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ELECTRIC CHARACTERISTICS OF LANGMUIR-BLODGETT FERROELECTRIC POLYMERS FILM: HIGH PYROELECTRIC COEFFICIENT AND LOW DIELECTRIC CONSTANT

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Abstract: The relative dielectric constant ε' and pyroelectric coefficient p of ferroelectric poly(vinylidene fluoride-trifluoroethylene) polymers P(VDF-TrFE) films grown on flexible substrates by Langmuir-Blodgett (LB) technique were measured, and room temperature figure of merit was obtained as 1.4 $Pa^{-1/2}$ at 1kHz. The result implies that LB P(VDF-TrFE) copolymer films are potential materials for pyroelectric detectors. This enhancement of figure of merit could be attributed to good crystallinity and highly planar ordered molecular chains in the LB films.

Key words: ferroelectric copolymer film; Langmuir-Blodgett film; figure of merit
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朗缪尔铁电聚合物薄膜的电学特性:高热释电系数和低介电常数

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摘要: 研究了利用朗缪尔技术(LB)生长在柔性基底上的聚偏氟乙烯和三氟乙烯的共聚物(P(VDF-TrFE))薄膜的电学性质. 通过测量相对介电常数和热释电系数, 发现薄膜在室温1kHz时的优值因子达到1.4 $Pa^{-1/2}$. 这表明利用LB技术生长的P(VDF-TrFE)薄膜是热释电探测器的优良候选材料. 优值因子的提高可能来源于LB薄膜的良好结晶性和分子链在平面内的高度有序性.

关 键 词: 铁电共聚物薄膜; 朗缪尔薄膜; 优值因子

Introduction

During the recent years, considerable experimental and theoretical efforts have been devoted to the study of ferroelectric thin film materials that have remarkably ferroelectric, dielectric, piezoelectric, and electro-optic properties. Due to prominent properties, ferroelectric thin films are essential components in a wide variety of applications including sensors and infrared detectors, nonvolatile memories, tunable microwave circuits or RF devices[1~5]. For infrared detectors, perfect materials should have huge pyroelectric coefficient, small dielectric constant and low dielectric loss. Classic perovskite-type ferroelectric materials have not only high pyroelectric coefficient but also high dielectric constant which is disadvantageous for infrared detectors. Although pyroelectric coefficient[6] of ferroelectric polymers is one order lower than that of perovskite-type ferroelectric materials, dielectric constants of ferroelectric polymers are two orders lower. In addition, ferroelectric polymers

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have appealing features, such as low synthesis temperatures (below 200 °C), low costs, ambient pressure and high chemical stability, etc. Consequently, polyvinylidene fluoride (PVDF) and copolymers with trifluoroethylene (TrFE) and tetrafluoroetylene (TeFE) are potential replacements for ferroelectric perovskites currently used in infrared detectors.

The P(VDF-TrFE) copolymers occur mainly in the ferroelectric β-and paraelectric α-phases. The permanent electric polarization is due to the influence of the highly electronegative fluorine on the polymer chain. The β-phase corresponds to all-*trans* (*TTTT*) molecular conformation, i. e. all the dipoles in each (CH_2-CF_2)-like monomer are aligned along the same direction that is roughly perpendicular to the polymer chain. The non-polar α-phase consists of an alternating *trans*(*T*) *gauche*(*G*) bonding configuration (*TGTG* pattern) in which neighboring units have antiparallel dipole moments. Depending on the processing techniques and conditions, the film properties associated with the chain motions and the inter- or intra- interactions, may be substantially different within the β-and α-crystalline and/or amorphous regions.

In this paper, we present a detailed investigation of the dielectric and pyroelectric properties of P(VDF-TrFE) films grown by Langmuir-Blodgett (LB) technique on aluminized flexible substrates. Our results indicate that good crystallinity, highly planar ordered and close parallel packing of the molecules in LB P(VDF-TrFE) copolymer films enhance the pyroelectric response.

1 Experimental details

Film growth by LB technique consists of depositing uniform molecular monolayer on solid substrates and allows full crystallization of the films, in contrary to bulk P(VDF-TrFE) copolymers or spin coating films which are usually semi-crystalline[7]. P(VDF-TrFE) films, whose compositions are 70% vinylidene fluoride mixed with 30% trifluoroethylene in mole ratio, are fabricated by the so-called horizontal LB technique as described elsewhere[8]. A solution of the copolymer is prepared with a concentration of about 0.05 wt.% in dimethyl sulfoxide. The films are transferred to an aluminium coated flexible substrate at a surface pressure of 5N/cm and consist of 50 monolayers. The thickness of one nominal monolayer is basically three times thicker than the molecular diameter, whose thickness is about 1.78 nm[8]. The total thickness of our 50 MLs copolymer is therefore of about 90 nm. In order to improve the crystallinity, these films were annealed at 140 °C for 5 h. Aluminium is evaporated onto the P(VDF-TrFE) films to form the capacitor structure with an area about 0.5 cm^2. The sample is then annealed at 120 °C for 2 h in atmosphere.

Here we used a variety of temperature-dependent techniques to investigate the same sample, which are beneficial to a better understanding of the behavior of P(VDF-TrFE) films. The temperature dependence of dielectric constants was measured by using an Agilent E4980A impedance analyzer with an ac drive voltage of 0.02 V at temperatures varying from 300 K to 400 K with a rate of 1 K/min. The frequency is varied from 1 kHz to 100 kHz. High resolution x-ray measurements at different temperature were performed on a highly accurate two-axis diffractometer in a Bragg-Brentano geometry with Cu-Kα wavelength issued from an 18 kW rotating anode generator, using a cryofurnace operating between 300 K and 400 K. The polarization versus electric field (*P-E*) hysteresis loops were measured by a Radiant Precision *LC* system at 1 kHz and various temperatures upon heating. The pyroelectric coefficient was measured by a dynamic technique[9].

2 Results and discussion

X-ray diffraction measurements of P(VDF-TrFE) film are shown in Fig 1. At temperatures below 340 K or above 385 K, only one phase is present, either the low-temperature ferroelectric β-phase ($2\theta = 19.5° \pm 0.5°$) or the high-temperature paraelelctric α-phase ($2\theta = 18° \pm 0.5°$). At temperature between 340 K and 385 K, there exists a mixture of the two phases, with one growing at the expense of the other. This is a clear sign of the structural change in P(VDF-TrFE) film which accompanies the phase transition. The disappearance of the β-phase Bragg peak in the x-ray diffraction pattern indicates that ferroelectric-paraelectric (F-P) phase transition temperature T_c is near 390 K. This phase transition is of first-order as α-and β-phases coexist in a

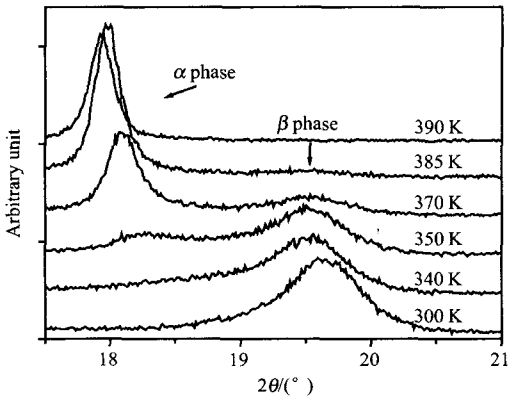

Fig. 1 X-ray diffraction pattern between 17.5° and 21° at temperature range from 300 K to 400 K
图 1 X 射线衍射图,扫描范围 17.5° ~ 21°,温度范围 300 ~ 400K

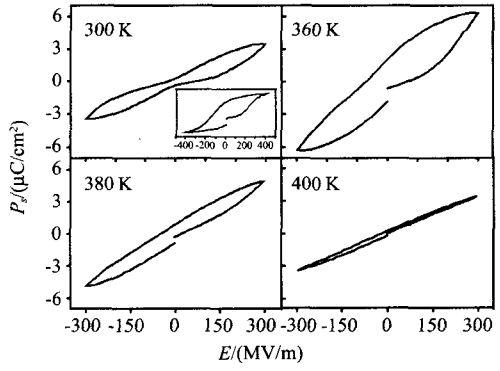

Fig. 2 *P-E* loops of P(VDF-TrFE) at different temperature. Inset shows the *P-E* loop under a 400 MV/m field at 300 K
图 2 P(VDF-TrFE)共聚物薄膜在不同温度下的电滞回线. 插图为 300 K 时,薄膜在 400 MV/m 电场下的电滞回线

wide temperature range from 340 K to 380 K on heating. Similar phenomenon has been reported by Choi *et al*[10] in surface phase transition of LB films.

The *P-E* loops at temperature range from 300 K to 400 K are presented in Fig. 2. Inset of Fig. 2 shows the *P-E* loop under a 400 MV/m field. Because film can be broken down under 400MV/m field above 350K, we measure the *P-E* loops under a 300 MV/m electric field upon heating. It can be seen that the polarization of P(VDF-TrFE) copolymer has a sharp change with temperature. The maximum of P_s is 6.3μC/cm² at 360K. Above 390K, the spontaneous polarization disappears and only polarization induced by electric field remains. Therefore, P_s is only 3.45μC/cm² at 400 K. The large change of polarization with temperature suggests a large pyroelectric response.

The pyroelectric current i_p was measured by a Keithley 6517 electrometer. The pyroelectric coefficient p calculated by $p = i_p/(A\omega\Delta T\cos\omega t)$ is $-26.7\mu C/m^2K$ at room temperature, where A is the area, ω is modulating frequency, and ΔT is the rate of change of the temperature. Compared with previous experiment results $-24\mu C/m^2K$ in spin-coated films[6], pyroelectric coefficient p of our sample is enhanced. However, our sample is much thinner than the spin-coated films. The spontaneous polarization and pyroelectric coefficient would be improved further with the increase of film thickness.

For pyroelectric detectors, relative dielectric constant ε' and dielectric loss tan δ of materials are important parameters. The responsivity of detectors is inversely proportional to ε'. Moreover, dielectric loss is one of noise sources which limit pyroelectric detector sensitivity. Fig. 3 shows the temperature dependence of the real part of the relative dielectric constant ε' and the dielectric losses tan δ on heating process as a function of frequency for P(VDF-TrFE) copolymer films. The F-P phase transition takes place at 388 K as evidenced by the maximum of the dielectric constant. This is in consistent with the result of *x*-ray diffraction. It is noticeable that the maximum of ε' is ~ 9 which is at least two orders less than that of classic perovskite-type ferroelectric materials[11,12]. The diagram of ε' and tan δ versus frequency is plotted in Fig. 4. It can be found that the dielectric losses are lower than 0.032 between 100 Hz to 10 kHz at room temperature.

The physics of pyroelectric detectors has been extensively analyzed and reviewed[13~17]. This analysis concerns both the thermal and electrical response of the detector and leads to the conclusion that voltage response is proportional to a figure of merit $F_v = p/[c'\varepsilon_0\varepsilon']$, where $c' = 2.7 \times 10^6$ J/m³K is volume specific heat, ε_0 is the permittivity of free space. Taken into account noise signals in particular application, the high value of figure of merit $F_D = p/[c'(\varepsilon_0\varepsilon'\tan\delta)^{1/2}]$ is more desirable. The figures of merit F_v and F_D are significant parameters in assessing the usefulness of a pyroelectric material. Room-temperature figures of merit of some pyroelectric materials are listed in Table I. It

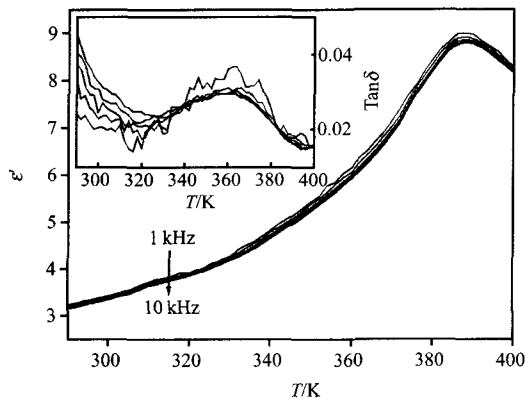

Fig. 3 Temperature variation of relative dielectric constant and losses (inset) for P(VDF-TrFE) film
图3 P(VDF-TrFE)共聚物薄膜的介电温谱和损耗(插图)

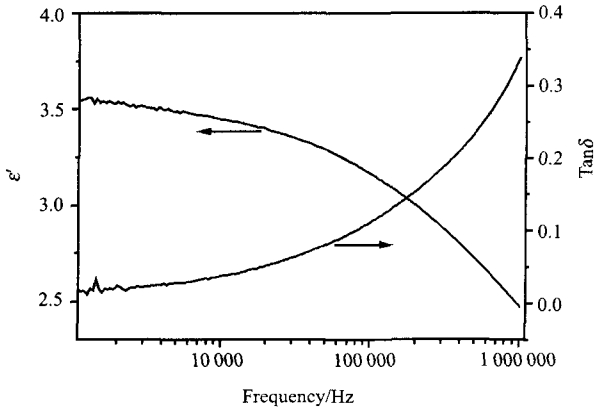

Fig. 4 Relative dielectric constant and losses versus frequency at room temperature
图4 室温下样品的相对介电常数和介电损耗随频率变化的关系

can be found that the figures of merit of LB film is slightly better than that of bulk for P(VDF-TrFE) 70/30. Due to trend of device miniaturization, films are more beneficial to practical application. Besides, it shows that F_D of P(VDF-TrFE) LB film is equal to that of PZT film. Compared to PZT film, the advantage of P(VDF-TrFE) film is nontoxic to environment.

In our opinion, the reason for enhancement of figures of merit should be associated with the special microstructure of LB films. It is well known that the LB copolymers demonstrate some exceptional features, such as good crystallinity, highly planar ordered and closed parallel packing of moleculars. LB growth technique decreases nonpolar clusters (nanometer size gauche segments) or defects and leads to arrangement of dipole moment more

表1 Room-temperature figures of merit of several ferroelectric materials

Table 1 几种铁电材料的室温优值因子

Material	f(kHz)	F_V(m^2/C)	F_D($\times10^{-5}$Pa$^{-1/2}$)
DTGS(crystal)	1	0.53	8.3 (Ref. 15)
$LiTaO_3$(crystal)	1	0.17	11.1 (Ref. 16)
PT(ceramic)	1	0.07	3.2 (Ref. 14)
PZT 25/75(film)	1	0.26	1.4 (Ref. 17)
P(VDF-TrFE) 70/30(bulk)	1	0.22	1.36 (Ref. 18)
P(VDF-TrFE) 70/30(LB film)	1	0.327	1.4

effective, which is beneficial to the enhancement of figures of merit. Consequently, LB P(VDF-TrFE) films can satisfy demands of uncooled thermal infrared detectors. Our work provides useful results in application of LB P(VDF-TrFE) films for practical detectors.

3 Conclusions

In summary, the dielectric and pyroelectric responses of LB P(VDF-TrFE) films were investigated. Relatively low dielectric constant ~ 9 and high pyroelectric coefficient ~ $-26.7\mu C/m^2K$ were obtained in our samples. Good crystallinity, highly planar ordered and close parallel packing of the molecules in LB polymer films enhance pyroelectric coefficient and figures of merit. It suggests that LB P(VDF - TrFE) film is a potential candidate besides classic ferroelectric materials for pyroelectric detectors.

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3　结论

采用 GSMBE 方法,生长了三种不同结构扩展波长 $In_xGa_{1-x}As$ 探测器材料,并制成了台面器件结构,分别测试了样品材料的表面形貌、X 射线衍射摇摆曲线和光致发光谱,结果表明 InAlAs/InGaAs 异质界面处的 DGSL 过渡层能够有效减少异质界面处的位错,减少非辐射复合中心,提高材料质量. 器件暗电流测试结果显示,反向偏压为 10mV 时,没有生长超晶格结构的暗电流为 0.521μA,生长超晶格结构的暗电流降到 0.480μA. 外延初始先生长 InP 缓冲层也能减少衬底自身带来的缺陷对外延层质量的影响,进一步改善探测器性能.

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