Remote plasma enhanced atomic layer deposition of ZnO for thin film electronic applications

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ARTICLE INFO

Article history:

Available online 28 May 2012

Keywords:

Remote plasma

Atomic layer deposition (ALD)

ZnO

Thin film transistor

ABSTRACT

This paper describes a systematic approach to analyze the simultaneous impact of various reactant plasma parameters of remote plasma enhanced ALD (PEALD) on the ZnO thin film properties. Particular emphasis is placed on the film stoichiometry which affects the electrical properties of the thin film. Design of Experiment (DOE) is used to study the impact of the oxygen plasma parameters such as the RF power, pressure and plasma time to realize semiconductor quality of ZnO thin film. Based on the optimized plasma condition, staggered bottom-gate TFTs were fabricated and its electrical characteristics were measured.

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1. Introduction

Zinc oxide is a metal-oxide semiconductor with considerable potential for applications in electronics, optoelectronics and sensors due to its wide and direct bandgap of 3.37 eV, large excitonic binding energy of 60 meV and its low cost [1,2]. There have been many reports on the deposition of ZnO using pulsed laser deposition (PLD) [3], molecular beam epitaxy (MBE) [4] and chemical vapor deposition (CVD) [5]. However, these depositions require high temperatures and it is difficult to perform large area deposition on low cost substrates. Recent attention has been focused on conventional ALD as the preferred growth method due to the low growth temperature, good crystallinity and good control of thickness, composition and uniformity [6–10]. ZnO thin film transistors fabricated with ALD ZnO have shown excellent electrical characteristics [6–8].

In the ALD process, diethyl zinc, DEZ and water are normally used as metal precursor and reactant, respectively. This is called thermal ALD and has been extensively studied and can be considered as a model system for ALD [6–10]. Recently, plasma assisted ALD method has been explored [11–20] and it is found that the use of plasma species as reactants allows more freedom in processing conditions and wider range of material properties compared with the conventional thermal ALD. The use of plasma also significantly reduced the OH impurity which affect the conductivity of the semiconductor film and induce defects in dielectric materials [16]. In the advent of this, remote PEALD has been widely reported

to form high quality dielectric films, particularly for high-k dielectric materials [18–20]. Very few have reported using remote PEALD for semiconductor layer especially ZnO film [11,12].

In this work, we study the remote PEALD process to deposit semiconducting and high quality ZnO layer for electronic device applications. Various plasma parameters were varied and their effects on ZnO film properties were investigated.

2. Experimental methods

2.1. Remote PEALD

Generally, ALD deposition technique on metal oxide is a cyclic and based on two self-limiting reactions: (1) metallization and (2) oxidation. These reactions are separately executed on a substrate surface at fixed temperature of 150 °C. DEZ ($\text{Zn}(\text{C}_2\text{H}_5)_2$) is used as the Zn metal precursor. During metallization cycle, DEZ is injected into the reactor at 50 ms and $\text{Zn}(\text{C}_2\text{H}_5)_2$ is chemisorbed to the substrate surface. After reaching saturation, residual $\text{Zn}(\text{C}_2\text{H}_5)_2$ and reaction products are removed by Ar purge. Subsequently, the $-\text{C}_2\text{H}_5$ ligands of the chemisorbed $\text{Zn}(\text{C}_2\text{H}_5)_2$ species are removed by a reaction with oxidant in the oxidation step. In this work, oxygen radicals were created by inductively coupled plasma source which is generated outside the deposition chamber. The O_2 flow was kept constant at 60 sccm during this cycle. To ensure only one reactant is present in the ALD chamber at a given time, oxygen is purged using Ar for 4 s before the next DEZ injection into the chamber. This constitutes one cycle and the substrate surface is ideally left with one monolayer of ZnO. Remote PEALD combines a high reactivity with low ion energy, typically below

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the threshold energy for plasma damage. Fig. 1 shows 2 cycles of remote PEALD process.

Design of Experiment (DOE) is used to study the impact of the oxygen plasma parameters such as the RF power, pressure and plasma time to realize semiconductor quality of ZnO thin film. DOE is a structured and organized method for statistically analyzing the relationships among factors affecting the process outputs. Reference [21] provides details on the DOE methodology. We have used the Box-Behnken design [21] in the DOE that includes 3 design points for all the plasma parameters that represent the experimental run to be conducted in the ALD. The 3 design points were RF power at 100, 250 and 400 W, plasma pressure at 15, 57.5 and 100 mTorr and plasma time at 2, 6 and 10 s. These parameters were varied simultaneously rather than one at a time which allows for the study of interactions between the factors.

We prepared ZnO films on 200 nm SiO₂/p-Si substrate. The deposition of ZnO film was carried out in Oxford Instrument's Flex-AL deposition tool. The Si wafers with 200 nm thermally grown SiO₂ were cleaned in acetone and IPA ultrasonically for 1 min, respectively. The samples were immediately loaded into the reactor and ALD process was performed based on DOE technique.

The deposited films were then characterized in X-ray photoemission spectroscopy (XPS) for surface material composition. The Hall mobility and resistivity of the ZnO films were measured by Hall-effect measurements using four-probe approach at a magnetic field of 0.5 T. For this test, quartz substrate was used to avoid any conductivity effect from the substrate.

2.2. TFT fabrication

From the optimized process condition, a staggered bottom gate thin film transistor was fabricated. This is to test if the ZnO film deposited has semiconductor characteristics. The ZnO thin film is patterned and Reactive Ion Etched (RIE) in CHF₃ before evaporating aluminium (Al) pads for the source and drain electrodes. The contacts were RTA annealed in Ar at 350 °C to improve the ohmic conductivity. The width (*W*) and length (*L*) of the TFT were 10 m and 5 m, respectively. The transfer characteristics and output characteristics were measured in HP4155C Parameter Analyzer.

3. Results and discussion

XPS is used to evaluate the content of ZnO film processed with different plasma parameters in the remote PEALD. This is important technique to study the effect of plasma parameters alone on the film quality since the DEZ dose cycle was kept constant. Fig. 2 shows the XPS spectrum obtained from a ZnO film processed at a plasma power of 100 W, plasma pressure of 57.5 mTorr and plasma exposure time of 2 s. The O1s and the Zn2p_{3/2} peaks are observed at about 531 eV and 1022 eV, respectively. The stoichiometry is determined

Fig. 1. Schematic diagram of remote plasma enhanced ALD cycle.

Fig. 2. XPS spectrum of ZnO film deposited with 2s oxygen plasma time in the remote PEALD.

from the O1s and Zn2p_{3/2} photoelectron peaks as shown in this work [22]. The C1s peak which is the carbon impurity appeared at 285 eV for all samples deposited. From this peak, we have also analyzed the carbon impurity content present in the ZnO films. The presence of carbon impurity in the ZnO film is due to the unreacted or by-product of the metal–organic precursor source. The carbon impurity can induce defect states in ZnO.

Meanwhile, the four probes Hall measurements give early indication of the semiconducting properties of the deposited ZnO films from the Hall mobility and resistivity, which are vital properties for typical thin film transistor (TFT) applications. Fig. 3 shows the contour plots of all four responses from the DOE model. These responses include the Zn/O ratio, the carbon impurity, Hall mobility and resistivity of the ZnO film. These contour plots are used to extract the ZnO film surface and electrical information and finally the desired operating conditions.

From the model analysis, it is found that plasma pressure and plasma time are the more significant factors than plasma power for determining ZnO film quality. Hence, the contour plot is used to give two plasma factors and the plasma power is fixed at 100 W. In Fig. 3(a), we observe the Zn and O compositions change as the plasma time and pressure being varied. The ZnO films become oxygen rich at plasma time greater than 8 s regardless of the plasma pressure. This is due to the insufficient Ar purge after the long exposure of the oxygen plasma. There could be some oxygen ions residues left which bound loosely onto the surface of the ZnO film resulting in highly oxygen rich film.

However, decreasing plasma time below 5 s and increasing plasma pressure higher than 50 mTorr drive the film to be more stoichiometric. Interestingly, carbon impurity decreased to <15 at.% as shown in Fig. 3(b). However, it is still high compared with other ALD ZnO films [6,8]. The carbon content can be further reduced by optimizing the DEZ dose time. This carbon content originated from the incomplete decomposition of DEZ and currently under investigation. Higher oxygen plasma and low pressure generally increases the carbon impurity. This increase is due to the insufficient Ar purge, which leads to the simultaneous presence of both precursors in the gas phase near the substrate resulting in chemical vapor deposition (CVD) type growth. CVD growth reactions can lead to particle formation such as carbon impurity which degrades device performance [20]. Very low plasma pressure during deposition (<50 mTorr) also results in very high carbon concentration. This result agrees well with the observed electrical properties from the Hall measurements. Fig. 3(c) and (d) show mobilities and resistivities of remote PEALD ZnO films as a function of plasma time and pressure at constant plasma power at 100 W.

Fig. 3. Generated contour plot of (a) Zn/O ratio, (b) carbon impurity in %, (c) hall mobility in cm^2/Vs and (d) resistivity in cm when plasma time and plasma pressure were varied at constant plasma power of 100 W.

Fig. 4. (a) Schematic diagram of the TFT structure. The ZnO and SiO₂ thickness were 20 nm and 200 nm, (b) optical microscope image of fabricated ZnO TFT, (c) I_D – V_G characteristics at $V_D = 10$ V and (d) I_D – V_D characteristics of the ZnO TFT.

For longer plasma exposure time, the Hall mobility of the ZnO film is reduced to $<1 \text{ cm}^2/\text{vs}$. During this time, the ZnO films consistently demonstrate an elevated film resistivity which is due to carbon impurity. As a result, the carrier scattering increases and reduces the mobility of the film.

Based on these findings, a good quality stoichiometric ZnO thin film with low carbon impurity, resistivity and high mobility can be achieved at plasma power of 100 W, plasma pressure of 57.5 mTorr and plasma exposure of less than 4s. With this optimized condition, a ZnO thin film was deposited at 1s plasma exposure time.

The measured carbon impurity is about 11% and Zn/O ratio is 1.02. This indicates at low plasma exposure time during remote PEALD, can exhibit a stoichiometric film with low carbon impurity.

A TFT was then fabricated using a 20 nm thick ZnO film deposited by remote PEALD at 150 °C with oxygen plasma time of 1 s, plasma power of 100 W and plasma pressure of 57.5 mTorr. Fig. 4(a) and (b) show the schematic diagram of the bottom-gate TFT structure and the optical image of the TFT device. Fig. 4(c) and (d) show the I_D – V_G transfer and I_D – V_D output characteristics. The ZnO TFT clearly operates in n-type enhancement mode with

threshold voltage of 2.5 V. The saturation mobility is estimated to be $0.33 \text{ cm}^2/\text{Vs}$. This value is consistent with the range of values from 0.06 to $17 \text{ cm}^2/\text{Vs}$ reported for as-deposited ALD ZnO TFTs [6,7,13,17,23]. The subthreshold swing is given by the maximum slope in the transfer curve in log scale and measured to be $2.3 \text{ V}/\text{dec}$. An $I_{\text{ON}}/I_{\text{OFF}}$ ratio of 5.9×10^7 was achieved. The output characteristics exhibited a clear pinch-off and saturation region. The mobility achieved is better than previously reported result on PEALD ZnO TFT [13] though can be further improved by optimizing DEZ dose for better film quality.

4. Conclusions

A semiconductor quality ZnO thin film was successfully deposited by remote PEALD. Film stoichiometry is reduced and carbon impurity content is increased by long oxygen plasma exposure time and very low plasma pressure. The results show film resistivity and carrier mobility are affected by presence of carbon impurity. The TFT from the optimized remote PEALD process operates in enhancement mode with threshold voltage of 2.5 V. It has a respectable $I_{\text{ON}}/I_{\text{OFF}}$ ratio of 5.9×10^7 and excellent output characteristics which exhibits distinct linear and saturation region. Finally, remote PEALD process has a great potential in producing semiconductor quality metal-oxide film.

Acknowledgments

This work was supported by the Malaysian Ministry of Higher Education and Universiti Teknologi Malaysia. The first author would also like to acknowledge the support of Southampton Nanofabrication Centre.

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