ZnO Nanostructure Thin Film Transistors on Plastic Substrate Prepared by Solution Method and PH Sensing Properties

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***Abstract* – We fabricated a ZnO nanostructures based TFT on plastic substrate by solution method under low temperature. ZnO nanostructures were prepared by zinc nitrate hexahydrate, and hexamethylenetetramine. The device shows hard saturation characteristics and exhibits a high off-resistance. The output characteristics devices also shows current saturation and pinch off behavior, in which the high of current saturation obtained 266 □A at VGS = 40 V and VDS = 42.5 V. The pH response on the electrical properties was also studied. It was found that the threshold voltage shifted from 10.21 V to 13 V as pH solution gradually increased. The Ion/Ioff for as grown TFTs and TFTs with pH response of 10.21 shifted from 1.86 x 105 to 7.03 x 106 at VDS = 20 V. The obtained sensitivity of devices was 1.05 V/pH.**

***Keywords*— ZnO nanostructure, plastic substrate, pH response, electrical behavior of transistors.**

I. INTRODUCTION

The flexible nano-electronics device is one of the future technologies in the past decade. The development of flexible electronics technology promises both to wide-range market and further investigation in which further accelerate and stimulate the development of this exciting field. Recently, flexible nano-electronics device have been extensively studied due to have the advantages and wide range application

Among semiconducting nanostructures, ZnO have been drawn much attention for the wide-range electronic and optoelectronic applications [1]-[5]. As chemical sensor, ZnO nanostructure is one of the most promising materials due to it has high surface-to-volume ratio, nontoxicity, chemical stability, electrochemical activity, and high electron communication features [6]. The change pH will create H^+ ions and/or OH^- in the solution and will release the metal atom in an amphoteric oxide. Since the changes of pH for very small volumes, the controlling the surface nanostructure morphology is still needed. Although studied of electrical properties of ZnO nanostructures thin films transistors (TFT) were recently reported [7]-[10], pH response of ZnO nanostructures TFT in electrolyte solutions are still under development. As we know that ZnO is an amphoteric substance, which reacts with either an acid or base of solutions and will generate current variation of TFT. Whereas most nanostructures material as pH sensors are use ZnO nanostructures with 80 nm diameter and 700 nm length and grown on the tip of borosilicate glass capillary [6] enable the application of highly sensitive of pH response. Although the effect pH of the solution to control the sensitive of the ZnO nanostructures as pH sensing material has been realized [6],[11], control of pH value by using release H^+ ions and/or OH^- of the solution to give a high mobility, drain to current on/off ratios and current density, and low threshold voltage of ZnO nanostructure TFTs is still not well reported. Therefore, these results provide both low temperature growth of ZnO nanostructure as active channel of flexible TFTs and pH sensing devices.

In this letter, we report the result obtained the ZnO nanostructures grown on plastic substrate and then further studied of electrical behavior of TFTs when its response at difference pH solutions.

II. EXPERIMENTS

In The ZnO nanostructure was fabricated using solutions method and was deposited using zinc nitrate hexahydrate, $Zn(NO_3)_2.6H_2O$ (Alfa Aesar, assay 99.998%) and hexamethylenetetramine (HMT) $C_{12}H_6N_4$ (Alfa Aesar, assay 99+%). The ITO-laminated plastic substrate of PET (Perm Top Co. Ltd., Taiwan) with ITO thickness and resistivity of 175 μm and 8 Ω/square, respectively, was used as the plastic substrate of the obtained films. The solutions were stored in a Teflon vessel and kept at temperature of 90 °C. The concentrations of $Zn(NO_3)_2.6H_2O$ and HMT were kept at an equimolar solution of 0.01 M in 20 ml deionized water solution. The ZnO growth process was also monitored during 10 hours. The pH values were adjusted by adding different amounts of 0.10 M natrium-hydroxide (NaOH) into the main solution. Subsequent to each process, the sample was removed from the main solutions before it was finally rinsed (with deionized water and dry nitrogen) and dried in a dry oven at 100 °C for 2 hours.

The ITO bottom gate of ZnO nanostructure TFTs were fabricated utilizing selective deposition of ITO by UV photolithography processes on ITO-laminated PET plastic substrate. The SiO_2 gate dielectric layer was deposited by using solution method. Based on our group previous study [12], the SiO_2 powder was added to hydrofluorosilicic acid (H_2SiF_6) and mixed with deionized water. Then 0.10 M H_3BO_3 was added and the solution was stirred for 20 minutes. Finally, the substrate was immersed into 40 °C treatment solution during 2 hours growth process. The substrate was then removed from the solution, washed with deionized water, and dried at dry oven at 100 °C for 2 hours. The ITO source and drain contacts were sputtered, which the channel length (L) and width (W) were 150 µm and 1500 µm, respectively. After finishing the clean process of the ITO-laminated PET substrate, the ZnO nanostructures based TFTs planar bottom gate was fabricated, and is shown in Fig 1(a).

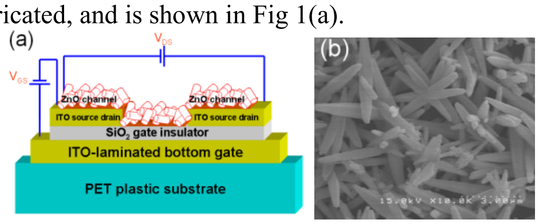

Fig 1. The flexible TFT devices based on ZnO nanostructure. (a) The schematic illustration devices structure. (b). the corresponding SEM image of ZnO nanostructure.

Here, we employ the TFTs planar bottom gate structure due to have an advantage such as increasing source and drain resistance causes the limitation the edges of the source and drain, the source and drain resistance due to the bulk conductivity through the channel is minimized.

The ITO bottom gate was produced by wet etching on ITO-laminated of PET substrate with 160 µm thick. Then, the SiO_2 gate dielectric layer was deposited by using solution method. Finally, before finishing deposit ZnO nanostructure as a TFT channel onto a 200-nm SiO_2 gate dielectric layer, the 175 nm-thick ITO source and drain contacts were sputtered. Meanwhile, the growth temperature was fixed at 95 °C with the concentration of $Zn(NO_3)_2.6H_2O$ and HMT were kept at 0.01 M and 0.20 M, respectively. The growth time was kept at 10.hours. The thickness of the films is 120 nm. The electrical properties of TFTs were measured by using Hewlet-Packard analyzer HP 4156B under atmospheric conditions. The data of pH response was recorded by using 1 µl drop of NaOH into distillated water.

Figure 1(b) shows the SEM pictures of the ZnO nanostructures on a SiO_2/ITO-laminated plastic substrate. It was found that the surface morphology of ZnO shows nanorods, tip-nanorods, and flower-like structure shape. It also can be seen that the ZnO nanostructures orientation shows the strong intensity of (110) reflection peak. This indicates that most ZnO have a hexagonal c-axis parallel to the substrate surface, which is also consistent with the result obtained form XRD data (not shown)

III. Results And Discussion

Since the capacitance as a function applied voltage ($C - V$) measurements of MOS capacitors provide a wealth of information about the structure, the $C - V$ characteristics of ZnO MOS diode measured at high frequency of 1 MHz and is shown in Fig. 2.

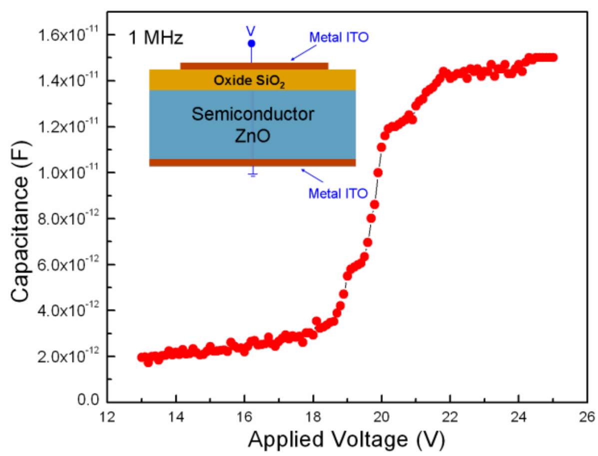

Fig 2. The $C - V$ characteristics of ZnO MOS-gate capacitor with measured at 1 MHz. Inset image of ZnO MOS structure.

It can be seen that no intermediate phase between oxide and semiconductor. The flatband conditions exist when no charge is present in the semiconductor so that the ZnO energy band is flat. In here, the flatband capacitance of 14.1 pF was obtained which flatband voltage at 2.9 V. Consequently, the major carrier density is constant.

Figure 3 shows the source-to-drain current (I_{DS}) as a function of the drain-source voltage (V_{DS}) curves of ZnO nanostructure TFT at difference gate-source voltage (V_{GS}) between 20 and 40 V, respectively. The measurement of the devices was taken at room temperature in the dark with the gate length and width was 150 and 1500 μm, respectively. Our device shows a hard saturation due to the slope of each I_{DS} curve at large V_{DS} shows a flat curve. The enhancement mode is necessary to create a conductive channel [13]. Our output characteristics devices also shows current saturation and pinch off behavior, in which by the fact that the slope of each I_{DS} curves is nearly constant flat for large V_{DS} indicating a large source to drain bulk resistance (R_B).

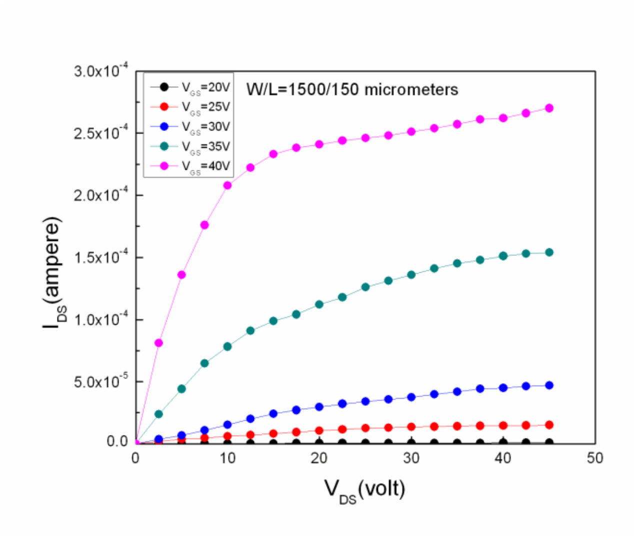

Fig 3. The output characteristics for flexible TFT ZnO nanostructure. Transfer characteristics for V_{DS} = 20 V.

This indicates that the entire thickness of the ZnO channel can be depleted of free electrons [14]. It can also be seen that our TFT saturates to a constant I_{DS} for V_{DS} >> (V_{DS} - V_T), which is desirable for most circuit applications. It is interesting to note that the high of current saturation obtained 266 μA at V_{GS} = 40 V and V_{DS} = 42.5 V. It may be caused to pinch off instead of velocity saturation in sub-120 nm thick ZnO typical metal–oxide–semiconductor transistors phenomena [15].

In order to study the pH response on the electrical behavior of ZnO TFTs, the devices were characterized before (as grown) and after immersing treatment at pH value of the solution. The transfer characteristic for ZnO TFT with dropped at pH of 8.30 and 10.21, and was compared without immersing treatment was shown in Fig 4. The transfer curves were measured at the same devices with the gate length and width was 150 and 1500 *μm*, respectively. It can be seen that the most of transfer curves shows an exponential increase of the drain current. It is interesting to note that the drain current shows linier increase curves at higher gate voltage region. As calculated by a linier region I_{DS} – V_{GS} and saturation region $I_{DS}^{1/2} - V_{GS}$ linier extrapolation to I_{DS} = 0, it was found that the threshold voltage (V_T) for as grown TFTs, TFTs with pH response of 8.30 and 10.21 was 20, 15 and 13 V. This result shows the important role regarding influence the electron depletion which affects the gate threshold voltage which proportional to the carrier concentration [16]. In electrolyte solutions, the metal oxide ZnO surface as active channel of TFT lead to significant hydroxyl group adsorption in which producing H^+ ions and/or OH^-. In general, reducing the device threshold voltage caused by different in work function as resulting of the energy diagram of the MOS structure formed by ITO, SiO_2 and ZnO.

Since the drain current on-to-off ratio (I_{on}/I_{off}) of devices with the enhancement mode behavior is key parameter for novel pH sensor application, the I_{on}/I_{off} was measured at room temperature. The I_{on}/I_{off} for as grown TFTs and TFTs with pH response of 10.21 shifted from 1.86 x 10^5 to 7.03 x 10^6 at V_{DS} = 20 V. This data confirms that the improvement the I_{on}/I_{off} due to the channel is induced on the body layer in the on state. The ratio of the average diameter to the length of the ZnO nanostructures decreased gradually as growth time increased. Therefore, the I_{on}/I_{off} of ZnO TFT increased gradually as pH value increased. This result agrees well with those several published reports [17]-[19]. It has been further confirm by measurement the field effect mobility μ of the obtained ZnO TFTs. In the saturation region, the μ was described by

$$I_D = \frac{WC_i}{2L}\mu(V_G - V_T)^2 \qquad (1)$$

When the device dropped by solution at pH of 8.30 and 10.21, the field effect mobility of transistors increased gradually from 9.4 cm^2/V.s to 13.4 cm^2/V.s as pH solution increased. In order to analyze the material parameters of transistors, the threshold slope of the transistor (S) was performed and calculated by following equation [20]:

$$S = \frac{\partial V_{GS}}{\partial[\log/ I_{Dsub}]} = \frac{qk_B T N_T d_s}{C_G \log_{10}(e)} \qquad (2)$$

The threshold slope also shifted from 1.4 V/decade to 2.6 V/decade as pH solution increased. The sensitivity of the devices can be estimated by [21]

$$Sensitivity \equiv \left|\frac{\Delta\varphi_0}{\Delta pH}\right| = \left|\frac{\Delta V_T}{\Delta pH}\right| = \left|\frac{\Delta V_{GS}}{\Delta pH}\right| \qquad (3)$$

and was 1.05 V/pH. It may cause the roughness of ZnO nanostructure surface which resulting defect on interface traps. Consequently, the threshold voltage of devices is quite high [22].

Based on our result above with comparing the other ZnO nanostructures TFTs that the lowering electrical properties of TFTs due to low-temperature deposition problem of ZnO nanostructures from aqueous solution in which resulting both insufficiency the thermal energy to induce the local bond of organometallic complexes $[Zn(H_2O)_2(HMT)_2](NO_3)_2$ formed in aqueous solution of $Zn(NO_3)_2$ and HMT for minimizing grain boundary defects [23]. However, our devices not only open up the possibility for fabrication low-cost flexible TFT but also potentially as pH sensing.

IV. Conclusion

In summary, we have fabricated the ZnO nanostructures on plastic substrate as active channel on TFT and study pH response on electrical behavior of transistors. The ZnO nanostructures based TFT under low temperature was fabricated and shows improvement in the sub-threshold slope, on/off ratio, and mobility as increasing pH solutions. These results demonstrated the capability of the device as pH sensor.

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