A Study of Spin coated a-IGZO TFT with Y-doped ZrO₂ Gate Insulators

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ABSTRACT

In this study, an indium gallium zinc oxide (IGZO) thinfilm transistor (TFT) based on Yttrium-doped ZrO₂ dielectric was studied. We revealed that a-IGZO/1:8 Ydoped ZrO₂ TFT deteriorated compared to a-IGZO/ZrO₂ TFT. On the other hand, a-IGZO/1:2 Y-doped ZrO₂ TFT had better overall properties than a-IGZO/ ZrO₂ TFT.

1 Introduction

Oxide semiconductor have attracted a lot of attention as a channel material of a thin film transistor. Because oxide semiconductor has superior electrical properties such as high field effect mobility, wide area uniformity, wide band gap, low temperature processability and solution processability compared to conventional Si TFTs [1]. Among them, amorphous indium gallium zinc oxide (a-IGZO) has attracted a lot of attention as it is recognized as an ideal TFT channel material for devices requiring high I_{on}/I_{off} ratio, high mobility at room temperature [2].

As integration and scaling accelerate, it becomes difficult to have the required low leakage current and high capacitance with ZrO_2 or HfO_2 alone.

Among them, there have been many studies to add Al2O3 with a large bandgap to improve the high leakage current characteristics of ZrO2 and HfO2, which are wellknown high-k materials [3, 4]. However, Al₂O₃ has a lower dielectric constant than ZrO₂. So, there is a disadvantage that the dielectric constant is reduced. On the other hand, Y-doped ZrO₂ has a leakage current lower and a higher dielectric constant than ZrO₂ at the same time. This is because Y has a larger ionic radius and lower electronegativity compared to Zr, which promotes large relaxation of adjacent O atoms in Y-doped ZrO₂. This shifts the charge state of the oxygen vacancies into the conduction band rather than the bandgap. In addition, Zr⁴⁺ ions are replaced by Y3+ ions, which introduce oxygen vacancies to compensate for the change of total charges, rearranging adjacent atoms of oxygen vacancies [5, 6]. So, unlike oxygen vacancy in other insulating films, it acts as a stabilizer in Y-doped ZrO₂.

Previous studied of adding Y₂O₃ to ZrO₂ mainly used pulsed lasers, ALD, and RF magnetron sputtering [5, 7, 8]. However, these equipments require a vacuum, making it difficult to process in the air. In particular, it was difficult to analyze the characteristics of different Y doping concentrations because pulse laser and RF magnetron sputtering require ceramic targets. However, the spin coating may be manufactured in the atmosphere, and characteristics according to the Y doping concentration may be analyzed.

In this study, an a-IGZO TFT with ZrO₂ having various Y doping ratios as a gate insulator was manufactured by spin coating and various analyzes were performed.

2 Experiment

2.1 Precursor Solution Synthesis

A 0.3 M ZrO₂ solution was synthesized by dissolving Zirconium(IV) Oxynitrate Hydrate (ZrO(NO₃)₂· xH₂O) in 2-Methoxyethanol (CH₃OCH₂CH₂OH). Also, 0.3 M Yttriu m-doped ZrO₂ solution was synthesized by dissolving Zi rconium(IV) Oxynitrate Hydrate(ZrO(NO₃)₂· xH₂O) and Y ttrium(III) nitrate hexahydrate(Y(NO₃)₃· 6H₂O) in 2-Meth oxyethanol (CH₃OCH₂CH₂OH). A 0.3 M of Y-doped ZrO 2 solution is mixed with Yttrium and Zirconium in a ratio of 1:8, 1:4, 1:2, respectively.

The a-IGZO solution was prepared by dissolving Indi um(\mathbb{II}) nitrate hydrate (In(NO₃)₃·xH₂O), Gallium(\mathbb{II}) nitr ate hydrate (Ga(NO₃)₃·xH₂O), and zinc acetate dihydrat e (Zn(CH₃COO)₂·2H₂O) in 2-methoxyethanol at a molar concentration of 0.1 M. The component ratio of In:Ga:Zn is 7:1:2. All solutions were stirred on a hot plate at 75°C for 12 hours and were filtered through a 0.1 μ m polytetr afluoroethylene (PTFE) syringe filter before spin coating.

2.2 Device Fabrication

The structure of a-IGZO TFTs with Y-doped ZrO₂ die lectric is shown in Fig. 1. Heavily doped p-type silicon w afer was used both as a substrate and as a gate electro de for the fabrication of TFT. The silicon wafer was clea ned with acetone, isopropyl alcohol, and deionized wate r in an ultrasonic cleaner for 20 minutes each. The UV/o zone treatment was performed for 10 minutes before spi n coating to remove organics on the surface of the silico n wafer and hydrophilize the surface. The ZrO₂ and 1:8, 1:4, 1:2 Y-doped ZrO₂ as gate insulators were spin-coat ed at 3000 RPM for 30 s on a silicon substrate. After co ating, the solvent was evaporated at 200 °C for 10 minut es to solidify. After repeating this two times, annealing p rocess was performed in s furnace at 800 °C for 1 hour. T he a-IGZO was spin coated at 4000 RPM for 30 s on gate insulator. The deposited films were annealed for 2 hours in UV/ozone treatment. Then, annealing process was perf ormed at 350 °C for 3 hours on a hot plate. The annealed a-IGZO films were patterned using photolithography. The wet etching was performed using HCI as etchant. The Al source-drain electrodes were deposited using a shadow mask via thermal evaporation. The channel width (W) and length (L) in this experiment are 1000 μ m and 200 μ m, re spectively. This shadow mask also has a circular shadow mask with an area of 0.0196cm² for capacitance measure ment.



Fig. 1 Schematic of the a-IGZO/ZrO₂ TFT and a-IGZO/Y-doped ZrO₂ TFTs.

3 Results

Fig. 2 shows the XRD patterns of ZrO_2 and Y-doped ZrO_2 fabricated by solution process. It can be seen that pure ZrO_2 has two crystalline phases: monoclinic and tetragonal. The crystal structure of Y-doped ZrO_2 has tetragonal, tetragonal, and cubic phases, respectively. In this case, 1:8 Y-doped ZrO_2 has a peak intensity of tetragonal phase higher than 1:4 Y-doped ZrO_2 .

It can be seen that the crystalline phase is stabilized from the tetragonal to the cubic phase as the Y doping concentration is increased to 1:2 Y-doped ZrO_2 . However, in 1:1 Y-doped ZrO_2 , the crystal phase has a rhombohedral structure and is no longer stable. It indicates that crystal phase stabilization through Y doping of ZrO_2 is possible up to 1:2 Y-doped ZrO_2 . So, we investigated additional analysis only up to 1:2 Y-doped ZrO_2 .



Fig. 2 XRD patterns of ZrO₂ and Y-doped ZrO₂ gate insulators.



Fig. 3 (a)Stoichiometry O/(Zr+Y) and (b) Atomic percent of V_0 and O²⁻ ions.

By adding Y to ZrO_2 , some of the Zr^{4+} ions are replaced by Y³⁺ ions. As a result, three O²⁻ ions are replaced instead of four O²⁻ ions, resulting in oxygen vacancies. Therefore, Fig. 3 (a) shows that the O²⁻ ions decrease as the Y doping concentration increases.

As shown in Fig. 3 (b), it can be seen that O^{2-} ions and oxygen vacancies are inversely proportional. Oxygen vacancies are reduced at 1:8 Y-doped ZrO_2 compared to ZrO_2 . But beyond that, it shows that the oxygen vacancies increase as the Y doping concentration increase.

Fig.4 shows the AFM images of ZrO₂ films according to the different Y doping concentrations. The surface roughness of gate insulator is an important parameter affecting the interface between the channel layer and the insulator layer [9]. The surface roughness is 0.61 nm, 0.68 nm, 0.52 nm, and 0.46 nm, respectively. The surface roughness is similar for ZrO₂ and 1:8 Y-doped ZrO₂, but slightly rougher for 1:8 Y-doped ZrO₂. As the Y doping concentration increased, the surface roughness decreased. In other words, 1:2 Y-doped ZrO₂ film has the smoothest surface.



Fig. 4 AFM images of gate insulators: (a) ZrO₂, (b) 1:8 Y-doped ZrO₂, (c) 1:4 Y-doped ZrO₂, and (d) 1:2 Y-doped ZrO₂.



Fig. 5 (a) shows the dielectric constant of Metal-Insulator-Metal (MIM) structure. The dielectric constants are 7.5, 8.4, 8.69, and 9.83, respectively, as the Y doping concentration increases. This indicates that as the doping concentration of Y increases up to 1:2 Y-doped ZrO_2 , the ZrO_2 phase is stabilized and the dielectric constant increases from 7.5 to 9.83. This is because cubic and tetragonal phase have much higher dielectric constants than monoclinic phase.

Fig. 5 (b) show the leakage current density. Based on 2 V, leakage current densities are 8.93×10-9, 2.39×10-8, 3.29×10⁻⁹ and 1.99×10⁻⁹, respectively. 1:8 Y-doped ZrO₂ has a higher leakage current density than ZrO2. But the leakage current density decreases as the Y-doping concentration increases beyond that. As shown in Fig. 3 (b), the oxygen vacancies of 1:4 Y-doped ZrO₂ and 1:2 Ydoped ZrO₂ increase, but the leakage current density decreases. This is because, in Y-doped ZrO₂, the adjacent atoms in the oxygen vacancies are relaxed because Y has a larger ionic radius and lower electronegativity than Zr (this changes the crystal structure as shown in Fig. 4). Due to this, the oxygen vacancies introduced by Y doping move to the conduction band, not the energy bandgap. As a result, electron trapping and defect creation are suppressed [6]. On the other hand, in the case of 1:8 Ydoped ZrO₂, the Y doping concentration is insufficient. So, oxygen vacancies do not move properly in the conduction band and remain within the energy band gap.



Fig. 6 (a) Transfer Characteristics and (b) extracted Subthreshold Swing.

Fig. 6 (a) shows the I-V characteristics of a-IGZO/ZrO₂ TFT and a-IGZO/Y-doped ZrO_2 TFTs. The drain voltage was applied at 1 V.

In Fig. 6 (b), SS increased and then decreased at 1:8 Y-doped ZrO₂. As shown in Fig. 2 and 4, the crystalline phase is changed as atoms are rearranged due to Y doping, which causes the surface roughness of the gate insulator to change. As the surface roughness of the gate insulator increases, the defect state creation at the gate insulator/channel interface increases, leading to an increase in SS. This can be confirmed through the similar tendency of Fig. 4 and Fig. 6 (b).

Table. 1 Average of electrical parameters.

Y:Zr	V _{тн} (V)	μ _{lin} (cm²V ⁻¹ s ⁻¹)	I _{on} /I _{off}	SS (V/dec)
ZrO ₂	1.68	0.55	1.84×10⁵	0.3
1:8	2.35	0.34	8.96×10 ⁴	0.37
1:4	2.1	0.46	1.87×10⁵	0.27
1:2	1.88	0.77	6.43×10⁵	0.22

Table.1 shows the average of the electrical parameters. The a-IGZO/1:8 Y-doped ZrO₂ TFT had the lowest μ_{lin} and l_{on}/l_{off} ratio. And it had the biggest V_{TH} and SS. On the other hand, a-IGZO/1:2 Y-doped ZrO₂ TFT had better overall properties than a-IGZO/ZrO₂ TFT. Compared to the conventional a-IGZO/ZrO₂ TFT, the a-IGZO/1:2 Y-doped ZrO₂ TFT increased μ_{lin} by about 1.4 times, the l_{on}/l_{off} ratio increased by about 3.49 times, and SS decreased by about 0.73 times.

4 Conclusions

We fabricated a-IGZO/Y-doped ZrO_2 TFTs. As the doping concentration of Y increases up to 1:2 Y-doped ZrO_2 , the monoclinic phase stabilizes into the cubic phase. However, as can be seen from the TFT transfer characteristic, the characteristic deteriorates at 1:8 Y-doped ZrO_2 . This is because the oxygen vacancies acting as stabilizers in Y-doped ZrO_2 were the least in 1:8 Y-doped ZrO_2 . Therefore, adding Y in a ratio of 1:8 to ZrO_2 is not sufficient to stabilize ZrO_2 .

In this study, Y doping concentration with superior properties than pure ZrO₂ was studied. As a result, compared to the conventional a-IGZO/ZrO₂ TFT, the a-IGZO/1:2 Y-doped ZrO₂ TFT increased μ_{lin} by about 1.4 times, the l_{on}/l_{off} ratio increased by about 3.49 times, and SS decreased by about 0.73 times. And the dielectric constant improved from 7.5 to 9.83. Therefore, we propose that 1:2 Y-doped ZrO₂ has excellent properties as gate insulators of a-IGZO TFTs.

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