Hafnium Oxide Nano-Film Deposited on Poly-Si by Atomic Layer Deposition

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Abstract

We reported that high dielectric hafnium oxide nano-film deposited by thermal atomic layer deposition on the poly-silicon film (poly-Si). The poly-Si film was produced by plasma enhanced chemical vapor deposition and excimer laser annealing. We used the hafnium chloride ($HfCl_4$) and water as the precursors and analyzed the hafnium oxide film by transmission electron microscope and secondary ion mass spectrometer. Hafnium oxide produced by the ALD method showed very good coverage on the rough surface of poly-Si film. While deposited with 200 cycles, these hafnium oxide films revealed a relatively smooth surface and good uniformity, but the cumulative roughness produced by the incomplete reaction was apparent when the amount of deposition cycle increased to 600 cycles.

1. Introduction

It is a trend to pursue high transparency, low drive voltage and low process temperature of transistor device manufacturing on plastic substrate for flexible display applications [1]. Therefore, active layer and isolator layer will need to possess transparent and thin properties. Nevertheless, the gate oxide layer gets thinner; the intensity of electric field applies on the gate oxide layer will be more and larger, that leads to the problem of high tunneling current and reliability of device in the future [2]. Furthermore, there are mainly physical vapor deposition (PVD) and chemical vapor deposition (CVD) in technology for thin film deposition in manufacture of flat panel display. These problems about control of thickness and uniformity generally limit CVD and PVD processes when the thickness of films deposited by CVD and PVD method are thinner than 10 nm and 20 nm respectively [3]. CVD processes only assure 100 % step coverage on aspect ratio of approximately 10:1 and PVD processes only offer 50 % step coverage even at 10:1 aspect ratios [3]. Therefore, it is difficult to uniformly deposit the atomic layers on a large area substrate for reducing the drive voltage of transistor and for increasing the reliability of every transistor. By using the atomic layer deposition (ALD) technologies [4] to deposit nano-scale thickness of thin film and using the new isolation materials to replace SiO_2 isolation layer for reducing tunneling current are required.

This study reported the gate dielectric film grown by thermal atomic layer deposition on poly-Si. The poly-Si film was formed by excimer laser anneal (ELA) and PECVD. We also characterized the morphologies and impurities of hafnium oxide thin film by transmission electron microscope (TEM) and secondary ion mass spectrometry (SIMS), respectively. It was revealed that the hafnium oxide film would include chlorine when the hafnium oxide film was deposited with the precursor of $HfCl_4$. Furthermore, the hafnium oxide film deposited by thermal ALD was rough when the number of deposition cycles was 600 cycles.

2. Experiment

Hafnium oxide thin film was produced by thermal atomic layer deposition consisted of two source chambers and a reactor in this experiment. These chambers heating were done using three resistive heaters. The temperatures were read by three thermocouple attached to the heater, so the temperature of these chambers was independently controlled in accuracy. We chose the hafnium chloride ($HfCl_4$) and water (H_2O) as the precursor of HfO_2 because that the cost of $HfCl_4$ and water was lower than the other precursor, and they were easily obtained. We set the deposition temperature of reactor at 300°C for these experiments. Additionally, the solid $HfCl_4$ precursor contained in the source chamber was used. The source chamber was maintained at 180°C to develop adequate vapor pressure. To improve the delivery, N_2 was used as the carrier gas. The valve upstream from the

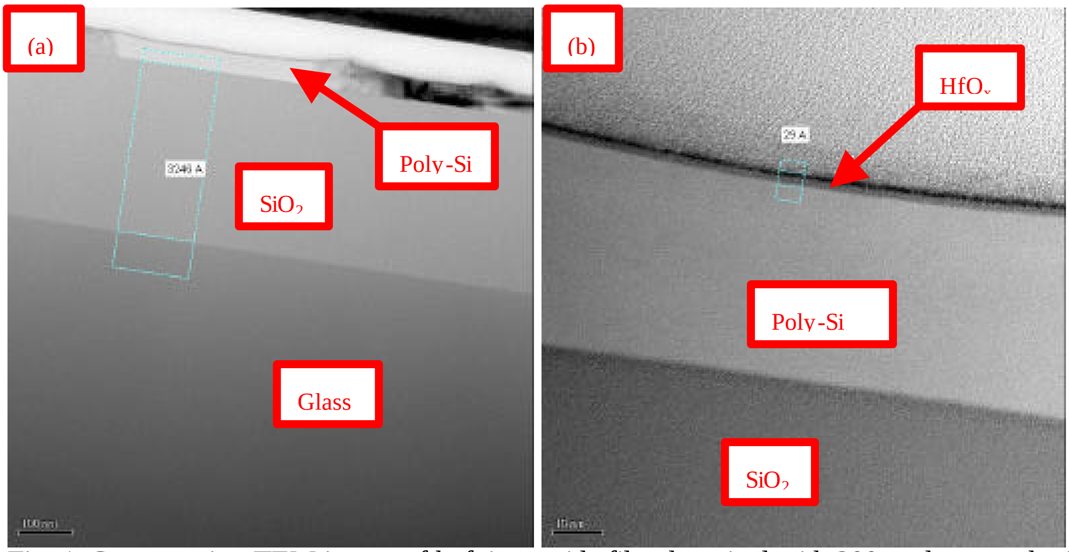

Fig. 1. Cross section TEM image of hafnium oxide film deposited with 200 cycles on poly-Si, (b) high magnification on the hafnium oxide film of (a).

source tube controlled the N_2 flow. The H_2O source was a glass jar, which was not heated. The steam from the glass jar was directly introduced to the reactor by carrier gas N_2. Two chemical reactions of $HfCl_4$ precursor pulse and steam pulse made up one basic cycle in this experiment. N_2 as a purging gas was introduced for the complete separation of the $HfCl_4$ precursor and steam. The deposition cycle consisted of the following steps: exposing the substrate to $HfCl_4$ carried by N_2 gas for 2 seconds, opening the N_2 purging gas valve for 3 seconds, exposing the substrate to steam carried by N_2 gas for 2 seconds, opening the N_2 purging gas valve for 3 seconds. The thickness of hafnium oxide film was controlled by the amount of deposition cycles. The thickness of hafnium oxide film increased with deposition cycles. For these experiments, the total time per cycle was 10 seconds, and the deposition conditions with 200 cycles and 600 cycles were carried out respectively.

The substrates used in this study were Corning 1737 glass (thickness of 0.7 mm). A buffer layer SiO_2 with thickness of 300 nm was first deposited on glass substrate by plasma enhanced chemical vapor deposition method, and 50 nm amorphous silicon film was then subsequently deposited by plasma enhanced chemical vapor deposition method. The excimer laser anneal was used for the crystallization of a-Si film.

3. Results and Discussion

Figure 1 is a TEM image of hafnium oxide ALD film deposited on poly-Si film showing that the film had a very smooth surface and uniformly covered on the surface of poly-Si. Moreover, the thickness of hafnium oxide film grown with 200 deposition cycles was only around 30 Å as shown in Fig. 1 (b). Figure 2 is a TEM image of hafnium oxide ALD film deposited on poly-Si film. It was obvious that the thickness of hafnium oxide film grown with 600 deposition cycles was about 170 Å as shown in Fig. 2 (b). However, there was obviously a very rough surface of the hafnium oxide film. Two factors may cause the roughness of the hafnium oxide thin film surface. The first one was that the oxidative power of the precursor such as H_2O was not enough. Park[5] and coworkers have used ozone and water as precursors to react with $HfCl_4$ and deposit hafnium oxide film. They found that the surface of the hafnium oxide film deposited with water was rougher than the hafnium oxide film deposited with ozone. Another one may be that there was not complete reaction of the adsorbed $HfCl_4$ during the formation of a monolayer of HfO_2 everywhere on the thin film surface. There will be no reaction of the adsorbed $HfCl_4$ and H_2O in parts of the thin film surface when the ligands were not completely removed. The thickness of the thin film was continuously increasing in parts of the thin film surface where the ligands were removed. In contrary, the thickness of thin film was not increasing in the other parts of the thin film surface where the ligands were not removed. Therefore the irregular surface was formed.

Figure 3 shows the SIMS depth profiles of the hafnium oxide films deposited with 600 cycles. It was obvious that the amount of chlorine as the main impurity in hafnium oxide film deposited with 600 cycle was also about 1 at.%, and there was carbon residue on the film surface due to exposing to ambient too long and carbon dioxide absorbed.

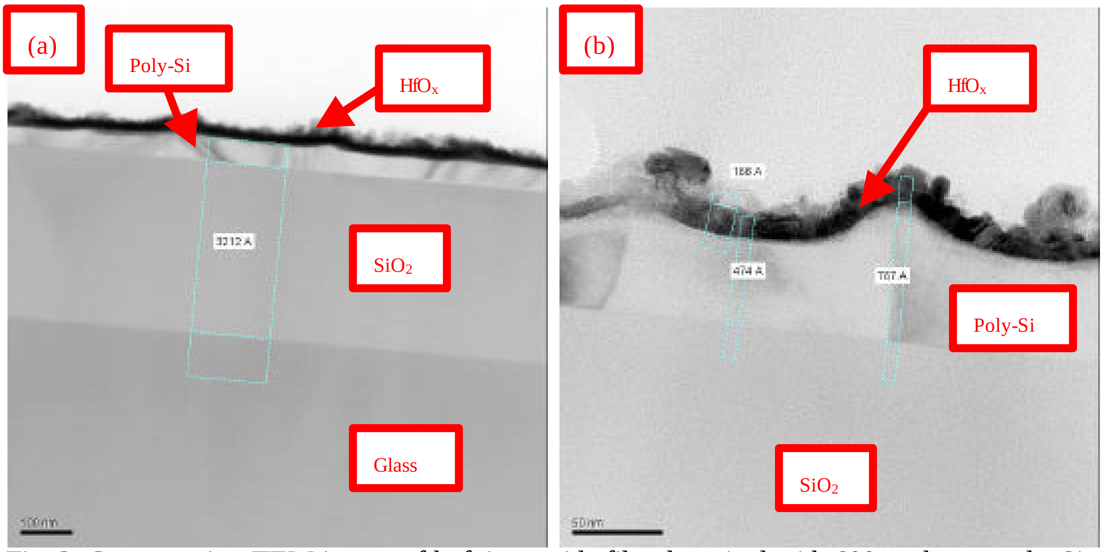

Fig. 3. Cross section TEM image of hafnium oxide film deposited with 600 cycles on poly-Si, (b) high magnification on the hafnium oxide film of (a).

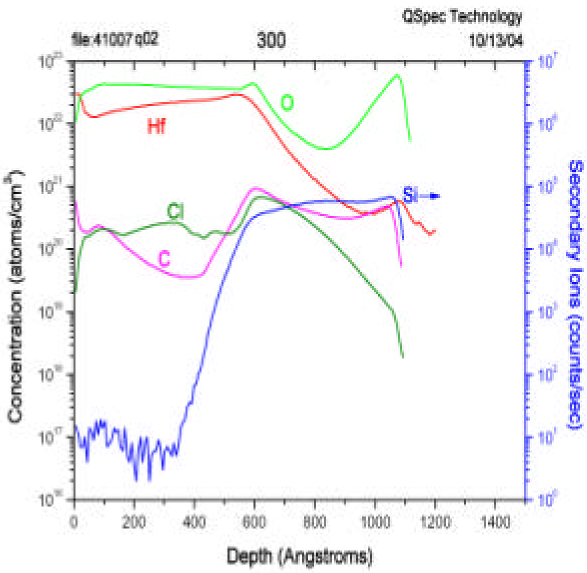

Fig. 4. SIMS spectra of the hafnium oxide film deposited with 600 cycles

The profile depth of hafnium oxide film in SIMS spectra was 500 ?. This depth was seriously affected by the rough surface of the hafnium oxide film.

4. Conclusion

Hafnium oxide films were successfully deposited by thermal ALD on poly-Si film produced by excimer laser annealing. The profiles of hafnium oxide films were investigated by TEM. SIMS characterized the compositions of hafnium oxide films. From the results of TEM images, hafnium oxide films deposited with 200 cycles showed a relatively smooth surface and good uniformity, but these cumulative roughness produced by the incomplete reaction was substantial and not neglected when the amount of deposition cycle was 600 cycles. The SIMS data confirmed the impurities in the hafnium oxide film deposited with 600 cycles. Hafnium oxide films deposited with $HfCl_4$ precursor contained 1 at.% of chlorine. A new precursor without chlorine is required in order to avoid eroding metal line thereafter. The deposition temperature of 300°C was too high for large area flexible display as well. Therefore, it needs to develop a low temperature plasma enhanced atomic layer deposition system for such applications.

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Reference:

[1] E. M. C. Fortunato, P. M. C. Barquinha, and Ana C. M. B. G. Pimentel, J. Appl. Lett. **85**, 2541 (2004)
[2] G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **89**, 5243 (2001)
[3] J. E. Crowell, J. Vac. Sci. Technol. A **21** (5), S88 (2003)
[4] T. Suntola, Mater. Sci. Rep. **4**, 261 (1989)
[5] H. B. Park, M. Cho, J. Park, S. W. Lee, and C. S. Hwang, J. Appl. Lett. **94**, 3641 (2003)