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Study on octadecylamine- HSBT intercalation compound/PVDF composite thin films and their ferroelectrical properties

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Ferroelectric composite thin films of x·C18A-HSBT/PVDF with different C18A-HSBT content (weight ratio of C18A-HSBT to PVDF, x=2.5%, 5%, 7.5%, 10%) were prepared by spin-coating method. The crystal structures of x·C18A-HSBT/PVDF thin films were analyzed by X-ray diffraction (XRD) measurements together with Fourier transform-infrared spectroscopy (FT-IR). The morphological studies of these samples were done via scanning electron microscopy (SEM). Experimental results demonstrated that both β -phase of PVDF and the layered perovskite C18A-HSBT co-existed in the x·C18A-HSBT/PVDF thin film samples. With an increase of C18A-HSBT content in the x·C18A-HSBT/PVDF thin films, both the dielectric constant and saturated polarizations were also increased. In addition, as the C18A-HSBT content increased, the leakage current density of the x·C18A-HSBT/PVDF thin films under the applied electric field was decreased.

Key words: PVDF, C18A-HSBT, Ferroelectric composite films, Remnant polarization.

Introduction

In recent years, great attention has paid to poly vinylidene fluoride (PVDF) ferroelectric materials utilized by many devices such as high energy density capacitors, pyroelectric thermal imaging devices, gate insulators in transistors, electro-optic light valves, energy harvesters due to their useful dielectric, ferroelectric, piezoelectric properties together with their excellent stability to chemicals, mechanical flexibility and biocompatibility [1]. However, the shortcomings of PVDF ferroelectric polymer related to lower ferroelectric properties and dielectric constant compared to those of ferroelectric ceramics will impede the large scale utilization of pure PVDF polymer in the abovementioned ferroelectric devices. To refer to the ferroelectric ceramics, lead zirconate-titanate (PZT) with conventional perovskite structure together with its compound possessing high dielectric constant, high dipole moment are the most widely used in commercial applications. In view of the toxicity of lead and its compound, environmental friendly lead-free ferroelectric materials should be substantially employed in the field of ferroelectric devices [2]. Fortunately, strontium bismuth tantalate (SBT) with the layered perovskite structure is also widely being used by the industry today. From the viewpoint of reliability, the SBT material will offer superior characteristics over PZT material. For example, there exists polarization degradation in PZT

ferroelectrical device [3]. Moreover, compared to that of PZT, SBT ferroelectric material are better imprint characteristics, low voltage/low power operation and scaling potential. On the other hand, it is further worth noting that although both PZT and SBT materials are currently used for ferroelectric devices in commercial, industry and radiation-hard applications, brittle property and high temperature processing are obstacles to their further applications. Therefore, in order to fabricate a ferroelectric device with low cost, good chemical stability, mechanical and ferroelectric properties, a hybrid ceramicpolymeric composite should be a good choice to tune both mechanical and ferroelectric properties. So far, some ferroelectric ceramic/PVDF composite materials, such as BaTiO₃ (BT)/PVDF, Pb(Zr,Ti)O₃(PZT)/PVDF have ever been investigated in some literatures [4, 5].

As we known, the initiative organic-inorganic hybrid composites fabricated by guest organic compounds intercalating into inorganic layered compounds will be of a better characteristic compared with the original organic or inorganic compounds [6]. Therefore, in this study, we would have firstly fabricated the intercalation materials of octadecylamine (C18A) into the acid-treated SBT with layered perovskite (HSBT), and then we synthesized the x·C18A-HSBT/PVDF composite thin film materials. The structural, dielectric, ferroelectric properties of x·C18A-HSBT/PVDF composite materials dependence on the C18A-HSBT content were thoroughly investigated.

Experimental

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Both PVDF powders and DMAC (N.N'-dimethyl-

Materials

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acetamide) solvent were supplied from Shanghai Ling Feng Chemical Reagent Co., Ltd. (China). The DMAC solvent was of reagent grade. SrBi₂Ta₂O₉ (SBT) nanopowders were self-made. The detailed fabrication process of SBT nanoparticles in our study could also be described in other literature [7].

Acid treatment of SBT

About 2.5 g SBT was dispersed in 500 mL of 3 M HCl for 5 days. The acid-treated product was centrifuged, washed with distilled water until free of (Cl⁻). The existence of Cl⁻ or not was determined by the addition of AgNO₃ solutions into the used distilled water to observe if there existed some white precipitates. The acid-treated SBT with free Cl⁻ was subjected to drying at 120 °C in baking oven, subsequently grinding for 10 minutes and then obtain the white HSBT powders.

The intercalation of octadecylamine (C18A) into HSBT

Octadecylamine (C18A) was dissolved in Tetrahydrofuran solvent to obtain 30 mL solutions with the concentration of 10%. The formed solution positioned on the magnetic stirring apparatus was firstly constant stirred at room temperature for about 48 hours, and then baked them in baking oven at 120 °C for drying. Finally, the drying products were ground to obtain the HSBT powders with C18A modification. For simplicity, the HSBT powders with C18A modification was simply referred to as the C18A-HSBT.

The fabrication of $x \cdot C18A$ -HSBT/PVDF composite thin films

The different amount of PVDF was separately dissolved in DMAC solvent at a fixed volume in different beakers. In order to get the fully dissolved PVDF solutions, these solutions in different beakers were magnetically stirred at 60 °C via water-bath heater. Meanwhile, the asprepared C18A-HSBT powders in different weight were also added into DMAC solvent in different beakers, followed by ultrasonic stirring for 20 minutes to obtain homogeneous C18A-HSBT suspensions for the next step spinning process. Finally, the PVDF solutions were poured into the C18A-HSBT to PVDF and subsequently vigorous mixed with a rotating stirrer accompanying by ultrasounds for 24 hrs with an aim to obtaining homogeneous suspensions.

In order to fabricate the x·C18A-HSBT/PVDF (x = 2.5%, 5%, 7.5%, 10%) thin films, the as-prepared x·C18A-HSBT/PVDF suspension solution above were firstly spin-coated on the cleaned ITO coated glass substrate (having resistance 60-120 Ω /sq) and crystalline Si substrate at a rate of 4000 rpm for 30 seconds, respectively. It should be pointed out in this study that the x·C18A-HSBT/PVDF (x = 2.5% to 10%) thin film samples grown on Si substrate were used to determine

the crystal structure of $x \cdot C18A$ -HSBT/PVDF thin films via XRD analysis, the $x \cdot C18A$ -HSBT/PVDF thin films grown on ITO coated glass substrate were used to characterize the electrical properties of films. And then the formed wet films were transferred into an air blowing thermostatic oven with furnace temperature of 60 °C for evaporating solvent. The coating and thermal treatment process was repeated ten times with an aim to obtaining a certain thickness films. The resultant films with a certain thickness were then placed into the air blowing thermostatic oven under 60 °C ambient for 48 hrs. When they were naturally cooled down to room temperature, these $x \cdot C18A$ -HSBT/PVDF thin films were ultimately obtained.

Structural and electrical characterizations

The crystal structure properties of x·C18A-HSBT/ PVDF (x = 2.5% to 10%) thin films on Si substrate synthesized were investigated by θ -2 θ method of XRD with a Cu Ka₁ (l = 0.15406 nm) source at 40 kV and 35 mA using an ARL XTRA powder X-ray diffraction diffractometer at a scan rate of 10 °/min. FT-IR spectrum were performed on a Nicolet FT-IR spectrophotometer (Nexus 470, Thermo Electron Corporation) using KBr disks at room temperature. The morphologies of the samples were examined by field emission scanning electron microscopy (SEM, FEI Nova NanoSEM 450). The thickness of the obtained films is about 2.0 µm by cross-sectional view of SEM. For electrical а measurements, silver with about 300 nm thickness was coated on the surface of the x·C18A-HSBT/PVDF thin films on ITO coated glass substrate with an area of 5.25×10^{-5} cm⁻² using a shadow mask. The ferroelectric hysteresis loops and leakage current behaviors of the Ag/ x·C18A-HSBT/PVDF /ITO capacitors were obtained using a ferroelectric tester (Radiant Technologies, Precision LC). The dielectric constant and the dissipation factors were measured by using an HP4294A impedance analyzer. The high-frequency capacitance-voltage characteristics of these samples were measured using Keithley 590 CV analyzer at one MHz with a bias sweep rate of 0.2 V/s. All the measurements were performed at room temperature.

Results and Discussion

XRD and FT-IR analyses

Fig. 1 demonstrates the XRD patterns of HSBT $(H_{1.8}[Sr_{0.8}Bi_{0.2}Ta_2O_7]$ in the protonated form) and C18A-HSBT powders. For comparison, the standard diffraction card (JCPDS#49-0609) for SBT powder standard sample is also indicated in the Fig. 1. The diffraction peaks of C18A-HSBT powders shifting toward the lower diffraction angle compared to that of HSBT is ascribed to the octadecylamine (C18A) intercalation into HSBT. Fig. 2 shows the XRD patterns of the x·C18A-HSBT/PVDF (x = 2.5% to 10%) thin films on Si substrate. The XRD peaks corresponding to



Fig. 1. XRD patterns of SrBi₂Ta₂O₉ (SBT) and C18A-HSBT.



Fig. 2. XRD patterns of the x \cdot C18A-HSBT/PVDF thin films on Si substrate (a) x = 2.5%, (b)x = 5%, (c) x = 7.5%, (d) x = 10%.



Fig. 3. FTIR spectra of the x·C18A-HSBT/PVDF thin films on ITO coated glass substrate (a) x = 2.5%, (b) x = 5%, (c) x = 7.5%, (d) x = 10%.

x-C18SBT and PVDF have been respectively denoted in Fig. 2. The peaks at $2\theta = 8.74^{\circ}$ associated with the reflection planes of (001) of the x·C18A-HSBT. As we



Fig. 4. SEM micrographs of the x·C18A-HSBT/PVDF thin films on ITO coated glass substrate: (a) x = 2.5% (b) x = 5% (c) x = 7.5% (d) x = 10% (e) cross-section image of x = 10% sample.

known, the peaks at $2\theta = 18.2^{\circ}$ and 20.1° are ascribed to a and b phases respectively of for standard PVDF powder sample [8]. Consequently, the XRD peak at 20.1 ° shown in Fig. 2 is originated from the β phases PVDF. Additionally, the structural characteristic of the x·C18A-HSBT/PVDF thin films on ITO substrates were further investigated by FI-IR spectra shown in Fig. 3 [9]. The characteristic absorption bands of β -phase PVDF are at 667, 880 and 1268 cm^{-1} , and the characteristic absorption bands of α -phase PVDF should appears at 531, 765 and 976 cm⁻¹. The disappearance of these characteristic absorption bands of α -phase PVDF indicates that there mainly exists in β -phase of PVDF for the x·C18A-HSBT/PVDF thin film samples. As a result, the XRD analysis for the PVDF shown in Fig. 2 is in good agreement with that determined by the FTIR spectra.

Morphology

The surface morphologies of the x·C18A-HSBT/ PVDF (x = 2.5% to 10%) thin films on ITO coated glass substrate determined by SEM were shown in Fig. 4, respectively. The contrast of pure PVDF membrane relative to the ITO glass substrate is unobvious. The surface of pure PVDF thin film is very flat and there exists no cracks. When C18A-HSBT powders were added into the PVDF, there existed some various protrusions on the surfaces of x·C18A-HSBT/PVDF thin films shown in Fig. 4(a-d), which were brought about probably due to incompletely wrapping of C18A-HSBT nanoparticles into PVDF materials. With the C18A-HSBT nanopartices added into the PVDF and thermally budgeted at 60°, the crystallinity of x·C18A-HSBT/ PVDF thin films was effectively improved. The crosssectional image of $x \cdot C18A$ -HSBT/PVDF (x = 10%) thin film was shown in Fig. 4(e). It can be seen from Fig. 4(e)



Fig. 5. Frequency dependence of the relative dielectric constant of the $x \cdot C18A$ -HSBT/PVDF (x = 2.5% to 10%) thin films on ITO coated glass substrate measured at room temperature.



Fig. 6. Dissipation factor (tanä) in dependence of frequency for the $x \cdot C18A$ -HSBT/PVDF (x = 2.5% to 10%) thin films on ITO coated glass substrate measured at room temperature.

that the $x \cdot C18A$ -HSBT/PVDF (x = 10%) thin film is flat. Meantime, no crack or void is also observed.

Correspondence of dielectric constant on frequency and dissipation factor.

The variations of dielectric constant as a function of frequency for the x·C18A-HSBT/PVDF (x = 2.5% to 10%) thin films on ITO coated glass substrate are shown in Fig. 5. It can be observed that with an increase of C18A-HSBT content in x·C18A-HSBT/ PVDF thin films, the dielectric constants of these x·C18A-HSBT/PVDF thin films also increase. What's more, for all the x·C18A-HSBT/PVDF thin films, the value of dielectric constant is high at lower frequencies and decreases with an increase in frequency. The characteristic can be explained according to the spacecharge relaxation phenomena wherein at low frequencies the space charges are able to follow the frequency of applied field. While at a higher frequency, they may not have time to undergo relaxation [10]. On the other hand, the dielectric loss (tanδ) for the x·C18A-HSBT/PVDF



Fig. 7. Electric hysteresis loops of the $x \cdot C18A$ -HSBT/PVDF (x = 2.5% to 10%) thin films on ITO coated glass substrate measured at room temperature.



Fig. 8. *I-V* characteristics of the $x \cdot C18A$ -HSBT/PVDF (x = 2.5% to 10%) thin films on ITO coated glass substrate measured at room temperature.

films shows a marked increase when the applied frequency is varied from 10^3 Hz to 10^7 Hz. Additionally, the dielectric loss (tanä) of x·C18A-HSBT/PVDF thin films shown in Fig. 6 will decrease with an increase of the C18A-HSBT content in the x·C18A-HSBT/PVDF thin films under an identical applied frequency.

Ferroelectric properties.

The polarization-electric field (P-E) hysteresis loops of the x·C18A-HSBT/PVDF (x = 2.5% to 10%) thin films on ITO coated glass substrate measured under the applied electric field up to 90 kV/cm are shown in Fig. 7. For the x·C18A-HSBT/PVDF (x = 2.5%) thin film, a ferroelectric hysteresis loop is observed with saturated polarizations of 5.04 μ C/cm² measured under the electric field of a 90 kV/cm. With an increase of C18A-HSBT content (x) in the x·C18A-HSBT/PVDF thin films, the saturated polarizations of the x·C18SBT/ PVDF thin films are also gradually enhanced. Compared to its counterpart, the x·C18A-HSBT/PVDF (x = 10%) thin film has the largest saturated polarizations of 10.06 μ C/cm². Owing to the polarization of C18A-HSBT being larger than that of PVDF, the enhance remnant polarization existed in the x·C18A-HSBT/PVDF thin films are probably ascribed to the addition of C18A-HSBT into the x·C18A-HSBT/PVDF thin films.

Current density

The variation in the current density with applied electrical field for x·C18A-HSBT/PVDF (x = 2.5% to 10%) thin films on ITO coated glass substrate measured at room temperature is given in Fig. 8. With the increase of C18A-HSBT content in the x·C18A-HSBT/PVDF thin films, the current density of x·C18A-HSBT/PVDF thin films under the applied electrical field also decreased. Compared to other counterpart, the current density with applied electrical filed at 90 kV/cm for $x \cdot C18A$ -HSBT/PVDF (x = 10%) thin films is the least and equal to 6.2×10^{-7} A/cm². This behavior could be explained as follows. When the amount of C18A-HSBT added into the PVDF matrix was increased, the more regular PVDF chains alignment would improve the crystalline of x C18A-HSBT/PVDF thin films subjected to thermal treatment. As a result, the phenomena of leakage current density existed in the x·C18A-HSBT/PVDF thin films decreased with the increase of C18A-HSBT content were determined from the Fig. 8. In addition, as reported in literature [11], the low dielectric loss at low frequency would reflect low leakage current.

Conclusions

In this paper, we reported the preparation of ferroelectric x·C18A-HSBT/PVDF (x = 2.5% to 10%) thin films by spin-coating method. The structural characteristic and surface morphology of the as-prepared films were determined by XRD, FT-IR and SEM, respectively. Both β -phase of PVDF, and the layered perovskite C18A-HSBT co-exist in the x·C18A-HSBT/PVDF (x=2.5% to 10%) thin film samples. with an increase of C18A-HSBT content in x·C18A-HSBT/

PVDF thin films, the values of dielectric constant of these x·C18A-HSBT/PVDF thin films also increase. The polarization-electric field loop of the x·C18A-HSBT/PVDF thin film samples exhibited enhanced saturated polarizations from 5.04 to 10.06 μ C/cm². Meantime, the C18A-HSBT nanoparticles added into the PVDF matrix could degrade the leakage current density of the x·C18A-HSBT/PVDF thin films under the applied electric field. These abovementioned results indicated that the x·C18A-HSBT/PVDF composite thin films with adjustable ferro-electrical properties could probably be of some favorable values for future applications ranging from broadband sensing to flexible energy scavenging.

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