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Low Temperature Solution Processed Hybrid Gate Insulators for High Performance Oxide Thin-Film Transistors

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ABSTRACT

High mobilities of ~30 cm^2/Vs in amorphous InGaZnO thin-film transistors were realized through application of a low temperature solution-processed hybrid gate insulator. The combination of high-k $BaTiO_x$ nanoparticles and a polysiloxane polymer matrix enables a lower process temperature of 300°C from 650 °C while ensuring enhanced performance and low leakage current.

1 INTRODUCTION

Gate insulators (GI) are crucial components of amorphous oxide semiconductor (AOS) thin-film transistors (TFT) and have a large influence on important TFT properties such as mobility (μ), operation voltage, and leakage current (I_g). Currently, SiO_2 is still widely used as the conventional gate insulator (GI) in most AOS TFT research. However, its relatively modest dielectric constant (*k*) of 3.9 pose an issue for achieving a large enough capacitance for ongoing miniaturization of high performance TFT devices. Thus, there has been a surge of research interest on high-*k* dielectric materials as GI of oxide TFTs for flexible and stretchable applications [1]. Utilizing high-*k* materials ensures high performance while exhibiting low voltage operation. Most high-*k* GI films are fabricated through vacuum process such as sputtering and atomic layer deposition to maintain suitable film quality. Nevertheless, vacuum deposition has a relatively high cost and requires lengthy and/or high temperature processes.

Solution process such as spin coating, spray-coating, and printing have been increasingly used for high-*k* GI deposition because of its relatively cheaper cost and potential for high throughput large area fabrication [2]. Still, there are major drawbacks when employing solution process such as higher leakage current due to impurities and defects which necessitates additional high temperature process (>500 °C). Here, we employ a strategy to ensure high performance (high-*k* and low leakage current) while reducing fabrication temperature by combining high-*k* inorganic nanoparticles with a hybrid organic/inorganic polymer matrix [3]. We demonstrate this using $BaTiO_x$ (BTO) nanoparticles and polysiloxane (PSX) to effectively lower the fabrication temperature to 300°C from the required high temperature process (~650 °C) for solution processed BTO films [4]. AOS TFTs with the high-*k* solution processed hybrid BTO/PSX gate insulators can achieve mobilities of up to ~30 cm^2/Vs with low I_g of <10^{-10} A. Comprehensive characterization and analysis of the electrical characteristics, composition, structure, and chemical bonding were also performed to investigate the improvement mechanism.

2 EXPERIMENT

2.1 TFT and MIM Fabrication

Heavily doped n-type Si substrates were initially cleaned through SPM cleaning. Prior to the deposition of the BTO/PSX layer, the native oxide of the Si substrate was removed by BHF etching. The BTO/PSX GI layer with a nominal thickness of 150 nm was then spin-coated at a main speed of 100 rpm and cured at 300 °C for 1 hr. The semiconductor channel used is a 70-nm-thick *a*-IGZO layer which was deposited at room temperature by radiofrequency magnetron sputtering. The *a*-IGZO layer was then patterned through standard UV photolithography and wet etching (HCl) process. A Mo/Pt metal stack with a thickness of 80 nm/20 nm were deposited and used as source/drain electrodes. Finally, annealing was performed at 300 °C in atmosphere (N_2:O_2 = 4:1) condition for 2 h. Using the same fabrication conditions, metal-insulator-metal (MIM) samples were also fabricated to analyze the dielectric properties of BTO/PSX films.

2.2 BTO/PSX Types and Characterization

Solution processed high-*k* BTO/PSX hybrid films with different deposition temperature (180 °C, 300 °C, and 500 °C) and BTO/PSX ratio (1.4/1.0 and 1.0/1.0) were used as gate insulator. Additional BTO/PSX films with supplementary properties such as fluorinated BTO/PSX and photosensitive type BTO/PSX films (positive and negative) are also introduced. Several characterization techniques were performed such as electrical characterization measurements, atomic force microscopy (AFM), X-ray diffraction (XRD), secondary ion mass spectrometry (SIMS) and X-ray photoelectron

spectroscopy (XPS) to analyze the electrical, physical, and chemical properties.

3 RESULTS AND DISCUSSION

Figure 1 demonstrates the importance of the process temperature and the PSX structure. For instance, the temperature dependence of the transfer characteristics shows that 300 °C is a sufficient temperature for the hybrid BTO/PSX film to be an effective GI. Although a higher on-current and switching characteristics can be obtained by using 180 °C, the off-current (~10^{-5} A) is quite high and the large on-current is likely due to substantial gate leakage current. Upon inspection of the film structure by a scanning electron microscope (SEM), the 180 °C sample showed incomplete film formation due to the non-uniform curing of the PSX layer at low temperatures. The silica part (marked red in Fig. 1(a)) of the PSX structure has an important role for the film formation by facilitating silanol condensation at low temperatures. This silanol condensation, and thus film formation, becomes more effective as the temperature is increased. Unsurprisingly, the off-current is drastically reduced to 10^{-8} A and 10^{-9} A, after 300 °C and 500 °C curing, respectively. AFM results also showed an improvement of the surface roughness at higher curing temperature. Nevertheless, 300 °C is still preferred as the fabrication temperature as it allows for the use of flexible substrates compared to 500 °C.

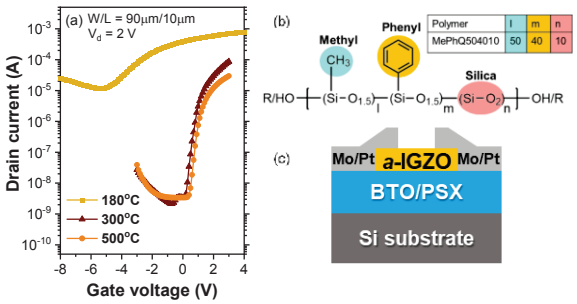

Fig. 1 (a) Temperature dependence of the transfer characteristics of $BTO_{1.4}PSX_{1.0}$ (b) PSX structure showing the methyl (l), phenyl (m), and silica (n) ratio. (c) Bottom gate top-contact TFT structure

The ratio between the BTO nanoparticles and PSX is also an important consideration. In general, having a greater ratio of BTO nanoparticles will improve the dielectric constant while a higher PSX ratio will enhance the flexibility, transparency, and reduce leakage current but at the cost of a lower dielectric constant. Films with a BTO/PSX ratio of 1.4/1.0 and 1.0/1.0 have a dielectric constant of 8.9 and 6.15, respectively. Higher dielectric constant can be achieved with higher BTO nanoparticle ratios but J-V measurements of MIM structure of BTO/PSX (70 wt.% BTO ratio) show high leakage current density.

From Fig. 2, both $BTO_{1.4}PSX_{1.0}$ and $BTO_{1.0}PSX_{1.0}$ samples show good switching behavior with no subthreshold degradation and high mobility of 23.81 cm^2/Vs and 30.17 cm^2/Vs, respectively, which is much better than SiO_2 GI samples (17.22 cm^2/Vs). At higher V_d, both hybrid GI also showed high μ and minimal V_{th} shift. Nonetheless, TFTs with higher BTO ratio GI have larger off current and I_g. From the XPS results, $BTO_{1.4}PSX_{1.0}$ film has more M-O bonding while higher Si-O bonding is observed in $BTO_{1.0}PSX_{1.0}$ film, as expected. The higher M-O ratio (more BTO nanoparticles) contributes to greater I_g since the BTO nanoparticles have poor dielectric breakdown strength. Moreover, introducing a large amount of high-*k* BTO nanoparticles into the low-*k* hybrid polymer matrix can induce increased void formation. The XPS results also show a higher M-OH bonding ratio for $BTO_{1.0}PSX_{1.0}$. High M-OH at the channel/GI interface can lead to hydrogen ionization and free electron consecutive release which can induce higher μ. The SIMS results also confirm higher H at the interface and its diffusion at the vicinity of the interface. In addition, the larger PSX ratio in $BTO_{1.0}PSX_{1.0}$ also improved surface roughness and thus, the TFT mobility.

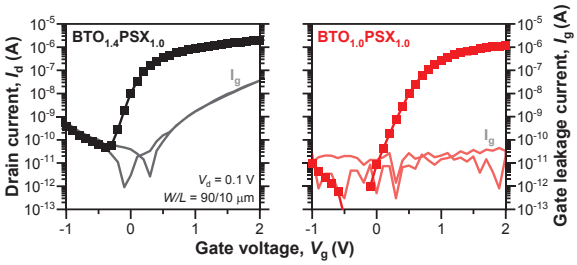

Fig. 2 Transfer characteristics and gate leakage current of $BTO_{1.4}PSX_{1.0}$ and $BTO_{1.0}PSX_{1.0}$

Additional functionalities such as fluorination and photosensitive property can also be incorporated to solution processed hybrid BTO/PSX. As shown in Fig. 3, fluorination can drastically reduce the off-current and gate leakage current of $BTO_{1.4}PSX_{1.0}$ by more than 1 order of magnitude while maintaining high μ of >20 cm^2/Vs (see Table I). Furthermore, improved hysteresis behavior (smaller hysteresis shift) of -0.17 V is observed for the fluorinated variant compared to 0.28 V for the non-fluorinated film. F incorporation in various TFT layers is known to enhance both TFT performance and stability.

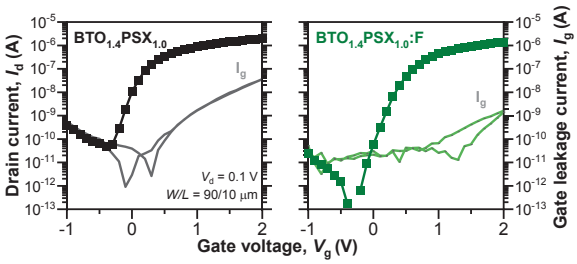

Fig. 3 Transfer characteristics and gate leakage current of $BTO_{1.4}PSX_{1.0}$ and fluorinated $BTO_{1.4}PSX_{1.0}$

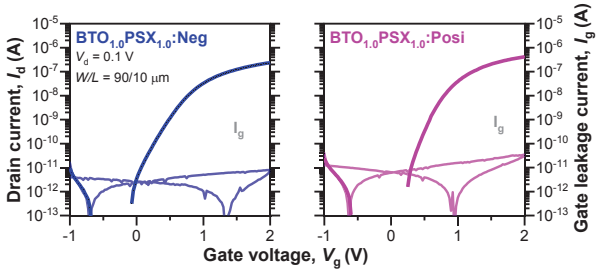

Fig. 4 Transfer characteristics and gate leakage current of photosensitive $BTO_{1.0}PSX_{1.0}$ (negative and positive type)

Table I. Comparison of electrical characteristics of *a*-IGZO TFT utilizing different gate insulator materials

Gate Insulator	Mobility (cm^2/Vs)	V_{th} (V)	*SS* (V/dec)	Leakage current (A)
$BTO_{1.4}PSX_{1.0}$	23.81	-0.16	0.18	~10^{-7}
$BTO_{1.0}PSX_{1.0}$	30.17	0.40	0.17	~10^{-10}
$BTO_{1.4}PSX_{1.0}$:F	21.86	0.16	0.16	~10^{-9}
$BTO_{1.0}PSX_{1.0}$ (Positive type)	11.16	0.62	0.10	~10^{-10}
$BTO_{1.0}PSX_{1.0}$ (Negative type)	6.55	0.59	0.17	~10^{-11}
Thermal SiO_2	17.22	4.56	0.33	~10^{-12}

Fig. 4 shows the transfer characteristics *a*-IGZO TFT with negative and positive type photosensitive $BTO_{1.0}PSX_{1.0}$ GI. Although the film formation process still needs to be optimized to improve mobility, both TFTs with photosensitive type hybrid GI have slightly lower leakage current (10^{-11} A) compared to $BTO_{1.0}PSX_{1.0}$ GI. J-V measurements also confirm this result with almost >1 order of magnitude reduction in the leakage current density of the MIM samples with photosensitive insulator films. A crucial advantage of these photosensitive films is the ease of forming patterned films through photolithography without employing any etching. Thus, fabrication steps can be reduced and etching-related degradation can be inhibited to fabricate high quality GI films. Photosensitive type GI will have interesting applications especially in TFTs with varying architectures such as top gate and vertical TFTs.

4 CONCLUSIONS

In this report, we demonstrated how the combination of BTO nanoparticles and PSX can be used to form solution processed high-*k* GI films at a low temperature of 300 °C to achieve high mobilities of up to ~30 cm^2/Vs and low leakage current of <10^{-10} A. We also showed that additional functionalization such as fluorination and photosensitive property can be augmented on hybrid BTO/PSX films to further improve its properties. Analysis of several characterization reveal that H at the interface and its diffusion can enhance the mobility of the *a*-IGZO TFT. These results show the large promise of solution-processed hybrid films as high-*k* GI for high performance oxide TFTs on flexible substrates.

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