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Electron Irradiation Effects on Ferroelectric Copolymer Langmuir-Blodgett Films

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The effect of irradiation on the ferroelectric properties of Langmuir-Blodgett films of the copolymer poly(vinylidene fluoride-trifluoroethelene) is investigated using 1.26 MeV electrons with dosages from 16 to 110 Mrad. Irradiation causes a systematic decrease in the phase transition temperature, coercive field and polarization of these thin films.

Keywords PVDF; Langmuir-Blodgett films; electron irradiation; ferroelectric films; relaxor

AIP Classification: 77.84.Jd; 78.90.+t; 77.80.-e; 77.80.Bh

Introduction

The discovery of ferroelectricity in thin films of poly(vinylidene fluoride-trifluoroethelene) (P(VDF-TrFE)) copolymers has elicited much attention from the scientific community for applications in memory, actuators, and transducers [1]. We have chosen the copolymer P(VDF-TrFE) 70:30 composition, which has a polarization of (10 μC/cm^2) and a phase transition temperature of 80°C, for this study.

Electron irradiation of the P(VDF-TrFE) copolymers has been studied for thin films ~10 μm–100 μm for spin cast and hot pressed films [2, 3]. Such studies have shown a change in phase transition temperature, structure, and melting temperature. Bharti et al. have shown that these copolymer films can be converted into a relaxor state using high energy electron irradiation for dosages >60 Mrad [3]. It is assumed that the irradiation breaks the crystal into micropolar regions that interact only through electrostatic coupling.

This study is performed using ultra thin (18–90 nm) Langmuir-Blodgett films, a technique pioneered by Palto et al. in 1995 [4]. The quality of these films is excellent, with high crystallinity and crystalline orientation, and they exhibit ferroelectric behavior in samples as thin as 1 nm [5]. Using irradiation we investigated the ferroelectric to relaxor transition in greater detail for Langmuir-Blodgett thin films.

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Experimental

The films used in this study were made on 1 mm thick glass substrates, on which two 50 nm thick, 1 mm wide Aluminum electrodes had been evaporated. The 70:30 copolymer was deposited to the desired thickness by the Langmuir-Blodgett technique described in detail elsewhere [6]. After deposition, another set of identical top Aluminum electrodes was evaporated onto the sample. Twenty-four samples were used in this study: three 10-monolayer samples, eighteen 20-monolayer samples, and three 50-monolayer samples. Only data for the 20-monolayer samples is reported in this paper. The samples were annealed at 120°C for two hours. Prior to irradiation each sample was characterized by measuring the ferroelectric-paraelectric phase transition temperatures, and coercive field using a Hewlett-Packard 4192A impedance analyzer.

The irradiation was performed at National Institute of Standards and Technology using a Van de Graff generator. The electron energy was 1.26 MeV with a fluence rate of 5.9×10^{11} electrons/cm^2/sec. The irradiation was performed under nitrogen atmosphere at room temperature. The samples were stacked vertically in three identical stacks, 8 samples deep. In this configuration, both exposure and electron energy will decrease as the beam passes through the stack. The dosages were measured for the top samples and determined to ±5%. The dosages were calculated for non-surface samples and ranged from 16 Mrad to 110 Mrad. Because of the sample configuration, direct measurement of dosage was not possible for the lower stacked samples; therefore ±5% is the lower limit error in these dosages.

Results

Figure 1 shows the capacitance versus temperature scans for three 20-monolayer samples of different dosages. We see a large shift in phase transition temperature for increased dosage for all 18 samples as summarized in Fig. 2. The change in T_C was found to be −0.52°C per Mrad dosage on cooling up to 60 Mrad, the heating phase transition temperature had a

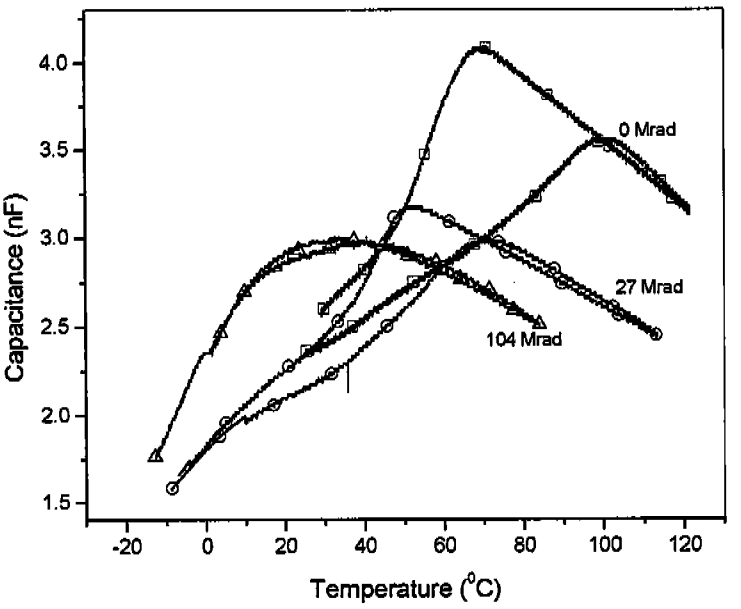

FIGURE 1 Capacitance vs. temperature scans for three 20-monolayer sample receiving different dosages. Notice the shift in heating and cooling phase transitions.

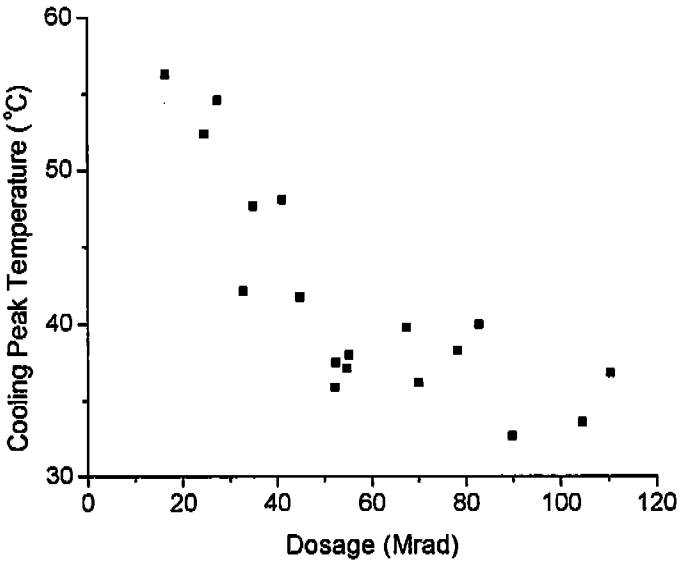

FIGURE 2 The change in cooling peak temperature as a function of dosage. For 20-monolayer samples the slope is found to be −0.52°C/Mrad.

slightly smaller slope of −.39°C/Mrad. This can be compared to a shift of: −1.3°C/Mrad for a 68/32 copolymer and beam energy of 1.2 MeV [7], −0.41°C/Mrad for a 60/40 copolymer and beam energy of 3 MeV [8], and −0.30°C for a 65/35 copolymer and beam energy of 3 MeV [9]. The data may be beginning to plateau as seen by Cheng et al. for dosages higher than 70 Mrad, but from our studies this cannot be determined conclusively. We also see a small decrease in the maximum capacitance after irradiation, however this value seems to be independent of dosage. Some of the spread in the data may have been caused by the comparatively small influence of electron average energy, which is higher for low

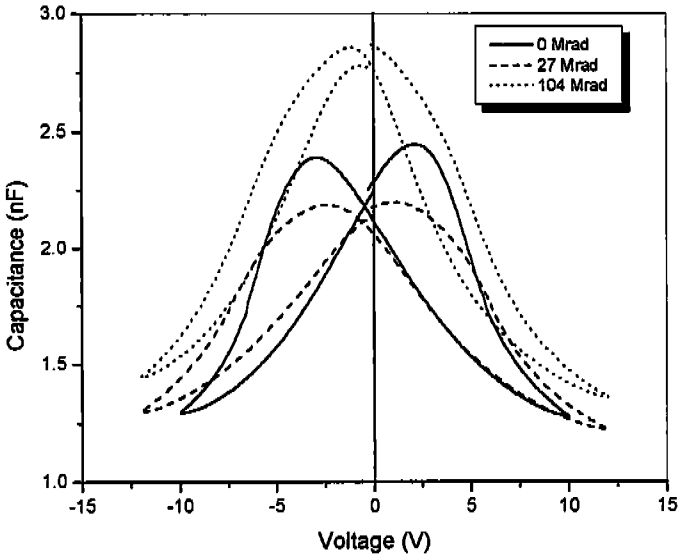

FIGURE 3 Capacitance vs. voltage "butterfly" curves for three 20-monolayer samples of different dosages.

dosages due to sample arrangement. A more detailed analysis is needed to isolate this contribution.

Figure 3 shows the "butterfly" capacitance, C(E) $\propto$ dD/dE, curves for three 20-monolayer samples of different electron dosages. The butterfly curves show peaks near the coercive voltage, the voltage at which the spontaneous polarization reverses direction [10]. The coercive voltage is shown to decrease with increased dosage and the dependence was found to be -26 mV/Mrad. The hysteresis as seen in the butterfly curves decreases as a function of dosage, this decrease corresponds to a decrease in remnant polarization. The decreasing coercive voltage and decreased remnant polarization support the theory that irradiation breaks the film up into micropolar regions. The increase in independent polar regions allows the film to switch more freely and at lower voltages. The decrease in polarization corresponds to damage and a possible increase in amorphous material.

Conclusions

Electron irradiation has a large effect on the ferroelectric properties of thin copolymer films. We have shown a -0.52°C change in phase transition temperature per 1 Mrad dosage and a -8.0 mV/Mrad change in coercive field. Changes are attributed to the increase in defects leading to micropolar regions. The elimination of thermal hysteresis and the large decrease in hysteresis in the butterfly curves support the idea that the films are being converted to a relaxor at high dosages.

Future endeavors may include characterization of structure changes with increased electron dosages, identifying the types of defects acquired during irradiation, and determining the dependence of switching speed with dosage. Also a more detailed analysis is needed to identify the effect of varying the electron energy.

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