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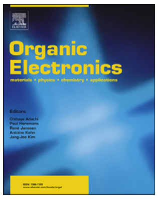

The formation of Cu_2O nanoparticles in polyimide using Cu electrodes via chemical curing, and their application in flexible polymer memory devices

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ABSTRACT

Flexible polymer memory devices were fabricated based on 4,4′-(hexafluoroisopropylidene)diphthalic anhydride-4,4′-oxydianiline (6FDA-ODA) polyimide (PI)/Cu_2O nanocomposite via chemical curing, heat treatment, and post-heat treatment at low temperature (<200 °C). Following the deposition of a Cu bottom electrode on a commercial PI film substrate, a PI precursor, polyamic acid (PAA) was spin-coated onto the Cu bottom electrode, and Cu was dissolved into the PAA, providing Cu ions for particle formation. The 6FDA-ODA PAA—Cu complex was imidized via chemical curing using acetic anhydride and triethylamine at 50 °C, and thermal treatment was performed at 200 °C in a reducing atmosphere to remove the solvent completely and precipitate Cu nanoparticles. Post-heat treatment was sequentially carried out at 150 °C in an oxidizing atmosphere to oxidize Cu to Cu_2O. The Al top electrode was deposited onto the 6FDA-ODA PI/Cu_2O nanocomposite film, and the flexible memory device with a crossbar array showed an ON/OFF ratio of ~10^4, endurance of 60 cycles, retention time of 10^4 s, and device yield of 86% (31 cells out of total 36 cells) under flat and bending conditions (bending radius ~1.5 mm) when the electrical measurements were performed in air at room temperature.

1. Introduction

The polymer-based nanocomposite is a promising candidate for applications in flexible memory devices due to flexibility, solution processability, low cost, good scalability, and 3D-stacking capability [1,2]. Various nanocomposites composed of a polymer matrix and nano-sized inorganic materials have been utilized as active layers in polymer memory devices, such as polystyrene/8-hydroxyquinoline/Au [3], pentacene/Al [4], *tris*-(8-hydroxyquinoline)aluminum/Al [5], polyvinylpyrrolidone/MoS_2 [6], poly(methyl methacrylate) (PMMA)/graphene [7,8], PMMA/ZnO [9], poly(N-vinylcarbazole)/Au [10], and polystyrene/Al_2O_3 [11]; however, the thermal instability of the polymers could lower performance and reliability of the polymer memory. In recent years, PI-based nanocomposites containing inorganic phases such as TiO_2 [12], ZnO [13,14], graphene [15], graphene oxide [16], 6-phenyl-C61 butyric acid methyl ester (PCBM) [17–19], and PIs containing donor and acceptor components [20–27] have been intensively studied, due to the outstanding thermal stability, chemical resistance, and excellent mechanical strength of PI [28], all of which lead to more reliable performance when applied in electronic devices and exposed to harsh environments.

For the synthesis of PI-based nanocomposites containing inorganic ingredients such as nanoparticles [13,14], graphene oxide [16], and PCBM [17,18], a PI precursor, polyamic acid (PAA), is often used because it can chemically react with a metal film, or be homogeneously mixed with inorganic elements. When PAA is used, thermal imidization is often performed near 300–350 °C [13–18], limiting the use of plastic substrates. Although thermal imidization can be performed at temperatures less than 200 °C [19,29], this may lead to insufficient imidization of PI [30,31], and could eventually affect the reliability of the polymer memory devices. In place of thermal curing at high temperature, PI can also be imidized with a high degree of imidization via chemical imidization at 22–65 °C, using an acid anhydride as a dehydrating agent and tertiary amine bases as catalysts, such as pyridine, 2-methylpyridine, triethylamine, and isoquinoline [32].

The donor-acceptor PIs have been synthesized as active layers in the polymer memory via chemical imidization, for which PAA was mixed with acetic anhydride and tertiary amine bases via stirring.

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The resulting solution was then poured into an excess amount of methanol or diethyl ether to precipitate PI [22–24]. This process allows the use of plastic substrates as well as glass or Si wafers because the pre-synthesized PI, which is dissolved in solvent, is spin-coated onto the substrates and heat treatment was performed at less than 100 °C [22–24]. However, this process of chemical imidization is not suitable for the synthesis of PI-based nanocomposites containing inorganic elements, because a loss of inorganic elements could occur during the process of PI precipitation and re-dissolution in solution.

We report here the fabrication of PI-based nanocomposites using chemical curing by immersing a soft-baked PAA-metal complex film into a solution of acetic anhydride and triethylamine. It is advantageous to immerse a PAA-metal complex film into a curing agent solution, because it does not need to precipitate PI and dissolve the PI powder in solvent. Moreover, the metal ions bonded with the PAA carboxylate ions remain in the film during chemical curing and the subsequent heat treatment to remove the solvent. We previously developed a simple method of nanoparticle formation in a PI film via thermal curing [31,33–40]. The PAA is spin-coated onto a metal film, and starts to dissolve the metal, forming a PAA-metal complex. Metal atoms rejected from the complex grow as nanoparticles during thermal imidization of PAA to PI. The imidization mechanism of chemical curing is the same as that of thermal curing, except that CH_3COOH is released during chemical curing instead of H_2O [32]. In chemical curing of PAA-metal complex films, the dehydrating agent and catalyst imidize PAA to PI, accompanying the reduction of metal atoms from a PAA-metal complex, and metal atoms agglomerate to form nanoparticles during heat treatment at less than 200 °C. The use of chemical curing can reduce the process temperature, allowing the use of plastic substrates such as polyetherimide and polyethersulfone, and enhance the imidization degree of PI.

In addition to the use of chemical curing, we fabricated nanoparticles using the bottom electrode without the addition of any metal precursor into PAA. By using the reaction between PAA and the metal electrode, metal ions are dissolved into PAA and form as nanoparticles near the electrode during chemical curing followed by heat treatment. These nanoparticles can act as charge-storage nodes for the polymer memory device. Until now, organic-inorganic nanocomposites as active layers of polymer memory devices have been prepared by spin-coating of the mixture solution composed of the pre-made inorganic elements or metal precursor and the polymer [3,6,9,10,12,16–19,41]. Assuming that the memory device has a crossbar architecture, the dispersion of inorganic elements between neighboring electrodes cannot be avoidable in this process. The incorporation of ceramic particles with high dielectric constant into a polymer or the construction of percolative systems by dispersing electrically-conductive metal particles or carbon materials can increase the dielectric constant of the polymer matrix [42], which may induce electromagnetic interference between parallel metal lines [32]. However, nanoparticles are dispersed only near the electrode in our memory device due to the local reaction which only occurs near the interface of the PAA and Cu electrode.

In this study, we propose the local formation of nanoparticles in a PI film by using the reaction of PAA and Cu bottom electrode via chemical curing and heat treatments at low temperature. The fabricated memory devices exhibited a high device yield of 86% with good memory performance.

2. Experimental

2.1. Materials

All chemicals were used as received. The PAA, is 4,4′-(hexafluoroisopropylidene)diphthalic anhydride-4,4′-oxydianiline (6FDA-ODA, LG Chem.), and the solvent is N-methyl-2-pyrrolidinone (Kanto Chemical Co. Inc.). The dehydrating reagent and catalyst for chemical imidization are acetic anhydride (Sigma–Aldrich) and triethylamine (Sigma–Aldrich), respectively. The substrate is a commercial PI film obtained from SKC Kolon (GL30, thickness: 25 μm).

2.2. Device fabrication and characterization

The commercial PI film was cleaned using sonication for 30 s in ethanol followed by 30 s in distilled water; the Ti (10 nm) as an adhesion layer and Cu (200 nm) as the bottom electrode were then sequentially deposited onto the PI film using a shadow mask in a direct current magnetron sputter. The 2.5 wt% 6FDA-ODA PAA was spin-coated onto the Cu/Ti/PI substrate at 500 rpm for 10 s and 3000 rpm for 30 s, and soft-baked at 135 °C for 30 min on a hot plate. The specimen was immersed into a mixture of acetic anhydride (1.7 mL) and triethylamine (2.5 mL) and chemically cured at 50 °C for 1 h in N_2 atmosphere. After being rinsed with distilled water and dried by blowing N_2, the specimen was heat-treated at 200 °C for 1 h in a reducing atmosphere (5% H_2/95% N_2), and then post-heat-treated at 150 °C for 1 h in an oxidizing atmosphere (1% O_2/99% N_2). Finally, the device was fabricated by depositing Al (100 nm) as the top electrode onto PI/Cu/Ti/PI substrate using a shadow mask in a thermal evaporator. The schematic of fabrication process is shown in Scheme 1. The memory features a 6 × 6 crossbar array with a total of 36 cells (Fig. S1(a)), and the electrode width and pitch size are approximately 440 μm and 1.3 mm, respectively. All electrical measurements were performed in air condition at room temperature using a semiconductor analyzer system (Keithley 2400 source meter). For measurements under bending condition, the flexible memory was completely wrapped around a straw with a diameter of approximately 3 mm (Fig. S1(b) and (c)). The distribution and size of nanoparticles were characterized using transmission electron microscopy (TEM, JEM 2010, JEOL). For ultraviolet–visible (UV–vis) spectroscopy (SHIMAZU 2450), 2.5 wt% PAA was spin-coated onto a sputtered 10-nm thick Cu film under 500 rpm for 10 s and 3000 rpm for 30 s, and soft-baked at 135 °C for 30 min on a hot plate. The chemical curing was performed under the same condition as above, and subsequent heat treatment was performed at 150, 175, or 200 °C for 1 h in a reducing atmosphere. Fourier transform infrared (FT-IR) measurement was performed to calculate the imidization degree, and details are described in the Supplementary Data.

3. Results and discussion

Fig. S1(a) shows a schematic of the PI/Cu_2O-based memory device with a 6 × 6 crossbar array. It is reported that the crossbar array is simple to make and enables maximum cell density [43]. The highly flexible PI substrate not only allows for extreme bending in the memory device (Fig. S1(b) and (c)), but also provides high thermal durability due to the complete aromatic structure [32]. The active layer of a 6FDA-ODA PI/Cu_2O nanocomposite film is sandwiched between Al top and Cu bottom electrodes, and each cell can be addressed as a TXBX coordinate point in which 'T', 'X', and 'B' represent the top electrode, coordinate numbers, and bottom electrode, respectively. For example, the cell marked with a dotted circle in Fig. S1(a) is addressed as T3B3.

Fig. 1(a) shows the cross-sectional TEM image of the polymer memory with an Al/PI–Cu_2O/Cu structure in which nanoparticles were well dispersed in the PI film. The average particle size is approximately 2.7 nm with a standard deviation of 0.6 nm (Fig. S2(a)), and the thickness of the nanocomposite is