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Dual role of Ag nanowires in ZnO quantum dot/Ag nanowire hybrid channel photo thin film transistors†

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High mobility and p-type thin film transistors (TFTs) are in urgent need for high-speed electronic devices. In this work, ZnO quantum dot (QD)/Ag nanowire (NW) channel TFTs were fabricated by a solution processed method. The Ag NWs play the dual role of dopant and providing the charge transfer route, which make the channel p-type and enhance its mobility, respectively. The best sample yields an on/off ratio (I_{on}/I_{off}) of 5.04×10^5 , a threshold voltage (V_T) of 0.73 V, a high field effect mobility (μ_{FE}) of $8.69 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and a subthreshold swing (SS) of 0.41 V dec^{-1} . Owing to the strong ultraviolet (UV) absorption and photo-induced carrier separation ability of ZnO QDs and the fast carrier transport of Ag NWs, the devices acquire a high external quantum efficiency (EQE) and ultra-fast response under 365 nm UV illumination. The UV-modulated ZnO QD/Ag NW hybrid channel photo TFTs have potential for future application in optoelectronic devices, such as photodetectors and photoswitches.

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Introduction

Thin film transistors (TFTs) based on metal oxide semiconductors are a key constituent for numerous optoelectronic devices such as sensors and displays. High mobility p-type TFTs are in urgent need for complementary metal oxide semiconductor (CMOS) technology. Wide-band gap metal oxide semiconductors, such as zinc oxide (ZnO),¹ zinc-indium-tin oxide (ZITO),² and indium-gallium-zinc oxide (IGZO)³ have been widely studied for TFTs. ZnO, owing to its abundance, low price, and being indium free, has great potential in the application of TFTs. Various dopants, such as H,⁴ Li,⁵ Na,⁶ Ca,⁷ B,⁸ Al,⁹ and Ti¹⁰ have been utilized to acquire better electrical performance. However, most research is focused on n-type TFTs. p-Type TFTs materials are limited to NiO,^{11–13} SnO,^{14–19} and Cu_xO.^{20–23} There is rarely a report about ZnO-based p-type TFTs due to the difficulty of p-type doping in ZnO.

Recent great progress in light emitting diode (LED) attracts the attention in quantum dots (QDs).²⁴ Quantum confinement effect makes QDs be considered as promising material for the optoelectronic devices. Thus, ZnO QDs with the appropriate band gap may be utilized in ultraviolet (UV)-related photo transistors. Compared with RF magnetron sputtering, pulsed

laser deposition, and atomic layer deposition, solution-processed colloid ZnO QDs can be synthesized at low-temperature to fulfill the progressive demands for low-cost devices. For one-dimensional nano-material, nanowires (NWs) have been widely studied due to the transport of carriers confined in one dimension. Recently, Zou²⁵ and Park²⁶ fabricated NWs and nanorods (NRs) thin film transistors and acquired high field effect mobility (μ_{FE}) owing to this property. The μ_{FE} are $110 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for In₂O₃ single NW TFTs and $1.77 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for ZnO NRs TFTs, respectively. The composite material combined with nanoscale components is the foremost scientific research now, which can take full advantage of these constituents. There were some reports about hybrid channel of ZnO and graphene with UV response.^{27–30} Herein, we employ the Ag NWs utilizing its good conductivity to improve hybrid channel mobility. Besides, Ag is doped into ZnO QDs by annealing, which realizes the ZnO based p-type TFTs. With strong light absorption and photo-induced carriers separation ability of ZnO QDs and fast carrier transport of Ag NWs, it is expected to fabricate these hybrid channel TFTs for the future photo-modulate transistors.

Experimental

Synthesis of colloid ZnO QDs

Colloid ZnO QDs were synthesized by the previous method with some modification.²⁴ In a typical reaction, 3 mmol zinc acetate hydrate and 30 mL dimethyl sulphoxide (DMSO) are loaded in a flask with magnetic stirring under ambient conditions. After zinc acetate being completely dissolved, 10 mL ethanol solution

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of 5.5 mmol tetramethylammonium hydroxide (TMAH) is added slowly. The reaction is proceeded for 2 h. The obtained stock was divided into 8 parts. Each part is precipitated by adding 5 mL ethyl acetate. After centrifugation, each one is redispersed in 2 mL ethanol with additional ligands of 30 μL 2-ethanolamine to stabilize the nanoparticles. The ZnO QDs are further washed with ethyl acetate and redispersed in 4 mL ethanol. The solution is filtered by 0.22 μL PTFE filter before use. The details of characterization of ZnO QDs are presented in the electronic ESI.†

Devices fabrication

Fig. 1a shows the fabrication process and framework of device. The channel is deposited on the p^{++} Si/300 nm SiO_2 of (100) orientation substrate. The wafers were purchased from University Wafer and cleaned in ultrasonic baths of acetone, ethanol and deionized water for 10 min, respectively, followed by drying with N_2 gas and oxide plasma treatment before used. Then, the Ag NWs film is grown by dip-coating technic. Ag NWs dispersed in ethanol were purchased from Jinan Shangke New Material Co., Ltd. The average length and width of Ag NWs are 60 μm and 80 nm, respectively. The concentration of Ag NWs is diluted to 0.1 mg mL^{-1} and the lifting speed of substrate is 10 $\mu\text{m s}^{-1}$. The NWs would self-assemble aligned owing to the surface tension and solvent evaporation. ZnO QDs were then spin-coated on the NWs film at 3000 rpm. for 35 s, twice. Subsequently, ambient annealing process at different temperature was carried out for 1 h. 100 nm thick Al electrodes were finally evaporated by electron beam evaporation technology with shadow mask as source and drain. The channel width and length were 1000 and 200 μm , respectively.

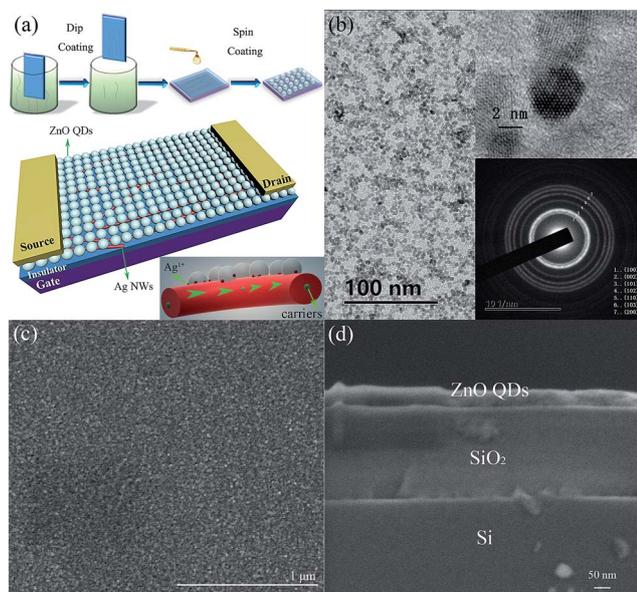


Fig. 1 (a) The schematic diagram of the TFT structure. (b) TEM image and HRTEM image of the ZnO QDs. (c) The surface SEM image of TFT. (d) The cross-section SEM image of TFT.

Characterization

Size and morphologies of ZnO QDs were characterized by high-resolution transmission electron microscopy (HRTEM, JEM-2100). The arrangement of Ag NWs, surface morphologies and cross-section of ZnO QDs film were observed by field-emission scanning electron microscopy (FE-SEM Hitachi S-4800). X-ray photoelectron spectroscopy with a monochromatic Al-K α (1486.6 eV) X-ray source (XPS, Thermo ESCALAB 250) measurements were performed to investigate whether Ag was doped into ZnO QDs after annealing. The performances of TFTs were tested with a semiconductor parameter analyzer (Agilent E5270B). The temporal response of UV was examined with a UVA-LED (365 nm).

Results and discussion

Characterization of hybrid channel

Fig. 1b shows the TEM image of ZnO QDs, and the inserts are HRTEM images. The diameters of ZnO QDs are 4 nm on average. The diffraction rings correspond to the X-ray diffraction (XRD) pattern in the Fig. S2 in the ESI,† which confirms the formation of ZnO phase. Fig. 1c and d are the surface and cross-section SEM images of TFT, respectively. Fig. 1c indicates that the spin-coated ZnO QDs film on the Ag NWs is smooth and flat. And the ZnO QDs film has a thickness of about 50 nm as shown in Fig. 1d.

To investigate the performance of TFTs and reveal the carrier transport of different morphological feature of Ag NWs, the TFTs are annealed at 100, 150, 200, and 300 $^{\circ}\text{C}$, respectively. From Fig. 2, Ag NWs keep the NW shape under 100 and 150 $^{\circ}\text{C}$, while melt into particles under 200 and 300 $^{\circ}\text{C}$. However, ZnO QDs barely have change from the SEM images (the insert graph in Fig. 2).

To clarify whether Ag was doped into ZnO QDs, XPS measurement was conducted on the sample annealed at 100 $^{\circ}\text{C}$.

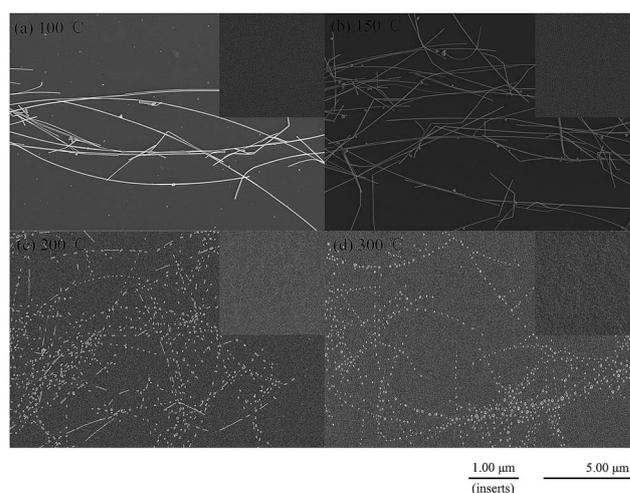
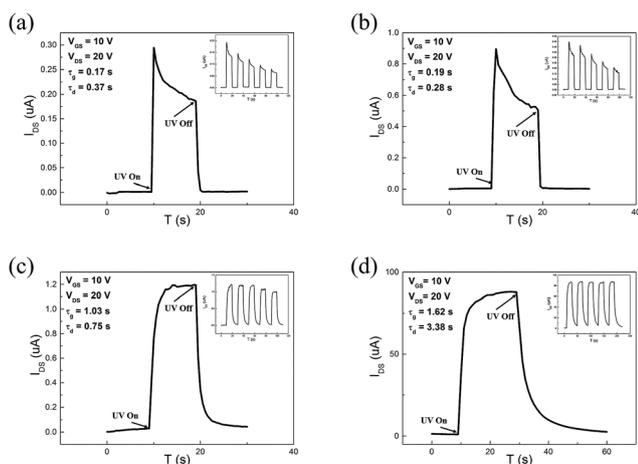


Fig. 2 The SEM images of Ag NWs at different annealing temperature (a) 100 $^{\circ}\text{C}$, (b) 150 $^{\circ}\text{C}$, (c) 200 $^{\circ}\text{C}$, (d) 300 $^{\circ}\text{C}$. Inserts are the corresponding surface of ZnO QDs film.



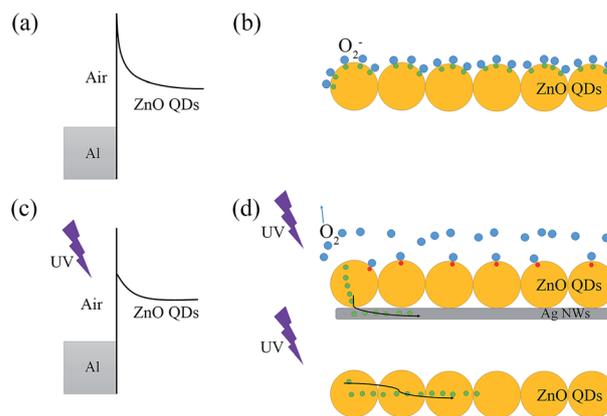
Table 1 Electrical parameters of TFTs with ZnO QDs/Ag NWs hybrid channel

Sample (at different annealing temp.)	V_T (V)	μ_{FE} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	SS (V dec^{-1})	I_{on}/I_{off} ($\times 10^5$)
100 °C	0.73	8.69	0.41	5.04
150 °C	3.33	1.74	1.41	0.36
200 °C	2.5	0.16	1.64	0.39
300 °C	15	0.52	1.26	0.09

**Fig. 5** The growth and decay of photocurrent of photo transistors at different annealing temperature (a) 100 °C, (b) 150 °C, (c) 200 °C, (d) 300 °C. Inserts are five repeated cycles.

200 and 300 °C. The characteristic times for growth (τ_g) and decay (τ_d) of the photocurrent are 0.17 and 0.37 s of sample annealed at 100 °C. In Fig. 5a and b, the photo current (I_{photo}) generates and rapidly soars to a maximum, while exposed to the ultraviolet. Due to the current crowding effect, the carriers accumulate in the NWs and I_{photo} will decrease to a stable value. When the UV light is off, the I_{photo} quenches to I_{dark} level. The response of UV is like our previous ZnO NR UV photodetectors.^{34–36} About samples annealed at 200 and 300 °C, the response is much slow and similar to the ZnO nanoparticles UV photodetector.³⁷ The time-resolved UV response confirms the charge transfer mechanism discussed above.

Fig. 6 depicts the energy band of surface ZnO QDs and the schematic diagram of charge transfer. As a result of the chemical absorbed O_2 on the surface of ZnO QDs without UV light, the oxygen molecules capture free electrons [$\text{O}_2(\text{g}) + \text{e}^- = \text{O}_2^-(\text{ad})$], which makes the band of ZnO QDs bend upward and create a low conductivity depletion region on the surface. The effect is particularly prominent in oxide semiconductors, especially in nano structures. Under UV illumination with photon energy higher than the semiconductor band gap, photo-induced hole–electron pairs generate. The photo-generated holes react with the chemisorbed oxygen [$\text{h}^+ + \text{O}_2^-(\text{ad}) = \text{O}_2(\text{g})$], resulting in increasing of free carrier concentration in the ZnO QDs and forming the carrier transport route in different situation, as shown in Fig. 6b and d.

**Fig. 6** The energy band of the surface ZnO QDs under (a) dark and (c) UV illumination, and the schematic diagram of the charge transfer under (b) dark and (d) UV illumination. Red dots = holes, and green dots = electrons.

Moreover, some significant UV response parameters are listed in Table 2. The calculated values are all applied at V_{GS} of 10 V and V_{DS} of 20 V. The responsivity (R) is used to indicate the photo-to-current efficiency. It is determined by the eqn (3):

$$R = \frac{I_{\text{photo}} - I_{\text{dark}}}{PS}, \quad S = L \times W \quad (3)$$

where P is the optical signal power density, and S is the effective photo-electric conversion area, respectively. The device performance can be expressed in terms of another vital parameter, external quantum efficiency (EQE), which is a function of photon flux density and incident photon energy as eqn (4):

$$\text{EQE} = \frac{I_{\text{photo}}/q}{P/h\nu} \quad (4)$$

where q is the quantity of one electron, h is the Plank constant, and ν is the frequency of absorbed photon. Note that the R and EQE both increase mainly by the I_{photo} in the same condition.

As discussed in XPS data, as-implanted Ag atoms by annealing occupy almost ideal substitutional Zn sites.³⁸ Ag atoms are incorporated in the form of point defects of Ag_{Zn} acceptor in $3d^{10}$ states, with part of the silver formed with silver oxide.³⁹ The Ag_{Zn} acceptor actualizes the formation of p-type ZnO. Besides, the heterojunction formed by ZnO QDs and Ag NWs makes the fast response of UV detection. The photo-induced carriers from UV illuminated ZnO are transferred to Ag NWs and transported away rapidly. The dual role of Ag NWs is depicted clearly in Fig. 1a.

Table 2 UV response parameters of ZnO QDs/Ag NWs hybrid channel TFTs

Sample (at different annealing temp.)	τ_g (s)	τ_d (s)	R (A W^{-1})	EQE (%)
100 °C	0.17	0.37	0.64	218
150 °C	0.19	0.28	2.33	793
200 °C	1.03	0.75	6.01	2048
300 °C	1.62	3.38	351	119 565



Conclusions

In summary, we have fabricated the photo-modulated p-type TFTs with ZnO QDs/Ag NWs hybrid channel, and cleared the charge transfer in the channel under UV illumination. At low annealing temperature of 100 and 150 °C, the Ag NWs firstly provide the Ag dopant and make the thin channel p-type as XPS measurements and TFTs transfer characteristic demonstrated. Moreover, Ag NWs play a role of charge transfer route, which enhances the μ_{FE} . The sample annealed at 100 °C yields an on/off ratio (I_{on}/I_{off}) of 5.04×10^5 , a V_T of 0.73 V, a μ_{FE} of $8.69 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and a SS of 0.41 V dec^{-1} . In addition, the TFTs show superior response of 365 nm UV illumination due to the surface ZnO QDs. Owing to the strong UV absorption and photo-induced carriers separation ability of ZnO QDs and fast carrier transport of Ag NWs, the devices display the high EQE and ultra-fast response. The sample annealed at 100 °C acquire a 0.17 s of τ_g , 0.37 s of τ_d , 0.64 A W^{-1} of responsivity, and 218% EQE. The UV-modulated ZnO QDs/Ag NWs hybrid channel TFTs have potential for the future application in optoelectronic devices, such as photodetector and photoswitch.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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