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Characterization of a Solution-processed YHfZnO Gate Insulator for Thin-Film Transistors

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Abstract

A solution-processed multicomponent oxide, yttrium hafnium zinc oxide (YHZO), was synthesized and deposited as a gate insulator. The YHZO film annealed at 600°C contained an amorphous phase based on the results of thermogravimetry, differential thermal analysis, and X-ray diffraction. The electrical characteristics of the YHZO film were analyzed by measuring the leakage current. The high dielectric constant (16.4) and high breakdown voltage (71.6 V) of the YHZO films resulted from the characteristics of HfO_2 and Y_2O_3, respectively. To examine if YHZO can be applied to thin-film transistors (TFTs), indium gallium zinc oxide TFTs with a YHZO gate insulator were also fabricated. The desirable characteristics of the YHZO films when used as a gate insulator show that the limitations of the general binary-oxide-based materials and of the conventional vacuum processes can be overcome.

Keywords: oxide compound, yttrium hafnium zinc oxide, solution process, gate insulator, TFT, electron affinity

1. Introduction

There are extensive reports on the use of binary-oxide-based materials such as HfO_2 [1], Y_2O_3 [2], Al_2O_3 [3], and ZrO_2 [4] as gate insulators in thin-film transistors (TFTs). The fabrication of gate insulators using these high-k dielectric materials increases both the capacitance, which improves the "on" current of the TFT, and the thickness, which simultaneously reduces the tunneling leakage current. Nevertheless, some disadvantages of using a binary oxide remain, such as its easy crystallization at a low temperature and the trade-off between the dielectric constant and breakdown voltage [5-7]. For example, although HfO_2 and ZrO_2 have higher dielectric constants than Y_2O_3 and Al_2O_3, they tend to have low breakdown voltages due to their large electron affinity. For these reasons, a multicomponent oxide was recently proposed as a solution [5-7].

Moreover, most methods that are used to deposit oxide-based materials as gate insulators involve the conventional vacuum processes, which are expensive or are limited to large-area deposition, such as pulse laser deposition [1], radio frequency DC magnetron sputtering [2], and atomic-layer deposition [3]. Solution processes are promising because of their simplicity, reduced cost, smooth surface, and good uniformity [8]. They are especially effective at accurately controlling the composition ratio for synthesizing multicomponent oxides.

This paper reports the characteristics of an yttrium hafnium zinc oxide (YHZO) film and the results of the analysis of oxide-based TFTs with YHZO. The desirable characteristics of this solution-processed multicomponent oxide when used as a gate insulator can ultimately result in its replacement of binary-oxide-based materials and of the conventional vacuum processes.

2. Experiment

The YHZO solution was synthesized by dissolving 0.1 M yttrium nitrate hexahydrate [$Y(NO_3)_3{\cdot}6H_2O$], 0.1 M hafnium chloride [$HfCl_4$], and 0.1 M zinc acetate dihydrate [$Zn(OAc)_2{\cdot}2H_2O$] in 25 mL 2-methoxyethanol (2ME). Monoethanolamine ($NH_2CH_2CH_2OH$) was added as a stabilizer, and acetic acid [CH_3COOH] was dropped into it to make a homogenous solution. The mixture was stirred for 1 h at 70°C and aged for at least 24 h. The mole ratio of Y:Hf:Zn was fixed at 3:1:1 to focus on the insulating prop-

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erties as a gate insulator rather than on the dielectric constant.

To prepare the TFTs, the conventional inverted staggered structure was used, and a heavily arsenic (n^+)-doped silicon wafer was used as a gate electrode. The YHZO solution was filtered through a 0.2-μm microfilter and was spin-coated at a speed of 3000 rpm for 30 s. The YHZO film was pre-annealed at 200°C for 5 min on a hot plate and was annealed at 600°C for 1 h in air ambient, using a furnace. The spin-coating and annealing procedures were repeated 15 times to optimize the electrical characteristics as a gate insulator. The indium gallium zinc oxide (IGZO) channel layer was deposited by spin-coating and was then annealed at 550°C for 2 h. The mole ratio of In:Ga:Zn was fixed at 3:1:2. Al metal was deposited using a thermal evaporator as the source and drain electrodes. The channel length (L) and width (W) of these TFTs were 100 and 1000 μm, respectively.

3. Results and Discussion

Thermogravimetry and differential thermal analysis (TG-DTA) was performed as shown in Fig. 1. The first endothermic reaction was observed within the range of 50-160°C and was accompanied by large weight loss due mainly to the removal of 2ME and the partial dissociation of zinc acetate into zinc monoacetate [9]. At 180-310°C, the second endothermic reaction occurred, indicating that the yttrium nitrate and hafnium chloride started to decompose and that the zinc monoacetate was completely converted into metal hydroxide [9, 10]. The exothermic peak at 370-380°C indicates that the metal hydroxides formed a multicomponent oxide via alloying. Simultaneously, small weight loss resulted from the dehydroxylation of the metal hydroxides, as shown in the inset of Fig. 1. Both the exothermic peak in the DTA curve and the weight loss in the TG curve, however, were much smaller than those for a general multicomponent oxide solution [10, 11], corresponding to the partial formation of YHZO crystals in this temperature region.

Fig. 2(a) shows the X-ray diffraction (XRD) pattern of the YHZO film annealed at 600°C to examine the possibility of crystallization. The (1 1-2) and (4 2-2) peaks, ascribed to the crystal phase of Y_2O_3, were observed at 33 and 62°, respectively. Based on these results, it is believed that the YHZO film did not completely form a multicomponent oxide, which coincides with the TG-DTA results. The yttrium was partially segregated and crystallized as Y_2O_3 because of the relatively large amount in the YHZO

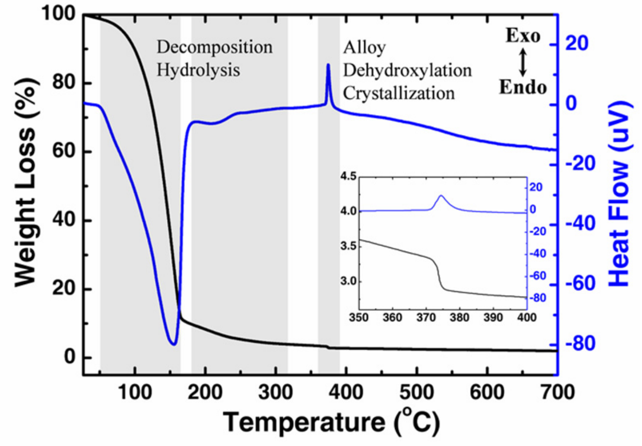

Fig. 1. TG-DTA curve of the YHZO solution.

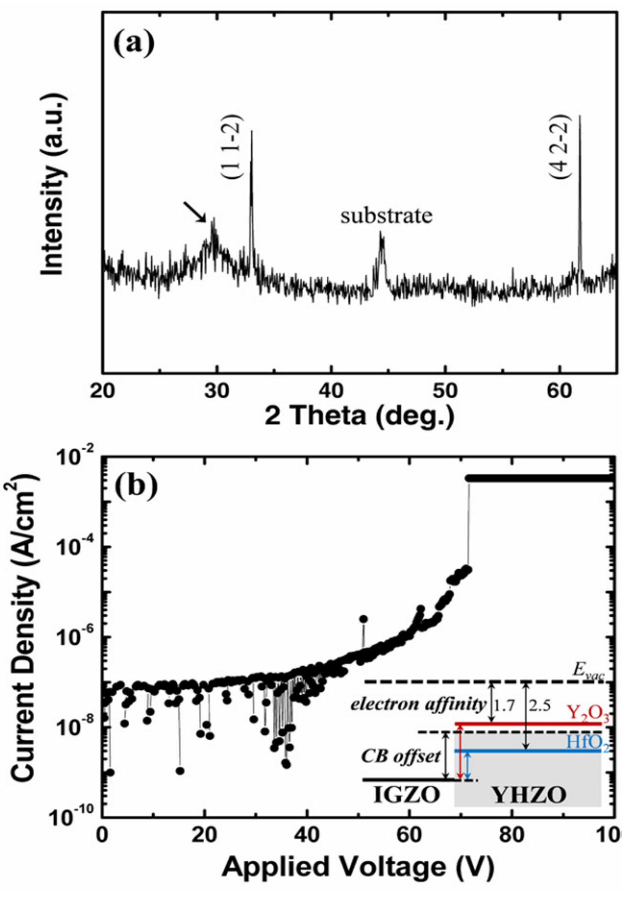

Fig. 2. (a) XRD pattern and (b) leakage current density of the YHZO film annealed at 600°C.

solution and because it has a lower crystallization temperature than hafnium [12, 13]. The small, broad peak seen near 30° (the arrow in Fig. 2(a)) is related to the (4 0 1) of Y_2O_3 or the (1 1 1) of $Y_2Hf_2O_7$. This peak is interpreted as an amorphous or nano-crystalline phase. No peaks ascribed to other material or crystal phases are observed in this XRD profile. Although the crystallization temperatures of the binary oxide Y_2O_3 [12] and HfO_2 [13] films deposited using the solution process were 400-500 and 500-550°C, respectively, the multicomponent oxide YHZO film was maintained in an amorphous phase despite annealing at 600°C. This may be due to the suppression of crystallization by the Y, Hf, and Zn in the YHZO film because of their different atomic radii and crystal phases. The crystal phases of Y, Hf, and Zn are cubic [12], monoclinic [13], and hexagonal [9], respectively, when grown through a solution process.

The electrical characteristics of the metal-insulator-metal structure (MIM) with the YHZO film were also analyzed by measuring the leakage current, as shown in Fig. 2(b). The leakage current density of the YHZO film was about $\sim 10^{-8}$ A/cm^2. This sufficiently low value for application in TFTs as a gate insulator was obtained for several reasons. The YHZO film formed a thin, dense film because of the low molarity of the YHZO solution, and the smooth surface resulted from the use of the spin-coating method and from annealing at a high temperature. The smooth surface of the YHZO film was confirmed via atomic-force microscopy, as shown in Fig. 3(a). The root-mean-square roughness, when deposited 15 times with annealing at 600°C, was 0.164 nm. Typically, the electric field increases from the valley to the peak of a rough surface, and the leakage current density increases exponentially with the increase in the electric field [14]. For these reasons, there is a low average leakage current density due to the net effect of the smooth surface and the low porosity of the YHZO film.

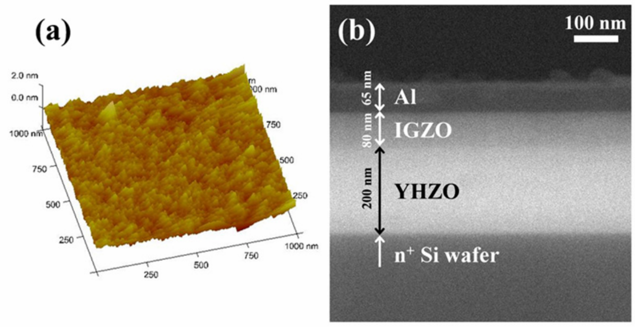

Fig. 3. (a) AFM image of the YHZO film. (b) Cross-sectional SEM image of the IGZO TFT with a YHZO gate insulator.

The breakdown voltage of the YHZO film was 71.6 V, which indicates that the breakdown takes place at an electric field of 3.58 MV/cm. The conduction band (CB) offset of oxide materials is generally smaller than the valence band offset, and both of these are related to the carrier injection into the oxide bands [6]. The CB offset of the YHZO film was considered due to the IGZO channel, which behaved as an n-channel transistor, as shown in the band diagram in Fig. 2(b). The relatively small electron affinity of Y_2O_3 [7] and the large amount of yttrium in the YHZO solution could have caused the high breakdown voltage of the YHZO film. Moreover, the performance of several depositions to optimize the film thickness may have also resulted in a high breakdown voltage. This process was performed via direct sequential deposition to prevent the surface from changing from hydrophilic to hydrophobic [12, 13]. As shown in the scanning electron microscopy (SEM) image in Fig. 3(b), the YHZO film was about 200 nm thick, and the deposition was done well. Here, the backscattered electron imaging (BSE) mode was used to distinguish the individual layers.

When the solution-processed YHZO film was annealed at 600°C, it showed an amorphous phase, with a dielectric constant of about 16.4 obtained via the capacitance-voltage measurement of the MIM structure (in a previous study [15]), a low leakage current density, and a high breakdown voltage, achieved by using a multicomponent oxide. Based on the possible application of a YHZO film as a gate insulator, oxide-based TFTs were also fabricated.

Fig. 4 shows the drain current (I_{DS})-gate voltage (V_{GS}) transfer characteristic of IGZO TFTs with a YHZO gate insulator. The field effect mobility in the saturation region (μ_{sat}) and the threshold voltage (V_{th}) calculated by fitting a straight line to the plot of the square root of I_{DS}-V_{GS}, were 0.29 cm^2/Vs and 3.45 V, respectively. The on-to-off current ratio was 1.22×10^5, and the subthreshold swing (S) was 0.80 V/decade. In particular, the maximum interface trap states (N_{SS}) were also analyzed for this S value, using eq. (1) [16].

$$N_{SS}^{\max} = \left(\frac{S\log(e)}{kT/q} - 1\right)\frac{C_i}{q}, \qquad (1)$$

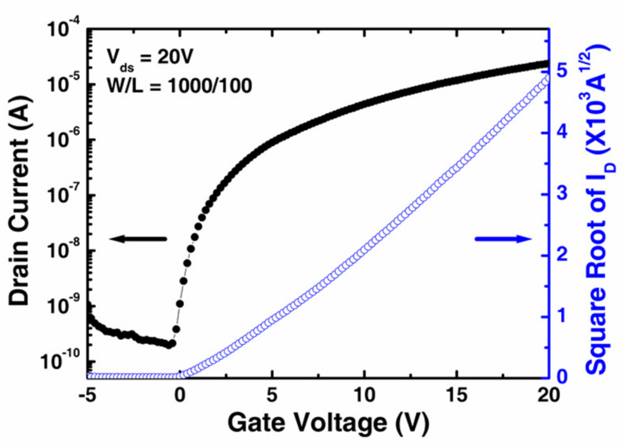

Fig. 4. Drain current-gate voltage transfer characteristic of the IGZO TFT with a YHZO gate insulator (L = 100 μm and W = 1000 μm).

where *k* is the Boltzmann constant, *T* is a room temperature, C_i is the gate insulator capacitance per unit area, and q is the elementary charge. This calculation indicates that N_{SS} had a relatively large value of 1.44×10^{14} cm^{-2} compared to an IGZO TFT with a conventional gate insulator [10] due to the rough interface. It caused trap charges between the nano-crystalline grains of the IGZO [10] and the partially segregated and crystallized Y_2O_3. These results suggest that the electrical performance of solution-processed YHZO films and IGZO TFTs with YHZO may be improved by optimizing the mole ratio of Y:Hf:Zn.

4. Conclusion

In summary, a YHZO solution was synthesized for a gate insulator, and IGZO TFTs with a YHZO gate insulator were fabricated. The YHZO film, a multicomponent oxide, has many advantages, such as an amorphous phase despite annealing at a high temperature, high-k properties, and good interface adhesion with an IGZO channel. The YHZO film annealed at 600°C was confirmed to have a low leakage current density of ~10^{-8} A/cm^2 and a high breakdown voltage. The transistor parameters μ_{sat}, on-to-off current ratio, V_{th}, and S were 0.29 cm^2/Vs, 1.22×10^5, 3.45 V, and 0.80 V/decade, respectively. These desirable characteristics of a multicomponent oxide as a gate insulator may overcome the limitations of binary-oxide-based materials and the conventional vacuum processes.

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