High performance thin film transistors using low-temperature solution-processed Li-incorporated In$_2$O$_3$/ZrO$_2$ stacks

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Abstract

We improved the performance of low-temperature solution-processed thin film transistors (TFTs) by lithium doping of In$_2$O$_3$/ZrO$_2$ gate stacks. Li incorporation into In$_2$O$_3$ reduced interface diffusion of ZrO$_2$ and improved channel mobility. Enhanced crystallization of Li-doped In$_2$O$_3$ thin films as well as the small equivalent oxide thickness of ZrO$_2$ were determined to be key factors in the observed improvement in device performance. An increase in the [Li]/[In$^3+$] ratio over the optimum value resulted in performance degradation, which we attributed to the formation of higher energy barriers due to grain boundaries.

1. Introduction

Low temperature solution-based oxide semiconductor/high-k dielectric stacks are of great interest in large-area flexible display applications because of their low process costs and large-area uniformity with reasonably high carrier mobility, low threshold voltage, and low leakage current [1–4]. Solution-processed inorganic dielectrics have many merits compared to their organic counterparts such as a high dielectric constant and long-term stability. In spite of these advantages, inter-diffusion during solution channel deposition can potentially degrade device performance and reliability.

Several strategies including combustion processing [2], foreign atom doping [5,6], and seeding layer preparation [7] have been reported to enhance the channel crystallization and performance of solution-processed oxide semiconductors at low temperature. In this work, we focused on low temperature solution-processed Li-doped In$_2$O$_3$/ZrO$_2$ stacks and examined channel crystallization, channel-dielectric inter diffusion, and the electrical performance of TFTs containing these stacks according to Li content.

2. Materials and methods

2.1. Low-temperature solution-processed In$_2$O$_3$ and ZrO$_2$ thin film fabrication

All precursors and solvents, namely zirconium oxynitrate hydrate (ZrO(NO$_3$)$_2$·xH$_2$O), indium nitrate (In(NO$_3$)$_3$·xH$_2$O), lithium nitrate hydrate (LiNO$_3$), and 2-methoxyl ethanol (2MeEtOH) were purchased from Aldrich and used as-received.

A 0.1 M ZrO$_2$ dielectric precursor solution was prepared by adding zirconium oxynitrate hydrate into 2MeEtOH solvent followed by stirring at room temperature for 12 h. A 0.3 M In$_2$O$_3$ oxide semiconductor precursor solution was prepared by dissolving In(NO$_3$)$_3$·xH$_2$O into 2MeEtOH and stirring the mixture at 40 °C for 2 h. Then, different amounts of LiNO$_3$ were added into the In$_2$O$_3$ precursor solutions and these solutions were stirred for an additional 2 h at 40 °C. Molar ratio of Li cations to In cations [Li]/[In$^3+$] was varied from 0% to 20%. All solutions were filtered with a 0.2-μm syringe filter before solution casting.

To fabricate the ZrO$_2$ dielectric, ZrO$_2$ precursor solution was spin-coated at 4000 rpm for 40 s, soft-baked at 100 °C for 10 min, and then hard-baked at 250 °C on a hot plate (air ambient) for 1 h. Multi-coating was used to fabricate a 23 nm-thick ZrO$_2$ dielectric. Li-doped In$_2$O$_3$ oxide semiconductor films were fabricated by spin-coating at 5000 rpm for 40 s, subsequent soft-baking at 100 °C on a hot plate for 10 min, and then hard-baking at 250 °C in a box furnace (air ambient) for 1 h.
2.2. Low-temperature solution-processed In$_2$O$_3$/ZrO$_2$ device fabrication

Fig. 1 shows the procedure used to fabricate coplanar bottom gate TFTs with Li-doped In$_2$O$_3$/ZrO$_2$ stacks and a highly doped p-type Si substrate as the bottom gate. First, 100 nm-thick commercial SiO$_2$ on highly doped p-type Si substrate was patterned by wet-etching using buffer oxide etchant (BOE) after exposure and development of a positive photoresist (PR) AZ 9000 layer on the substrate (Fig. 1a). On the active region, a 23 nm-thick ZrO$_2$ layer was prepared by multi-coating the ZrO$_2$ precursor solution followed by annealing (Fig. 1b). A 150 nm-thick ITO layer was deposited by DC sputtering the ITO target with 90% In$_2$O$_3$. The ITO layer was patterned into source and drain electrodes by wet etching in 4% HCl solution for 15 min after PR coating, exposure, and development (Fig. 1c). Li-doped In$_2$O$_3$/ZrO$_2$ stacks were completed by Li-doped In$_2$O$_3$ thin film fabrication. Li-doped In$_2$O$_3$ layers were finally patterned by wet etching in 1% HCl within several seconds. The final structure of Li-doped In$_2$O$_3$/ZrO$_2$ TFTs is shown in Fig. 1d: these TFTs had a width of 150 μm and length of 14 μm. ITO/ZrO$_2$/p-Si capacitors were also used to characterize the dielectric properties of ZrO$_2$ films of different thicknesses.

2.3. Characterization

Physical thicknesses of the Li-doped In$_2$O$_3$ and ZrO$_2$ thin films were measured by high-resolution X-ray diffractometry (HR XRD, X’Pert – PRO MRD) using the X-ray reflectivity (XRR) of the thin films, and values were confirmed using a spectroscopy ellipsometer (SE MG-1000). Surface topography of the In$_2$O$_3$ thin films was characterized by atomic force microscopy (AFM, Multimode 8, Bruker). Crystallization of the thin films was investigated by HR XRD (X’Pert – PRO MRD). Chemical bonds were confirmed by X-ray photoelectron spectroscopy (XPS, K-Alpha Thermal Scientific). Capacitance was measured using an HP 4980A. Electrical properties of capacitors and TFTs were measured using a semiconductor analyzer (Agilent 4155C).

3. Results and discussion

The dielectric characteristics of ZrO$_2$ thin films are shown in Fig. 2. Standard surface X-ray photoelectron spectroscopy (XPS) spectra (Fig. 2a) of the ZrO$_2$ films were obtained using an X-ray spectrometer (K-Alpha Thermal Scientific) with K$_\alpha$ radiation. The atomic composition of ZrO$_2$ thin film (Fig. 1b) was approximately 2 O atoms per 1 Zr atom, which indicated good oxidation of the low-temperature solution-processed ZrO$_2$ dielectric. The equivalent oxide thickness (EOT) was extracted from capacitance-voltage (CV) plots (Fig. 2c); these plots revealed a low EOT with reasonable physical thickness. A relative dielectric constant

![Fig. 1. Li doped In$_2$O$_3$/ZrO$_2$ TFT fabrication process: (a) active patterning of SiO$_2$, (b) ZrO$_2$ dielectric deposition, (c) ITO deposition and patterning, (d) In$_2$O$_3$ deposition and patterning.](image1)

![Fig. 2. ZrO$_2$ dielectric characterization: (a) surface XPS spectra; (b) atomic composition of ZrO$_2$ thin film with three coats extracted from depth profile XPS; (c) EOT and physical thickness according to number of coatings, and (d) leakage current density.](image2)
of solution-based ZrO2 was determined to be approximately 40. Leakage current was significantly reduced in multi-coated ZrO2 films. The 23 nm-thick ZrO2 film showed reasonable leakage current after TFT fabrication.

High-resolution XRD spectra of Li-doped In2O3 thin films with various Li contents are shown in Fig. 3. Crystallization of the active layers improved gradually with Li incorporation, even at lower process temperatures (below 250 °C, data not shown). The XPS results (not shown) proved the existence of intermediate product, InOOH, which contains weak bonds, In-OH. Those bonds can be broken during heating with Li+ doping because Li+ is very strong oxidizing agent (reduction potential: −3.04). The decomposition from InOOH to In2O3 under Li+ assistance was significantly increased, which explained the crystallization enhancement.

In2O3/ZrO2 interfaces with and without Li incorporation were studied using time-of-flight secondary ion mass spectroscopy (TOFSIMS) (Fig. 4). While the stack without Li showed significant inter-diffusion of In and Zr atoms, the stack with Li incorporation had an abrupt interface between In2O3 and ZrO2. This result suggests that amorphous phase of In2O3 film has higher diffusion coefficient of Zr atoms compared to crystalline phase. This improvement of the interface may be one of the key advantages of Li doping of In2O3.

Transfer curves of the TFTs were greatly enhanced by Li doping by up to 13.5% (Fig. 5a). The threshold voltage (Vt), subthreshold swing (SS), and field effect mobility (μFE) of the In2O3/ZrO2 TFTs improved up to a [Li+]/[In+] ratio of 13.5%. The maximum mobility of Li-doped In2O3/ZrO2 TFTs was 60 cm²/Vs at the lowest interface trap density (lowest SS) of 0.18 V/decade. We attributed the enhancement in mobility to crystallization of the channel material and the resulting fine interface and lower EOT of the ZrO2 dielectric. By monitoring the dependence of effective mobility on electric field with different Li doping contents, the scattering from 0.2 to 0.6 MV/cm was significantly reduced, which resulted to the mobility enhancement of the Li doped In2O3/ZrO2 TFTs.

AFM images of In2O3 thin films with various [Li]/[In] ratios are shown in Fig. 6. Nano-islands formed at a higher Li content, which is clearly seen in Fig. 6c with 13.5% Li. In combination with XRD results, we suggested that the growth of In2O3 crystals would reduce the amorphous In2O3 – amorphous ZrO2 contact area and
increase the crystallized In$_2$O$_3$ – amorphous ZrO$_2$ contact area, which affects the inter-diffusion of In and Zr atoms at the active/dielectric interface during annealing. The 16.8% Li sample had much larger islands (Fig. 6d), which indicated that further addition of Li atoms over an optimum value resulted in the formation of grain boundaries in In$_2$O$_3$ thin films, thereby increasing the energy barrier. TFTs with over 20% Li TFTs did not display reasonable transfer characteristics (data not shown).

4. Conclusions

Li-doped In$_2$O$_3$/ZrO$_2$ TFTs fabricated by a low temperature solution process had high mobility and a high $I_{ON}/I_{OFF}$ ratio. Low temperature crystallization of In$_2$O$_3$ films enhanced by Li incorporation improved the In$_2$O$_3$/ZrO$_2$ interface and therefore the mobility, SS, and $V_T$ values of the TFTs. The optimum Li content was determined to be 13.5%, with a mobility of 60 cm$^2$/Vs. A further increase in Li content degraded TFT device performance, most likely due to the formation of grain boundaries.

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