HfSi<sub>x</sub>O<sub>y</sub>-HfO<sub>2</sub> Gate Insulator for Thin Film Transistors

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We propose a new technique to grow HfSi<sub>x</sub>O<sub>y</sub>-HfO<sub>2</sub> film on Si substrate by using a 500 °C process, and demonstrate the feasibility of multi-layered high-k oxide film (i.e., HfSi<sub>x</sub>O<sub>y</sub>-HfO<sub>2</sub>) as alternative gate insulator for thin film transistors (TFTs). Hf metal films were directly deposited on Si wafers at substrate temperatures of 25 ∼ 400 °C by using a non-reactive rf-magnetron sputtering system. Oxidation at 500 °C in dry O<sub>2</sub> ambient and subsequent annealing at the same temperature in N<sub>2</sub> ambient result in electrically stable multi-layered HfSi<sub>x</sub>O<sub>y</sub>-HfO<sub>2</sub> gate insulator for TFTs. We also investigate the effects of the substrate temperature on the physical and electrical properties of HfSi<sub>x</sub>O<sub>y</sub>-HfO<sub>2</sub> films, and show that substrate temperature must be set at 25 °C for the sputtering of Hf metal films to obtain optimum electrical characteristics (e.g., high dielectric constant, no hysteresis phenomenon, and low leakage current).

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I. INTRODUCTION

The development of reliable gate oxides, especially at low processing temperature, is an important issue for TFT research [1]. Specifically, gate oxides grown at low temperature have to exhibit good electrical and physical properties such as low leakage current, low interface trap density, and minimum value of hysteresis window [2,3]. One of the candidates for satisfying these requirements is multi-layered high-k film such as HfSi<sub>x</sub>O<sub>y</sub>-HfO<sub>2</sub>. Since the multi-layered HfSi<sub>x</sub>O<sub>y</sub>-HfO<sub>2</sub> film consists of both amorphous HfSi<sub>x</sub>O<sub>y</sub> and polycrystallized HfO<sub>2</sub>, the leakage current through the gate oxide can be minimized due to the mismatch of pinholes located at each layer. It has been reported that the HfSi<sub>x</sub>O<sub>y</sub> film remains amorphous, even after subjection to relatively high temperature processing [4]. Therefore, the Si-HfSi<sub>x</sub>O<sub>y</sub> interface may satisfy the requirement for low interface trap. Furthermore, the desired value of effective dielectric constant can be easily controlled through the thickness change of HfSi<sub>k</sub>O<sub>y</sub> (k 15 ~ 25) [5] and HfO<sub>2</sub> (k ~ 30). For example, the ratio HfSi<sub>k</sub>O<sub>y</sub>/HfO<sub>2</sub> might be minimized to obtain a higher value of effective dielectric constant. The HfSi<sub>k</sub>O<sub>y</sub> and HfO<sub>2</sub> films can be formed either by atomic layer deposition (ALD) [6] or by sputtering [7]. For the sputtering method, both reactive deposition using a hafnium-metal target and direct deposition using a hafnium-oxide target were widely employed [7]. Although the ALD technique has unique properties such as the exact controllability for both film thickness and composition, the contamination problems originating from the hafnium sources still have to be tackled. Furthermore, regardless of deposition techniques, it may be unavoidable to employ a more complicated processing sequence for growing the multi-layered high-k film such as HfSi<sub>k</sub>O<sub>y</sub>-HfO<sub>2</sub>. Recently, our group demonstrated that the oxidation of Hf thin film deposited on Si substrate results in a HfO<sub>2</sub>/HfSi<sub>k</sub>O<sub>y</sub> stack layer [4]. Moreover, we showed that the HfO<sub>2</sub>/HfSi<sub>k</sub>O<sub>y</sub> stack layer allows us to maintain the excellent interfacial property due to the presence of the amorphous HfSi<sub>k</sub>O<sub>y</sub> thin film, while the effective dielectric constant can be further increased by forming the HfO<sub>2</sub> layer on HfSi<sub>k</sub>O<sub>y</sub>. In this work, we explore the applicability of multi-layered HfSi<sub>k</sub>O<sub>y</sub>-HfO<sub>2</sub> film as alternative gate insulator for TFTs. Specifically, the roles of substrate temperature on the physical and electrical properties of HfSi<sub>k</sub>O<sub>y</sub>-HfO<sub>2</sub> films are investigated.

II. EXPERIMENTS

Hf metal films were deposited on 6 to 12 Ω-cm (100) p-type Si wafers by non-reactive rf-magnetron sputtering at different substrate temperatures (25, 200, and 400 °C). A metallic hafnium disc (99.9%) of 4-inch diameter was used as the sputtering target, and argon (Ar) was
Fig. 1. (a) High-resolution TEM image of HfSi$_x$O$_y$-HfO$_2$ film. The Hf metal film was oxidized at 500 °C for 240 min in a conventional furnace and subsequently N$_2$-annealed at the same temperature for 1 min by using a rapid thermal processor. (b) The amorphous silicate layer is clearly shown in a magnified view of (a).

Fig. 2. AFM images of the surface morphology of HfO$_2$ film: Hf metal was deposited at (a) room temperature, (b) 200 °C, and (c) 400 °C. The RMS values in (a), (b), and (c) were 0.35, 0.42, and 0.71 nm, respectively.

used as the plasma generation gas. The base and deposition pressures were $5 \times 10^{-7}$ and $8 \times 10^{-2}$ Torr, respectively. The deposition was performed at plasma power of 30 W for 10 − 15 min, resulting in an Hf thickness of 19 − 29 nm. Hf metal films deposited on the Si substrate were subjected to oxidation in O$_2$ ambient at 500 °C for 240 min in a furnace. The post-oxidation annealing of some oxidized samples was then performed in N$_2$ ambient at 500 °C for 1 min by using a rapid thermal processor. Palladium (Pd) was thermally evaporated on the samples by using a shadow mask, and the gate area was $\sim 2 \times 10^{-4}$ cm$^2$. Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) were used to determine the thickness of the films and to investigate the interfacial layer between HfO$_2$ and Si substrate. Atomic force microscopy (SEIKO SPA400) was used to investigate the surface morphology of HfO$_2$. High frequency capacitance-voltage ($C-V$) measurement was performed by using a Boonton 7200 capacitance meter at 1 MHz. Current density-voltage ($J-V$) curves were measured by stepping the voltage and measuring the current with a HP 4145B semiconductor parameter analyzer.

III. RESULTS AND DISCUSSION

The data shown in Figure 1 represent typical high-resolution TEM images of the HfSi$_x$O$_y$-HfO$_2$ stacked layer obtained in this work. Figure 1(a) demonstrates that the oxidation and subsequent N$_2$-annealing of Hf metal film result in the HfSi$_x$O$_y$-HfO$_2$ stacked layer on the Si substrate, consistent with the previous results [4]. Figure 1(b) shows a magnified view of the selected area of Figure 1(a). As is clear in Figure 1(b), the oxidation and annealing of the Hf film result in thick (i.e., 26 nm) polycrystalline HfO$_2$ and thin (i.e., 2 nm) amorphous HfSi$_x$O$_y$ simultaneously. In addition, the HfSi$_x$O$_y$-Si interface shows no indication of interface roughness due to the heat treatment during the oxidation and annealing cycles.
The effects of substrate temperatures on the physical and electrical properties of HfSiO$_x$-HfO$_2$ films were investigated, and the results are shown in Figures 2-5. AFM images shown in Figure 2 represent the effects of substrate temperature on the surface morphology of HfO$_2$ film. HfO$_2$ films shown in Figures 2(a), (b) and (c) were formed by the oxidation and subsequent annealing of Hf metal deposited at 25, 200, and 400 °C, respectively. It is clearly shown in Figure 2 that the roughness of the HfO$_2$ film increases as substrate temperature rises. Especially, the RMS value rapidly increases at 400 °C. This phenomenon can be explained from the viewpoint of the structural change of Hf metal film due to substrate temperature: for instance, the grain size of Hf metal film increases as substrate temperature rises, resulting in an increased RMS value after oxidation and annealing.

Figure 3 shows the Hf 4f and Si 2p XPS spectra of HfSi$_x$O$_{3-x}$-HfO$_2$ films formed by the oxidation and subsequent annealing of Hf metals deposited at 25, 200, and 400 °C. It is known that the peak located at 16.8 eV is caused by the Hf-O bonding state [8], suggesting that the top layer of the multi-layered high-k film obtained in this work is HfO$_2$. In addition, the data shown in Figure 3(a) indicate the shift of the Hf 4f$_{7/2}$ peak as a function of the substrate temperature. This phenomenon demonstrates that the structural properties of HfSi$_x$O$_y$-HfO$_2$ films could be affected by the substrate temperature set for the Hf metal sputtering process. Since the shift of peaks toward higher binding energy represents higher oxygen content in the films, the results of Figure 3(a) may suggest that the grain size of Hf metal film deposited at room temperature is the smallest, resulting in the highest oxidation rate and subsequently the highest value of oxygen content. The Si 2p XPS spectra in Figure 3(b) show peaks at 103 eV, which have been assigned to silicate, consistent with the data shown in Figure 1. Interestingly, there is no significant change in the peak intensity of silicate. Therefore, the compositional properties of HfSi$_x$O$_y$ silicate layer may be less sensitive than those of HfO$_2$ as a function of substrate temperature.

The C–V and J–V characteristics of the Si/HfSi$_x$O$_y$-HfO$_2$/Pd capacitor are shown in Figures 4 and 5, respectively. The C–V and J–V data clearly show that the substrate temperature set for the Hf metal deposition process is a critical processing parameter for obtaining reliable electrical characteristics. In Figure 4, C–V characteristics are plotted for the Si/HfSi$_x$O$_y$-HfO$_2$/Pd capacitors prepared from Hf metal films deposited at 25, 200, and 400 °C, respectively. A hysteresis window was observed in all samples, but was almost negligible for the one prepared with Hf metal film deposited at 25 °C. The hysteresis phenomenon is caused by the interface and/or bulk defects. Therefore, the results in Figure 4 suggest that Hf metal films deposited at high temperature (e.g., 400 °C) may be insufficiently oxidized at 500 °C, resulting in the defects that cause the hysteresis phenomenon.

The $J$–$V$ data shown in Figure 5 also support this idea. The current density at a given voltage is dependent on the substrate temperature. For example, the lowest value of $J$ was obtained with the samples deposited at room temperature, since the defects generated at this temperature are minimized as shown in Figure 4.

### IV. CONCLUSION

In this work, we propose a new and simple technique to form very reliable HfSi$_x$O$_y$-HfO$_2$ films for gate insulator in TFTs. Oxidation and annealing of Hf metal films deposited directly on Si substrate result in multi-layered HfSi$_x$O$_y$-HfO$_2$ films. Based on the TEM and XPS data, we identified that the amorphous layer located between the Si and HfO$_2$ layers is HfSi$_x$O$_y$ film. We also discuss the effects of substrate temperature on the physical and electrical properties of HfSi$_x$O$_y$-HfO$_2$ films. The surface morphology, chemical composition, and electrical properties such as $C$–$V$ and $J$–$V$ were all sensitive to substrate temperature. We show that substrate temperature must be set at 25 °C for the sputtering of Hf metal films to obtain the best electrical characteristics (e.g., high dielectric constant, no hysteresis phenomenon, and low leakage current).

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### REFERENCES