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OPTICAL AND ELECTRIC PROPERTIES OF POLY (VINYLIDENE FLUORIED-TRIFLUOROETHYLENE) THIN FILM BY LANGMUIR-BLODGETT TECHNIQUE

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Abstract: Poly (vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) thin films were deposited on polyimide substrate using horizontal Langmuir-Blodgett(LB) technology. X-ray diffractions indicate that the films have good crystallinity with (110) preferential orientation for films with different thickness. The optical dispersion of the films were measured by variable-angle spectroscopic ellipsometry. The data Ψ and Δ at multiple incident angels ($\theta=75°$ and $85°$) were fitted using the Cauchy model. The refractive index, extinction coefficient, absorption coefficient and thickness of each film were obtained. The ferroelectric of the films were studied. The remnant polarization is up to $6.3\mu C/cm^2$. The coercive field is 100MV/cm. The dielectric measurement for the film shows two distinctive phase transitions, ferroelectric-paraelectric phase transition and β relaxation.

Key words: Langmuir-Blodgett technology; P(VDF-TrFE) films; spectroscopic ellipsometry; electric property
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LB 法制备的 P(VDF-TrFE)共聚物薄膜其光学和电学特性研究

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摘要:运用郎缪尔-布尔吉特法在聚酰亚胺衬底上制备聚偏氟乙烯及三氟乙烯(P(VDF-TrFE))共聚物薄膜.不同厚度薄膜的X射线衍射结果表明,薄膜具有良好的结晶特性,取向为(110).运用波长范围为300～1300nm的椭圆偏振光谱仪对薄膜光学特性进行了表征;运用Cauchy模型对不同角度($\theta=75°$和$85°$)测得的Ψ和Δ数据进行了拟合.获得了P(VDF-TrFE)薄膜的光学参数n, k, α以及薄膜的厚度.另外对薄膜的铁电性质的测量,其剩余极化达到了$6.3\mu C/cm^2$,矫顽电场为100MV/cm.介电测量得到了薄膜两个明显的相变,铁电-介电相变以及β弛豫.

关 键 词:LB技术;P(VDF-TrFE)薄膜;椭圆偏振光谱;电学特性

Introduction

The polymers based on polyvinylidene fluoride (PVDF) have attracted attention of many research groups for their ferroelectric properties and many applications. For instance, their dielectric, piezoelectric, pyroelectric and ferroelectric can be used in capacitors, piezoelectric actuators, infrared detector and ferroelectric memories, respectively[1~5]. Compared to the traditional perovskite ferroelectric thin films, the

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PVDF-based ferroelectric thin films have many advantages, for example, fabrication at low temperature, easily integrated with silicon technique, and environment friendly[2,3,5]. In PVDF-based ferroelectric thin films, the copolymer PVDF-trifluorethylene (TrFE) film has been studied for its special ferroelectric. There are several methods to prepare the P(VDF-TrFE) thin films, including spin coating[2,3], evaporation[6] and Langmuir-Blodgett(LB) technique[4,7~9]. In 1995, P(VDF-TrFE) thin films were successfully prepared using LB method[7]. With this method, it is possible to prepare a single layer of the film in mono-molecular thickness.

In this paper, high quality P(VDF-TrFE)) thin films were prepared on polyimide substrate using horizontal LB technology. The optical characteristics of P(VDF-TrFE) LB films were investigated in the wavelength range of 300 ~ 1300 nm by the variable-angle spectroscopic ellipsometry (VASE). The optical constant spectra were obtained. The ferroelectric and dielectric properties were also studied in this paper.

1 Experimental procedures

1.1 Preparation of the P(VDF-TrFE) LB films

The copolymer P(VDF-TrFE) with a composition ratio of 70/30 mol% was dissolved in dimethylformamide to form a dilute solution (0.01% wt) for LB transfer at room temperature. The P(VDF-TrFE) films were deposited on the Al-coated polyimide substrates by LB technology at a surface pressure of 5 mN/m. Top electrode was formed by thermal evaporating aluminum through a metal mask. A plot of surface pressure versus area is shown in Fig. 1. As can be seen, each transferred layer of the film has nearly identical area. That is to say, the thickness of every deposition layer of the film is equal. After the transferring, the film was annealed at 135℃ for 8 hours in air to improve its crystallinity.

1.2 Characterization of the P(VDF-TrFE) LB films

The X-ray diffraction (XRD) data were obtained using a Bruker AXS/D8 Discover Cu Kα Diffraction meter with an X-ray wavelength of 0.15406 nm. We report the optical dispersion of P(VDF-TrFE) LB films over the wavelength range from 300 nm to 1300 nm by variable-angle spectroscopic ellipsometry analysis (W-VASE with Auto RetarderTM) and record $\psi(\lambda,\theta)$ and $\Delta(\lambda,\theta)$ for the incident angels of 75° and 85° for the P(VDF-TrFE) LB film. The measurements were carried out at room temperature. The polarization versus electric field (P-E) hysteresis loops were measured using a Radiant Precision LC system. The dielectric spectrum was measured using the Agilent 4980A impedance analyzer with an ac drive voltage of 0.02 V at different temperatures. Temperature was varied at a rate of 2K/min controlled by a cryostat (MMR Tech., Inc.).

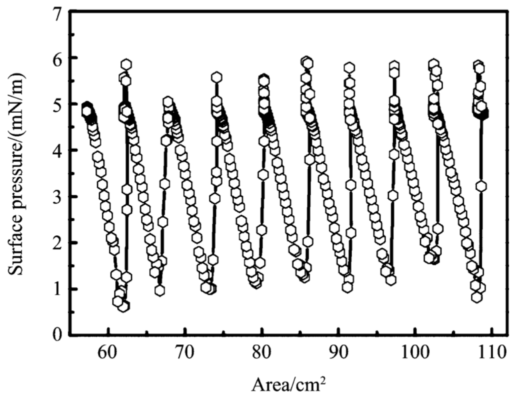

Fig. 1 The dependence between surface pressure and area when transferring the P(VDF-TrFE) films by LB technique
图 1 运用 LB 技术生长 P(VDF-TrFE)薄膜时的表面压和面积的关系

2 Results and discussion

2.1 Crystalline structure of the P(VDF-TrFE) LB films

Fig. 2 shows the XRD pattern of the P(VDF-TrFE) films with 2,5,10,20 and 100 LB transfer layers respectively. It can be seen in this figure that the films exhibit a typical diffraction pattern of β phase, which has a strong (110) peak at 19.6°. The intensity of the peak increases with the thickness of the film for thinner films with deposition layers less than 20. For film with layers more than 20, the XRD intensity keeps unchanged. This result reflects the changes in crystallinity of the thin film with the thickness of films. The intensity of the peak for the 2, 5, 10 and 20 layers samples increased with the increased thickness, suggesting that the crystallinity of the films increased. As shown

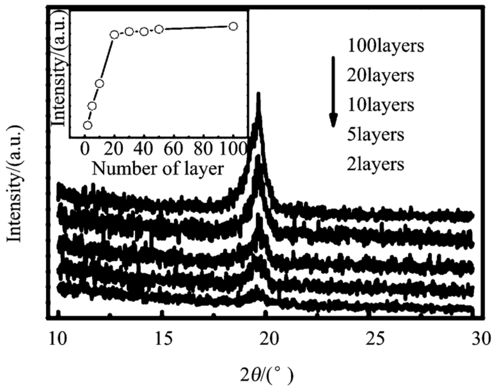

Fig. 2 XRD patterns of the P(VDF-TrFE) thin films with different thickness. The inset is the dependence between the number of transfer layer and the peak of diffraction intensity

图2 不同厚度P(VDF-TrFE)薄膜X射线衍射图谱. 插图为薄膜层数与衍射峰值关系

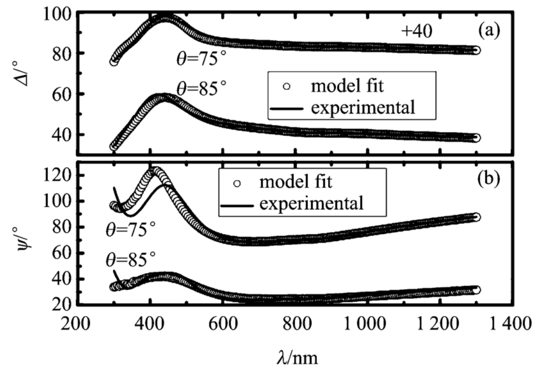

Fig. 3 The ellipsometry spectra of the P(VDF-TrFE) thin film (a) $\psi(\lambda,\theta)$ (b)$\Delta(\lambda,\theta)$. The circle is experimential data , the solid line is the fitted data

图3 P(VDF-TrFE)薄膜的椭圆偏振光谱图(a)$\psi(\lambda,\theta)$(b)$\Delta(\lambda,\theta)$. 图中圆圈数据是实验数据,实线为拟合数据

in inset of Fig. 2, with the thickness of film up to 20 transfer layers, the intensity of the peak does not change greatly. It can be explained by the thickness will induce the films crystallinity.

2.2 Optical dispersion properties of the P(VDF-TrFE) LB films

The optical properties of the P(VDF-TrFE) LB films were obtained by VASE. The ellipsometric basic parameters are the angels ψ and Δ, which are defined by the complex reflectivity ratio: $\rho = r_p/r_s = \tan\psi\exp(i\Delta)$ [10,11], where r_p and r_s are the complex reflection coefficients of the light polarized parallel and perpendicular to the plane of incidence, respectively. The dielectric constant $\varepsilon = \varepsilon_1 + i\varepsilon_2$ can be calculated by fitting the measured data with Cauchy model. Then, the optical constants, refractive index n and extinction coefficient k are decided as follows $n = 1/\sqrt{2}\sqrt{\sqrt{\varepsilon_1^2+\varepsilon_2^2}+\varepsilon_1}$, $k = 1/\sqrt{2}\sqrt{\sqrt{\varepsilon_1^2+\varepsilon_2^2}-\varepsilon_1}$. The measured and the fitted data, ψ and Δ, of the 40 transfer layers P(VDF-TrFE) LB films are shown in Fig. 3 (a) and 3(b), respectively. The experimental data are shown by the circle, and the fitted spectra are shown by solid lines. The data were obtained by 5 nm steps at incident angles of 75° and 85°. We analyzed these experimental data by a model of (Ambient/P(VDF-TrFE)/Al/ Polyimide). It can be seen from Fig. 3 that the fitted data fit well to experimental data for the P(VDF-TrFE) films in the entire wavelength range. However, there are some small deviations between the fitted and the experimental data that can be observed in Fig. 3(a) and 3(b). It is result from depolarizing some detected polarized light[10]. The thickness of 40 transfer layers P(VDF-TrFE) LB films is 80.63nm. The average thickness of one LB transfer layer is about 2.02nm, which is similar to other group results [2].

Fig. 4 shows optical constants spectra of P(VDF-TrFE) thin film, (a) n, (b) k. The inset is the α The refractive index n (λ) and extinction coefficient k (λ) were obtained and is shown in Fig. 4(a) and 4(b) respectively.

The refractive index n of the P(VDF-TrFE) LB films decreases as the wavelength increases in the 300 ~1300 nm wavelength region. The dispersive curve of the P(VDF-TrFE) film of refractive index are very flat

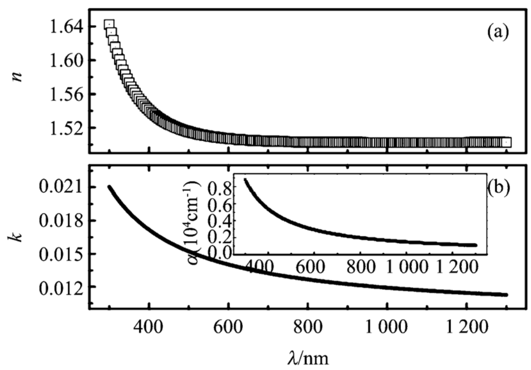

Fig. 4 Optical constants spectra of P(VDF-TrFE) thin film (a)n (b)k. The inset is the α

图4 P(VDF-TrFE)薄膜的光学参数 (a)折射率n (b)消光系数k (b)中插图为吸收系数α

above 650 nm and rise sharply at shorter wavelength. It is a typical dispersive curve near the electronic inter-band transition. The value of the refractive index n is 1.506 at the wavelength $\lambda = 633$ nm, which is close to the values of P(VDF-TrFE) reported by Berge, et al[12]. The absorption coefficient of the P(VDF-TrFE) LB films obtained by $\alpha = 4\pi k/\lambda$ is shown in Fig. 4 (b) inset. As can be seen, the absorption coefficient decreases with increasing wavelength.

2.3 Ferroelectric properties of the P(VDF-TrFE) LB films

Fig. 5 shows the hysteresis loop of the Al/P(VDF-TrFE)/Al capacitor measured at various applied voltages range from 5V to 35V.

The P(VDF-TrFE) LB film is characterized by well-saturated polarization electric field switching curves. At an applied voltage of 35V, the remnant polarization Pr is 6.3μC/cm^2 and the coercive field E_c is about 100MV/cm. The well saturated PE loops is related to the β phase and the good crystallinity of the P(VDF-TrFE) LB film.

2.4 Dielectric properties of the P(VDF-TrFE) LB films

The temperature dependence of dielectric properties for 50 transfer layers P(VDF-TrFE) LB films is shown in Fig. 6.

The data are derived at frequency of 1 kHz. The temperature range is from 220K to 420K. The circle and square lines represent data obtained in heating and cooling process, respectively. As is shown in Fig. 6, the curie temperature T_c (388K) on heating process is obviously higher than that (356K) on the cooling process. It suggests that the phase transition is a first-order type. In addition, there is a broad dielectric loss peak is around at 248K. This dielectric relaxation is similar to the dielectric relaxation of P(VDF-TrFE, 65:35 mol%), which have been found and assigned to β relaxation [9].

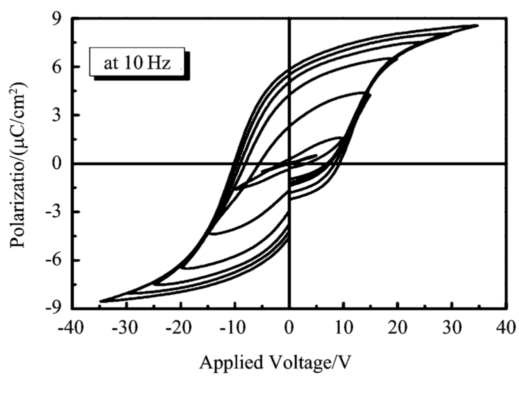

Fig. 5 P-E curves of the P(VDF-TrFE) thin film at 10Hz with different applied voltages

图 5 P(VDF-TrFE)薄膜在 10Hz 时不同电压下的电滞回线

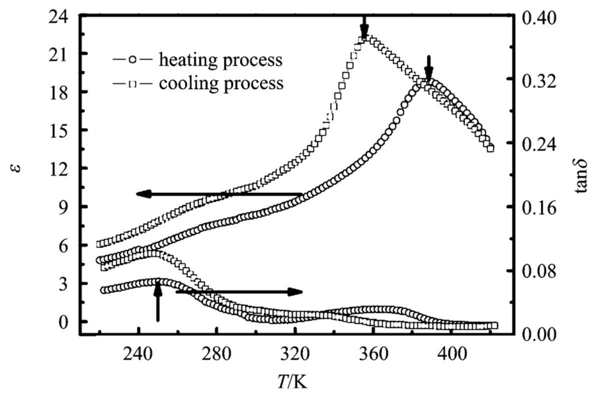

Fig. 6 Temperature dependence of the dielectric constant and dissipation factor for P(VDF-TrFE) thin film at 1kHz, the red circle and black square line are the heating and cooling process respectively

图 6 P(VDF-TrFE)薄膜 1KHz 时的介电温度谱图,圆圈和方块线分别代表升温和降温过程

3 Conclusions

In summary, good crystallinity P(VDF-TrFE) films have been prepared on Al coated polymide substrates by Langmuir-Blodgett(LB) technology. The optical characters of the P(VDF-TrFE) films were investigated by variable-angle spectroscopic ellipsometry over a range from 300 ~ 1300nm. The thickness of the thin film obtained by analysis is about 2 nm per deposition layer. The P(VDF-TrFE) films showed good ferroelectricity with a remnant polarization of 6.3 μC/cm^2 and the coercive field E_c of 100MV/cm. The dielectric measurement for the film shows two distinctive phase transitions. One is ferroelectric-paraelectric phase transition and the other is belonging to β relaxation.

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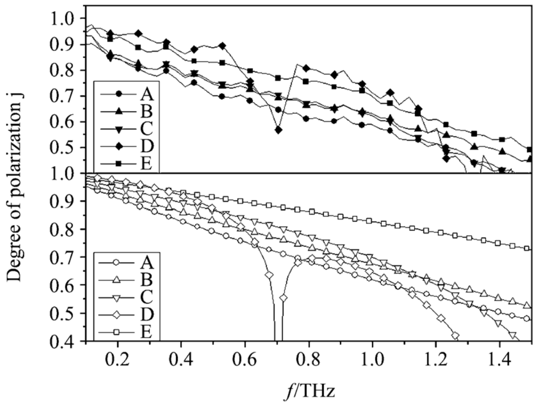

图5 五个实验样品偏振度j与频率的关系(空心线为通过模拟的数据计算得到的结果,实心线为通过实验数据计算得到的结果)
Fig. 5 Frequency-dependence of degree of polarization for 5 various grating structures (Solid line symbols for the result of experiment, Hollow Line symbols for the result by FDTD simulation)

模拟.研究结果表明,在太赫兹波段(1)P偏振的超强透射来源于金属波导的横向半波共振;P偏振的透射率频谱分布受woods反常调制;(2)S偏振整体透射率较低,这是因为对于金属狭缝来说只支持S偏振电磁波的消逝模式传播,并且透射率光谱受到截止波长的调制作用;(3)当刻蚀宽度一定时,在占空比$f = a/L = 0.5$左右线栅的偏振特性较好.因此,要改善线栅的偏振效果,需要使得线栅周期和刻蚀线宽越小越好,同时要满足占空比在0.5左右.这些结论为制作太赫兹波段的线栅型偏振片提供有益的参考.

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