Ultrathin silica film derived with ultraviolet irradiation of perhydropolysilazane for high performance and low voltage organic transistor and inverter

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In recent years, organic electronic devices have become more and more popular, such as organic solar cell (OSC) [1–4], organic light emitting diode (OLED) [5–7] and organic thin film transistor (OTFT) [8–11] by virtue of their light weight, easy-processing and flexibility. As OTFT could be used as functional device or drive circuit to activate other devices [12,13], the development of OTFT becomes more urgent in practical applications. Low voltage operation as one of the major performances is very important to apply OTFT in low power consumption situations, especially in wearable and portable devices. As we all know, dielectric layer plays an important role to modulate the operation voltage of OTFT. Utilization of ultrathin dielectric film is an effective method to construct low voltage transistor. Therefore, new dielectric materials and novel processing methods for ultrathin dielectric films are two main ways to adjust the energy consumption performance of OTFT. Generally, most dielectric materials are composed of polymers or inorganic oxides [14,15]. For polymers, although the cheap and easy-process features make them popular in organic electronics [16,17], ultrathin polymer film has a risk of leakage. Inorganic oxides, such as silica and alumina, generally have excellent stability and low leakage even with ultrathin thickness, but they are usually prepared by physical vapor deposition (PVD) [18], chemical vapor deposition (CVD) [19], sol-gel [20] and atom layer deposition (ALD) [21], etc., which usually need high temperature, expensive equipment, and complex procedures. Therefore, from the standpoint of performance,

preparation of ultrathin inorganic oxides layer through low cost and mild condition is highly meaningful for the construction of low voltage OTFT.

Silica is one of the most extensively used inorganic dielectric oxides because of its high performance and mature processing [22–25]. However, the traditional processes are not compatible with modern organic electronics and large-scale production that generally requires low-cost and low temperature process. Recently, silica derived from solution precursor conversion method has drawn more and more attention. The most common solution precursor is perhydropolysilazane (PHPS) which possesses basic chemical structure of $[-Si(H_2)-NH-]$ and usually goes through the hydrolysis, condensation and oxidation reaction of active Si–N bond and Si–H bond to form silica [26–32]. In our previous work, the conversion is finished by thermal annealing of PHPS on a hot plate [33]. Despite lower power consumption method, it may be not completely compatible with organic electronics due to the thermal annealing procedure. Some polymer substrates with low glass transition temperature cannot endure the annealing temperature [34–36]. Therefore, we further exploit milder silica preparation method based on PHPS. In this letter, we introduce an ultraviolet irradiation conversion to fabricate ultrathin silica film and further apply the as-fabricated silica film in organic transistors. The silica film shows highly dense and smooth surface, which presents high electrical performance in capacitors and transistors, indicating that this method is suitable for large-scale production.

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Figure 1 The schematic diagram of silica film-based transistor and reaction mechanism of ultraviolet irradiation conversion method.

In the fabrication progress, PHPS precursor was first diluted into 5 wt% with butyl ether (99%, purchased from Aldrich sigma), and then the solution was dropped onto the surface of heavily doped silicon substrate and spin-coated with 4000 rpm for 30 s by spin coater (KW-4A, purchased from the Institute of Microelectronics of Chinese Academy of Sciences) in a glove box. After that, the sample was irradiated by 172 nm ultraviolet light for 30 min with a power of 1 kW, and the distance between the light source and substrates is 2 cm. The oxygen concentration in the glove box maintained at 4%. During irradiation, PHPS was converted into silica. The thickness is 60 nm measured by spectroscopic ellipsometry (M-2000DI).

The reaction mechanism of PHPS conversion into silica is shown in Fig. 1. Prager *et al.* [37] pioneered the research on the mechanism of ultraviolet irradiation conversion method. They demonstrated the high-energy UV photons can excite the Si–N bond breakage. After bond breakage in the chain, silicon-free radicals are oxidized by oxygen to form Si–O–Si bond. The surface morphology of silica film (Fig. 2a) was characterized by atom force microscope (AFM), revealing a dense and smooth surface. The root mean square roughness (RMS) of the film is only 0.5 nm. This feature satisfies the requirements of dielectric layer in high performance organic transistors. To test the chemical component of silica film, X-ray photoelectron spectroscopy (XPS) spectrum was measured. As shown in Fig. 2b, sharp silicon peak and oxygen peak are clearly observed at 103 and 533 eV, respectively, which demonstrate the film is composed of silicon dioxide. The carbon peak may result from the adsorbed organic contaminants during the storage and transferring, or atmospheric carbon dioxide. To measure the degree of PHPS-to-silica conversion, the atomic contents of the

Figure 2 (a) AFM image of the SiO₂ film. (b) XPS spectra of the SiO₂ film. (c) XRD spectra of the silicon substrate and SiO₂ film. (d) The schematic diagram of silica film-based capacitor. (e) The function of capacitance versus frequency. (f) The current leakage of silica film under different electric field.

obtained film were provided in Fig. S1, where the O/Si mole ratio of 1.97 indicates the high efficiency of this conversion method [38]. Crystallization state of silica has strong influence on the dielectric properties. In Fig. 2c, X-ray diffraction (XRD) spectrum of the silica film shows no visible diffraction peaks (X-ray source is Cu Kα θ/2θ scan), indicating the completely disordered arrangement of atoms. The amorphous property contributes to high barrier properties to ions and small molecules, and is also

Figure 3 AFM image (a) and XRD spectrum (b) of pentacene. (c) Transfer curve and mobility of pentacene transistor. AFM image (d) and XRD spectrum (e) of PDI-8CN2. (f) Transfer curve and mobility of PDI-8CN2 transistor.

beneficial to preventing current leakage under applied voltage bias.

A capacitor with sandwich structure (Fig. 2d) was fabricated to test the electrical performance of the silica film. Square Au pad electrode was deposited on surface of silica film. We measured the capacitance of silica film from 200 Hz to 0.1 MHz, and the capacitance maintains a high average value of 53 nF cm^{-2} in the range of 200–1000 Hz, which is comparable to the theoretical value (57.5 nF cm^{-2}) of thermally oxidized silicon with same thickness. When the frequency increased from 200 Hz to 0.1 MHz, the capacitance only decreased by 10% (Fig. 2e). The stability of this silica film under high frequency endows it with applicable possibility in logic circuit. Besides the capacitance, leakage current is another important parameter to evaluate the electrical performance of dielectric materials in practical application. As shown in Fig. 2f, the silica film could suffer high electric field strength up to 1.3 mV cm^{-1} , while keeping the current leakage under $2 \mu\text{A cm}^{-2}$. This value is low enough to

keep the capacitor not to breakdown in electronic devices.

We utilized the silica film as dielectric layer to construct organic transistor and verify the practical potential of the silica film in electronic devices. The silica film prepared by ultraviolet irradiation conversion has an ultra-flat surface, so it should be beneficial for the growth of crystalline organic semiconductor film. In Fig. 3 and Fig. S2, we fabricated p-type organic transistor and n-type organic transistor, and measured their morphologies and electrical properties. All fabrication process and characterization were conducted in air. Firstly, the silica films were treated by oxygen plasma at 150 W for 3 min, and then modified by octadecyltrichlorosilane (OTS, purchased from Aldrich Sigma) in vacuum oven at 60°C for 1 h. After cleaning with chloroform and ethanol, the silica films were dried. For transistor fabrication, semiconductors and gold electrodes were deposited successively (Fig. 1). For p-type organic transistor, pentacene was deposited in vacuum deposition system with rate of 0.05 Å s^{-1} . The AFM image (Fig. 3a) shows that the grains

are big and dense. The sharp peak of XRD spectrum (Fig. 3b) stems from (001) crystal plane, indicating its high crystallinity. Such morphology and crystallization are beneficial for high mobility in transistor. As expected, the transfer curve of pentacene device in Fig. 3c shows high mobility up to $0.74 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Significantly, this device can be operated under a voltage as small as 3 V, which mainly benefits from the high capacitance of ultrathin (60 nm) silica dielectric layer as well as the high quality of semiconductor film grown on the silica surface. The on/off ratio, threshold voltage and subthreshold slope are derived to be 10^3 , -0.7 V , and 277 mV dec^{-1} , respectively. *N,N'*-bis(*n*-octyl)-dicyanoperylene-3,4,9,10-bis(dicarbox imide) (PDI-8CN2) was deposited on silica in vacuum deposition system with rate of 0.1 Å s^{-1} to further test the generality of silica dielectric for the n-type semiconductor. The AFM image (Fig. 3d) and XRD spectrum (Fig. 3e) also show a good film quality and crystallinity. The mobility of PDI-8CN2 device has a high mobility of $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ compared to the counterpart of thermally oxidized silicon based device. The on/off ratio, threshold voltage and subthreshold slope are calculated to be 10^3 , -0.39 V , and 398 mV dec^{-1} , respectively. We also fabricated transistors based on 100 nm thermally oxidized SiO_2 dielectric to reflect the actual performance of the transistors under our experimental conditions. The electrical data were presented in Fig. S3 and Table S1. The performance of the devices based on silica by ultraviolet irradiation conversion method have comparable even better low voltage operation performance, which indicates good potential in organic electronic devices.

The above results demonstrate that silica film may serve as dielectrics for both p-type and n-type organic transistors, which indicates that the silica film has good potential in the complementary digital circuits. With this regard, we fabricated a complementary inverter based on pentacene transistor and PDI-8CN2 transistor. The schematic diagram is shown in the inset of Fig. 4a. p-Type transistor is the load transistor, and n-type transistor is the drive transistor. The inverter was constructed on 60 nm as-prepared silica film. Heavily doped silicon was used as gate electrode and substrate. After modifying the silica film by OTS, 20 nm pentacene and 30 nm PDI-8CN2 were deposited on both sides of silica with substrate temperature of 45 and 100°C , respectively. Finally, Au electrodes were deposited on top of two kinds of semiconductor with sharing drain electrode by shadow mask. The channel length (L) and width (W) of pentacene transistor are 50 and $500 \mu\text{m}$, while the L and W of PDI-8CN2 transistor are 50 and $1,000 \mu\text{m}$. The static

Figure 4 (a) The static VTC of inverter. Inset: the schematic diagram of inverter. (b) The gain characteristics of complementary inverter.

voltage transfer curves (VTC) of this inverter under different applied V_{DD} is presented in Fig. 4a. When a low voltage was inputted, a clear high voltage was outputted, and similarly, a high inputted voltage got a low outputted voltage. This process corresponds to the logic state conversion, just like “0” state and “1” state conversion. By extracting the data from VTC, the voltage gain was obtained at different V_{DD} in Fig. 4b. The gain ranged from 6–8 V is high enough to drive more complicated circuits. These results illustrate the performance of silica film has a good potential in logic circuit.

In summary, the ultraviolet irradiation conversion from PHPS to silica is an efficient way to fabricate ultrathin, dense and smooth silica film. The film presents excellent electrical properties such as low leakage current and high electric field tolerance. All of these characteristics are beneficial for the construction of high performance and low voltage transistors and circuits. Consequently, it is of significance to apply the method in organic electronic industry because of its mild process conditions and high performance.

Received 12 December 2017; accepted 17 January 2018;
published online 1 February 2018

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Acknowledgements The authors are grateful to the National Natural Science Foundation of China (21573277, 51633006 and 51503221), the National Key Research and Development Program (2016YFA0200700), the Key Research Program of Frontier Sciences of Chinese Academy of Sciences (QY2DBSSWSLH031), and the Natural Sciences Foundation of Jiangsu Province (BK20150368).

Author contributions Li L designed the experiments; Wang Z and Guo S fabricated device; Liang Q assisted in the film fabrication. Wang Z measured performance and wrote the paper with support from Li L, Xing F, Zhang Z, Dong H and Hu W. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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紫外光辐照全氢聚硅氮烷制备超薄二氧化硅膜及其在有机晶体管和反相器中的应用

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摘要 二氧化硅是一种常见且非常重要的介电材料, 但是其传统的制备方法例如物理气相沉积, 化学气相沉积等无法适应大规模生产以及有机电子工业. 本论文介绍了一种简单的制备二氧化硅超薄膜的方法, 即利用紫外光辐照全氢聚硅氮烷, 使其转化为二氧化硅. 这种方法所制备的二氧化硅超薄膜具有超平的表面以及非常低的漏电. 此外, 我们还将该二氧化硅超薄膜应用于有机晶体管和反相器电路中, 这些器件均表现出良好的电学性能. 这些结果表明该方法制备的二氧化硅超薄膜具有很好的实际应用前景.