Effect of UV-ozone treatment on the bias-stress stability of indium-zinc-oxide thin-film transistors fabricated by using a sol-gel process

Ho Yong Chong and Tae Whan Kim*
Department of Electronics and Computer Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea

Thin film transistors (TFTs) with indium-zinc-oxide (IZO) channel layers were fabricated by using a solution process. The channel and the SiO$_2$ insulator layers were exposed to ultraviolet (UV)-ozone to investigate the effect of UV-ozone treatment. The enhancement of the subthreshold slope of the UV-ozone-treated TFTs was dominantly attributed to a decrease in the defect density and an increase in the adhesion due to the ozone treatment on the SiO$_2$ insulator layer. The positive-bias temperature stress results for the UV-ozone-treated IZO thin film showed that the threshold voltage shift and the subthreshold slope variation of the TFTs with an UV-ozone-treated IZO thin film were smaller than those with an as-deposited IZO thin film, indicative of an enhancement in the bias-stress stability. X-ray photoelectron spectroscopy spectra showed that the number of the oxygen vacancies and the number of trap sites for the as-deposited IZO film were larger than those of the UV-ozone-treated IZO film.

Key words: Indium-zinc-oxide thin-film transistors, Bias-stress stability, UV-ozone treatment, Sol-gel process.
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Introduction

Active-matrix liquid-crystal displays have currently emerged as excellent candidates for potential applications in flat-panel display devices, which typically use amorphous Si thin-film transistors (TFTs) as gate-driver and pixel-switching devices [1]. The active-matrix liquid-crystal displays have drawbacks and limitations, such as low mobility, light sensitivity to visual light, and device instability. Zinc-oxide (ZnO)-based semiconductor layers have attracted a tremendous amount of attention as an active channel material because they offer transparency and high performance in comparison with amorphous Si layers [2, 3]. TFTs based on solution-processed ZnO layers are feasible alternatives to TFTs formed by using vacuum deposition techniques for potential applications in low-cost, large-area, and flexible substrates, such as displays and consumer electronics [4-6]. Even though some studies on the electrical characteristics of ZnO-based-TFTs have been performed, investigations concerning their instabilities under applied bias voltages or thermal stresses are still necessary if they are to be applied to flat-panel devices [7].

The long-term application of a positive gate bias stress to ZnO-based TFTs deteriorates the electrical performance of the threshold voltage ($V_{th}$) shift and the image sticking of the display devices. The $V_{th}$ shift of the driving TFTs for the pixels of liquid-crystal displays significantly lowers the luminance and causes image sticking in which a faint outline of a previously-displayed image remains visible on the screen [8, 9]. Electrical instability in TFTs is dominantly attributed to the occurrence of a $V_{th}$ shift when the device is subjected to a constant voltage or drain current for a certain duration [10]. Furthermore, solution-processed oxide-semiconductor TFTs suffer from a severe bias-stress instability for device operation because of numerous, undefined defect states that can inhibit reproducible, reliable performance [11].

This paper reports data for the effect of ultraviolet (UV)-ozone treatment on the bias-stress stability of indium-zinc-oxide (IZO) TFTs fabricated by using a sol-gel process. The relative improvement in the stability of the TFTs against electrical stress during device operation under ambient conditions was investigated. Photoluminescence (PL) measurements were performed to investigate the optical properties of the IZO thin films. X-ray photoelectron spectroscopy (XPS) measurements were performed in order to characterize the stoichiometry of the samples, and current-voltage measurements were carried out to investigate the electrical characteristics of the fabricated IZO TFTs.

Experimental Details

The solution of the IZO precursor was synthesized with a sol-gel method by dissolving 0.1-M zinc acetate dihydrate [Zn(CH$_3$COO)$_2$ $\cdot$ 2H$_2$O] and indium nitrate hydrate [In(NO$_3$)$_3$ $\cdot$ xH$_2$O] in 2-methoxyethanol. After
the solution had been stirred at 70 °C for 1 hr to make a transparent and homogeneous solution, the stirred solution was spin-coated on the SiO$_2$/Si substrate at a speed of 2500 rpm for 25 sec. A 200-nm SiO$_2$ layer, acting as a gate dielectric layer, was thermally grown on top of the heavily-boron $p^+$-doped Si wafer. A 20-nm-thick IZO active layer was formed and annealed at 350 °C for 30 min. An Al electrode with a thickness of 200 nm was deposited as a source and a drain electrode. The structure used for characterizing the fabricated TFTs was an inverted, staggered, bottom-gate structure. The electrical characteristics of the solution-processed IZO TFTs were measured at room temperature with a semiconductor parameter analyzer (Agilent B1500). The positive-bias temperature stress (PBTS) measurements were carried out at high temperature in air and in the dark environment. A stress voltage was applied only to the gate while keeping the source and the drain grounded in order to create a uniform electric field across the channel interface. Heavily-doped n-type Si substrates with a 200-nm SiO$_2$ layer were ultrasonically cleaned for 20 min with acetone and methanol. Then, the substrates were cleaned by using an UV-ozone treatment at a wavelength of 207 nm for 10 min in order to compare contact angles and device characteristics of TFTs with an UV-ozone treated layer to those of TFTs with an untreated SiO$_2$ insulator layer. Because the surface energy of the SiO$_2$ surface cleaned by using the UV-ozone treatment is higher than that of a contaminated SiO$_2$ surface, while water droplets of the same amount dropped on each surface spread widely on the clean surface and have a small contact angle, the spread on the contaminated surface is narrow, and the contact angle is large [12].

Results and Discussion

The contact angle of a water drop on the SiO$_2$ surface was significantly decreased from 31 ° to 7 ° due to the ozone treatment, as shown in the inset of Fig. 1. The improved water wettability resulting from the UV-ozone cleaning of the entire surfaces of the samples and from the UV-ozone treatment was attributed to the conversion of hydrophobic surfaces into hydrophilic ones [13]. UV-ozone treatment might improve the adhesion between the SiO$_2$ insulator layer and the solution material for the channel layer due to its hydrophilic characteristics due to the smaller contact angle. The defect density on the substrate is reduced by using an UV-ozone treatment, which is attributed to its ability to produce a protective oxide and to remove residual hydrocarbons [14]. The value of the subthreshold slope (SS) of the IZO thin film decreased from 0.91 to 0.76 V/dec because of the UV-ozone treatment. The improved SS value for the UV-ozone-treated device indicates that the defect density of interface decreased due to a portion of the adsorbed oxygen being removed from the thin-film surface due to the UV-ozone treatment, which might reduce the negative surface charge and eliminate residual contaminants [15]. When the UV-ozone cleaning was applied to the surface of the SiO$_2$ insulating layer, the $I_{on}/I_{off}$ ratio of $2.5 \times 10^3$ for the TFTs with an UV-ozone-treated SiO$_2$ layer was similar to that for the TFTs with an as-deposited insulating layer ($2.7 \times 10^5$). The device performances of the TFTs with an UV-ozone-cleaned IZO film were much better than those of the TFTs with an as-deposited SiO$_2$ layer, resulting in a sharper SS. The mobility ($1.7 \text{cm}^2/\text{V} \cdot \text{sec}$) of the IZO thin film decreased from $1.5 \times 10^{-5}$ to $1.5 \times 10^{-5}$ because of the UV-ozone treatment, which is attributed to its ability to produce a protective oxide and to remove residual contaminants [14]. The value of the subthreshold slope (SS) of the IZO thin film decreased from 0.91 to 0.76 V/dec because of the UV-ozone treatment. The improved SS value for the UV-ozone-treated device indicates that the defect density of interface decreased due to a portion of the adsorbed oxygen being removed from the thin-film surface due to the UV-ozone treatment, which might reduce the negative surface charge and eliminate residual contaminants [15]. 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IZO TFTs resulted in a relatively large shift of the $V_{th}$ of 18 V in the positive direction, the UV-ozone-treated IZO transistors had a relatively small $\Delta V_{th}$ of 6.36 V, after applying the same PBTS, as shown in Fig. 3.

The $V_{th}$ of the TFTs with an UV-ozone-treated IZO layer is smaller than that of the TFTs with an untreated IZO, indicative of better bias-stress stability. The positive $V_{th}$ shift for the oxide TFTs under PBTS originates from the charge trapping and the defects in the film [16, 17]. While a shift of the $V_{th}$ without a significant variation of the SS during the stress time is attributed to simple charge trapping in the gate dielectric layer and/or at the channel/dielectric interface, a positive shift in the $V_{th}$, together with a variation in the SS value, is related to the creation of defects within the oxide semiconductor channel [17]. The charge trapping and the defects near the channel-dielectric interface under a gate voltage stress are different from each other when an UV-ozone treatment is applied to the IZO channel. The charge trapping typically originates from electron trapping due to $O_2$ adsorption on the channel surface under a positive-bias stress [16]. The positive $V_{th}$ shift is attributed to the negative charge screening of the applied gate voltage [18]. A lower effective gate bias results in a smaller current flow through the channel resulting from the negative charge trapping [18]. However, a positive shift of the $V_{th}$, together with a variation in the SS, originates from the creation of defects within the oxide semiconductor channel. The SS value for the TFTs with an untreated IZO film rapidly increases from 0.8 initially to 2.43 at 3,600 sec which that of the IZO film exhibits a relatively small variation from 0.59 to 1.3, as shown in Fig. 3. While the large variation in the SS value for the TFTs with an untreated IZO film is closely related to the creation of more defects within the IZO oxide-semiconductor channel during the stress, the relatively small SS for the TFTs with an UV-ozone-treated IZO film is related to charge trapping at the channel/dielectric interface. The termination of the defects at the IZO/dielectric interface and in the IZO bulk is attributed to a decrease in the number of oxygen vacancies acting as n-type dopants in IZO materials and to the interaction of the ambient-passivated in interface states after the UV-ozone treatment [19, 20]. UV-ozone treatment improved the bias-stress stability and reduced the $V_{th}$ shift and the variation in the SS slope for TFTs.

The relative ratios of the oxygen-related defects were determined by using XPS analyses to investigate the oxygen vacancies in UV-ozone-treated and untreated IZO films. Fig. 4(a) shows the XPS spectra for the O 1s peaks of the as-deposited or UV-ozone-treated indium-zinc-oxide film. The spectra were fitted by using three Gaussian functions. (b) PL spectra of the as-deposited or UV-ozone-treated indium-zinc-oxide thin film.

![Fig. 3. $\Delta V_{th}$ and $\Delta SS$ as functions of the bias stress time under the PBTS condition.](image1)

![Fig. 4. (a) X-ray photoelectron spectra of the O 1s peaks for the as-deposited or UV-ozone-treated indium-zinc-oxide film. The spectra were fitted by using three Gaussian functions. (b) PL spectra of the as-deposited or UV-ozone-treated indium-zinc-oxide thin film.](image2)
high-binding-energy, the medium-binding-energy, the low-binding-energy component, and the total O 1s peak areas, respectively. The ratio of O$_2$/O$_1$, which is related to the oxygen deficiency, decreased after UV-ozone treatment from 33.2 to 27.7%, and the ratio of O$_3$/O$_1$, which is related to O$^2-$ ions, increased from 57.3 to 63%. This result indicates that the oxygen vacancies and the trap sites of the as-deposited IZO film were larger than those of the UV-ozone-treated IZO film. PL spectra for the as-deposited and the UV-ozone-treated IZO thin films were observed to investigate the effect of the UV-ozone treatment and are shown in Fig. 4(b). The peak intensity of the near-band-edge emission at 3.1 eV is increased by the UV-ozone treatment. These results confirm the utility of UV-ozone cleaning [24].

Conclusions

TFTs with IZO channel layers were fabricated by using a solution process. The channel layer and the SiO$_2$ insulator layer were each exposed to UV-ozone to investigate the effect of UV-ozone treatment. The water contact angle at the SiO$_2$ surface was significantly decreased to 7° from 31° due to the ozone treatment on the SiO$_2$ insulator prior to the deposition of the IZO channel layer. The improved SS after ozone treatment on the SiO$_2$ insulator layer might be dominantly attributed to both the decreased organic contamination due to the cleaning and to the increased adhesion. The PBTS results confirmed that the $V_{th}$ shift and the variation of the SS slope of the TFTs with an UV-ozone-treated IZO film were smaller than those of the TFTs with an as-deposited IZO film, indicative of improved bias-stress stability due to UV-ozone treatment. XPS spectra showed that the numbers of oxygen vacancies and trap sites in the as-deposited IZO film were larger than those in the UV-ozone-treated IZO film. These results can help to improve understanding of the effect of UV-ozone treatment on the stability properties of IZO TFTs fabricated by using a sol-gel process.

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