Applied Surface Science 254 (2008) 6987-6990

Contents lists available at ScienceDirect

# Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Effect of modifying a methyl siloxane-based dielectric by a polymer thin film for pentacene thin-film transistors

Sang-Il Shin, Jae-Hong Kwon, Jung-Hoon Seo, Byeong-Kwon Ju\*

Display and Nanosystem Laboratory, College of Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea

#### ARTICLE INFO

Article history: Received 26 February 2008 Received in revised form 5 May 2008 Accepted 6 May 2008 Available online 13 May 2008

PACS: 85.30.Tv 72.80.Le 73.61.Ng 73.61.Ph

Keywords: Organic thin film transistor Pentacene Polymer film Solution processed

# 1. Introduction

Organic thin-film transistors (OTFTs) have received considerable attention for organic electronics [1,2]. So far, a high performance for OTFTs has been obtained by employing nonsoluble inorganic gate dielectrics, such as thermally grown silicon dioxide (SiO<sub>2</sub>), plasma-enhanced chemical vapor deposited silicon nitride (Si<sub>3</sub>N<sub>4</sub>), and ion-sputtered alumina (Al<sub>2</sub>O<sub>3</sub>) [3]. Solutionprocessed materials have recently become attractive for fabricating OTFTs because high performance films can be formed easily by spin, drop, spray coating, and printing methods at room temperature. The use of methyl-siloxane-based spin-on-glass (SOG) as a gate dielectric has demonstrated that a sol-gel reaction can lead to the formation of a solution-processed inorganic dielectric without sacrificing good electrical properties [4–6]. This approach has several advantages, namely, no moisture and hysteresis problems are encountered, the ability to fill gaps as small as 100 nm is provided to achieve complete regional planarization, and the resulting planarization interlayer has good

## ABSTRACT

We report on the fabrication of pentacene thin-film transistors (TFTs) utilizing a spun methyl siloxanebased spin-on-glass (SOG) dielectric and show that these devices can give a similar electrical performance as achieved by using pentacene TFTs with a silicon dioxide (SiO<sub>2</sub>) dielectric. To improve the electrical performance of pentacene TFTs with the SOG dielectric, we employed a hybrid dielectric of an SOG/cross-linked poly-4-vinylphenol (PVP) polymer. The PVP film was deposited onto the spun SOG dielectric prior to pentacene evaporation, resulting in an improvement of the saturation field effect mobility ( $\mu_{sat}$ ) from 0.01 cm<sup>2</sup>/(V s) to 0.76 cm<sup>2</sup>/(V s). The good surface morphology and the matching surface energy of the SOG dielectric that was modified with the polymer thin film allow the optimized growth of crystalline pentacene domains whose nuclei are embedded in an amorphous phase.

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dielectric properties in multilevel IC devices [4–7]. The SOG dielectric contains 15 wt% methyl (CH<sub>3</sub>) groups and minimal density hydroxyl radicals (OH) bonded to silicon (Si) atoms in the siloxane (Si–O–Si) backbone. This chemical structure is very similar to that of SiO<sub>2</sub>. In previous research, many studies have reported on the effect of modifying the SiO<sub>2</sub> dielectric by several kinds of polymer films [8–11]. These works reported that a modification layer placed between the pentacene film and the SiO<sub>2</sub> dielectric gives advantages in optimizing the growth conditions for the pentacene film, which in turn leads to high performance pentacene TFTs.

In this study, we have found that pentacene TFTs with a spun SOG dielectric showed a similar electrical performance to pentacene TFTs with a SiO<sub>2</sub> dielectric. To improve the electrical performance of pentacene TFTs with a spun SOG dielectric, we employed a cross-linked poly-4-vinylphenol (PVP) film that served as a modification layer on the SOG dielectric. The PVP layer forms an interface that interacts less with organic semiconductors (OSCs) while inorganic dielectrics lead to some undesirable interface interactions with the OSC materials [11–13]. We confirmed that the enhancement of the saturation field effect mobility ( $\mu_{sat}$ ) in pentacene TFTs that were modified with the PVP film were related to other characteristics, including the





<sup>\*</sup> Corresponding author. Tel.: +82 2 3290 3237; fax: +82 2 3290 3671. *E-mail address*: bkju@korea.ac.kr (B.-K. Ju).

<sup>0169-4332/\$ -</sup> see front matter  $\circledcirc$  2008 Elsevier B.V. All rights reserved. doi:10.1016/j.apsusc.2008.05.092

surface energy, the roughness of PVP film, and the crystalline structure of the pentacene film.

# 2. Experimental

Fig. 1 shows a schematic of the pentacene TFTs with the SOG dielectric that was modified with the PVP film and the chemical structures of the SOG and PVP materials. A glass substrate with an indium-tin oxide (ITO) layer of 150 nm thickness was used as a substrate and as a bottom gate electrode. To form the inorganic dielectric, the SOG (Accuglass 512B, Honeywell) solution was spun onto the ITO glass. The spun SOG film was baked at 80 °C for 1 min and at 250 °C for 1 min on a hot plate, and then, it was fully cured in a furnace at 425 °C for 1 h in a nitrogen environment. For comparison, a highly doped p-type Si wafer with a 500 nm thick SiO<sub>2</sub> dielectric layer was used as the substrate and the gate electrode.

To prepare the PVP (Sigma–Aldrich, Mw ~20,000) solution, the PVP powder was mixed with propylene glycol monomethyl ether acetate (PGMEA) with 13 wt%. We added poly melamineco-formaldehyde methylated (Sigma–Aldrich, Mwn ~511) into the PVP solution with a ratio of 1:20. To modify the SOG dielectric surface, the PVP solution was coated on the SOG dielectric, and this was cured at 200 °C for 5 min on a hot plate to enforce the cross-linking of the polymer. The thicknesses of the different films that were measured using a surface profiler (Alpha-step) were 750 nm and 450 nm for the SOG and PVP, respectively.

A 70 nm thick pentacene (Sigma–Aldrich, ~99% purity) active layer was deposited on the different dielectrics with a deposition rate of 0.3 Å/s under a base pressure of  $1 \times 10^{-6}$  Torr. Torr. The 250 nm thick Au source and drain electrodes were deposited through a shadow mask by a thermal evaporator. The channel width and length were 1000  $\mu$ m and 100  $\mu$ m, respectively. The electrical characteristics were measured in order to evaluate the electrical performance of the TFTs using a semiconductor characterization system (Keithley SCS 4200) in a dark box.

#### 3. Results and discussion

Fig. 2 shows a cross-sectional field-emission scanning electron microscope (FE-SEM) image, and an elemental energy dispersive X-ray (EDX, Horiba EX-200) measurement was carried out for the SOG dielectric. From Fig. 2(a), the FE-SEM image indicates that the spun SOG dielectric is homogeneous and it has a flat surface property. As shown in the EDX result, the average atomic percentage ratio of O to Si was  $2.19 \pm 0.07$ . This value was similar to that of the thermally grown  $SiO_2$  (the O/Si ratio of  $SiO_2$  is 2) [14]. Through the heat treatment used in the fabrication process, the amount of the silanol (Si-OH) group in the spun SOG dielectric gradually decreased while the amount of the Si–O–Si group increased. This condensation reaction was thermally induced to generate a Si-O-Si network, thereby consuming the hydroxyl radical (OH). On the other hand, the amount of the methyl  $(CH_3)$  group was unchanged [4]. The carbon atom in a SOG dielectric is not independent element; it is bound with hydrogen to produce a hydrocarbon. Because the hydrogen element in the CH<sub>3</sub> group does not emit X-rays, our EDX analysis could not detect the percentage of carbon and hydrogen in the SOG dielectric.

To improve the performance of OTFTs, the role of the interface between the gate dielectric and the OSC is important [15,16]. Among other things, the surface roughness of the gate dielectric is a primary factor for obtaining high carrier mobility because the mobility in thermally grown pentacene on a dielectric film is influenced by the  $\pi$ -orbital overlap between neighboring pentacene molecules. If the dielectric film has poor surface roughness, then this roughness leads to valleys in the channel region, and these valleys may act as carrier traps with a number of scatterings. Fig. 3(a)–(c) shows atomic force microscopy (AFM, XE-100) images and the contact angles of SiO<sub>2</sub>, SOG, and SOG that was modified with the PVP film, respectively. The root-mean-square (RMS) roughness of the SOG dielectric was 0.51 nm, indicating that it is smaller than the 1.08 nm roughness of the SiO<sub>2</sub> dielectric. The SOG dielectric that was modified with the PVP film had a 0.44 nm



**Fig. 1.** The chemical structures of (a) SOG, (b) PVP, and (c) a schematic of the pentacene TFTs with spun SOG that was modified with PVP film.



**Fig. 2.** (a) A FE-SEM image of the cross-section of the SOG dielectric and (b) an EDX analysis of the SOG dielectric showing the average percentage of the stoichiometrical amount.



Fig. 3. The AFM images and contact angles of different dielectrics with (a) SiO<sub>2</sub>, (b) SOG, and (c) SOG that was modified with PVP. The AFM images in (d), (e), and (f) show the morphologies of the pentacene films corresponding to (a), (b), and (c), respectively.

roughness, which is very smooth. It was reported that the analogous surface energy of the dielectric film compared to that of the pentacene film contributes to the considerable enhancement of mobility, which produces an improvement in the threshold voltage in the pentacene TFTs [9]. In addition, Yoneya et al. have found that most of the carriers in pentacene TFTs were transported through the effective channel, which has a thickness of less than 3 nm from the dielectric surface [17]. Because the initial optimized growth of the pentacene film is determined by the dielectric/ pentacene film interface, the surface energy is very important. To calibrate the surface energy of different films, we measured the contact angles using deionized water and ethylene glycol as reference liquids, and we used the following equation [18],  $(1 + \cos \theta)\gamma_r = 2(\gamma_s^p \gamma_r^p)^{1/2} + 2(\gamma_s^d \gamma_r^d)^{1/2}$ , where  $\gamma_s$  and  $\gamma_r$  are the surface energy of the sample and reference liquid components. The superscripts 'p' and 'd' refer to the polar and dispersion components of the surface energy, respectively. Two reference liquids of known surface energies are deionized water ( $\gamma_r^d$ : 21.80 mJ/m<sup>2</sup>;  $\gamma_r^p$ : 51.00 mJ/m<sup>2</sup>) and ethylene glycol ( $\gamma_r^d$ : 29.29 mJ/m<sup>2</sup>;  $\gamma_r^p$ : 18.91 mJ/m<sup>2</sup>). The surface energies of the SiO<sub>2</sub> and SOG dielectric were 61.3 mJ/m<sup>2</sup> and 25.7 mJ/m<sup>2</sup>, respectively. Because the CH<sub>3</sub> group in the SOG dielectric is a hydrophobic alkyl functional group, the wetting property of the SOG surface exhibited a very non-polar characteristic, which coincides with low surface energy. The surface energy of the SOG dielectric that was modified with the PVP film matched that of the pentacene film  $(38 \text{ mJ/m}^2)$  [19]. Fig. 3(d)–(f) shows AFM images of the pentacene films on the different dielectrics. There have been reports that a small grain size of OSCs in OTFTs can cause a considerable decrease in the mobility due to an increase in the number of grain boundaries that may act as carrier trap sites [20,21]. The pentacene film on the SOG dielectric that was modified with the PVP film exhibited a well-formed dendritic structure with an average grain size of 1.4 µm, as shown in Fig. 3(f). The RMS roughness values of the pentacene film on the SiO<sub>2</sub>, SOG, and SOG that was modified with PVP film were 8.41 nm, 6.95 nm, and 5.75 nm, respectively. From our results, we believed that the grain size can be increased and the crystal disorder can be decreased in the pentacene film by using an SOG dielectric that is treated with a PVP film to produce a very smooth surface morphology and a surface energy that is similar to that of pentacene film.

We also calculated the capacitance per unit area by  $C = \epsilon_0 \epsilon_r A t^{-1}$ , where  $\epsilon_0$  is the free space permittivity, *A* is the area of the capacitor electrode, and *t* is the thickness of the dielectric film. For the thermally grown SiO<sub>2</sub> dielectric, the capacitance per unit area was 6.90 nF cm<sup>-2</sup>. For the SOG dielectric film, the capacitance was 7.84 nF cm<sup>-2</sup>. Because the structure of the SOG dielectric that was modified with the PVP film was a series connection, the



**Fig. 4.** Square root of the drain current–gate voltage  $(\sqrt{-I_D}-V_G)$  curves (circles) and  $\log_{10}(-I_D)-V_G$  (squares) of the pentacene TFTs with the SiO<sub>2</sub> and SOG dielectrics. These plots were obtained at a drain voltage ( $V_D$ ) of -60 V.



**Fig. 5.**  $I_D-V_D$  curves of the pentacene TFTs with spun SOG that was modified with the PVP film. The  $V_G$  ranges from 0 V to -60 V in 10 V steps. (Inset)  $\sqrt{-I_D}-V_G$  and  $\log_{10}(-I_D)-V_G$  curves of the modified TFTs were obtained at  $V_D = -60$  V.

total capacitance per unit area of the SOG dielectric that was modified with the PVP film decreased to  $3.93 \text{ nF cm}^{-2}$ .

The electrical characteristics, such as the saturation field effect mobility ( $\mu_{sat}$ ), the threshold voltage ( $V_{th}$ ), and the on/off current ratio were determined from the  $log_{10}(-I_D)-V_G$  and  $\sqrt{-I_D}-V_G$ curves shown in Fig. 4. The pentacene TFTs with a SiO<sub>2</sub> dielectric exhibited a small on-state current ( $I_{\rm on}$ ) of 1.73  $\mu$ A, a  $\mu_{\rm sat}$  of 0.02 cm<sup>2</sup>/(V s), a current on/off ratio of 10<sup>4</sup>, and a  $V_{\rm th}$  of -24 V. Similarly, the pentacene TFTs with spun SOG exhibited a  $\mu_{sat}$  of 0.01 cm<sup>2</sup>/(V s), a current on/off ratio of  $10^4$ , and a  $V_{\rm th}$  of -18 V. In contrast, Fig. 5 shows the output characteristics  $(I_{\rm D}-V_{\rm D})$  and the inset transfer characteristics  $(\log_{10}(-I_D)-V_G)$  and  $\sqrt{-I_D}-V_G$ obtained from the pentacene TFTs with the SOG dielectric that was modified with PVP film. Compared to Fig. 4, it can be found that the magnitudes of the  $\mu_{sat}$  and  $I_{on}$  produced by the pentacene TFTs with the SOG dielectric that was modified with the PVP film were significantly larger than those of the TFTs without PVP layer. We also observed a positive shift of the  $V_{\rm th}$ , which allows a lower operating voltage in the OTFTs. As shown in the  $I_D-V_D$  curves of Fig. 5, the lack of I<sub>D</sub> crowding at low V<sub>D</sub> establishes a low-resistance ohmic contact between the Au electrode and the pentacene film. In addition, there is a good saturation state at high  $V_{\rm D}$ , indicating a depletion region in the pentacene active layer. The pentacene TFTs with SOG dielectric that was modified with the PVP film exhibited improved electrical characteristics, including a high  $\mu_{sat}$  of 0.76 cm<sup>2</sup>/(V s), an  $I_{on}$  of 51.74  $\mu$ A, a current on/off ratio of  $\sim 10^4$ , and a  $V_{\rm th}$  of less than -1 V. We found that forming the PVP film prior to the evaporation of pentacene gave rise to an increase in the  $\mu_{\rm sat}$  of the pentacene TFTs with SOG dielectric, which resulted in an improvement of the  $V_{\rm th}$ . This result indicates that it was more feasible for the pentacene molecules to bind with the polymeric tails of the organic molecules on the PVP film.

## 4. Conclusions

This work demonstrates the solution-processed fabrication and operation of high performance pentacene TFTs using a spun SOG inorganic dielectric that was modified with a thin film of PVP polymer. The use of the spun SOG dielectric offered easy and lowcost fabrication of OTFTs compared to vacuum-deposited inorganic dielectrics. To improve the electrical performance of our TFTs with the SOG dielectric film, we employed hybrid dielectrics of SOG dielectric/cross-linked PVP film by a simple spin coating method. Conclusively, it is believed that the good surface morphology and the matching surface energy of the SOG that was modified with the PVP film had a positive influence on the crystallization of the pentacene molecules, which improved the electrical performance of the pentacene TFTs.

#### Acknowledgement

This work was supported by the National Research Laboratory (NRL, ROA-2007-000-20111-0) Program of the Ministry of Science and Technology (Korea Science and Engineering Foundation).

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