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Effects of Annealing on an IGZO-Metal Interface

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The interface reaction between a metal layer and a layer of amorphous indium-gallium-zinc oxide was investigated. Oxygen atoms at the interface bond to the metal atoms and form metal oxide. The reaction depends on the annealing temperature and ambient conditions. The thickness of the metal oxide at the interface increased with the annealing temperatures. The reaction relies on the Gibbs free energy for oxidation. Ta, which has low Gibbs free energy formed a 33 nm layer of tantalum oxide at an annealing temperature of 450 °C. The HR-TEM and EDX observation showed that the metal oxide thicknesses were 5, 10, and 33 nm at annealing temperatures of 350, 400, and 450 °C, respectively. The thicknesses obtained with both Ar and oxygen gas were 4, 8, and 21 nm, respectively. The lower oxide thicknesses were attributed to the lower number of oxygen vacancies in the IGZO deposited using Ar and oxygen, which was identified by XPS analysis.

Keywords: Interface, Oxidation, Oxide Semiconductor, Tantalum.

1. INTRODUCTION

Thin-film transistors (TFTs) are widely used in display backplanes and TFTs based on silicon are the most common. Amorphous silicon TFTs are mainly used for active matrix liquid crystal displays (AMLCDs), and polycrystalline silicon TFTs are mainly used for active matrix organic light emitting diode (AMOLED) displays. Recently, oxide TFTs have been used for AMOLED televisions due to their higher mobility than amorphous silicon TFTs and lower processing costs than poly crystalline silicon TFTs. The most common material for oxide TFTs is amorphous indium-gallium-zinc oxide (a-IGZO) [1–4].

Since high contact resistance reduces the drain current, low contact resistance is important for high-performance TFTs. In silicon based TFTs, ohmic contact is accomplished by a highly doped region of silicon. The highly doped silicon reduces the contact resistance between the silicon and source/drain metal electrodes due to the narrow Schottky barrier.

In amorphous IGZO TFTs, the source/drain metal is in contact with IGZO oxide. Ohmic contact between the metal and IGZO layers is important and has been investigated to improve the performance of IGZO TFTs [5–13]. The metal atoms that contact the IGZO become oxidized, and the oxide cations reduce their oxidation state. These interfacial oxidations form a thin metal oxide layer in the source/drain contact, which increases the contact resistance [11–13]. The oxygen in IGZO bonds to metal atoms which leads to a thin metal-oxide layer that increases the contact resistance of oxide TFTs.

For a certain metal such as Al, a thin metal oxide layer between IGZO and metal is observed immediately after sputter deposition. During the deposition, thin metal oxide formed at the interface between the IGZO and metal [12]. High temperature annealing after deposition also thickens the metal oxide through additional oxidation. It is important to understand the oxidation process between IGZO and metal electrodes to control the source/drain contact resistance. Ta has the lowest oxide formation energy among several metals such as Al, Ti, Mo, Ta. Therefore, Ta has large tendency to be oxidized and tantalum oxide is an important dielectric material in terms of high dielectric insulator. The oxidation behavior of Ta has been investigated by many researchers including the stress effect of the oxidation to Ta film [14–20]. In device, Ta based materials have been found suitable as barriers against Cu diffusion and usually contacts to insulator and the reaction of Ta with insulator is also important. Therefore, the reaction of Ta with SiO_2 have been investigated, also. The Ta interacts with SiO_2 to form tantalum oxide or tantalum silicide [20]. In IGZO TFT, the interfacial reaction occurs between Ta and IGZO layer. In this study, interfacial oxidation of Ta was investigated in terms of the thin insulator. *An interfacial oxide is very thin and useful for the very thin*

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Figure 1. Cross sectional structure of a sample.

dielectric devices including MOSFET (metal oxide semiconductor field effect transistor) and MIM (metal insulator metal) devices. Thin insulator is a mostly important issues in the scaling down of electronic devices as well as IGZO TFT. The scaling includes the decrease of the gate insulator thickness of MOSFET which is the most widely used device. The thinner gate dielectric of the MOSFET provides faster speed and less power which are essential requirements in circuits. For the application to the electronic devices, the control of its thickness and electronic properties are important. The high dielectric constant of the tantalum oxide is an additional advantage of the interfacial oxide in the realization of the low voltage devices. In TFT also, thin gate insulator provides high speed and less power in the circuit applications.

2. EXPERIMENTAL DETAILS

A 100 nm thick Ta layer was deposited on a cleaned glass substrate by DC magnetron sputtering without substrate heating. The process pressure was 5 mTorr with an Ar flow rate of 20 sccm. A 23 nm IGZO layer was deposited on the Ta layer by RF magnetron sputtering at a substrate temperature of 250 °C. The target ratio of the In_2O_3: Ga_2O_3: ZnO composition was 1:1:1 for the IGZO and the process pressure was 6 mTorr.

Two kinds of IGZO layers were prepared: one that was sputtered with Ar gas only (30 sccm) and another that was sputtered with Ar and O_2 gas (Ar: O_2 = 22.5 sccm:7.5 sccm). After deposition of the IGZO layer, it was annealed for 1 hour at temperatures from 350 to 450 °C under O_2 atmosphere. After annealing, top metal electrodes with 0.8 mm diameter were deposited with a shadow mask, as shown in Figure 1. The interface was investigated by high resolution transmission electron microscope (HR-TEM) and energy dispersive X-ray spectroscopy (EDX). The currents between bottom metal and top metal were measured under dark condition to characterize the electrical property of the interface. The IGZO oxygen bonds were investigated by X-ray photoelectron spectroscopy (XPS).

3. RESULTS AND DISCUSSION

The main reaction between a metal and an oxide is a redox reaction. One metal atom is oxidized and the other is reduced. The metal oxidation and the oxide reduction at the interface are described by $M + M^*O_x \rightarrow MO_y + M^*O_{x-y}$. The metal used in this study was Ta, and the oxide was IGZO. The Gibbs free energies for the oxidation of these elements are important in the reaction. The Gibbs free energy of Ta_2O_5 is −1911.2 kJ/mol, while those of In_2O_3, Ga_2O_5 and ZnO are −830.7, −998.3, −348.1 kJ/mol, respectively. The lower Gibbs free energy of Ta_2O_5 results in Ta oxidation at the Ta/IGZO interface and the formation of tantalum oxide.

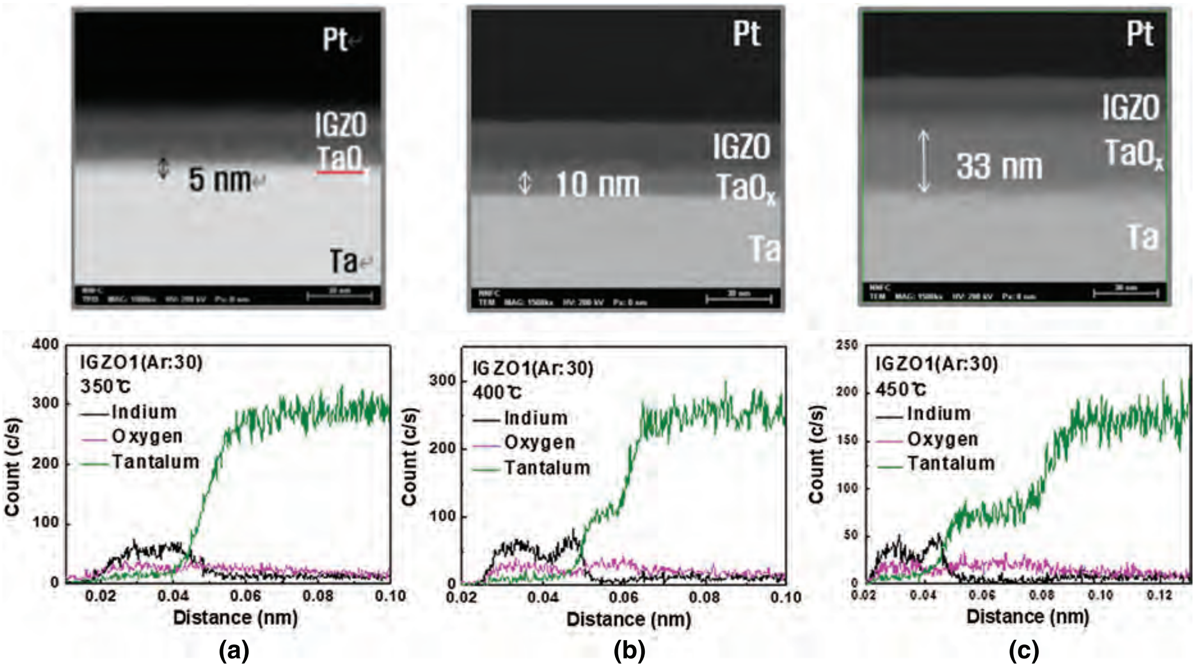


Figure 2. HR-TEM images and EDX results at annealing temperatures of 350 °C (a), 400 °C, (b) and 450 °C (c).

One of the important parameters that determine the thickness of the metal oxide is the diffusion coefficient of the oxygen in the IGZO and tantalum oxide. The diffusion coefficient is a function of the temperature. Oxygen diffuses to the metal/IGZO interface and forms metal oxide. As the reaction proceeds, the metal oxide thickness increases, which means the oxygen must diffuse across the metal oxide to undergo the oxidation reaction with the metal.

The HR-TEM images of the interfaces obtained at annealing temperatures of 350, 400 and 450 °C are shown in Figure 2. The annealing was performed under oxygen atmosphere. Oxygen atoms entered the surface of the IGZO and diffuses into the metal-IGZO interface. Oxygen replacement at the surface and diffusion in the IGZO were observed at a relatively low temperature under 300 °C [21].

Figures 2 also shows the EDX results for a-IGZO deposited with Ar gas only. The HR-TEM images show a thin layer between the IGZO and Ta layers. The Ta composition decreases near the interface and decreases to zero at the IGZO layer. The decrease of the Ta concentration and increase of the oxygen concentration show the formation of TaO_x at the interface. The depth independent composition of Ta and Oxygen indicates stoichiometric TaO_x where the composition of Ta and oxygen remains constant. The TaO_x thickness was estimated from this flat region and the HR-TEM images as 5, 10, and 33 nm for annealing temperatures of 350, 400 and 450 °C, respectively.

The oxygen atoms in the atmosphere exchange into the IGZO, diffuse to the IGZO-metal interface, and form metal oxide. The exchange rate at the surface and the diffusion coefficient in the IGZO affect the formation of metal oxide at the interface. The diffusion coefficient of the IGZO relies on the defect density and oxygen vacancies of the IGZO layer. Thus, we changed the sputtering gas during the deposition of the IGZO layer. It has been reported that the oxygen vacancies decrease as the oxygen ratio increase. The diffusion coefficient becomes higher as the number of oxygen vacancies increases, so the thickness of the metal oxide at the interface would be higher than with fewer oxygen vacancies.

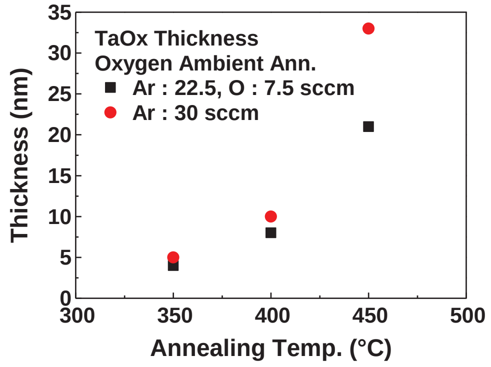


Figure 4. Interfacial oxide thickness versus annealing temperatures.

The interface was compared to that of IGZO deposited with Ar and oxygen (Ar: $O_2 = 22.5$ sccm: 7.5 sccm). Figure 3 shows the HR-TEM and EDX results for samples annealed at temperatures of 350, 400 and 450 °C. The estimated thicknesses were 4, 8, and 21 nm, respectively.

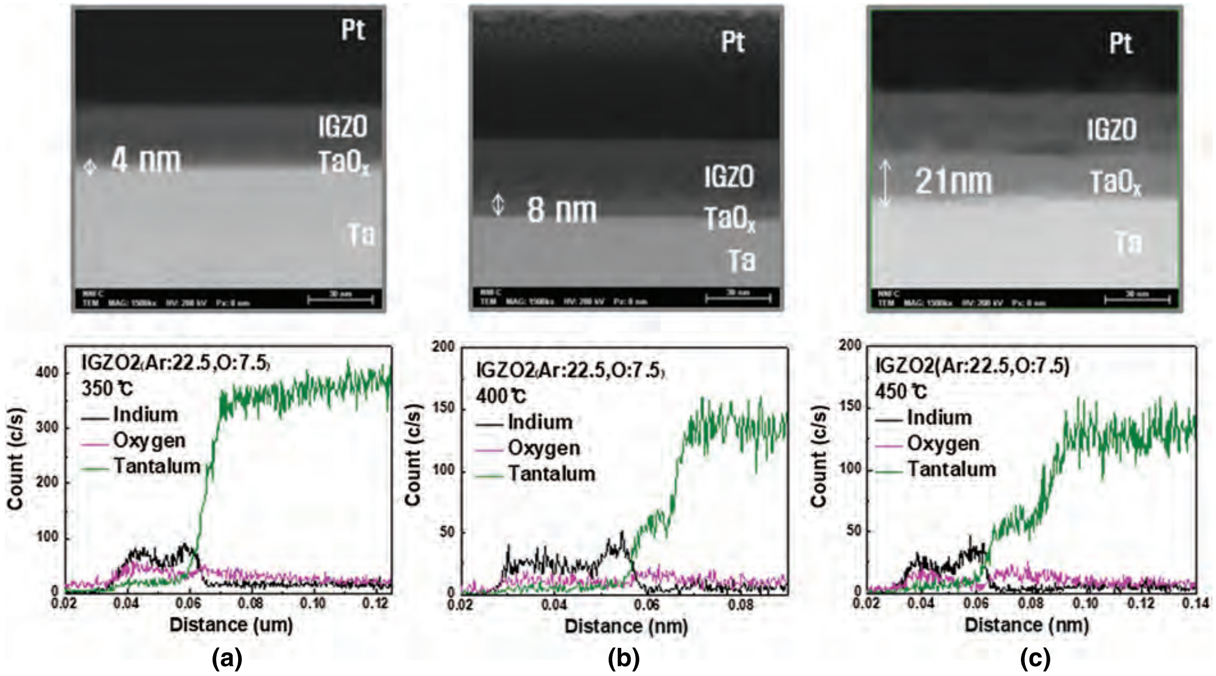
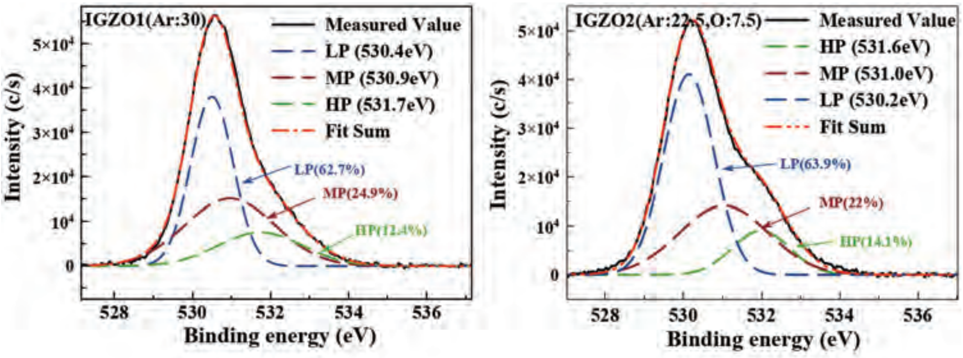
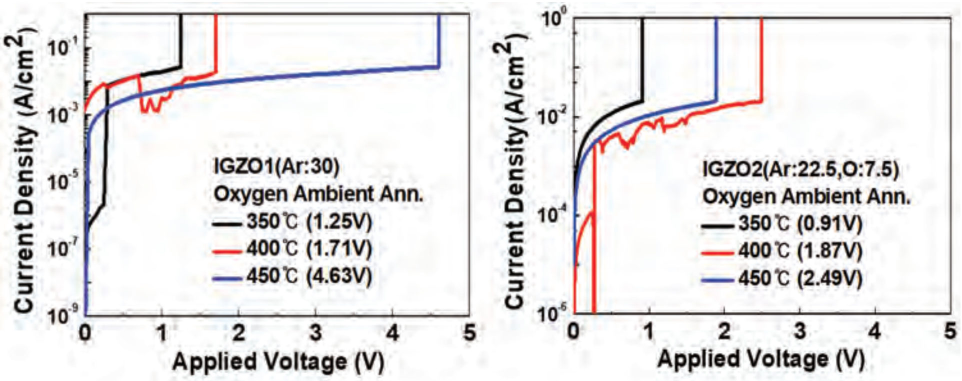


Figure 3. HR-TEM images and EDX results at annealing temperatures of 350 °C (a), 400 °C (b) and 450 °C (c) for IGZO deposited with Ar and O_2 (Ar: $O_2 = 22.5$ sccm:7.5 sccm).



(a) (b)

Figure 5. XPS results for IGZO deposited with Ar gas only (a), and with Ar and oxygen (b).



(a) (b)

Figure 6. Electrical properties of interfacial oxide. Currents were measured between top and bottom Ta metal electrodes, for IGZO deposited with Ar gas only (a), and with both Ar and oxygen gas (b).

The interfacial oxide was thinner for the IGZO deposited with Ar and oxygen as shown in Figure 4. The IGZO deposited with Ar gas only shows thicker interfacial oxide. The number of oxygen vacancies is larger in the IGZO deposited with Ar gas only, so the oxygen diffusion coefficient is also larger.

Figure 5(a) shows the XPS results for IGZO sputter deposited with Ar gas only and Figure 5(b) shows the result obtained with Ar and oxygen gas (Ar: O_2 = 22.5 sccm: 7.5 sccm). The O 1*s* XPS spectra were fitted using three Gaussian peaks related to the low, middle, and high peaks (LP, MP, and HP) centered at approximately 530.2–530.4, 530.1–530.9, and 531.6–531.7 eV, respectively. The LP is associated with O^{2-} ions surrounded by In, Ga, and Zn metal atoms in a fully oxidized stoichiometric IGZO system. The MP can be attributed to O^{2-} ions in the oxygen deficient regions in the IGZO matrix and is related to oxygen vacancies. The HP is related to the chemisorbed or dissociated oxygen or to O–H bonds near the film surface [22–31].

The MP area was 24.9% for the IGZO deposited with Ar gas only, but it was 22.0% when using Ar and oxygen. With the addition of oxygen during the deposition of the IGZO, the oxygen vacancies were reduced due to the oxygen gas, which removes or reduces the oxygen vacancies.

The diffusion coefficient is higher in defective material with dangling bonds or vacancies. The higher number of vacancies when using Ar gas only results in thicker interface oxide then when using Ar and oxygen gas. This is consistent with dependency of the diffusion coefficient on the density of oxygen vacancies.

For the electrical properties of the interface metal oxide, voltages were applied between the top and bottom Ta electrodes. The currents were measured as shown in Figure 6. Higher thickness resulted in higher breakdown voltages.

4. CONCLUSION

The Ta interface with an IGZO layer was investigated to explore the interface oxidation of the Ta metal. The interface reaction was compared between IGZO layers deposited with Ar gas only and with both Ar and oxygen gas. The interface reaction was enhanced by increasing of the annealing temperatures from 350 to 450 °C.

The HR-TEM and EDX observation showed that the metal oxide thicknesses were 5, 10, and 33 nm at annealing temperatures of 350, 400, and 450 °C, respectively. The thicknesses obtained with both Ar and oxygen gas were 4, 8, and 21 nm, respectively. The lower oxide thicknesses were attributed to the lower number of oxygen vacancies in the IGZO deposited using Ar and oxygen, which was identified by XPS analysis. For the IGZO deposited with Ar only, the breakdown voltages were up to 4.6 V which is enough for the gate insulator for the application to the TFT operated with low operation voltages under 1 V.

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