The effect of plasma damage on electrical properties of amorphous GaInZnO film

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Abstract

The effect of plasma damage was investigated on amorphous gallium-indium-zinc oxide (a-GIZO) films and transistors. Ion-bombardment by plasma process affects to turn semiconductor to conductor materials and plasma radiation may degrade to transistor electrical properties. All damages are easily recovered with a 350°C thermal annealing.

1. Introduction

Transparent oxide semiconductors have recently gained much attention for applications in the consumer electronics, transportation, business, and military fields [1]. In particular, transparent ZnO based thin film transistors (TFTs) offer an attractive alternative to amorphous Si TFTs because of their high mobilities (>10cm^2/Vs) and low process temperature (<250°C), compared to those of amorphous Si TFTs, which makes ZnO-based TFTs a very promising low-cost and large-size backplane for active-matrix organic light-emitting diode (AM- OLED) displays [2]. Conventional polycrystalline Si TFTs, which are used as a backplane for AMOLED displays, suffer from the non-uniformity of their mobility and threshold voltage, due to the existence of grain boundaries. To circumvent this problem, complex pixel circuits such as those containing 6 transistors plus 2 capacitors have to be adopted, which causes the TFTs to have a low yield and high cost [3,4] Therefore, it is evident that the development of amorphous ZnO-based TFTs is critical for the fabrication of competitive AMOLEDs.

Very recently, the Hosono group reported high performance TFTs with amorphous gallium-indium-zinc oxide (a-GIZO) channel layers deposited by PVD [5-6]. But in terms of practical process, most works are based on simply fine metal mask (FMM) and never considered critical process issues in preparing a photolithography patterning.

Although a few researchers reported a plasma effect on ZnO based materials [5-6], there is no report in dry etch induced electrical and physical evaluation of *a*-GIZO thin film. In this paper we investigated the effect of plasma on electrical properties of transparent thin-film transistors using *a*-GIZO for an active channel.

2. Experimental

The TFT devices were fabricated as follows: After the common gate of MoW sputtered on silica glass in a radio frequency (RF) sputter, silicon nitride was successively deposited in a plasma enhanced chemical vapor deposition (PECVD) system as a gate insulator layer. ~ 50nm thick amorphous IGZO films deposited at room temperature by a RF sputter using an GIZO (mol% 1:1:1) target.

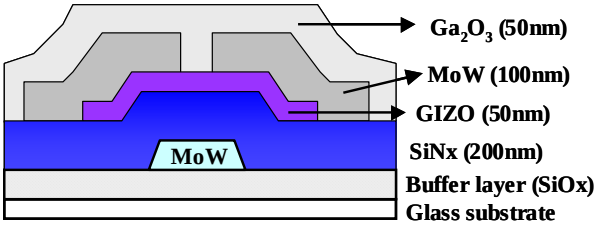


Fig 1. The scheme of bottom-gate oxide TFT

a-IGZO films were patterned by shadow mask. Then source/drain electrode of MoW sputtered in a RF sputter and patterned by shadow mask. Next, Ga_2O_3 sputtered in a RF sputter as a passivation layer as shown in Fig 1. After completing process, TFTs were divided two groups for plasma damage experiment. One was exposed for 30 s to Ar (25sccm)/CHF_3 (25sccm) plas-ma using a RIE (Oxford Instruments PlasmaLab System) etch tool. The other was exposed for 30 s to CF_4(200sccm) plasma using a ICP (ICD Company) etch tool. Then all TFTs were annealed at 350°C for 1h in N_2 atmosphere. The roughness and resistivity of films are measured by atomic force microscopy (AFM) and four point probes, respectively. The carrier concentration and hall mobility are determined by hall measurement system. The device parameters, such as the field effect mobility (μ_{FE}) and the threshold voltage (V_{th}), were extracted I_d-V_g characteristics by least-square fitting to the field effect transistor's gradual channel approximation equation. The channel width and length of TFTs were 1000μm and 150μm.

3. Results and discussion

There are two kinds of damage caused by plasma gases such as surface and bulk damage. [7] The surface damage has been mainly caused by ion bombardments. In terms of the inverted staggered TFT, various gases (such as Ar, SF_6, O_2, and Cl_2 etc.) have usually exposed on the channel layer itself after an active process.

Figure 2 shows the resistivity of the a-GIZO thin film as a function of the Ar plasma exposure time. As-deposited a-GIZO thin film usually had a high resistivity (>10^4 Ωcm) when oxygen gas was used as the reactant source. In this study, upon its exposure to the Ar plasma (30sec), the resistivity of the a-GIZO film dramatically decreased by approximately seven orders of magnitude from >10^4 Ωcm to 5.90×10^{-3} Ωcm. Interestingly, the resistivity of the a-GIZO film decreased further to 2.93×10^{-3} Ωcm when the plasma exposure time was increased to 120sec, then seemed to become saturated. The resistivity of the a-GIZO films did not return to its original value (>10^4 Ωcm) under ambient conditions (in air, at room temperature) for 1 week but retained its plasma-treated value. To elucidate whether the dependence of the resistivity of the a-GIZO films on the Ar plasma treatment comes from the change in the carrier mobility or net carrier concentration, Hall effect measurements were performed for the a-GIZO thin films. As shown in the inset of Fig. 2, the net electron concentration of the a-GIZO film rapidly increases from 10^{14} cm^{-3} (as-deposited, [8]) to 10^{20}~10^{21} cm^{-3} upon its exposure to the Ar plasma. In contrast, the electron mobility of the a-GIZO films is approximately 6~7 cm^{-3} independent of the Ar plasma treatment time. Therefore, it is clear that the huge change in the resistivity of the a-GIZO film is due to the creation of the net electron carriers during the Ar plasma treatment.

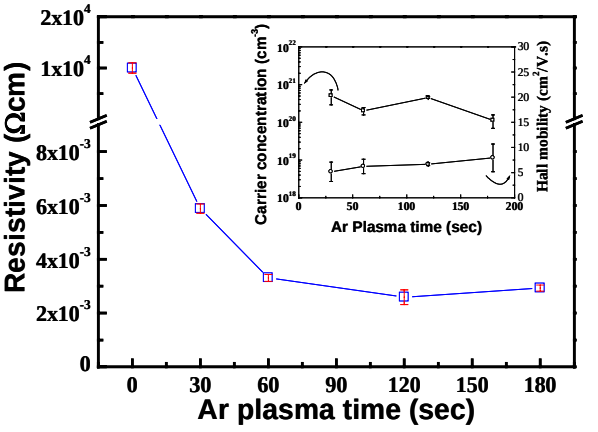


Figure 2. The resistivity of a-GIZO thin films as a function of an Ar plasma exposure time. The net electron carrier concentration and Hall mobility of a-GIZO thin films was shown in the inset of fig. 2.

The morphology and roughness of the a-GIZO films were also investigated as a function of the Ar plasma exposure time, as shown in Fig. 3. The as-deposited a-GIZO thin film was very smooth (Fig.3(a)), but the film became rougher as the exposure time was increased to 30 sec, as shown Fig. 3(b). The surface of the a-GIZO films was modified and tended to become smoother again by the re-sputtering mechanism with increasing Ar plasma time. This implies that the energetic Ar ion bombardment may sputter the surface of the a-GIZO thin films, which may be the reason for the creation of the huge electron concentration. Energetic ion bombardment is known to induce the preferential sputtering of the relatively light atoms from the surfaces of Ⅱ-Ⅵ or Ⅲ-Ⅴ group semiconductors as a result of the physical momentum transfer between the ions in the plasma and the atoms on the material surface, for example, oxygen in ZnO or nitrogen in GaN [9]. Therefore, it is quite reasonable to assume that the oxygen on the a-GIZO film surface is dissociated by

the Ar ion bombardment and, thus, the net electron concentration of 10^{20} ~10^{21} cm^{-3} is due to the formation of an oxygen deficient surface layer as compared to the bulk GIZO film. The change of the cation concentrations (In, Ga, and Zn) on the surface was analyzed using XPS. The In concentration in the Ar plasma treated surface was relatively higher than that of the as-deposited sample, but those of Ga and Zn were relatively lower in the Ar plasma treated surface. In fact, the concentration of the cations (Ga, In and Zn) showed a variation of approximately 3~5 atomic % due to the difference of the sputtering yield (not shown). It is noted that the resistivity of the Ar plasma-treated GIZO films increased by more than 3 orders of magnitude after annealing (300C, 1hr) in an air environment. However, there was no difference in the cation composition of the Ar plasma-treated GIZO films before and after annealing.

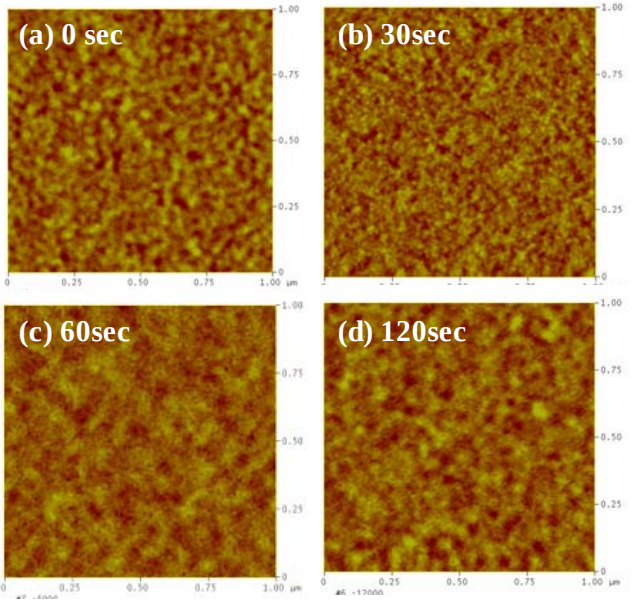
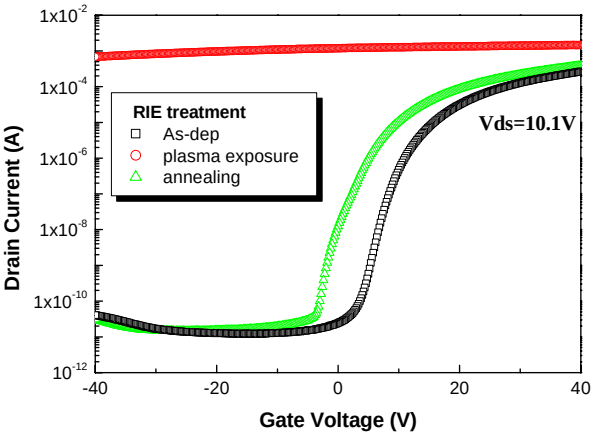


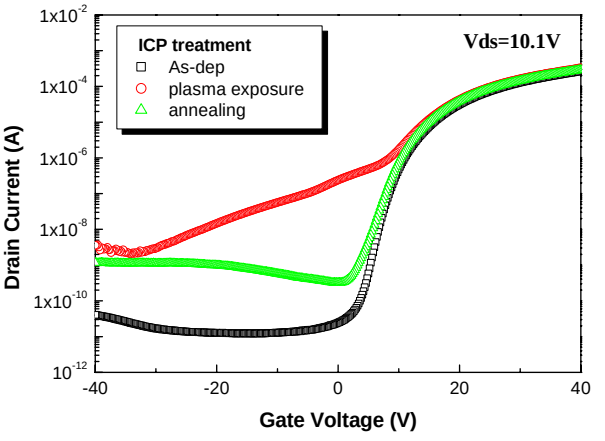
Figure 3. AFM image of a-GIZO film as a function of an Ar plasma time: (a) 0 sec, (b) 30 sec, (c) 60 sec and (d) 120 sec.

Therefore, it is believed that the dramatic change of the electron concentration upon the exposure to the Ar plasma comes from the oxygen deficiency on the a-GIZO film surface rather than the variation in the cation composition. This result is consistent with a previous report on ZnO film [10].

On the other hand, to investigate the effect of TFTs electrical properties by plasma gases, we fabricated a TFT with Ga_2O_3 layer as a passivation layer to prevent a direct damage of channel layers. Figure 4 shows the effect of electrical properties depending on various plasma gases (such as Ar, CHF_3, and CF_4 etc.), which are general reactants for oxide or metal dry etch patterning. As shown in figure 4, an as-deposited TFT with Ga_2O_3 (50nm) has 4.2 cm^2/V.sec of saturation mobility (μ_{sat}), 5.6V of threshold voltage (Vth), 1.37 V/dec. of sub-threshold voltage swing (S.S.) and 2×10^7 of on-off current ratio (Ion/off). After plasma gas like Ar/CHF_3 or CF_4 ignites on the TFT for 30 sec, the devices are significantly degraded.



(a) Ar/CHF_3 plasma exposure under 600W for 30 sec



(b) CF_4 plasma exposure under 500W bias + 2.4KW source for 30 sec

Fig. 4. Transfer characteristics before/after various plasma gases exposure. The recover of transfer curves after thermal annealing (350°C, for 1hr under N_2 gas).

In case of RIE treatment (Ar/CHF_3gas, 600W bias for 30 sec), the semiconductor channel layer turns to conducting materials, which seems to be induced from high carrier concentrations. Moreover, SS and Ioff current are increased considerably in both RIE and ICP treatments (CF_4 gas, 500W bias for 30 sec).

There are two kinds of damages caused by plasma process: the surface damage and the bulk damage. As mentioned before, the surface damage is mainly caused by ion bombardment. In terms of the inverted *a*-GIZO TFT, ion bombardment occurs at the top of the Ga_2O_3 passivation layer (50nm). But the depth of surface damage layer has been reported about 60 Å. [11] Therefore, this kind of surface damage does not contribute to the abnormal TFT behaviors.

The bulk damage can be caused with two sources: [6] the plasma radiation, e.g., UV and other high energy photons, which could create defects in channel and interface layers; the surface charge buildup which could severely damage the Ga_2O_3 passivation layer. When the TFT, covered with quartz (t~0.5mm) plate, is exposed to same plasma condition, it shows similar TFT behaviors like figure 4 (not shown). If the quartz plate can block the ion bombardment and charge buildup, all damages should come from the plasma radiation.

Based on abnormal behaviors (Vth, S.S., and Ioff), it is believed that plasma radiation and high-energy photon could create native defects (oxygen vacancies (V_o) and Zn interstitials (Zn_i)) in *a*-GIZO channel and the interface of SiNx and *a*-GIZO. The increment of native defects can result in high carrier concentration and charge traps, which can increase off-current and S.S. Especially, as the plasma power density and time increase, the damage also may increase. The RIE process (600W, Ar/CHF_3) shows more severe abnormal properties than ICP (500W bias, CF_4). Although the exposure time in this experiment is the similar as that in the real etching condition, the real radiation time is longer than these tests.

An annealing process is adopted to repair those damages in TFTs. After the damaged TFTs are annealed at 350°C for 1 hr under N_2 circumstance, the transfer characteristics get recovered to as-deposited status. Both the threshold voltage, the off current, and S.S decrease drastically. It has repaired damages in channel and interface layers as annealing time goes on. The annealing result is independent of the environment except hydrogen.

4. Summary

In summary, we reported the observation of plasma damages on the *a*-GIZO thin film and inverted TFT structure. The surface damage on *a*-GIZO thin films can change semiconducting to conducting layers, resulting from increasing carrier concentration (oxy-gen vacancies) by ion bombardments. In case of inverted TFTs with Ga_2O_3 passivation layer, the plasma process also happened in significant damages of the channel and interface layers, creating defects and traps. The Vth, S.S. and Ioff are drastically changed after plasma treatment. These damages were contributed mainly by the radiation and slightly by charge buildup. These damages were easily recovered with 350°C thermal annealing process.

5. References

1. H. Ohta and H. Hosono, *Material Today*, 42 (2004)
2. P. F. Carcia, R. S. McLean, M. H. Reilly, and G. Nunes, Jr., *Appl. Phys. Lett*., 82 1117 (2003)
3. J. H. Lee, W. Nam, B. K. Kim, H. S. Choi, Y. M. Ha, and M. K. Han, *IEEE Electron Device Letters*,27, 830 (2006)
4. S. H. Jung, W. J. Nam, and M. K. Han, IEEE Electron Device Letters, 25, 690 (2004)
5. A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S.F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, and M. Kawasaki, *Nat. Mater.*, 4, 42 (2005)
6. H. Yabuto, M. Sano, K. Abe, T.Aiba, T. Den, H. Kumomi, K. Nomura, T. Kamiya, and H. Hosono, *Appl Phy. Lett*., 89 112123 (2006)
7. Y. Kuo, *Appl. Phys. Lett.*, 61 (23), 2790 (1992)
8. A. Takagi, K. Nomura, H. Ohta, H. Yanagi, T. Kamiya, M. Hirano, H. Hosono, *Thin solid Films*, 486 38 (2005)
9. J. M. Lee, K. K. Kim, S. J. Park, and W. K . Choi, *Appl. Phys. Lett*. 78, 3842 (2001)
10. J. M. Lee, K. M. Chang, S. W. Kim, C. Huh, I. H. Lee, and S. J. park, *J. Appl. Phys*. 87, 7667 (2000)
11. Y. Kuo and M. Crowder, *J. Electrochem. Soc*., 139, 548 (1992)