

ZnO에서 질소 불순물에 의한 p-type Capacitance

P-type Capacitance Observed in Nitrogen-doped ZnO

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Abstract - We studied p-type capacitance characteristics of ZnO thin-film transistors (TFT's), grown by metal organic chemical vapor deposition (MOCVD). We compared two ZnO TFT's: one grown at 450°C and the other grown at 350°C. ZnO grown at 450°C showed smooth capacitance profile with electron density of $1.5 \times 10^{20} \text{ cm}^{-3}$. In contrast, ZnO grown at 350°C showed a capacitance jump when gate voltage was changed to negative voltages. Current-voltage characteristics measured in the two samples did not show much difference. We explain that the capacitance jump is related to p-type ZnO layer formed at the SiO₂ interface. Current-voltage and capacitance-voltage data support that p-type characteristics are observed only when background electron density is very low.

Key Words : ZnO, MOCVD, CV characteristics, TFT, Nitrogen, Display

1. Introduction

Zinc oxide (ZnO) has attracted considerable attention as promising semiconductor for utilization in display devices. Various growth methods, such as molecular beam epitaxy [1,2], sputtering [3], pulsed laser deposition [4], and metalorganic chemical vapor deposition (MOCVD) [5] have been used. Among these, MOCVD has advantages for industry applications, because it can be applied to large size substrates more easily. MOCVD-grown ZnO thin-film transistors (TFT) usually show large negative threshold voltage due to native defects, and this problem was solved by using growth interruptions [6].

Another important issue in MOCVD grown ZnO is realization of p-type TFT. One of the difficulties of p-type doping in ZnO is due to the self-compensation process. The donor-like native defects, such as zinc interstitial and oxygen vacancy, are dominant defects in ZnO, resulting in n-type behavior. In order to achieve p-type conduction in ZnO, these donor-like defects should be suppressed or eliminated. According to Zhang et al. [7] and Lee et al., [8] the donor-like defects can be suppressed at oxygen-rich (O-rich) condition, and it was possible to obtain intrinsic p-type conduction in ZnO.

However, under the O-rich condition, the concentration of acceptor-like defects such as zinc vacancy, oxygen interstitial, and oxygen antisite remains low due to their high formation enthalpies. Nevertheless, p-type ZnO thin films can be realized without doping by suppressing the donor-like defects [9-12].

We studied p-type characteristics of ZnO films by measuring capacitance characteristics. Capacitance data can give local information about carrier type and density at a specific depth. Our results show that capacitance increases at negative gate voltages, and we interpret that as an evidence of p-type ZnO.

2. Experimental Results

Our MOCVD system has a horizontal reactor operating at atmospheric pressure. ZnO films were grown at temperatures between 350 and 650°C. Diethylzinc (DEZ) was used for Zn source, and O₂ was used for O source. DEZ was fed through a bubbler kept at 10°C. with a N₂ flow of 40 sccm. N₂ was employed as a carrier gas with a flow of 4000 sccm, and O₂ flow was 2500 sccm. ZnO films were grown on heavily doped p-type Si substrates (10^{19} cm^{-3}) with a thermal oxide of 150 nm thickness. The thickness of ZnO film was between 30 and 50 nm. TFT structure was fabricated by evaporating Al through a shadow mask (channel length = 15 μm, width = 500 μm). Excess ZnO film outside of active device area was etched away by diluted acetic acid, while the TFT was protected by photoresist. Capacitance was measured by an Agilent E4980A LCR meter, with frequencies between 1 kHz and 1 MHz. Currents were measured by Keithley 2400 sourcemeters.

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Fig. 1 shows p-type capacitance measured in ZnO films. Nitrogen was introduced into ZnO during N₂ annealing at 800°C. Capacitance increased at negative gate voltages, which indicates positive charge increase in ZnO. P-type capacitance was observed up to 1 MHz frequency. It is known that nitrogen introduces acceptor level at 200 meV above valence band edge. The 800°C annealing converted n-type ZnO to an insulator, because the newly added acceptor levels decreased background electron density significantly.

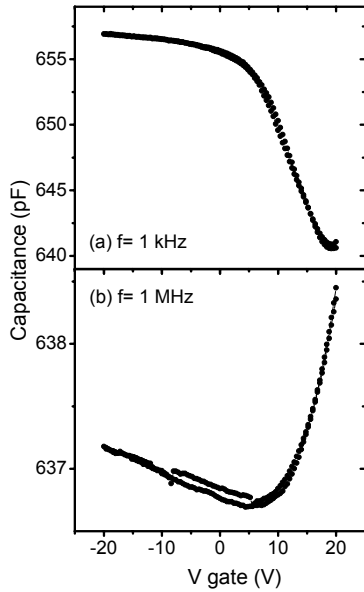


Fig. 1 P-type capacitance measured in ZnO, at (a) 1 kHz and (b) 1 MHz frequencies. Capacitance increases at negative gate voltages.

p-type capacitance was also observed in ZnO samples grown at 350°C. Figs. 2 and 3 are current and capacitance characteristics measured in two TFT's, one grown at 450°C. (Fig. 2), and the other at 350°C (Fig. 3). The figures show that capacitance data are very different, although current data are almost identical. Fig. 2 shows typical n-type capacitance characteristics, but Fig. 3 shows large capacitance jumps at zero gate voltage. It is known that at the initial stage of ZnO growth there are intermediate layers, which have different electrical characteristics than the normal ZnO layer. It appears that these intermediate layers have p-type characteristics, which can explain the large capacitance jumps.

In Fig. 4, p-type TFT currents were observed when carrier density was very low, and the drain currents showed space-charge limited behavior. Space-charge limited current shows non-linear voltage dependence, because the applied voltage increases carrier density. This effect can be more pronounced when carrier density is very low. It appears that underlying p-type currents

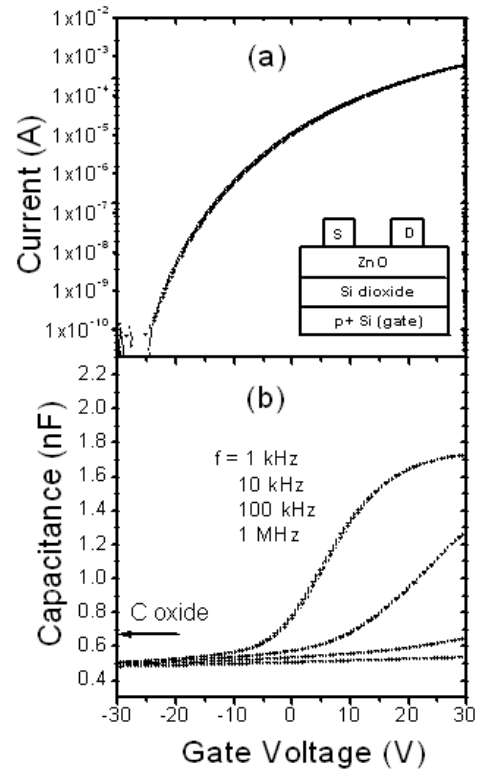


Fig. 2 Current-voltage (a) and capacitance-voltage (b) characteristics of ZnO TFT grown at 450°C.

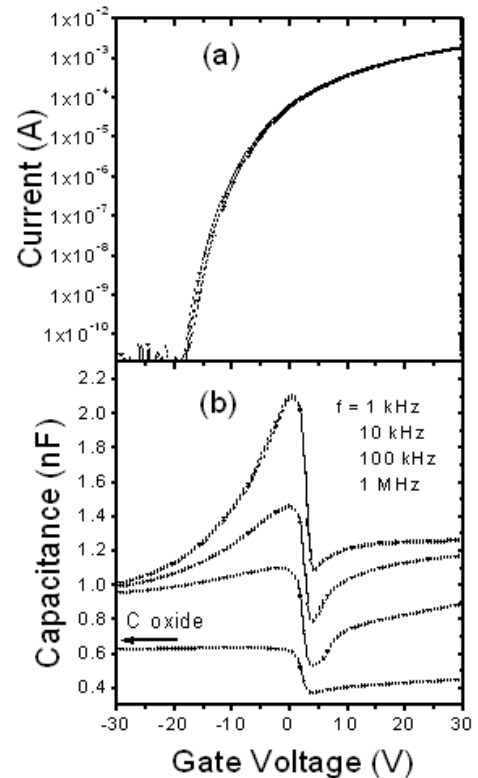


Fig. 3 Current-voltage (a) and capacitance-voltage (b) characteristics of ZnO TFT grown at 350°C.

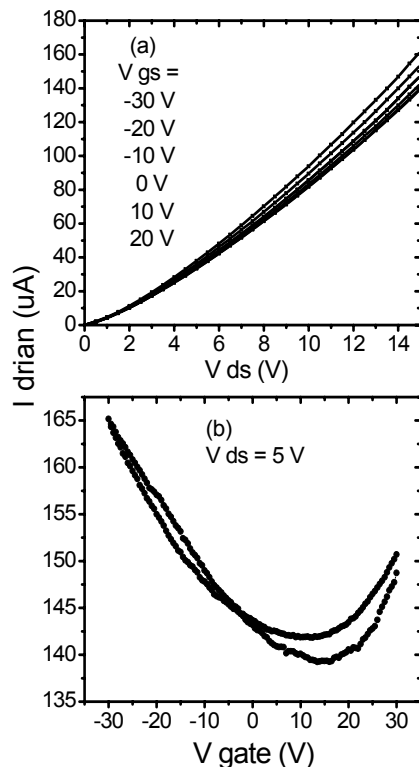


Fig. 4 TFT currents measured by sweeping (a) drain-source voltage and (b) gate-source voltage. Although currents increase at negative gate voltages, they show space-charge limited current.

become more pronounced when n-type defects are removed.

3. Conclusions

We demonstrated realization of p-type characteristics in ZnO grown by MOCVD. Nitrogen was used for p-type dopants. Capacitance increased at negative gate voltages, and we interpret that as a result of p-type ZnO. P-type current-voltage characteristics were measured in ZnO TFT structure, but the current was low because carrier density was decreased by compensation.

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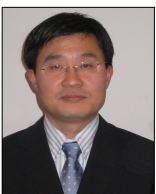
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