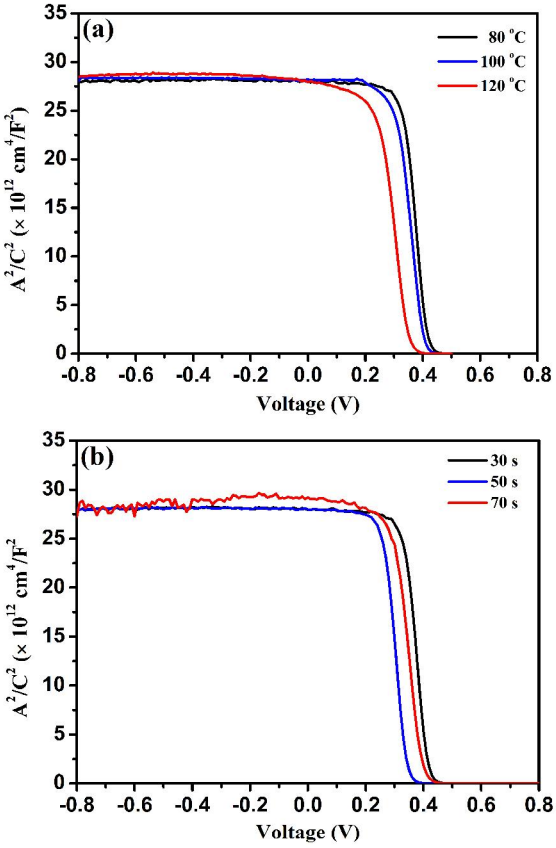

Fig. 2. C-V characteristics of Schottky diodes with different PE-ALD ZnO deposition conditions: (a) the O_2 plasma time 5 s and deposition temperatures of 80, 100 and 120 °C, (b) the ZnO deposition temperature at 80 °C and O_2 plasma times of 30, 50, and 70 s.

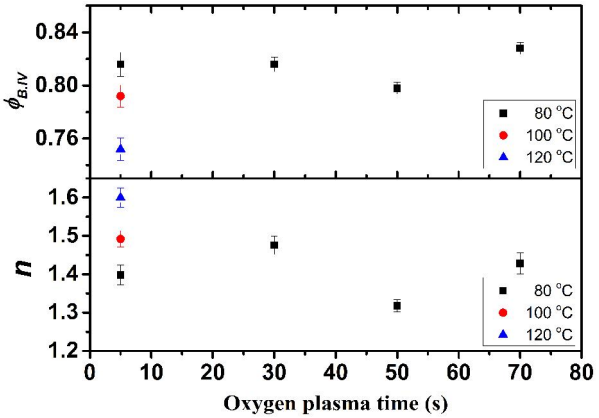

Fig. 3. Barrier heights and ideality factors of Schottky diodes with different PE-ALD ZnO deposition conditions. Five devices were tested for each ZnO deposition condition and error bars stand for standard deviation.

A summary of the area ratios of the two components of the O 1s is given in Table II, and shows that the O-H area fraction is correlated with N_{dep}. However, from the characteristics shown in Fig. 1(b), the diode processed at 80 °C with a 50 s O_2 plasma time gives the most favorable characteristics, seemingly in contradiction of the requirement of a lower carrier density.

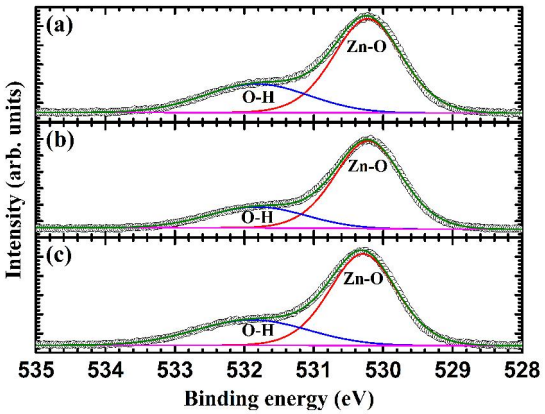

Fig. 4. XPS O 1s spectral results of PE-ALD ZnO films processed at 80 °C with O_2 plasma times of (a) 30 s, (b) 50 s, and (c) 70 s.

TABLE II. RELATIVE PERCENTAGE OF Zn-O AND O-H CURVE AREAS CALCULATED FROM XPS RESULTS FOR ZnO THIN FILMS PROCESSED AT 80 °C WITH DIFFERENT OXYGEN PLASMA TIMES (30, 50, AND 70 s)

Oxygen plasma time	Zn-O	O-H	O-H/Zn-O
30 s	0.69	0.30	0.43
50 s	0.74	0.25	0.34
70 s	0.68	0.31	0.46

Variation in the surface roughness of the ZnO films and metal contacts will influence the device performance. AFM images of PE-ALD ZnO films processed at 80 °C with different oxygen plasma times (30, 50, and 70 s) are shown in Fig. 5(a), 5(b), and 5(c) respectively. The scanned ZnO surface area was 1×1 μm^2. No significant changes in the roughness of the PE-ALD ZnO films with increasing plasma time were observed. The root mean square (rms) roughness of the surface is around 1 nm and variation does not exceed ±0..05 nm for all three samples. The AFM images of the metal contacts are shown in Fig. 5(d) and 5(e). The rms surface roughness of Ti and Ag_xO were 0.55 nm and 0.74 nm respectively, which demonstrates low rms surface roughness of the metal contacts. It is still not clear why the parameters n and $\phi_{B,IV}$ were affected by O_2 plasma time. One possible explanation is that different O_2 plasma times result in differences in crystal orientation at the ZnO surface [17], which in turn causes inhomogeneity of barrier heights and defect densities, resulting in a concomitant variation of the ideality factor.

IV. CONCLUSIONS

We have identified the conditions to realize good quality Schottky diodes based on PE-ALD ZnO thin films. We have demonstrated that low temperature (80 °C) with relatively long O_2 plasma time (> 30 s) PE-ALD is the key to produce ZnO films with net doping concentration lower than 10^{17} cm^{-3}. ZnO films processed at 80 °C with a O_2 plasma time of 50 s exhibited the best device characteristics, featuring an ideality factor of 1.33, an effective barrier height of 0.80 eV, and an On/Off ratio of 3.11×10^5.

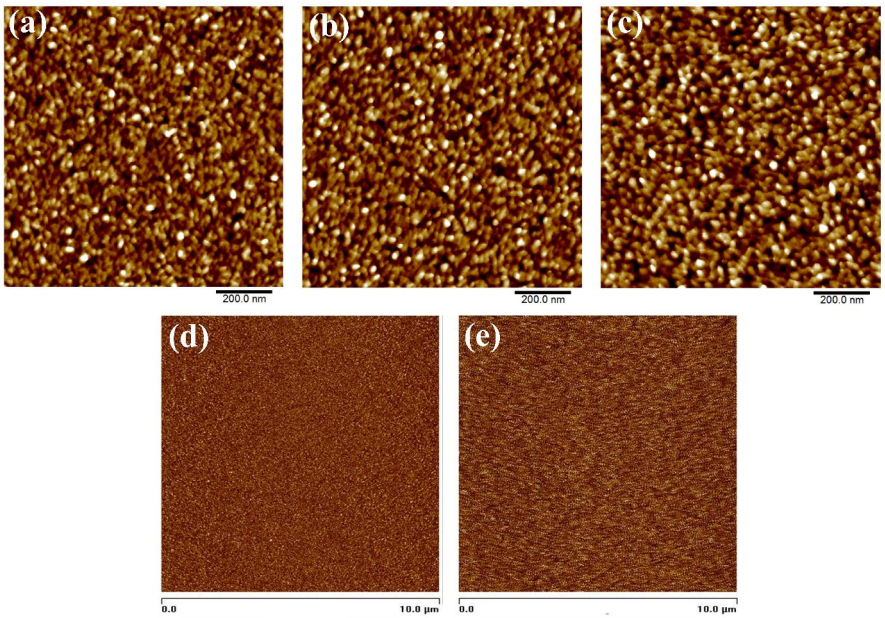

Fig. 5. AFM images of (a) PE-ALD ZnO film processed at 80 °C with O_2 plasma time at 30 s, (b) PE-ALD ZnO film processed at 80 °C with O_2 plasma time at 50 s, (c) PE-ALD ZnO film processed at 80 °C with O_2 plasma time at 70 s, (d) Ti, and (e) Ag_xO.

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