Ferroelectric Polymer P(VDF-TrFE) in Nonvolatile Memory Devices

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Abstract

In recent years, with rapid demand growth of wearable devices, flexible electric devices with high performance are urgently needed because of the shortages of traditional semiconductor equipments, such as non-flexibility and complex preparation process. As a typical kind of ferroelectric polymer, poly (vinylidenefluoride-ran-trifluoroethylene) (P(VDF- TrFE)) possesses excellent ferroelectricity and has been used in flexible ferroelectric memories. In this article, recent progress of P(VDF-TrFE) in nonvolatile memory devices is reviewed, including nanostructured ferroelectric capacitor memories, ferroelectric rectifying diodes and ferroelectric field effect transistors, along with opportunities and challenges in device applications.

Keywords

P(VDF-TrFE); Ferroelectric; Application.

1. Introduction

Although ferroelectrics are a class of versatile materials, the exploration time span of ferroelectrics is relatively short, which began with Valasek's study of hysteresis phenomenon in Rochelle salt in 1920[1]. In less than one century, due to their excellent dielectric, piezoelectric, pyroelectric and ferroelectric properties, ferroelectrics have been widely used in machinery sensing, optical detection, information storage, and so on[2, 3]. Among these properties of ferroelectrics, ferroelectricity is the most extraordinary one, which manifests bistable polarization that can be reversed repetitively under external electric field. Thus, information writing and reading can be realized with the characteristics of ferroelectric polarization reversal, which provides broad prospects for high performance nonvolatile memories.

Because of the stable polarization states require strong thermodynamic stability, all ferroelectric materials found so far possess crystal structure. Early ferroelectric studies were all focused on inorganic materials. Compared to inorganic crystalline materials, the crystalline phase of the polymer is more complex due to their long molecular chains. With excellent piezoelectric and ferroelectric properties, polyvinylidene fluoride (PVDF) based polymers have been extensively studied for the past over seven decades. Although PVDF was first synthesized in the 1940s, whether PVDF is ferroelectric material is still uncertain, owing to the significant characteristic parameter Curie point was not found. Until 1981, this dispute was solved with the synthesis of vinylidene fluoride and trifluoroethylene copolymer (P(VDF-TrFE)), whose Curie temperature is lower than its melt point[4].

Because its excellent performance of stable non-volatile information retention, effective writing and reading process and high polarization reversal rate, ferroelectric memories will play an important role in information storage in the future. At the same time, flexible electronics technology aiming at flexibility and wearability has developed rapidly in recent years, which has promoted polymer ferroelectric memory to become an important part of information storage in the future. Among them, the research of memory utilizing P (VDF-TrFE) as the core component has become one of the hotspots in memory research field. Here, the brief background of ferroelectric polymer is introduced, and then recent progress of ferroelectric polymer in nonvolatile memories including nanostructured ferroelectric capacitor memories, ferroelectric rectifying diodes and ferroelectric field effect transistors is reviewed. At last, the opportunities and challenges in device applications will be discussed.

2. Ferroelectric Polymer Materials

The ferroelectricity of copolymer P(VDF-TrFE) originates from the directional arrangement of dipole molecules in lamellar crystals, thus, the polarization reversal of copolymer P(VDF-TrFE) inevitably involves the rotation of molecular chains. In addition, the polarization reversal process of P(VDF-TrFE) is closely related to its multi-layer condensed state structure[5]. Therefore, the crystallization state and molecular orientation of P(VDF-TrFE) are closely related to the ferroelectric properties of P(VDF-TrFE). In the past long-term studies, it has been found that strain-induced, electric and magnetic field-induced, and space-constrained induced methods can be used to control the crystallization status and molecular orientation of specific polymers[6-9].

In polymer materials, due to the strong polarity of C-F bond and similar size of fluorine atom and hydrogen atom, crystalline fluorine-containing polymers such as PVDF and its copolymers have strong ferroelectric property. Some crystalline polymers that containing other polar groups, such as polyvinyl chloride (C-Cl), polyacrylonitrile (C-CN) and so on, also have ferroelectric, but, the polarization is relatively weaker than PVDF-based polymers[10].

PVDF polymer usually exhibits a semi-crystalline state, and its crystalline portion forms α phase without further treatments. Under force field and/or electric field, PVDF can also forms β, γ and δ phases[11]. Among these four crystal phases, the α phase is most easily obtained and nonpolar, in which the molecules packed with TGT$^{\overline{G}}$ type in an antiparallel arrangement. In the other three polar phases, the β phase with all-trans conformation possesses the strongest ferroelectricity, whose polarization is close to twice that of γ and δ phases.

However, the PVDF β phase is hard to be obtained, and the preparation process needs carefully controlled stretching and high electric field. In contrast, the copolymer P(VDF-TrFE) with the molar ratio of VDF/TrFE around 2/1 can obtain the ferroelectric phase directly from solution, which greatly reduces the difficulty of the acquisition of ferroelectric phase and increases the compatibility in industrial device process. The coercive electric field of P(VDF-TrFE) thick films is about 50 MV/m, which means that in order to meet the needs of ~5 V low voltage electronic module, its thickness can not be higher than 100 nm. While, what's worse is that the coercive electric field increases to 70-150 MV/m when the film thickness decreases to lower than 100 nm[12]. Therefore, opportunities and challenges coexist in memory application of ferroelectric polymer.

3. Nonvolatile Ferroelectric Polymer Memories

This century is an era of network and information technology explosion. More and more information come into our daily life, which puts forward higher requirements for large capacity, high storage density, fast speed and non-volatility of information storage. Recently, ferroelectric capacitors, rectifying diodes and field effect transistors are the three main realization forms in the research of ferroelectric polymer memories.

3.1 Nanostructured Ferroelectric Capacitor Memories

For capacitive nonvolatile ferroelectric memory, each structural unit in the P(VDF-TrFE) nanostructure array can be used as a storage unit. In order to achieve high-density ferroelectric polymer memories, it is necessary to reduce the size of ferroelectric structure units. On the other hand, the property of ferroelectric polymer materials is desiderated to be optimized further, for the purpose of achieving high read and write rate under standard voltage.

In the past several decades, a series of competitive micro-nano preparation methods have been proposed and widely used in both research and industrial process, such as micro-contact printing[13], dip-pen lithography[14], scanning-probe-based techniques[15] and nano-imprinting lithography

(NIL)[16]. These methods partially replacing the expensive and complex processes, for instance, deep-UV and E-beam lithography, have greatly facilitated the preparation process. NIL is a low cost, high yield, reusable and high resolution micro-nanofabrication method. NIL is especially suitable for direct micro-nanostructuring of soft materials, such as linear and conjugated polymer film materials.

For crystalline polymers, NIL can not only realize the construction of micro- and nano-structures, but also control the alignment of internal molecules and crystals through confined environment, thus improving the properties of polymer crystalline materials[17]. Utilizing NIL method, Hu et al successfully prepared high-density arrays of nanostructures with silicon template, and found that each P(VDF-TrFE) nanocolumn can be used as a storage unit for information storage[18]. The read-write voltage is less than (+5V) and the density of storage reaches around 40 Gbit/inch. Chen et al. found a much more cost-effective method for nanostructure preparation with anodic aluminum oxide (AAO) template, and the storage density can reach about 80 Gbit/inch[19].

Since the crystalline orientation and structure of ferroelectric polymers act as decisive roles in its polarization reversal behavior, the ferroelectricity of nanostructured P(VDF-TrFE) can be improved by NIL process. In P(VDF-TrFE) nano-imprinted nanostripes, well-defined crystalline lamellar orientation and regular polarization domains were found, with high polarization domain reversal speed[5].

3.2 Ferroelectric Rectifying Diodes

Ferroelectric rectifying diodes are another prototype of memory devices that can realize nonvolatile read and write of information. Under polarization field modulated by P(VDF-TrFE), the carrier injection barrier between semiconductor and electrode can be controlled, and then the current flowing through semiconductor will be influenced effectively with tunnelling injection and charge accumulation[20].

In the past nearly one decade, this method of storing data in ferroelectric rectifying diodes has been widely studied by numerous researchers. In 2008, using solution blending and film cast, Asadi et al. successfully prepared phase-separated composite films of p-type semiconductor irregular polythiophene and P(VDF-TrFE)[21]. Their relevant results show that the polarization field produced by P(VDF-TrFE) can effectively modulate the switching currents with good repeatability of data reading and writing, and difference between on and off currents can be more than 20 times. Taking advantages of conductive ink PEDOT:PSS as the electrode, a diodes-type all-organic ferroelectric memory with high switching ratio and low reading voltage was successfully fabricated by Khan et al., which is based on the phase separation membrane formed by n-type semiconductor PCBM small molecule and P (VDF-TrFE)[22].

At the range of nanoscale, the composite thin films prepared by blending method show obvious inhomogeneity, which makes it hard to downscale the structural units. In order to solve this problem of unit size reduction, van Breemen et al. prepared patterned surface-modified electrodes by micro-contact printing, and obtained ordered composite films with 500 nm characteristic size by reasonably controlling the composition of P(VDF-TrFE) and semiconductor Poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT), and the results show the storage density was successfully improved[23].

3.3 Ferroelectric Field Effect Transistors

From the view of electronic industry, field effect transistors are the most convenient way of ferroelectric polymer application in memories. The current switching between source and drain through semiconductor can be modulated by the state of ferroelectric polarization. For n-type semiconductors, in general, when the vector of polarization directs to semiconductor, the majority carrier electrons will accumulated in transistor channel and the current is large (on state), while the vector directs opposite to semiconductor, the current is relatively little (off state).

Using P(VDF-TrFE) as functional dielectric layer, Gelinck et al. firstly realized all-organic ferroelectric field effect transistors, which can work at 10 V low operating voltage, with a switch ratio of over 1000 and good retention for hours[24]. In order to improve the storage density, in 2011, Tripathi et al. successfully obtained a single field effect transistor memory cell with four current states by constructing P (VDF-TrFE) micron lines. Their results show ferroelectric multilevel storage is realized in one single memory unit, which provides a new idea for memory device design of ferroelectric polymer P(VDF-TrFE)[25].

In order to meet the flexibility requirement of future memories, many different functional materials have been applied in the design of memory devices. Graphene is one of the materials with the highest strength, good toughness and can be bent nondestructively. Heidler et al. successfully prepared low-cost ferroelectric field effect transistor memory using graphene flakes and P(VDF-TrFE) as semiconductor and bias layer, respectively, and this graphene based memory device shows excellent performance in both retention time and cycle endurance[26].

4. Summary and Prospects

In summary, recent studies of three main types of P(VDF-TrFE) nonvolatile memories are demonstrated, including nanostructured ferroelectric capacitor memories, ferroelectric rectifying diodes and ferroelectric field effect transistors. Ferroelectric capacitor memories are the easiest approach among them in high storage density device realization, and the storage density can reach to nearly 80 Gbit/inch. However, the data reading procedure is a destructive storage process, in which P(VDF-TrFE) is prone to fatigue under continuous or intermittent electric field. At present, all organic non-destructive ferroelectric memory has been a hotpot of these research works, however, problems still exist in increasing storage density furtherly.

As a functional polymer with application potential in memory devices, whether a P(VDF-TrFE) structure unit can play a storage role when its size is further reduced is still unknown. Two main problems need to be solved. Firstly, how the ferroelectric properties of P (VDF-TrFE) change with the further reduction of lateral size; secondly, how the carrier modulation effect of P(VDF-TrFE) nanostructures on the surrounding semiconductors. Taking these problems into consideration, the polarization reversal behavior of nanostructured P(VDF-TrFE) and carrier modulation mechanism should been studied. These two aspects of research will help to deepen the understanding of P(VDF-TrFE) ferroelectric properties and functional mechanism in storages, on the other hand, provides references for design and optimization of future wearable devices.

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