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Synthesis of Silver Nanoparticles for Organic Bistable Memory Device Applications

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Abstract: Poly (vinyl pyrrolidone) (PVP) capped spherical silver nanoparticles (Ag NPs) were synthesized using polyol process. In this process, silver nitrate (AgNO_3) acts as precursor, ethylene glycole (EG) as reducing agent and PVP as capping agent. Field emission scanning electron microscopy images revealed the spherical geometry of nanoparticles with narrow size distribution. The sharp linear absorption band confirmed the high monodispersity in size and shape of nanoparticles. Bistable memory devices were fabricated by embedding synthesized nanoparticles between two tris-(8-hydroxyquinoline)aluminum (Alq_3) layers and memory characteristics were studied using current-voltage (I-V) characteristics. When the applied voltage exceeds a threshold value (6.5 V), the device suddenly switches from a low current OFF state to a high current ON state. The device exhibited an ON/OFF current ratio of more than 100 at a read voltage of 4 V. The OFF state of the device could be recovered by applying a negative voltage pulse above -5 V. Applied voltage induced transfer of electrons between Ag NPs and Alq_3 layers is proposed to be responsible for switching between different conducting states. Present study indicates that the Ag NPs synthesized using polyol process have strong potential in non-volatile organic memory applications.

Keywords: Synthesis of Silver Nanoparticles for Organic Bistable Memory Device Applications.

Introduction

In past few years, organic semiconductor devices such as solar cells, light emitting diodes, transistors and memory devices, have gained considerable research attention due to their mechanical flexibility, tunable optoelectronic properties, ease of manufacturing and low cost processing¹. Among these, bistable memory devices have showed rapid progress as key elements of organic integrated circuitry². Compared to their inorganic counter parts, organic memory devices (OMDs) have many advantages like high data storage, high response speed and large area device fabrication³. Moreover, the OMDs can offer superior physical and electronic properties. The basic feature of a memory device is its ability to switch between two or more conducting states at the same applied voltage, with conductivity differs in several orders of magnitude. The phenomenon of electrical bistability has been investigated in both thermally evaporated and solution processed organic thin films for more than 30 years^{4,5}. Memory effect has been demonstrated in various device architectures such as single organic layer sandwiched between two electrodes⁶, polymer-metal nanoparticle blend structures³, tri-layer organic/metal nanoparticle/organic structures⁷ and donor-acceptor systems⁸. Among

these, tri-layer device architecture is one of the promising structures to study the memory effect. The tri-layer structure consists of organic layer/metal nanoparticle layer/organic layer sandwiched between two electrodes. The bistability can be achieved by applying voltage pulses with different polarities. Ma and co-workers demonstrated the memory effect in tri-layer 2-amino-4,5-imidazoledicarbonitrile (AIDCN)/Al nanoparticle/AIDCN device⁹. This device exhibited one million read-write-erase cycles with an ON/OFF current ratio of more than 10^6 . Switching time of the device is less than 10 ns. The importance of metal nanoparticles in tri-layer OMDs was reported by Francesco et al. in theoretical and simulations point of view¹⁰. The crew suggested that the switching between different conducting states is due to the applied voltage induced charge trapping and de-trapping in metal nanoparticles. Bozano et al. have studied the effect of different metal nanoparticles, electrodes and organic materials on the performance of tri-layer memory devices¹¹. The performance of tri-layer memory device is sensitive to size and density of metal nanoparticles that are difficult to control using thermal evaporation technique. In present investigation, we synthesized Ag NPs using a solution based synthesis procedure called polyol process, which offers good control on size and morphology of nanostructures¹². Organic bistable memory devices were fabricated by embedding these synthesized Ag NPs between two Alq₃ layers, sandwiched between indium tin oxide (ITO) and Al electrodes.

Experimental

Synthesis of silver nanoparticles

Ag NPs were synthesized using polymer mediated polyol process. In this process, AgNO₃ (99.0%, Sigma Aldrich) acts as precursor, EG (99.0%, Merck) as reducing agent and PVP (99%, M_w= 55000 g/mol, Aldrich) as capping agent. The molar ratio of repeating unit of PVP and Ag NO₃ was kept as 0.11. Initially, EG solution of PVP (0.027 mol l⁻¹) and Ag NO₃ (0.25 mol l⁻¹) was vigorously stirred at room temperature in two necked round bottom flask with reflux condenser, followed by heating the solution up to 120°C at a heating rate of 7.5 °C min⁻¹. Then, the reaction mixture was kept at 120°C for 30 min. The scheme of Ag NP growth is shown in fig. 1(a). In polyol method, particle size and shape are very sensitive to process parameters such as concentration of AgNO₃, PVP/AgNO₃ molar ratio, reaction time and temperature¹². When the reaction mixture is heated, the temperature of the reactants increases gradually and leads to the reduction of Ag⁺ species to Ag⁰. Initially, many nucleation centers are formed when the temperature of reaction mixture is raised to 120°C and they grow slowly as nanoparticles with protective agent PVP. It is observed that the nanoparticle size increases with increase in reaction time. The solution went through a series of colour changes, including light yellow, dark yellow and greenish yellow. The final solution appeared green-ochre at the reaction media and dark ruddy-red at the meniscus. The solution was repeatedly washed with ethanol to remove excess of PVP and EG for further characterization. Field emission scanning electron microscopy (FE-SEM) (HITACHI, SU6600) was used to study the size and shape of synthesized Ag NPs. For FE-SEM studies, the films were prepared by drop casting the solution onto a cleaned ITO glass slide, followed by drying at room temperature. The FE-SEM was performed at accelerating voltages 10-15 kV. UV-Vis Near-Infrared spectrophotometer (Perkin Elmer-Lambda 35) was used to record the linear absorption spectra of synthesized nanoparticles.

Fabrication of memory device

The tri-layer memory device with structure, ITO/Alq₃ (20 nm)/Ag NPs/Alq₃ (20 nm)/Al, was fabricated to investigate the memory characteristics (Fig. 1(b)). Initially, the patterned ITO was cleaned thoroughly in acetone, isopropyl alcohol and de-ionized water sequentially. Both the Alq₃ layers were deposited by thermal evaporation at a base pressure of 1×10^{-5} mbar. The middle Ag NPs layer was prepared by drop casting ethanol solution of Ag NPs onto bottom Alq₃ layer followed by annealing at 50-60°C. Finally, 80 nm thick Al strips were deposited by thermal evaporation through a shadow mask. Thickness of various layers was determined using quartz crystal thickness monitor. The I-V characteristics of the memory devices were measured using precision source measure unit (Agilent, B2902A).

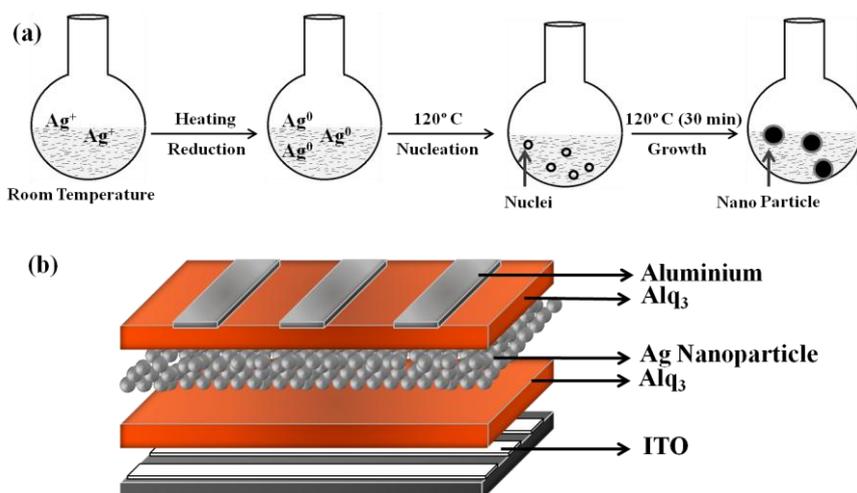


Fig. 1. (a) Schematic illustration of growth of Ag NPs using polyol method and (b) schematic diagram of the memory device architecture.

Results and Discussions

Fig. 2(a) shows the FE-SEM image of synthesized nanoparticles. This image reveals the presence of spherical nanoparticles with diameter 40-50 nm. Linear absorption spectrum of synthesized Ag NPs is shown in fig. 2(b). The sharp absorption band centered at 424 nm indicates the high monodispersity in size and shape of nanoparticles. Fig. 3(a) shows the I-V characteristics of the memory device obtained by sweeping the voltage from -8 to +8 V and then back to -8 V. During the voltage sweep from -8 to +8 V, the device remains in high resistance (OFF) state until a threshold voltage ($V_{th} \sim 6.5$ V) is applied to the device. The sudden change in current was observed at V_{th} and current reached the maximum value at ON voltage ($V_{on} \sim 7$ V). The device remains in low resistance (ON) state until an OFF voltage ($V_{off} \sim -5.5$ V) is applied to the device. The fabricated device exhibits an ON/OFF current ratio of more than 100 at a read voltage of 4 V. The solid and open circles in the fig. 3(a) represents the voltage sweeps from -8 to +8 V and +8 to -8 V, respectively.

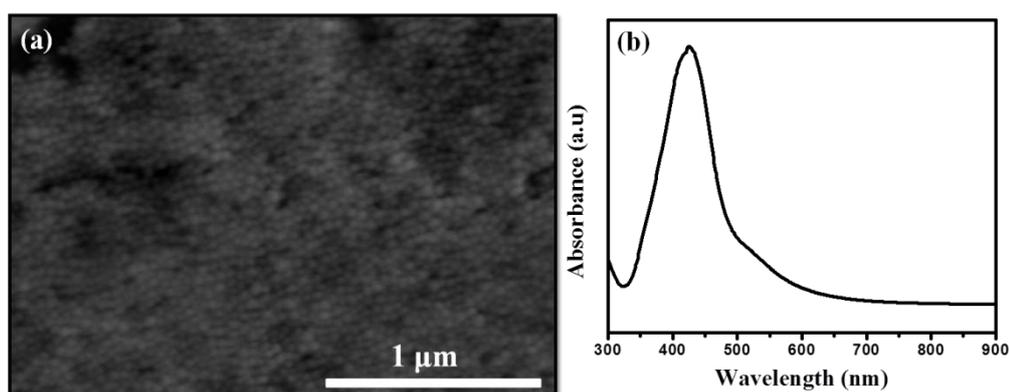


Fig. 2. (a) FE-SEM image of synthesized Ag NPs drop casted on ITO coated glass substrate and (b) UV-Vis NIR spectrum of Ag NPs in ethanol.

Based on experimental results, we propose a mechanism for memory device operation. The conductance switching is due to applied voltage induced charge transfer between Ag NPs and Alq_3 layers. At low bias, the device exhibits low conductivity due to lack of charge carriers in organic layer. When applied voltage is large enough, the electrons from the highest occupied molecular orbital (HOMO) of Alq_3 may get enough energy to tunnel through PVP layer into the core of Ag NPs as shown in fig. 3(b). Consequently, the charge carriers are generated in organic layer and metallic core, which change the device from OFF state to ON state. The insulating PVP layer prevents the recombination of generated charge carriers after the removal of applied voltage. The device remains in its ON state until a reverse electric field is applied to remove the electrons from metallic core.

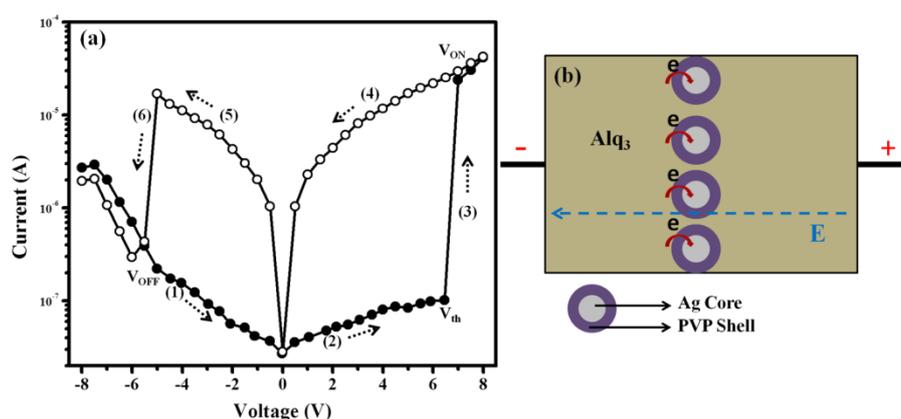


Fig. 3. (a) I-V characteristics of the memory device with structure ITO/Alq₃/Ag NPs/Alq₃/Al, obtained by sweeping voltage from -8 V to +8 V and back to -8 V and (b) schematic illustration of the operating mechanism of memory device.

Conclusions

In conclusion, organic memory devices were fabricated using Alq₃/metal nanoparticles/Alq₃ as the active medium inserted between ITO and Al electrodes. Polyol method was used to prepare the metal nanoparticles instead of commonly used thermal evaporation technique. This method offers precise control on the size and morphology of nanoparticles. The fabricated device shows bistability with an ON/OFF current ratio of more than 100 at a read voltage of 4 V. The ON and OFF states of the device can be accessed by applying an ON voltage around 6.5 V and an OFF voltage around -5.5 V, respectively. Present investigation indicates that the current switching is due to applied voltage induced transfer of electrons between Ag NPs and Alq₃ layers.

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