Characterization of proton irradiated copolymer thin films for microelectromechanical system applications

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The electrostrictive response of proton irradiated poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] thin films, deposited on silicon (Si) substrates, has been characterized. By applying an ac field to the copolymer films, the induced surface displacement of the film along the thickness direction was measured using a laser interferometer. After the proton irradiation, the electric field induced strain response of the copolymer film is enhanced. Since the copolymer films are laterally clamped by the rigid substrate, the films cannot vibrate freely. At a proton dose of 50 Mrad, the effective electrostrictive coefficient $M_{\mathrm{eff},33}$ of P(VDF-TrFE) thin film on Si is $0.07\times 10^{-18}\ \mathrm{V}^2/\mathrm{m}^2$ which is ~25 times smaller than that of bulk sample under the same irradiation dose ($M_{33}=1.76\times 10^{-18}\ \mathrm{V}^2/\mathrm{m}^2$). Using bulk micromachining to etch away most of the Si substrate, an actuator in the form of a suspended membrane was fabricated. The effective electrostrictive coefficient at the center of the membrane $M_{\mathrm{eff},33'}$ increased to $0.67\times 10^{-18}\ \mathrm{V}^2/\mathrm{m}^2$ due to the weakening of the substrate clamping effect. The resonance characteristics of the actuators based on these irradiated copolymer films were studied. [DOI: 10.1063/1.2435342]

Polymer materials with electromechanical properties such as piezoelectricity are of interest in many fields of acoustics, where they are used in a large number of applications including sonars, loudspeakers, ultrasonic transducers, and actuators. Polymers have the advantages of being light weight, easy to process, and low cost. Renewed interest in polymers for electromechanical applications has been generated due to the discovery of a large electrostrictive effect in electron-irradiated poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE),[1–3] which makes these materials attractive in transducer applications. Its properties can be used in applications which require large displacements and compact size, as in the case of micromachined transducer used in the construction of microelectromechanical systems (MEMSs).

A diaphragm is a typical structure in microphones to detect the acoustic pressure-induced deflection. In a piezoelectric microphone, the electroacoustic sensor consists of a piezoelectric thin film deposited on a diaphragm. The acoustic pressure-induced deflection of the diaphragm creates a bending strain field in the piezoelectric thin film that generates a voltage across the piezoelectric film via the converse piezoelectric effect. The concept of ferroelectric-based acoustic MEMS has been proven. The earliest implementation of a piezoelectric microphone was by Royer *et al.*[4] More recently, Kim *et al.*[5,6] used ZnO in an audio microphone. Organic films, such as aromatic polyurea and PVDF, have been integrated into a microphone structure by Schellin *et al.*[7] However, these results were obtained after the PVDF has been poled. Without permanent polarization, electrostrictive materials [e.g., irradiated P(VDF-TrFE)] have strain that can be varied under different bias fields. They may be good candidates as active elements in tunable acoustic transducers for both sensing and actuation.

Usually, in a bulk sample, the sample is free to expand or contract in all directions. Optimum electromechanical behavior is obtained. When a thin film is attached to a substrate, it is free to expand along its thickness dimension, but its motion is constraint in the plane of the film to a great extent. There are few reports on the effect of substrate clamping on the electrostrictive coefficient of irradiated copolymer thin film on Si substrate. In this study, the performance and the electrostrictive strain responses in proton irradiated P(VDF-TrFE) thin film integrated on Si substrate and on a suspended membrane structure are reported.

Figure 1 shows that the process starts with the back etched of silicon with a $2.5\times 2.5\ \mathrm{mm}^2$ opening at the back formed by KOH anisotropic wet etching. The second step was the deposition of bottom aluminum (0.1 μm) electrode using magnetron sputtering. The third step consists of the spin coating of the 56/44 mol % P(VDF-TrFE) layer. The thickness of the film depends on the concentration of the copolymer in methylethylketone (MEK). The thickness of the film as measured by an α-step surface profilometer was about 2.2 μm, using a 13 wt % copolymer in MEK solution. Then, annealing was carried out at 120 °C for 2 h in order to achieve higher crystallinity. After that, proton-irradiation treatment was carried out in an accelerator located at the Chinese University of Hong Kong (High Voltage Engineering Europa B.V., The Netherlands) at ambient temperature with a 3 MeV proton (H^+ ion) beam. The doses used in this investigation were 0, 20, 30, and 50 Mrad. Finally, the top aluminum electrode was sputtered onto the sample.

In this study, the membrane deformation by the P(VDF-TrFE) thin film is measured with a scanning laser

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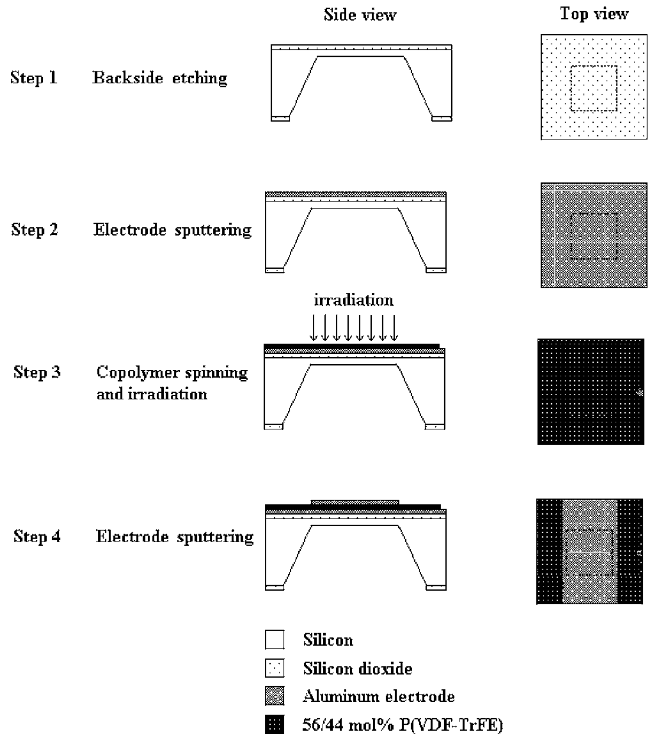

FIG. 1. Fabrication process of the P(VDF-TrFE) thin film on a membrane structure and top view of the electrode pattern.

interferometer.[8] The sample holder is controlled by an X-Y stacked translation stages. In principle, the longitudinal strain (S) of a material can be related to the electrostrictive coefficient (M_{33}) as follows:

$$S = M_{33}E_3^2, \tag{1}$$

where E_3 is the electric field perpendicular to the film surface.

When a sinusoidal signal is superimposed on the sample,

$$E = E_o \sin(\omega t), \tag{2}$$

where E_0 is the amplitude of the electric field applied perpendicular to the film surface.

The induced field strain S is given as

$$S = \left(\frac{1}{2}M_{33}E_0^2\right) + (d_{33})E_0 \sin(\omega t) + \frac{1}{2}M_{33}E_0^2 \sin(2\omega t). \tag{3}$$

Equation (3) possesses three components: a constant strain, a first-order term (at frequency f), and a second-order term (at frequency $2f$). In our interferometer the constant strain is compensated by a feedback arrangement, and is therefore not taken into account. The first-order term is a piezoelectric term, and the second-order term depends on electrostriction only. Thus, the M_{33} coefficient can be obtained by measuring the 2ω component of strain.

$$M_{33} = 2\frac{S}{E_o^2}. \tag{4}$$

For the measurement of the electrostrictive coefficient M_{33} of thin films one has to keep in mind that the film is clamped to a substrate. Therefore, the ratio of strain S and electric field E^2 does not represent the M_{33} of the free sample but gives only an effective coefficient ($M_{\mathrm{eff},33}$). The sample was mounted on a sample holder and adjusted so that the laser beam was normal to the vibration surface of (a) the P(VDF-TrFE) film on a Si substrate without back etching and (b) at the center of the membrane (with Si back etched). The proton irradiated P(VDF-TrFE) film was excited by an ac voltage at 5 kHz generated by a Tektronix AFG310 arbitrary wave form generator, and strain of the film was then measured at the second harmonics (10 kHz) using a lock-in amplifier. Figures 2(a) and 2(b) show that the strain S is proportional to the square of the applied field E^2 in completely clamped copolymer films irradiated with different doses. The values of $M_{\mathrm{eff},33}$ and $M_{\mathrm{eff},33'}$ are deduced according to Eq. (4), which can be determined by 2 times the slope. The $M_{\mathrm{eff},33}$ and $M_{\mathrm{eff},33'}$ results, as shown in Table I, are summarized together with the earlier results of 30 μm bulk samples obtained by hot compression molding.[9] As expected, the $M_{\mathrm{eff},33}$ increases after irradiation. At the proton dose of 50 Mrad, $M_{\mathrm{eff},33}$ on bulk Si substrate approaches 0.07×10^{-18} $\mathrm{V^2/m^2}$. It is seen that the clamping of the film to the

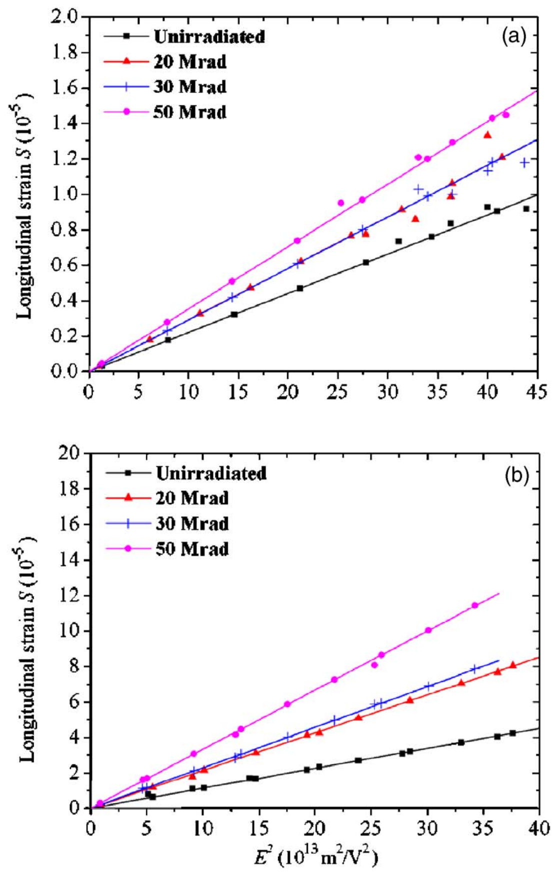

FIG. 2. (Color online) Longitudinal strain (S) as a function of the square of applied electric field E^2 for various proton doses. Effective electrostrictive coefficient of P(VDF-TrFE) (a) on Si ($M_{\mathrm{eff},33}$) and (b) at the center of the membrane with Si back etched ($M_{\mathrm{eff},33'}$) can be evaluated by Eq. (4).

TABLE I. Comparison of the electrostrictive coefficients of proton irradiated P(VDF-TrFE) at 10 kHz.

Dose	M_{33} for bulk sample (10^{-18} m^2/V^2)	$M_{\mathrm{eff},33}$ for film on Si (10^{-18} m^2/V^2)	$M_{\mathrm{eff},33}$ for film at the center of the suspended Si membrane (10^{-18} m^2/V^2)
Unirradiated	0.3	0.044	0.23
20	0.43	0.057	0.43
30	0.44	0.058	0.46
50	1.76	0.071	0.67

TABLE II. Material properties of the thin films in the P(VDF-TrFE) membrane.

Material	Y (GPa)	ρ (kg/m^3)	υ	t (μm)
Silicon	150	2500	0.172	30
Silicon dioxide	70	2200	0.17	1.3
Aluminum	69	2700	0.36	0.1
P(VDF-TrFE)	0.7	1900	0.43	2.2

rigid substrate results in a significant reduction of the measured $M_{\mathrm{eff},33}$ compared to the electrostrictive coefficients of the unconstrained material M_{33} (1.76×10^{-18} m^2/V^2). $M_{\mathrm{eff},33'}$ (0.67×10^{-18} m^2/V^2) on the suspended Si membrane is higher than $M_{\mathrm{eff},33}$ but lower than M_{33}.

The resonance characteristics of the membrane actuator with 50 Mrad copolymer film as the active element have been studied. By calculation, the resonant frequency of a clamped square membrane is proportional to the membrane thickness t and inversely proportional to the size of the square, which can be estimated by the equation[10]

$$f_r = 1.654\frac{t}{L^2}\sqrt{\frac{Y}{\rho(1-\upsilon^2)}}, \tag{5}$$

where L is the length of the square membrane, Y is Young's modulus, ρ is the density, and υ is Poisson's ratio. Rule of mixtures is used to determine effective Young's modulus, the effective density, and effective Poisson's ratio for the P(VDF-TrFE) membrane.[11] Listed in Table II are the material properties of the thin films in the P(VDF-TrFE) membrane. The calculated resonant frequency is 68 kHz. Experimentally, the displacement at the center of the membrane was measured as a function of frequency under an ac driving field of 6.5 MV/m, as shown in Fig. 3. The fundamental resonance of the membrane is found at 56.2 kHz. The displacement profiles of the membrane along the lateral direction at both resonance and off-resonance frequencies were also measured under an electric field of 16 MV/m. As shown in Fig. 4, a symmetric and broad profile is observed. Although the applied field is in the thickness direction, the film movement in the thickness direction also causes bending of the membrane. The maximum off-resonance deflection amplitude at the center of the membrane (measured at 10 kHz) is approximately 0.3 nm. At resonance (measured at 56.2 kHz), the maximum amplitude is up to 15 nm.

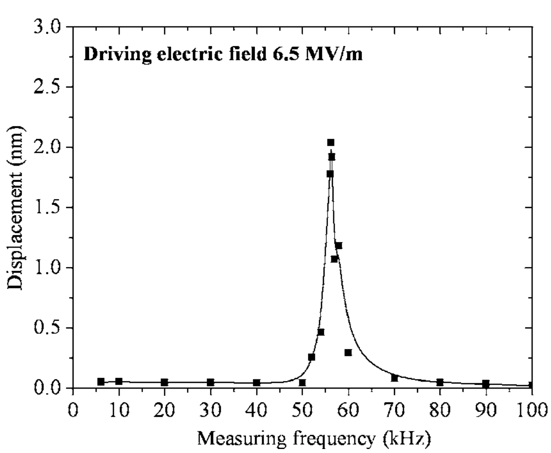

FIG. 3. Displacement vs measuring frequency at the center of a membrane spin coated with P(VDF-TrFE) film irradiated with 50 Mrad. (Frequency measured at the second harmonic of driving frequency.)

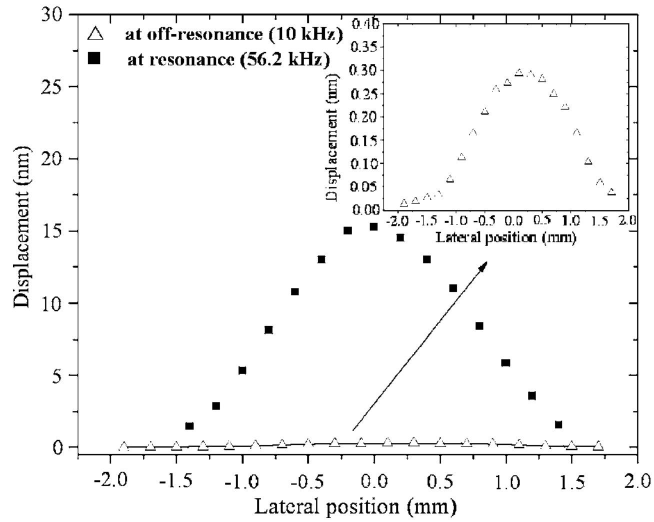

FIG. 4. Displacement across the membrane spin coated with P(VDF-TrFE) film irradiated with proton dose (50 Mrad) under 16 MV/m. Maximum displacement at the center of the membrane is observed in both measurements off-resonance (see inset) and at resonance. The solid line is drawn to guide the eye. Inset: Enlarged view of the off-resonance profile.

To summarize, the substrate clamping effect in 56/44 mol % P(VDF-TrFE) copolymer films irradiated with proton doses ranged from 20 to 50 Mrad was investigated. The results give an estimation of the proportion of the reduction due to the clamping effect. This is important in giving an idea in designing membrane devices for a particular application. The effective electrostrictive coefficient $M_{\mathrm{eff},33}$ of irradiated P(VDF-TrFE) film on silicon substrate is significantly ($\sim$25 times) smaller than M_{33} of the bulk sample, presumably due to substrate clamping. At the center of a membrane structure, $M_{\mathrm{eff},33'}$ is higher than $M_{\mathrm{eff},33}$ but lower than M_{33}. The resonant frequency of the membrane depends on the size and thickness of the membrane. Films on the membrane, due to the decrease in clamping, have performances different from those of the completely clamped films.

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