

Nonvolatile electrical memory effect observed in the silver quantum dot embedded polyimide thin film

Guo-Feng Tian (田国峰), Sheng-Li Qi (齐胜利), Zhan-Peng Wu, De-Zhen Wu* (武德珍)

College of Material Science and Technology, Beijing University of Chemical Technology, Beijing
100029, PR China (北京化工大学)

Abstract

Because of the small size effect, surface effect and quantum effect, metal nanoparticles show a different light, heat, electric, magnetic, catalytic properties compared with bulk materials. Therefore, metal nanoparticles are often incorporated into polymer to prepare functional materials. In this paper, via in-situ formation, a novel hybrid polyimide film containing silver nanoparticles has been fabricated using a soluble polyimide as matrix which is synthesized by one step method and (1,1,1-trifluoro-2,4-pentadionato) silver(I) (AgTFA) as the silver source. The size of silver nanoparticles in polyimide matrix is about 6.4nm through TEM. The current-voltage characterization shows that the hybrid material exhibits a nonvolatile memory behavior.

Key words: polyimide, memory, nanoparticle, silver

Introduction

Metal nanoparticles have been investigated intensively in recent years because of the potential application in the optoelectronics, catalysis, magnetic materials and biosensors.¹⁻⁶ Therefore, metal nanoparticles are often incorporated into polymer to prepare functional materials which could be used as field-effect transistors, light-emitting diodes, and solar cells.^{7,8} Conductance switching phenomena has also been observed in many polymer films embedded with granular metal islands like Mg, Ag, Al, Cr, Cd, Se, Au nano-particles (NPs) to serve as the trapping sites (nano-trap memories).⁹⁻¹² Among the various metal nanoparticles, silver nanoparticles have been widely investigated because they exhibit unusual optical, electronic, and chemical properties, which depend on their sized and shape and open many possibilities with respect to technological applications.¹³

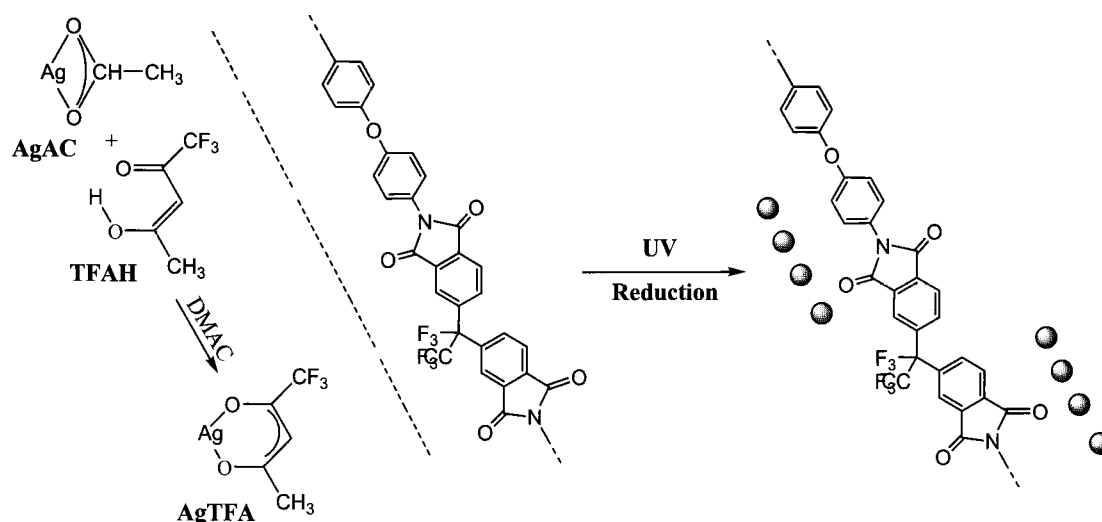
In earlier works on polymer memory, a number of polymer such as PMMA, PVK and polyaniline have been used as matrix to fabricate the polymer/NPs hybrid materials.¹⁴⁻¹⁶ But polyimide, with excellent thermal and mechanical properties, high-temperature stability and chemical inertness, has rarely been investigated as the matrix because of the complicated procedure. In this report, a new method using a soluble polyimide to incorporated with silver NPs was proposed to simplify the fabrication process. And due to the electron capture and release properties of the “nano-traps” formed by the silver nanoparticles in polyimide matrix, polyimide/silver nanohybrid materials with memory functional properties were obtained.

Experimental Section

Preparation of polyimide (6FDA/ODA)/silver nanohybrid films: AgAc is insoluble in DMAC and the 6FDA/ ODA polyimide resin. However, AgAC could be brought into solution when equivalent or

* Corresponding author: Tel.: +86 10 6442 1693; fax: +86 10 6442 1693.
E-mail address: wdz@mail.buct.edu.cn (De-zhen Wu).

more TFAH is dissolved in DMAC. Thus, silver-containing solution was prepared by first dissolving silver acetate in a small volume of TFAH-containing DMAC, followed by addition of the polyimide solution. Triple equivalent TFAH was used in our experiment to dissolve the AgAC. The formation of AgTFA complex has been demonstrated perviously in the literature and introduced to the solution in situ as illustrated in Scheme 1.^{17, 18} Doped polyimide solutions were cast as films onto ITO glass plates. After held in the ambient environment to remove the solvent, the films were treated under a UV light.



Scheme 1. Illustrative protocol for the preparation of polyimide (6FDA/ODA)/silver nanohybrid films via in situ single-stage self-metallization process.

Results and Discussion

A representative transmission electron microscope (TEM) image of silver nanoparticles is shown in Figure 1, which proved the generation of nanoparticles with a unified shape. The resulting particles, which have an identical size of 6.4nm, were well dispersed in the polyimide matrix without aggregation.



Figure 1 Typical TEM image of silver nanoparticles in the hybrid films

The current-voltage characteristic of the hybrid material memory device is shown in Figure 2a. In the first positive sweep from 0 V to -1.5 V, an abrupt increase in current was observed at a switching threshold voltage of about -0.8 V. The device jumps to a high conductivity state (ON state) from the low conductivity state (OFF state) corresponding to the “writing” process. The device remains in a high conductivity (ON state) during the subsequent second sweep from 0 to -1.5 V and does not relax to the OFF state even after the applied voltage has been removed. So a 1V voltage can be used for reading and this memory point is corresponded to “1” in binary system. As the voltage sweeps from 0 to 3V, a decrease in current is observed at a threshold voltage about 2.5 V, corresponding to the “erasing”

process for the memory device. The fourth line shows that the memory device can maintain its “Off state” after the power has been turned off. The device could be further written or erased when the switching threshold voltages were reapplied, indicating that the memory device was rewritable (sweeps 5 to 8). I-V measurements on the device without silver nanoparticles with the same fabrication conditions were performed to investigate the charge storage role of the silver nanoparticles (Figure 2b). There is no significant change in current, indicating that the electrical bistability of the hybrid material can be attributed to the existence of silver nanoparticles.

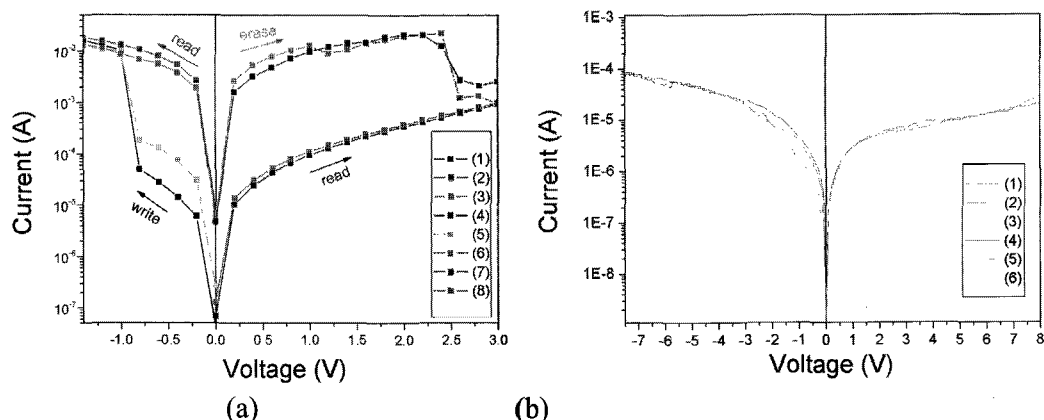


Figure 2. Current-voltage (I-V) characteristic of (a) the ITO/polyimide(6FDA/ODA)/silver nanohybrid film/Au memory device (Au electrode diameter: 1mm); (b) the ITO/polyimide(6FDA/ODA) film/Au memory device (Au electrode diameter: 1mm).

Conclusions

As a summary, a functional polyimide (6FDA/ODA)/silver nanohybrid material has been synthesized in our present work. Semiconductor parameter analysis on the sandwiched ITO/polyimide (6FDA/ODA)/silver nanohybrid film/Au memory device suggests that the material shows nonvolatile electrical bistability.

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CONCLUSIONS

The series of novel polyimide-silica hybrid thin films were synthesized from pyromellitic dianhydride(PMDA), 4, 4'-oxydianiline(ODA) and hyperbranched silicone polymers containing amine via thermal imidiazation. Results revealed that the heat resistance of hybrid thin films increased with the increasing the content of hyperbranched silicone polymers. At the same time, hybrid thin films had good mechanical properties.

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