

Low Temperature Preparation of Hafnium Oxide Thin Film for OTFT by Atomic Layer Deposition

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(Received November 24 2008, Accepted December 17 2008)

Hafnium dioxide (HfO₂) thin film as a gate dielectric for organic thin film transistors is prepared by plasma enhanced atomic layer deposition (PEALD). Mostly crystalline of HfO₂ film can be obtained with oxygen plasma and with water at relatively low temperature of 200 °C. HfO₂ was deposited as a uniform rate of 1.2 Å/cycle. The pentacene TFT was prepared by thermal evaporation method with hafnium dioxide as a gate dielectric. The electrical properties of the OTFT were characterized.

Keywords : Hafnium oxide, Thin film, ALD, OTFT

1. INTRODUCTION

Organic molecular thin film transistors have been widely studied due to their potential for applications related to large area, low-cost electronics and their compatibility with flexible substrate[1]. The carrier mobilities that are observed for organic thin film transistors (OTFT) fabricated from pentacene are comparable with those of amorphous silicon and have attractive interest. The use of an organic gate dielectric is likely to be an ideal case in the development of all-organic transistor for organic electronics. Therefore, most of works about gate insulators are related to organic materials and silicon dioxide. However, the OTFT with organic gate dielectrics showed electrical instabilities such as the bias stress effect and hysteresis [2,3]. Inorganic gate dielectrics show relatively stable characteristics with the gate bias and hysteresis. Recently, hafnium dioxide is considered as a potential gate dielectric due to its relatively high dielectric constant around 30 and large band gap around 5.68 eV[4].

Atomic layer deposition (ALD) for semiconductor industry is used for the fabrication of uniform and dense thin films due to the easy control of thickness and improved film quality at relatively low temperature. Plasma enhanced (PE) ALD with shower head reactor and ALD with traveling-wave reactor were used for metal oxide film fabrication on silicon wafer by using plasma and water as reactants, respectively[5]. Recently, there was a report on the HfO₂ as a potential substitute for SiO₂ gate insulator, however, they reported the

interfacial properties of HfO₂ as a ALD film on the silicon wafer[6].

In this paper, we prepared and characterized HfO₂ thin film by PEALD to investigate the effect of thin film quality and prove low temperature process for the compatibility of flexible substrates. OTFT with the inorganic dielectric was characterized.

2. EXPERIMENTAL

HfO₂ films were deposited on 4" n-type silicon wafer after cleansing by ALD at the temperature 200 °C. The source delivery system for ALD is using bubbler type delivery system like Fig. 1. As a source of hafnium tetrakis(ethylmethylamino) hafnium (TEMAH) was used. Oxygen plasma and water were used as oxygen precursors for thin film fabrication. The reactor pressure was maintained 0.6 Torr with the Ar purging of 100 sccm. During the reaction TEMAH and oxygen plasma were sequentially injected into the reactor chamber to form HfO₂ monolayer on the substrate. ALD cycle consisted of the injection of TEMAH for 0.5 s, Ar for 5 sec, O₂ gas for 0.5 sec, and additional O₂ with r.f. power of 60 W, and final purge. In order to fabricate pentacene TFT, gold (Au) as a source and drain was used and deposited by thermal evaporator with show mask. Pentacene was also deposited by thermal evaporator with show mask. The thickness of a source and drain, and pentacene semiconductor were 70 nm and 60 nm, respectively.

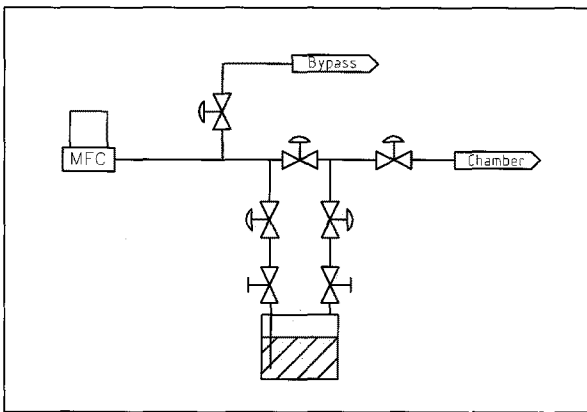


Fig. 1. Schematic diagram of bubbler type source delivery system for ALD.

3. RESULTS AND DISCUSSION

The growth rate of thin film (average film thickness per cycle) was examined as a function of precursor pulse time and reaction cycle. The growth rate was about 1.2 Å/cycle and it was reasonable higher rate comparing previous ALD methods[7]. They used HfCl_4 as a source precursor and water as reactant. The obtained the thickness of 0.95 Å/cycle at 200 °C and 0.64 Å/cycle at 300 °C. We used a different source of TEMAH and reactant of oxygen plasma and water, and also different system. Even though in water system in our experiment, similar result of growth rate was obtained.

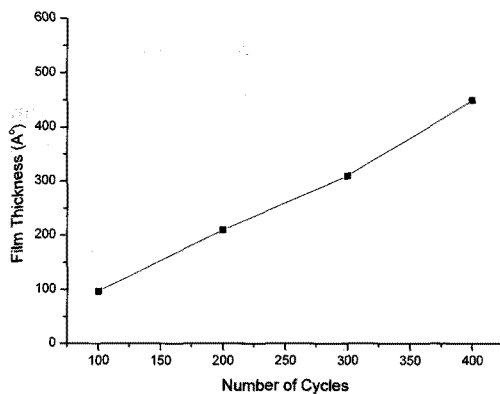


Fig. 2. Total film thickness of HfO_2 with reaction cycles.

We changed the distant of showerhead type reactor in the process module to see the uniformity of the HfO_2 film. The effect of showerhead distant on the thickness is not a critical factor, however, it showed about small differences between the distances. Considering the experimental error the difference of thickness between distant is negligible in this system.

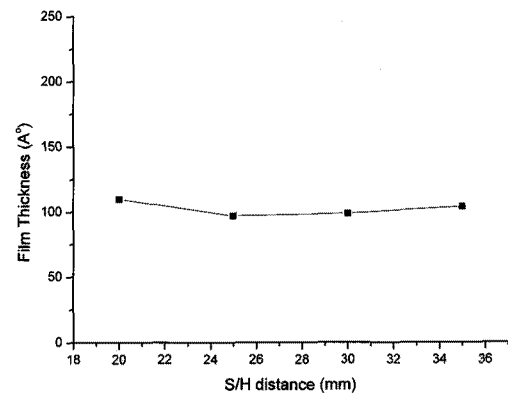


Fig. 3. Effect of showerhead distance in the process module on the HfO_2 film thickness.

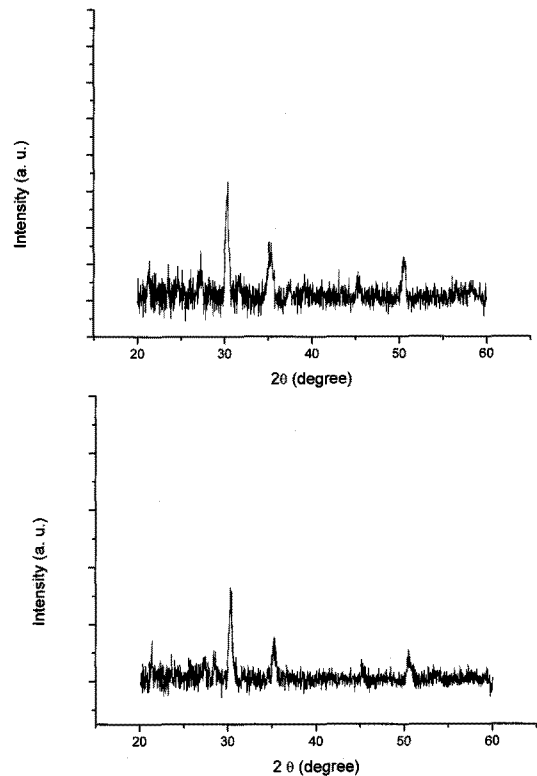


Fig. 4. X-Ray diffraction pattern of hafnium oxide prepared on glass with water (above) and oxygen plasma (below).

The crystallographic orientation of prepared HfO_2 film was examined by an X-ray diffractometer (XRD). Polycrystalline structure of HfO_2 film was obtained. It was reported that the hafnium oxide films prepared by ALD at 200 °C was amorphous while the film deposited at 300 °C was partially crystalline. And the films deposited at 400 °C were mostly crystalline as monoclinic and orthorhombic[7]. In this experiment,

crystalline HfO_2 of (111) direction at 31.1° and (002) direction at 35.1° shows preferred orientation with minor peak of (-111) at 27.3° . In this experiment, therefore, mostly crystalline of HfO_2 film can be obtained at relatively low temperature at 200°C comparing previous result. The plastic substrates can be applied to this system for the flexible display applications.

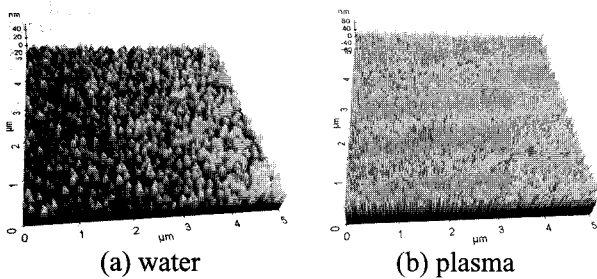


Fig. 5. AFM topography of hafnium oxide film.

From AFM topography in Fig. 5, the surface roughness of OTFT devices is compared with water and oxide plasma reactants, respectively. Hafnium oxide prepared with water looks more uniform than that with plasma. The peak to valley of water is 39 nm while that of plasma is 138 nm. The roughness of water is 0.9 nm while that of plasma is 2.8 nm.

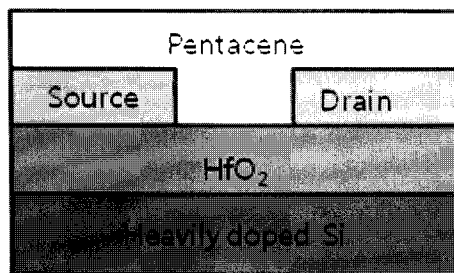


Fig. 6. Schematic structure of OTFT.

The structure of OTFT in this experiment is bottom contact. Silicon wafer as a gate was used for fabrication. The thickness of hafnium prepared by ALD is about 500 \AA . Gold was used for source and drain metal. Pentacene was deposited to 600 \AA by thermal evaporator with $0.3 \text{ \AA}/\text{sec}$ rate. No self assembly monolayer (SAM) was used in this experiment. Figure 6 shows the schematic diagram of the structure of TFT for this research.

The transfer curve as in Fig. 7 show the on-to-off ratio of this device is not high and subthreshold slope is very

steep. The threshold voltage (V_t) and the saturation mobility were obtained by fitting the straight line of the square root of I_d versus V_g from Fig. 7. The dimension of TFT was width of $1000 \mu\text{m}$ and length of $50 \mu\text{m}$, and the ratio of W/L was 20. The mobility of $0.19 \text{ cm}^2/\text{Vs}$, and the threshold voltage of 2.0 V , subthreshold slope of 0.3, and on-to-off ratio of 10^3 were obtained. This TFT operates in enhancement mode since there is some no measurable drain current at a gate voltage of 0 V . So the negative bias is required to induce a conducting channel and the channel conductivity increases with decreasing gate voltage to negative region. Usually, there was a big negative shift of threshold voltage in the pentacene organic TFT with organic gate dielectrics, however, this result shows a different story. Ions migration and mobile ions originating from organic dielectrics are the main reason for voltage shift. For inorganic dielectric such as hafnium oxide prepared by ALD technology shows dense thin film, the voltage shift is not expected. The on-to-off ratio is relatively small. However, the subthreshold slope shows good characteristic.

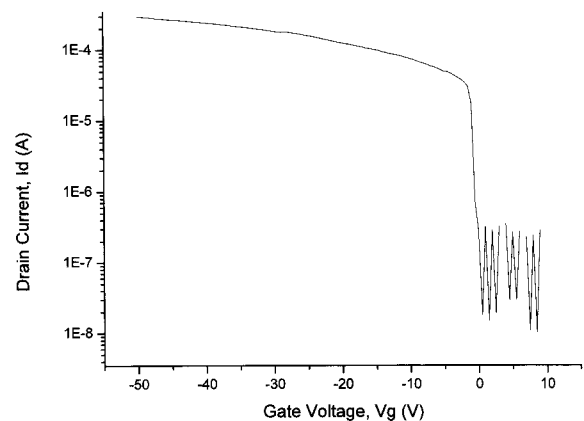


Fig. 7. Transfer curve of pentacene TFT with a hafnium gate dielectric on silicon wafer. $W/L = 1000/50 \mu\text{m}$.

4. CONCLUSION

By ALD method, mostly crystalline of HfO_2 films can be obtained with oxygen plasma and with water at relatively low temperature of 200°C . HfO_2 was deposited as a uniform rate $1.2 \text{ \AA}/\text{cycle}$. OTFT device prepared with pentacene and hafnium dioxide gate dielectric on silicon wafer was characterized. P-type enhancement mode OTFT was obtained with moderate mobility, good subthreshold slope, and threshold voltage. The on-to-off ratio of drain current is relatively lower than other OTFT devices.

ACKNOWLEDGMENTS

This research was supported by the academic research fund of Hoseo University in 2005 (20050304).

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