Electrical Characteristics of Solution-processed Hafnium-aluminum Oxide Gate Insulator with Addition of Hydrochloric Acid for a-IGZO Thin-Film Transistors

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Keywords: High-k, Hafnium-aluminum oxide, Solution process, a-InGaZnO thin film transistor, Hydrochloric acid.

ABSTRACT

This paper introduces a study on solution-processed $HfAlO_x$ dielectric films prepared by different ratios of Hf and Al applied to amorphous indium-gallium-zinc oxide(a-IGZO) thin-film transistors (TFTs). We also investigated the influence of hydrochloric acid (HCl) incorporation on the electrical characteristics of $HfAlO_x$ dielectric films.

1 Introduction

Recently, amorphous indium-gallium-zinc oxide (a-IGZO) thin-film transistors (TFTs) have been applied in flat panel displays such as liquid-crystal displays (LCDs) and organic light-emitting diode displays (OLEDs) owing to the advantages of low processing temperature, good optical transparency, excellent mobility, and large area uniformity [1]. However, it has been reported that a-IGZO TFTs are driven at high voltage to have high mobility. To reduce the power consumption, the capacitance of a gate insulator should be high to operate TFT at low gate voltage [2]. Therefore, the thickness reduction of the conventional SiO_x gate insulator layer was proposed to increase the capacitance. However, thin gate insulators are limited by high leakage current because of the tunneling effect. To suppress leakage current by oxide tunneling, the SiO_x gate insulator can be replaced with thicker high-dielectric-constant (high-k) gate insulators [3].

The high-k materials are such as aluminum oxide (Al_2O_3) [4], hafnium oxide (HfO_2) [5], zirconium oxide (ZrO_2) [6], and titanium oxide (TiO_2) [7] have been studied for use as gate insulators in a-IGZO TFTs. Among high-k dielectric materials, HfO_2 has a high dielectric constant of approximately 25, a relatively large bandgap (~5.8 eV), and good thermal and chemical stability on various substrates but tends to exhibit poor insulation properties such as low breakdown voltage and a high leakage current density [8]. Conversely, Al_2O_3 has a relatively low dielectric constant of approximately 9 and high breakdown voltage compared to HfO_2 [10]. Therefore, A large body of prior work has investigated the use of hafnium aluminum oxide ($HfAlO_x$) to simultaneously achieve a high dielectric constant and low leakage current by combining the advantages of HfO_2 and Al_2O_3.

There has been a growing body of research that explores $HfAlO_x$ films using the vacuum-based deposition method [9-11]. Although the vacuum-based deposition method has advantages, the high fabrication cost restricts its areas of application. The solution process offers the advantages of low cost and component controllability.

Up to date, few studies had reported $HfAlO_x$ film coating using the solution process. Particularly there has not been intensively investigated on the electrical characteristics of solution-processed $HfAlO_x$ gate insulators with various ratios of Hf and Al for oxide TFT. Therefore, to further explore the practical application of $HfAlO_x$ gate dielectric, it will be very interesting to investigate the properties of $HfAlO_x$ film coating by low-cost and component-controlled sol-gel methods.

2 Experiment

2.1 Precursor solution synthesis

The $HfAlO_x$ precursor solutions were synthesized by dissolving hafnium dichloride oxide octahydrate ($HfCl_2O \cdot 8H_2O$) and aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) in 2-methoxyethanol (2-ME) of 5 ml as a solvent. The molar ratio of Hf:Al was HfO_x, 3:1, 1:1, 1:3, AlO_x, and the total concentration was 0.2 M. The HCl-added precursor solutions were prepared by adding 35 % HCl of 1 ml to the prepared $HfAlO_x$ precursor solutions. The a-IGZO precursor solution was prepared by dissolving indium nitrate hydrate ($In(NO_3)_3 \cdot xH_2O$), gallium nitrate hydrate ($GaN_3O_9 \cdot xH_2O$), and zinc acetate dehydrate ($Zn(C_2H_3O_2)_2 \cdot 2H_2O$) in 2-ME as a solvent. The total concentration was 0.15 M, and the molar ratio of indium:gallium:zinc was 7:1:2. All precursor solutions were stirred at 75 °C for 11 h 30 min and filtered through a 0.1 μm polytetrafluoroethylene (PTFE) syringe filter before spin coating.

2.2 Device fabrication

A heavily doped p-type silicon wafer was used as a substrate for the fabrication of a metal-insulator-metal device. The substrate was cleaned using an ultrasonic cleaner in acetone, isopropyl alcohol, and deionized water and treated with UV/ozone for 15 min. The $HfAlO_x$ precursor solution was spin-coated on the UV ozone-treated substrate at a rotation speed of 3000 rpm for 30 s, and the solvent was removed by baking at 200° C for 10 min. After repeating this process three times, the

$HfAlO_x$ film with HCl added was annealed at 450° C for 1 h under ambient air conditions. Then, a 70 nm aluminum top electrode was deposited on the $HfAlO_x$ film by thermal evaporation using a shadow mask.

a-IGZO TFTs with bottom gate and top contact structures were fabricated using $HfAlO_x$ with HCl addition of 1 ml as the gate insulator layer. The synthesized $HfAlO_x$ solution was deposited by spin coating at 3000 rpm for 30 s, and the solvent was evaporated by baking at 200 °C for 10 min, and this process was repeated three times. The deposited film was annealed at 450 °C for 1 h in ambient air conditions. The synthesized a-IGZO solution was spin-coated on the gate insulator at 4000 rpm for 30 s. The a-IGZO film was treated with UV/ozone for 2 h to improve the properties of the IGZO film. They were then annealed at 350 °C in ambient air for 3 h and patterned by photolithography. 70 nm thick aluminum source and drain electrodes were deposited by thermal evaporation through a shadow mask. The channel width (W) and length (L) are 1000 μm and 200 μm, respectively.

2.3 Device characterization

The physical properties were investigated using atomic force microscope (AFM, NX-10, PSIA) and X-ray photoelectron spectroscopies (XPS, ESCALAB 250, Thermo Scientific) to obtain the surface morphology, chemical bonding of the $HfAlO_x$ films. The electrical properties such as capacitance-voltage (C-V) and current-voltage (I-V) characteristics of solution-processed $HfAlO_x$ thin films and a-IGZO TFTs were measured using an Agilent 4284A LCR meter and an Agilent 4145B semiconductor under dark ambient conditions. Transfer characteristics (I_D-V_G) were measured by sweeping V_G from -2 V to 5 V at V_D=1 V. C-V characteristics were measured by sweeping V_G from -2 V to 2 V. The electrical parameters of the samples were extracted from the transfer curves and C-V curves at room temperature.

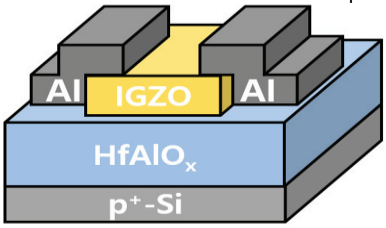

Fig. 1 Schematic of the a -IGZO TFTs using the $HfAlO_x$ as gate insulator

3 Results and discussions

Fig. 2 shows the leakage current density (I_{leak}) of solution-processed $HfAlO_x$ film of Hf:Al=1:1 ratio without and with the presence of HCl. The leakage current density was reduced from 1.67×10^{6} to 0.51×10^{9} A/cm^2 at 0.5 MV/cm by adding HCl to the precursor solution. In addition, a low breakdown voltage of 0.76 MV/cm showed for $HfAlO_x$ film, but a breakdown voltage was not observed even at 2.5 MV/cm for $HfAlO_x$ film with HCl addition. This result of the improved leakage current is attributed to HCl acting as a catalyst to increase metal oxide bonding, thereby reducing oxygen vacancy, and improving insulation [12].

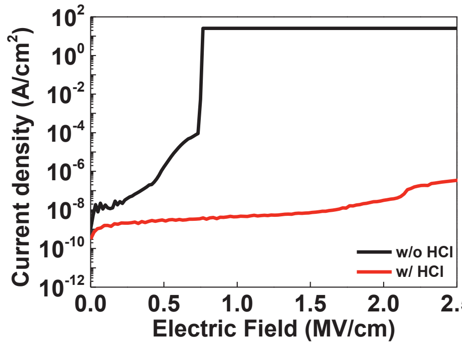

Fig. 2 Leakage current density of Al/$HfAlO_x$/p+Si devices without or with HCl

To analyze the result of the decrease in leakage current density of the $HfAlO_x$ film with HCl addition, the $HfAlO_x$ thin film in the molar ratio of Hf:Al=1:1 was investigated through XPS as shown in Fig. 3. The deconvolution results of the O1s peak of the $HfAlO_x$ film produced two peaks centered at 530.4 and 532.1 eV. The peak centered at 530.4 eV corresponds to a metal oxide (Hf-O-Al) bond that represents the form of a complete metal-oxygen bond. The peak centered at 532.1 eV can be expected to be associated with oxygen vacancies (V_O) related to oxygen with incomplete bonds [12, 13]. As the addition of HCl to the $HfAlO_x$ film, the fraction of Hf-O-Al bonds increases from 75.37% to 78.96%, and the fraction of V_O decreases from 24.43% to 21.03%. These results indicate that HCl acts as a hydrolysis catalyst to cause a rapid oxidation reaction, and the addition of HCl accelerates the formation of metal oxide bonds in the $HfAlO_x$ film. In addition, V_O refers to a defect state that can act as a path through which a leakage current flows, and a decrease in V_O means that there are few defect states in the $HfAlO_x$ film. Therefore, it is possible to decrease the V_O by increasing the formation of Hf-O-Al bonds, which reduces the number of defect states and suppress the leakage current density through the $HfAlO_x$ film.

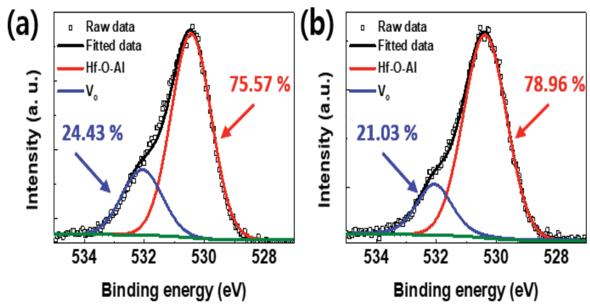

Fig. 3 XPS spectra for O1s core levels from $HfAlO_x$ films (a) without HCl and (b) with HCl

Fig. 4 displays the leakage current density (I_{leak}) and the dielectric constant (k) of solution-processed $HfAlO_x$ film of various ratios of Hf and Al with the addition of HCl. I_{leak} gradually decreases with increasing AlO_x contents, and 1.98×10^{-5}, 1.08×10^{-6}, 4.19×10^{-7}, 2.05×10^{-7}, 1.50×10^{-8} A/cm^2 at 2.5 MV/cm for HfO_x, Hf:Al=3:1, Hf:Al=1:1, Hf:Al=1:3, and AlO_x, respectively. A relatively wide bandgap of AlO_x affects the leakage current reduction. The average values of the dielectric constant are 9.20, 7.96, 7.28, 5.91, and 5.36, respectively. It is known that the dielectric constant of AlO_x is generally lower than that of HfO_x [8].

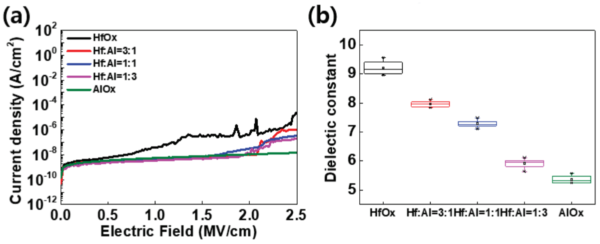

Fig. 4 (a) Current density and (b) dielectric constant of Al/$HfAlO_x$/p+Si devices with different $HfAlO_x$ film with HCl

The surface morphologies of the $HfAlO_x$ dielectric films were also investigated by AFM, which are shown in Fig. 5(a)–(e). The root-mean-square (RMS) values of the roughness are 0.86, 0.48, 0.43, 0.39, and 0.23 nm for HfO_x, Hf:Al=3:1, Hf:Al=1:1, Hf:Al=1:3, and AlO_x, respectively. The surface roughness of the gate insulator layer is an important factor related to electrical properties such as breakdown voltage and subthreshold swing (SS). The increased breakdown voltage from HfO_x to AlO_x film is probably due to the surface properties because the non-uniform surface condition increases the local electrostatic field and causes high leakage current. In particular, the surface becomes smoother with an increment of the AlO_x content, which is assumed to result in a smaller radius of aluminum ions than that of hafnium ions, and the volume of the film structure is contracted upon AlO_x addition [10].

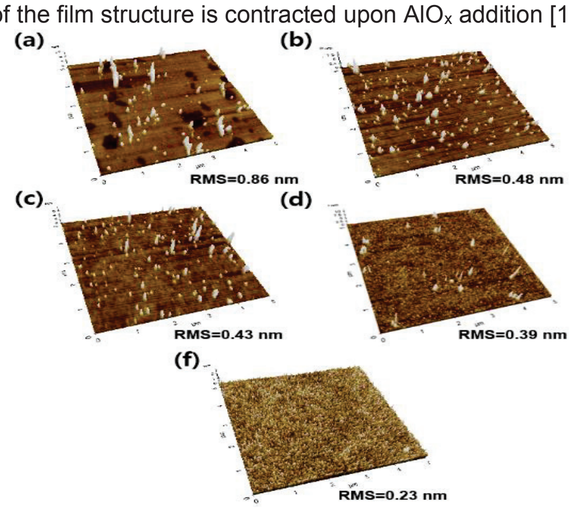

Fig. 5 Surface morphology of (a) HfO_x, (b) Hf:Al=3:1, (c) Hf:Al=1:1, (d) Hf:Al=1:3 and (e) AlO_x films

Fig. 6 illustrates the transfer characteristics of the solution-processed a-IGZO TFTs for $HfAlO_x$ films with various ratios as the gate insulator layer. The electrical parameters of the average value are listed in Table 1. The V_{th} shifts in the negative voltage direction as the HfO_x content increase. As the content of HfO_x increases, the capacitance increases. The higher capacitance requires a smaller gate voltage to fully deplete the active layer. Therefore, high capacitance caused a lower V_{th}. [13]. Field-effect mobility (μ_{FE}) increased from 2.48 to 3.63 cm^2 /V·s with increasing HfO_x contents. In general, as the capacitance of the gate insulator increases, the μ_{FE} of solution-processed oxide TFTs increases because of the variable-range-hopping percolation model [14]. Because the increment of capacitance makes electrons rapidly fill the lower-lying localized states, which allows the additionally accumulating electrons to occupy the upper-lying localized states. Consequently, the electrons easily jump to the neighboring localized states in the percolating path, which result in increasing μ_{FE}. The subthreshold swing (SS) decreases with increasing AlO_x content. It indicates that the number of defect states is reduced in the $HfAlO_x$/a-IGZO interface by increasing the AlO_x contents. It can be confirmed that the interface quality improved through the increase of the AlO_x content as shown in Fig. 6. The leakage current density decreases as the AlO_x content increases in the $HfAlO_x$ film, and the I_{off} of the different $HfAlO_x$ films are 2.9×10^{-10}, 7.07×10^{-11}, 6.29×10^{-11}, 5.35×10^{-11}, 3.11×10^{-11} at -2 V for HfO_x, Hf:Al= 3:1, Hf:Al=1:1, Hf:Al=1:3, and AlO_x, respectively. Because the barrier height of Hf:Al=3:1, Hf:Al=1:1, Hf:Al=1:3, and AlO_x films are higher than that of HfO_x film, leakage current can also be suppressed [11]. Comparing electrical properties of different $HfAlO_x$ films, a-IGZO TFT with $HfAlO_x$ gate insulator of Hf:Al=1:1 exhibited excellent electrical properties, such as μ_{FE} of 2.59 cm^2/V·s, SS of 0.08 V/dec, and I_{on}/I_{off} ratio of 1.50×10^7.

Table. 1 Summary of extracted parameters of a-IGZO TFTs with different $HfAlO_x$ gate insulators

	V_{th} (V)	$\mu_{lin.}$ (cm^2/V·s)	SS (V/dec)	I_{on}/I_{off}
HfO_x	0.03	3.46	0.13	1.01×10^6
Hf:Al=3:1	0.15	3.39	0.08	1.27×10^7
Hf:Al=1:1	0.22	2.95	0.08	1.50×10^7
Hf:Al=1:3	0.24	2.88	0.08	5.01×10^6
AlO_x	0.28	2.48	0.07	3.24×10^6

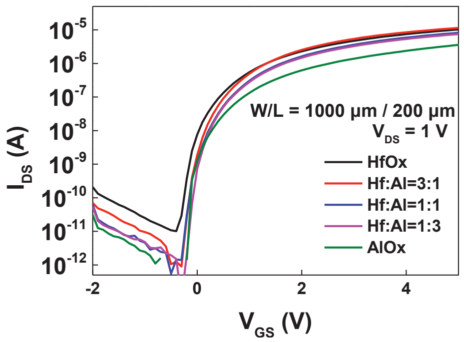

Fig. 6 Transfer characteristics of a-IGZO TFT with different $HfAlO_x$ films

4 Conclusions

a-IGZO TFT with different ratios of $HfAlO_x$ dielectric films with HCl addition were fabricated by solution process. The leakage current decreased from 1.98×10^{-5} to 1.50×10^{-8} A/cm^2 at 2.5 MV/cm with increasing AlO_x content and the mobility increased from 2.48 to 3.46 cm^2/V·s with increasing HfO_x content. Furthermore, the a-IGZO TFTs using $HfAlO_x$ gate insulator with the molar ratio of Hf:Al=1:1 exhibited superior current-driving capability with high μ_{FE} and I_{on}/I_{off} ratio, because the dielectric properties were improved by adding HCl to the $HfAlO_x$ film.

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