Reduction of Oxide Defects in $ZrO_2/Al_2O_3/ZrO_2$ Dielectrics by Incorporating Hydrogen Peroxide

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ABSTRACT

Capacitance- and current-voltage characteristics of $ZrO_2/Al_2O_3/ZrO_2$ (ZAZ) capacitors with an addition of hydrogen peroxide (H_2O_2) were identified. From the results, leakage current and interface trap density of the H_2O_2-doped devices decreased due to reduction of oxygen vacancies in ZAZ layers. H_2O_2 effect on the electrical behaviors was qualitatively analyzed.

1 INTRODUCTION

Recently, solution-processed oxide semiconductor thin-film-transistors (oxide TFTs) has been extensively studied due to high throughput, homogeneity, excellent compositional control, simple and low cost [1-2]. Some researchers reported oxide TFTs using high-κ materials as a gate insulator for achieving low operating voltage and high speed [3]. Among the high-κ materials, multi-stacked ZrO_2/Al_2O_3 layers have been attracted considerable attention due to high dielectric constant and low leakage current [4]. However, ZrO_2 has stability issues resulting from the oxygen vacancies and research groups have tried to reduce the oxide defect using high pressure O_2 annealing and O_2 plasma treatment [5]. These methods, however, require high cost and additional process. In this study, we introduce $ZrO_2/Al_2O_3/ZrO_2$ (ZAZ) capacitors which are excellent for achieving high speed, on/off-current ratio, and low operating voltage of the TFTs compared with conventional SiO_2 gate dielectric. Capacitance-voltage (C-V) and current density-voltage (J-V) properties of the devices with H_2O_2 incorporation into ZrO_2 layer are discussed.

2 EXPERIMENTAL DETAILS

Figure 1 shows the structures of fabricated device. The ZAZ capacitors were fabricated on p-type silicon substrates which cleaned by RCA method. A 0.2 M Al_2O_3 solution was prepared by dissolving aluminum chloride ($AlCl_3$) in the mixture of ethylene glycol ($C_2H_6O_2$) and acetonitrile (CH_3CN). And a 0.3 M ZrO_2 solution was prepared by dissolving zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) in 2-methoxyethanol ($C_3H_8O_2$). And then, H_2O_2 was incorporated into the pure ZrO_2 solutions. These solutions were stirred at 80 °C at 1000 rpm for 18 and 5 hours, respectively. The prepared solutions were spin-coated at 3000 rpm for 30 seconds. After a pre-annealing process at 250 °C for 10 minutes on a hot plate, the post deposition annealing process was performed under the temperature of 600 °C for 1 hour by rapid thermal annealing (RTA) process. The electrode Al was deposited by e-beam evaporator. C-V properties were evaluated at 100 kHz frequency using an Agilent E4980A precision LCR meter and current density-voltage (J-V) characteristics were observed using the Agilent B1500A analyzer.

3 RESULTS and DISCUSSIONS

Figure 2 shows the hysteresis C-V characteristics of ZAZ capacitors measured at 100 kHz. We confirmed that oxide capacitance increased by incorporating H_2O_2 compared to pure ZAZ structure. The values of κ for H_2O_2-incorporated and pure ZAZ films were ~ 30 and ~ 24, respectively. The flat-band voltage shifted to the negative bias direction from 0.59 V to 0.06 V. Also, hysteresis (ΔV_{FB}) of H_2O_2-incorporated ZAZ capacitors has a smaller than the ZAZ capacitors without an incorporated H_2O_2. This implies that H_2O_2 reduced negatively charged oxide traps in the film leads to a decrease in the charge trapping [6]. And the extracted electrical parameters of the devices are summarized in Table 1.

Figure 3 shows the density of the border traps in the fabricated ZAZ capacitor with and without H_2O_2. The border traps are oxide traps located in near-interfacial. And extracted the density of the border traps according to equation (1) [7-8].

$$N_{bt} = \left(\frac{1}{q}\right) \int |C_{reverse} - C_{forward}| \quad (1)$$

As shown in Figure 3 and Table 1, N_{bt} drastically decreased from 4.26 x 10^{11} for pure ZAZ to 2.63 x 10^{10} cm^{-2} for H_2O_2-incorporated ZAZ. These result from the passivation of near-interface by oxygen atoms due to the H_2O_2 dissociation.

To identify the quality of interface between gate insulator and Si substrate, we calculated interface trap density (D_{it}) by the Terman's method.

$$D_{it} = \frac{C_{ox}}{q^2}\left(\frac{dV_G}{d\phi_s} - 1\right) - \frac{C_s}{q^2} \qquad (2)$$

The calculated D_{it} using above equation (2) decreased from 2.40 x 10^{11} for H_2O_2-undoped device to 6.99 x 10^{10} cm^2eV^{-1} for H_2O_2-doped device as shown in Figure 4 and Table 1. These results indicated that oxygen atoms in the H_2O_2 reduced oxygen related trap resulting in decrease of D_{it}. Accordingly, we confirmed that incorporating of H_2O_2 to pure ZAZ films leads to an improvement the quality of dielectric films.

Figure 5 shows the J-V characteristics of ZAZ capacitors with and without H_2O_2. The values of leakage current of ZAZ capacitors evidently decreased from 2.31 x 10^{-7} to 2.07 x 10^{-9} A/cm^2 by incorporating H_2O_2. This indicates that an addition of H_2O_2 reduces oxygen vacancies of the film by providing oxygen atoms to the dielectric/Si interface accompanying by reduction of leakage path through the dielectrics.

4 CONCLUSIONS

In this paper, H_2O_2 was employed as a dopant in ZAZ stacks for improving interfacial characteristics and reliability. The incorporation of H_2O_2 into ZAZ reduced leakage current, interface traps, border traps by passivating the defect sites in the ZrO_2 layer. We recommend the H_2O_2-doped ZAZ layers as a gate insulator for high performance TFTs.

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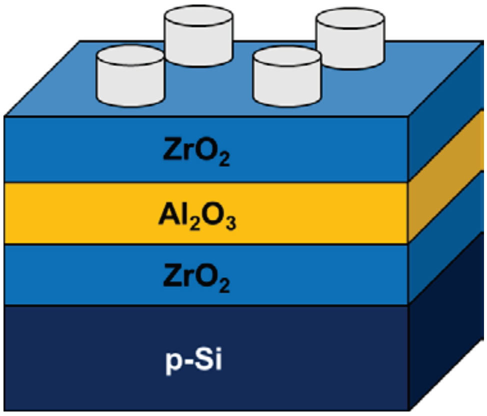

Fig. 1 Structures of fabricated ZrO_2/Al_2O_3/ZrO_2 capacitors

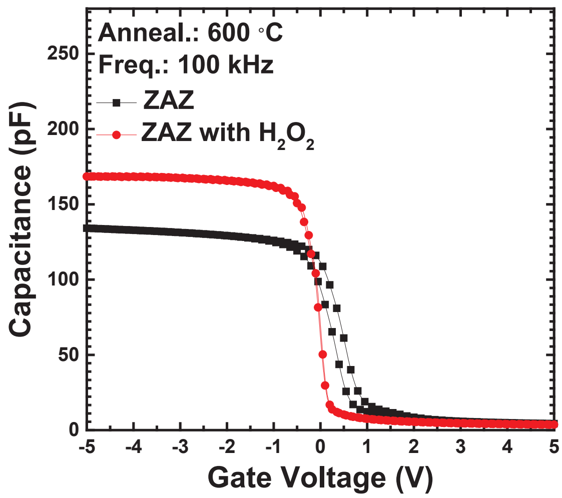

Fig. 2 Hysteresis C-V characteristics of solution-processed ZrO_2/Al_2O_3/ZrO_2 capacitors with and without H_2O_2.

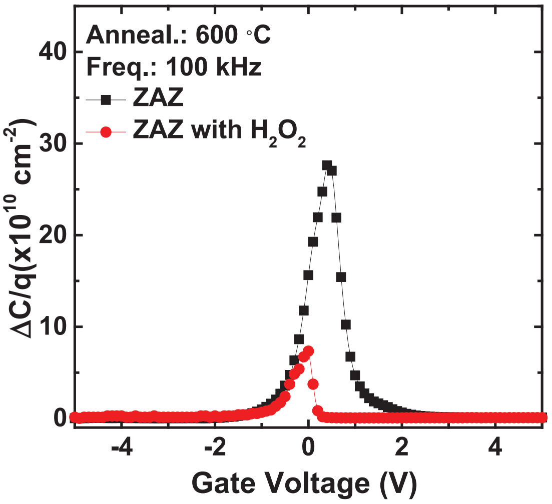

Fig. 3 Calculated border trap densities for solution-processed $ZrO_2/Al_2O_3/ZrO_2$ capacitors with and without H_2O_2

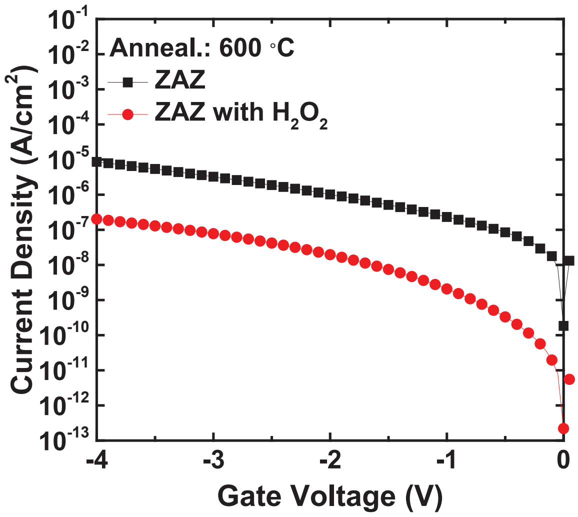

Fig. 5 Current density versus Gate Voltage for $ZrO_2/Al_2O_3/ZrO_2$ capacitors with and without H_2O_2

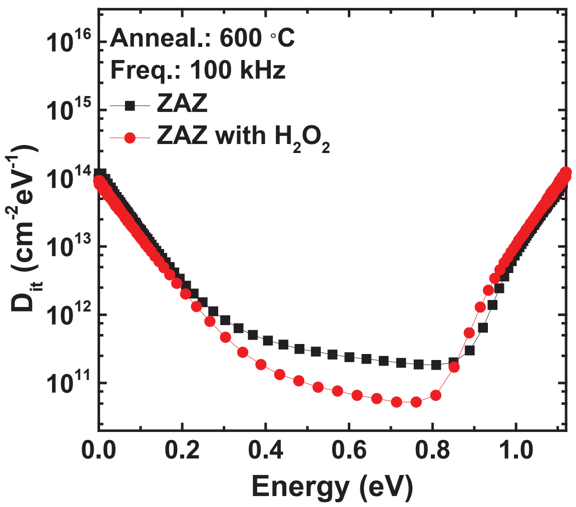

Fig. 4 D_{it} distribution of the pure $ZrO_2/Al_2O_3/ZrO_2$ capacitors and H_2O_2-doped $ZrO_2/Al_2O_3/ZrO_2$ capacitors

Table. 1 Extracted the value of electrical parameters of $ZrO_2/Al_2O_3/ZrO_2$ capacitors

	ZAZ	ZAZ+H_2O_2
C_{OX} (pF)	134	168
Dielectric constant (κ)	23.57	29.55
ΔV_{FB} (V)	-0.17	-0.01
D_{it} ($cm^{-2}eV^{-1}$)	2.40 x 10^{11}	6.99 x 10^{10}
N_{bt} (cm^{-2})	4.26 x 10^{11}	2.63 x 10^{10}
Leakage current (A/cm^2) (@ -1 V)	2.31 x 10^{-7}	2.07 x 10^{-9}