Abstract—We present an electrical-bistability device based on MIM-sandwiched structure. Poly(N-vinylcarbazole) (PVK) mixed with gold nanoparticles (GNPs) serve as the active layer between two metal electrodes. After applying a voltage, the as-fabricated device can transit from low conductivity state to high conductivity state. By simply using a reverse bias, the high conductivity state can return to the low conductivity state. An ON/OFF current ratio as high as 10^5 at room temperature has been achieved. The memory effect is attributed to electric-field-induced charge transfer complex formed between the PVK and the GNPs. The device shows a good stability under stress test for both states and exhibits a high potential on Flash-type memory applications.

Index Terms—Electrical bistability, gold nanoparticle (GNP), memory effect, poly(N-vinylcarbazole) (PVK), thin-film device.

I. INTRODUCTION

In the past years, organic semiconductor materials have exhibited strong potentials as the active materials in different electronic devices, such as light-emitting diodes [1], field-effect transistors [2], logic gates [3], optocouplers [4], photodetectors [5], and lasers [6]. Very recently, organic memory devices attract a lot of attention due to their simplicity in structure, good scalability, low-cost potential, 3-D stacking capability, and large capacity for data storage. Rather than encoding “0” and “1” as the amount of charge stored in a cell in silicon devices, organic memory stores data, for instance, based on the high and low conductivity response to an applied voltage. Different types of memory devices, such as Flash-type memory [7]–[12], write-once-read-many-times memory [13]–[15], and dynamic-random-access memory [16], have been demonstrated. For some devices, the memory effect comes from the materials themselves. Examples of these materials include Rose Bengal [7], DDQ [8], poly[3-(6-methoxyhexyl) thiophene] [9], PEDOT [13], PPEu [14], PCBM/TCNQ [15], and PFOxPy [16]. There is another kind of nanoparticle-based organic memory device [10]–[12], where the organic material itself has no memory effect and the memory effect is a result of the nanoparticle incorporated. An organic bistable memory device by embedding aluminum nanoparticles in an organic layer through thermal evaporation [10] has been demonstrated. However, an accurate control of aluminum deposition process is needed. Later, a polymer memory device has been reported by using mixture of gold nanoparticles (GNPs), 8-hydroxyquinoline (8HQ), and polystyrene (PS) [12]. The 8HQ serves as the electron donors, the GNPs serve as the electron acceptors, and the PS only serves as matrix and plays no role in the memory effect.

In this letter, we report on the fabrication and operation of a MIM structured nonvolatile memory device using poly(N-vinylcarbazole) (PVK) containing GNP as the active layer between two electrodes. In our device, the PVK serves as both the matrix and electron donor [17], and the GNP serves as electron acceptors. The as-fabricated device exhibits a low conductivity property and can be programmed to high conductivity state, with a high ON/OFF current ratio up to five orders of magnitude. The high conductivity state can also be erased to the low conductivity state by only using a reverse bias. It has the strong potential on Flash-type memory device applications.

II. EXPERIMENTAL

The chemical structures of the PVK and GNP are shown in the inset of Fig. 1(a). The PVK was obtained from Aldrich Chemical Co., and the GNP was prepared by the two-phase growth method [18]. Fig. 2 shows the transmission electron microscopy picture of the GNP, with a size distribution of 1.5–6.5 nm. The PVK:GNPs solution was prepared by mixing the PVK and GNPs with a weight ratio of 12:1 into the toluene solvent. The inset of Fig. 1(b) shows the basic device structure consisting of the PVK:GNPs film sandwiched between a TaN bottom electrode and an Al top electrode. The TaN was sputtered onto the SiO_2 covered Si substrate through a shadow mask with 200-µm wide lines. The shadow mask was used to pattern and define the electrode area. The toluene solution of PVK:GNPs was sequentially spin-coated on the TaN, followed by solvent evaporation in a vacuum chamber at 10^{-5} torr under 60 °C for 9 h. The thickness of the polymer film was about 130 nm, as measured by a step profiler. Finally, the top Al electrode was thermally evaporated with linewidth of 200 µm at a pressure of ∼10^{-7} torr through a shadow mask. The top and bottom electrodes were aligned perpendicular to each other, so as to define an active cross area of 200 × 200 µm. A
Fig. 1. (a) UV-visible absorbance spectra of GNP, PVK, and PVK:GNPs in THF solutions \((1 \times 10^{-5} \text{ mol/L})\). Inset: Molecular structure of the PVK and schematic structure of the GNP. (b) UV-visible absorbance spectra of GNP, PVK, and PVK:GNPs films on quartz (the curves are normalized for a better view). Inset: Schematic diagram of the Al/PVK:GNPs/TaN MIM memory device.

control sample based on PVK-only solution was also prepared. Electrical measurements were carried out using a HP 4156A semiconductor parameter analyzer in a dark chamber with the TaN electrode grounded. All electrical measurements were conducted under ambient condition without any encapsulation.

### III. Results and Discussion

The UV-visible absorption spectra of GNP, PVK, and PVK:GNPs in THF solution \((1.0 \times 10^{-5} \text{ mol/L})\) and as a thin film on quartz are shown in Fig. 1(a) and (b), respectively. The GNP shows a broad absorption band extending through the entire UV-visible spectrum. The undoped PVK solution exhibits three strong absorption bands at 295, 331, and 344 nm (correspond to the \(1A \rightarrow 1L_a\) and \(1A \rightarrow 1L_b\) transitions), with the absorption edge at about 370 nm [19]. Due to the low concentration of GNP in solution, PVK:GNPs mainly shows the absorption peaks of the undoped PVK. However, the absorption edge of PVK:GNPs has also been extended into the long wavelength range. As shown in Fig. 1(b), the GNP and undoped PVK film exhibit similar absorption behavior as they are in solution, while the absorption peaks of PVK:GNPs film are obviously broadened. This phenomenon has probably arisen from the interaction between the GNP and PVK in solid state when excited by UV irradiation. The far distance between GNP and PVK in dilute solution can prevent such an interaction. The charge transfer complex formed between the GNP and PVK in the solid state can extend the delocalization of carbazole moiety, and thus broaden the absorption peaks [20].

The memory effect of the device is observed in the \(J-V\) characteristics of the Al/PVK:GNPs/TaN sandwich device, as shown in Fig. 3. The \(J-V\) characteristics are recorded by scanning the applied voltage from 0 to 4 V and then going back to 0 V. It distinctively displays two conducting states. With an applied voltage on the as-fabricated device, although the current increases slowly with the voltage, the current remains low. The current density is in the range of \(10^{-8} \text{ A/cm}^2\) at 1 V. This is the low conductivity state \(\text{OFF-state}\). When the applied voltage is increased further to \(\sim 3 \text{ V}\), a sharp increase in the current is observed, indicating the device transition from the \text{OFF}-state to a high conductivity state \(\text{ON-state}\). This transition from the \text{OFF}-state to the \text{ON}-state serves as the “writing” process for the memory device. For the programmed device, the device shows a high current for the voltage applied. The current density at 1 V is about \(10^{-3} \text{ A/cm}^2\). This current is five orders of magnitude higher than that in the \text{OFF-state}. The inset (a) of Fig. 3 shows the ratio of the \text{ON} to the \text{OFF}-state current as a function of the applied voltage. The distinct biellectrical states in the voltage ranging from 0 to 2 V allow a low voltage (e.g., 1.0 V) to read the “0” or “OFF” signal (before writing) and “1” or “ON” (after writing) signal of the device. Curve 2 in Fig. 3 shows a sweep from 0 to 4 V after the first sweep. It can be seen that the device, after reaching its high conductivity state, remains in this \text{ON-state} even turning off the power. The \text{ON-state} can be returned to the \text{OFF-state} by applying a reverse bias as indicated in curve 3, where the current density suddenly drops to \(10^{-8} \text{ A/cm}^2\) at \(-1.7 \text{ V}\), corresponding to the “erasing” process for the memory device. The erased state (“0”) could be further written to the high conducting state (“1”) when a switching threshold voltage is applied.

Fig. 3. Typical \(J-V\) characteristics of the Al/PVK:GNPs/TaN device. Inset: (a) The \text{ON/OFF} current ratio as a function of applied voltage and (b) \(J-V\) characteristics of the Al/PVK/TaN device.
indicating that the memory device is rewritable, as indicated in curve 4. The write and erase processes can be repeated for about 50 times. Besides, no memory effect was observed from Al/PVK/TaN device, as shown in the inset (b) of Fig. 3.

The electrical bistability suggests that the Al/PVK:GNPs/TaN devices can be used as nonvolatile Flash-type memory. Since stability is a very important characteristic to memory device, the stability of the device was characterized under a constant voltage stress of 1.0 V, as shown in Fig. 4. Little degradation in current density for both the ON- and OFF-states was observed during the test. The thermal stability of the device in both the ON- and OFF-states was also measured. The device was found to be stable in both its ON- and OFF-states from room temperature to around 70 °C (Inset of Fig. 4). The response time for both write and erase processes has also been measured. The device in the OFF-state can be switched back to the ON-state by a pulse of 6 V with a width of 1 μs. The device in the ON-state can be switched back to the OFF-state by a pulse of −10 V with a width of 1 μs.

Electrical bistability and memory effect in the Al/PVK:GNPs/TaN devices are due to the incorporation of GNPs in the PVK. By mixing the GNPs into the PVK polymer, the PVK serves both as the matrix for GNPs and electron donor since it has a strong capability to provide electrons [17], while the GNPs act as electron acceptors. Since PVK is dominant in the active layer of our devices, it serves as the path for charge carrier transport. When a high electric field is applied to the device, the electric-field-induced charge transfer complex between the PVK and GNPs will be formed with the PVK positively charged and the GNPs negatively charged. The distortion due to the presence of a charge tends to change the electronic states in the vicinity of the charge such that the HOMO energy level shifts upward and the LUMO energy level shifts downward [21]. This change will decrease the bandgap and increase the conductivity of the organic materials. It is known that charge transfer complex strongly depends on the electric field. For the devices in the ON-state, a reverse bias could cause the charge transfer complex return back to their original states, and hence, the device will be erased to its OFF-state.

IV. CONCLUSION

In summary, a novel polymer memory device, based on the spin-coated PVK:GNPs mixture film, has been demonstrated. In this device, the PVK serves as matrix and electron donor, and GNPs serve as electron acceptors. Due to the charge transfer complex formation between the PVK and GNPs under the electric field and its capability of returning to their original states, the device can be switched between the low conductivity state and high conductivity state. At a specified voltage, the device exhibited two conductivity states with an ON/OFF current ratio up to $10^5$. The device remains in either state even after the power has been turned off, and shows a good stability under stress test. This device has the potential use for low-cost Flash-type memory applications.

REFERENCES


