Nonvolatile Memory Thin Film Transistors using CdSe/ZnS Quantum Dots-PMMA Blend Layer as Floating Gate
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1. Introduction
Recently, the flash memory and nonvolatile memory with the floating gate structure are the most popular storage media of mobile devices due to the high reproducibility of data. Nevertheless, the data loss problem is a main research topic. For the purpose of reducing the storage data loss, novel memory structures are continually developed. The ferroelectric materials, such as poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) \cite{1}, and poly-m-xyylene adipamide \cite{2}, have extensively replaced the dielectric layer of the organic thin film transistors (OTFTs) to store the necessary data by the electric dipoles and polarization effect. The charge electret materials with the charge-storage or slow polarization characteristics, such as polyvinyl alcohol (PVA) \cite{3} and polystyrene \cite{4} are also suitable as the gate dielectric for the memory devices application. Moreover, the nanoparticles are also used to replace the floating gate in the conventional flash memory. These devices exhibit low leakage current and long retention time. In this article, we fabricate and characterize the OTFTs using the core/shell CdSe/ZnS quantum dots (QDs)-poly(methyl methacrylate) (PMMA) blend layer as floating gate. After blend layer was modified with PMMA/toluene solution, the strong memory effect and electric characteristics are significantly improved.

2. Experimental Details
The device configuration of the nonvolatile memory organic thin film transistor (NMOTFTs) using the surface-modifying QDs-PMMA blend layer is shown in Fig. 1 (a). The fabrication process of the device is carried out on the heavily doped n-type silicon (Si) wafers as the gate electrodes. First of all, the QDs are capped with the trictylphosphine oxide (TOPO) and well-dispersed in toluene with the concentration of 10 mg/ml. Subsequently, PMMA is blended into the QDs-solution with a concentration of 2 wt. % and stirred for 24 hours. Fig. 1 (b) shows the transmission electron microscopy (TEM) image of the QDs. The average diameter of the QDs is 5.4 nm. The molecular weight of PMMA is 996,000. After the QDs-PMMA blend solution preparation, silicon dioxide (SiO\textsubscript{2})-coated Si substrates are cleaned by the acetone and isopropyl alcohol in an ultrasonic bath and then the blend solution is spin-coated on SiO\textsubscript{2} film at 1000 rpm for 40 seconds, followed by baking at 70 °C for 1 hour. The thicknesses of SiO\textsubscript{2} and polymer blend films are 300 and 100 nm, respectively. The surface of the blend film is then modified by spin-coating 2 wt. % PMMA-toluene solution at 7000 rpm for 40 s. Afterward, a 60-nm-thick pentacene film is deposited on the modified blend film as the channel layer through the shadow mask by using thermal evaporation under a vacuum level of 1×10\textsuperscript{-6} Torr. Finally, the source and drain electrodes are formed by thermal evaporating Au through a shadow mask. The thickness of Au film is 150 nm. The channel length and width are 100 and 500 μm, respectively. The devices characterization after fabrication is carried out by using the sourcemeter system (model 2400, Keithley Instruments Inc.) in a nitrogen-filled glove box. Moreover, the alpha-step profile-meter and tapping mode atomic force microscope (AFM) are also used to measure the thickness and surface morphology of the composite film, respectively.

3. Results and Discussion
Fig. 2 shows the x-ray diffraction (XRD) spectra of the pentacene films on the non-surface-modified and surface-modified blend layers. The XRD is carried out in the symmetric reflection coupled 0-2θ arrangement. The XRD patterns are obtained using Cu Kα radiation (λ=1.5406 Å) and wide-angle graphite monochromator. Here, the x-ray diffraction of both pentacene films show the same characteristic diffraction peaks position. The peaks at 2θ = 5.7°, 11.5°, and 17.2° can be attributed to the thin film phase (00l') of pentacene, and the other diffraction peaks at 2θ = 6.1°, 12.2°, 18.4° and 24.0° are associated with the triclinic bulk phase (00l) of pentacene \cite{5}. For the pentacene film on the non-surface-modified QDs-PMMA blend layer, the peak intensity of the thin film phase is not significant than that of the triclinic bulk phase. Especially, the diffraction

![Fig. 1 (a) The device configuration of the nonvolatile memory OTFTs and (b) TEM images of the QDs used in this experiment.](image-url)
intensities of the both phases are much weaker when com-
pared with that of the pentacene film on the sur-
face-modified QDs-PMMA blend layer. This result sug-
gests that a crystallite quality of pentacene film grown on
the surface-modified QDs-PMMA blend layer surface is
better than that on the non-surface-modified QD-PMMA
blend layer. From the peaks position, the interlayer spacing
(d-spacing) for both pentacene films is simultaneously ob-
tained to be 15.4 Å by Bragg’s law.

Fig. 2 XRD spectra of the pentacene films on the
non-surface-modified and surface-modified blend layers.

Fig. 3 (a) shows the write-read-erase-read (WRER)
cycles of the OTFTs with the surface-modified
QDs-PMMA blend layer. The writing and erasing operation
are carried out by applying a gate-source voltage \( V_{\text{GS}} \) of
+150 V and -150 V for 10 seconds, respectively. The
memory states are read out with a small \( V_{\text{GS}} \) of -5 V. Dur-
ing the measurement, the drain-source voltage is fixed at
-40 V. High probing drain-source current \( I_{\text{DS}} \) is defined to
be on state and low \( I_{\text{DS}} \) is defined to be off state of the fab-
ricated memory unit. The probed \( I_{\text{DS}} \) at on state is one or-
der of magnitude higher than that of the off state. The de-
vices can be operated for more than 100 times without any
current degradation. Fig. 3(b) shows the retention charac-
teristics of the OTFTs with the surface-modified
QDs-PMMA blend layer. The on- and off states of the de-
vice can be clearly discriminated. Nevertheless, the full
charge loss occurs after about 10^6 seconds.

4. Conclusions
In conclusion, the nonvolatile memory organic thin film
transistors (OTFTs) using core/shell CdSe/ZnS quantum
dots (QDs)-poly(methyl methacrylate) (PMMA) blend
layer as floating gate have been fabricated and charac-
terized. It can be observed that the OTFTs using
QDs-PMMA blend layer surface-modified with the PMMA
solution showed a strong memory behavior and good elec-
tric performance. The memory behaviors are attributed to
the charge storage/discharge effect in the QDs-PMMA
blend layer. Under the programming and erasing operations,
good programmable memory characteristics are obtained.
In addition, the retention characteristics showed a good
reliability.

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