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Fabrications of PVDF Gratings: Final Report for LDRD Project 79884

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Abstract

The purpose of this project was to do some preliminary studies and process development on electroactive polymers to be used for tunable optical elements and MEMS actuators. Working in collaboration between Sandia National Labs and The University of Illinois Urbana-Champaign, we have successfully developed a process for applying thin films of poly (vinylidene fluoride) (PVDF) onto glass substrates and patterning these using a novel stamping technique. We observed actuation in these structures in static and dynamic measurements. Further work is needed to characterize the impact that this approach could have on the field of tunable optical devices for sensing and communication.

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Fabrications of PVDF gratings: Final Report for LDRD Project 79884

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We explored the use of the electroactive polymer poly (vinylidene fluoride) (PVDF, Aldrich Chemical Company) in a tunable photonic structure that uses a voltage-driven high resolution molded relief grating of PVDF. Average Mw and glass transition temperature (Tg) of pure PVDF is ~534,000, and -38.0 . And, Mass density (ρ_m), relative permittivity ($\varepsilon/\varepsilon_0$), refractive index is 1.78x10^3kg/m^3, 12~13, and 1.42, respectively. Average Mw, inherent viscosity and Tg of PMMA is 120,000, 0,2, and 114.0 , respectively. A 10wt% PVDF was produced by dissolving PVDF powder in 99% n,n-dimethyl acetamide (DMA, Sigma Chemical). Poly-methyl methacrylate (PMMA) was added (final conc. is 2wt%) for good adhesion of PVDF on glass or Au substrate and increasing the proportion of the β-phase PVDF [1,2]. The PVDF in this case is α-phase crystalline. The β-phase, which has improved piezoelectric response, can be made by rolling and drawing the α-phase PVDF film.

Soft lithographic embossing methods formed gratings from this form of PVDF. Figure 1 shows the fabrication procedures for this lithographic manipulation, and for integrating the resulting PVDF structure into a simple tunable device. First, a thin film metal electrode (5nm/50nm Ti/Au) was deposited onto a glass substrate by electron-beam evaporation through a shadow mask. Spin casting PVDF at 1,000 rpm formed a uniform film with thickness of ~2μm. Baking the sample at 65 on a hot plate drives off the residual DMA solvent. To emboss the relief structure, the PVDF was heated to ~170 on a hot-plate to slightly melt the film. Placing a poly(dimethylsiloxane) (PDMS, Sylgard 184; Dow Corning) elastomeric stamp with a line grating structure onto the heated film for 20~30min, allowing the film to cool and then removing the PDMS completed the embossing process. For the experiments described here, the line width, spacing and depth of the relief grating on the PDMS surface were 1.86μm, ~2μm, and 740nm, respectively. A top electrode (2nm/30nm Ti/Au) was formed on the molded PVDF film by electron beam evaporation through a shadow mask. Aluminum tape was attached to the edges of both top and bottom electrodes to facilitate connections to power supplies and multimeters; the junctions between the aluminum tape and the electrodes were coated by silver paint.

Figure 2 presents a schematic illustration of the device structure and actual images of a representative device. As deposited and patterned with the procedures described above, the PVDF is not an electro-active. Electrical poling is necessary to obtain significant piezoelectric response. This poling process involves heating the molded PVDF structure to 150 hot-plate and applying an external bias using the top and bottom electrodes to generate ~200kV/cm electric fields for 3hr. During and after cooling the sample, we maintained the external bias for ~1hr. Figures 3 and 4 show scanning electron, optical and atomic force micrographs of the relief structures. The molded grating structures are not significantly altered during the poling process.

As a first method to characterize the response of the gratings to applied voltages, we mounted the completed devices into an atomic force microscope, and measured the structure of relief for different applied voltages. As a control, we also measured devices that did not undergo the poling process. Data corresponding to such a sample are shown in Fig. 5a; there is no change in the relief depth with applied voltage. Figure 5b gives the response of a working device. The relief depth decreases by ~15 nm as the voltage increases from 0 to 10 V. Above 10 V, the relief does not change appreciably with applied voltage.

The literature shows that the piezoelectric strain coefficient of pure poled PVDF is d_{33}=-20~-33 x10^{-12}m/V. [3],[4]. We can estimate relief depth changes Δl_{33} of piezoelectric sample by that simple equation.

(1) $\Delta l_{33} = d_{33}\, l_3\, E_0$

Where, Δl_{33} is a relief depth change of sample, l_3 is initial depth, and E_0 is electric field.
But, PMMA blending can vary the piezoelectric activity of PVDF. Also, piezoelectric activity of PVDF is temperature dependent. We observed very large depth changes from PVDF line grating sample. Predicted depth change of regular square or flat film, which consisting of pure PVDF, is ~1nm. But, predicted depth changes of embossing structure like line grating is not same with square or flat film, because, the thickness and electrode shape is different with flat film or square.

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Figure Captions

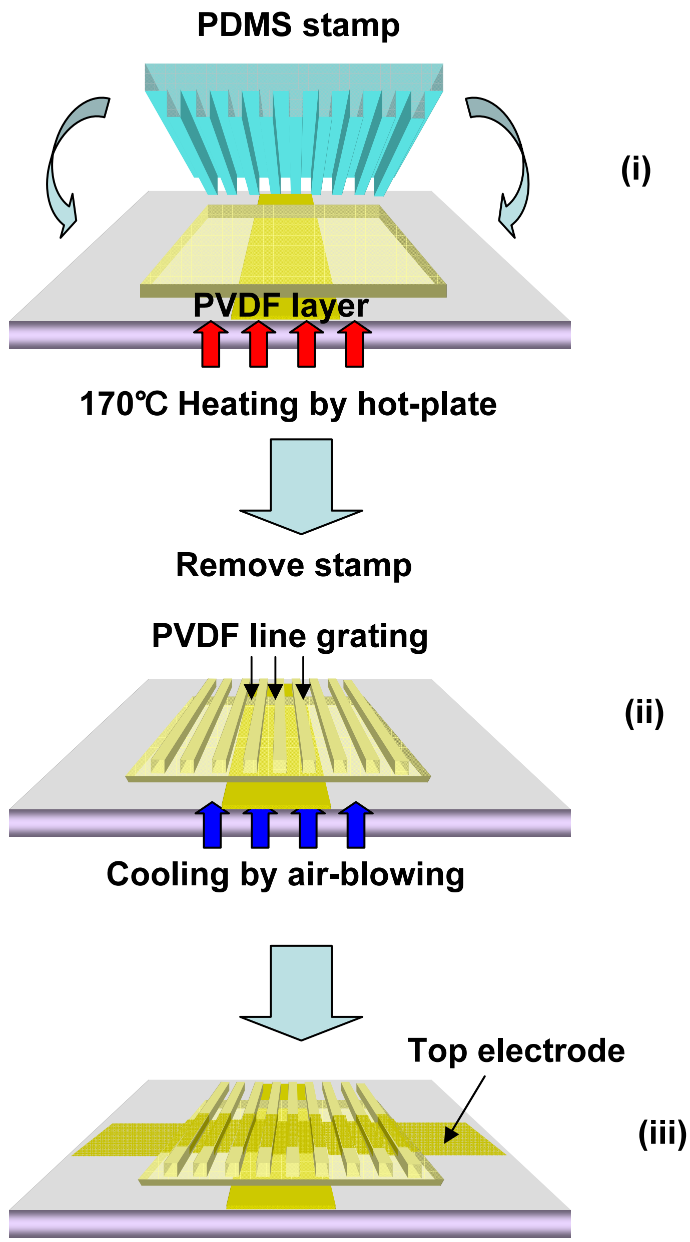
Figure 1. Fabrication procedures for PVDF line grating: (i) PVDF film onto Au(50nm)/Ti(5nm) electrode by spin coater, and PDMS stamp to fabricate PVDF grating, (ii) PVDF grating from PDMS stamp, (iii) Au(30nm)/Ti(2nm) top electrode deposition on PVDF grating.

Figure 2. (Top) Schematic structure and poling process of PVDF line grating sample and (Bottom) Its low resolution real image: (a) Au(30nm)/Ti(2nm) top electrode, (b) PVDF line grating with thickness 0.8~1.5μm, (c) connection to external bias with 200kV/cm for poling the PVDF grating, (d) Al tape for good electric conductivity between electrode and external power supply, (e) glass substrate, (f) coat between electrode and Al tape by silver paint, (g) Au(50nm)/Ti(5nm) bottom electrode, (h) 150 heat by hot-plate for fluent and plastic PVDF.

Figure 3. Top view SEM images of (a,b) PDMS line grating stamp and (c,d) PVDF replica from stamp a,b, and 45° tilted (e) and cross section (f) view of PVDF replica.

Figure 4. (a) Optical microscope image and 20μm scan size AFM images of PVDF replica: (b) top view, and (c) 3D view.

Figure 5. Average depth changes of (a) unpoled and (b) poled PVDF line grating sample under external bias from 0 to 24V obtained from AFM observation: 20μm scan size AFM images show 4 waves, and depth changes were measured from difference of maximum height and minimum depth of left one wave in each AFM image.



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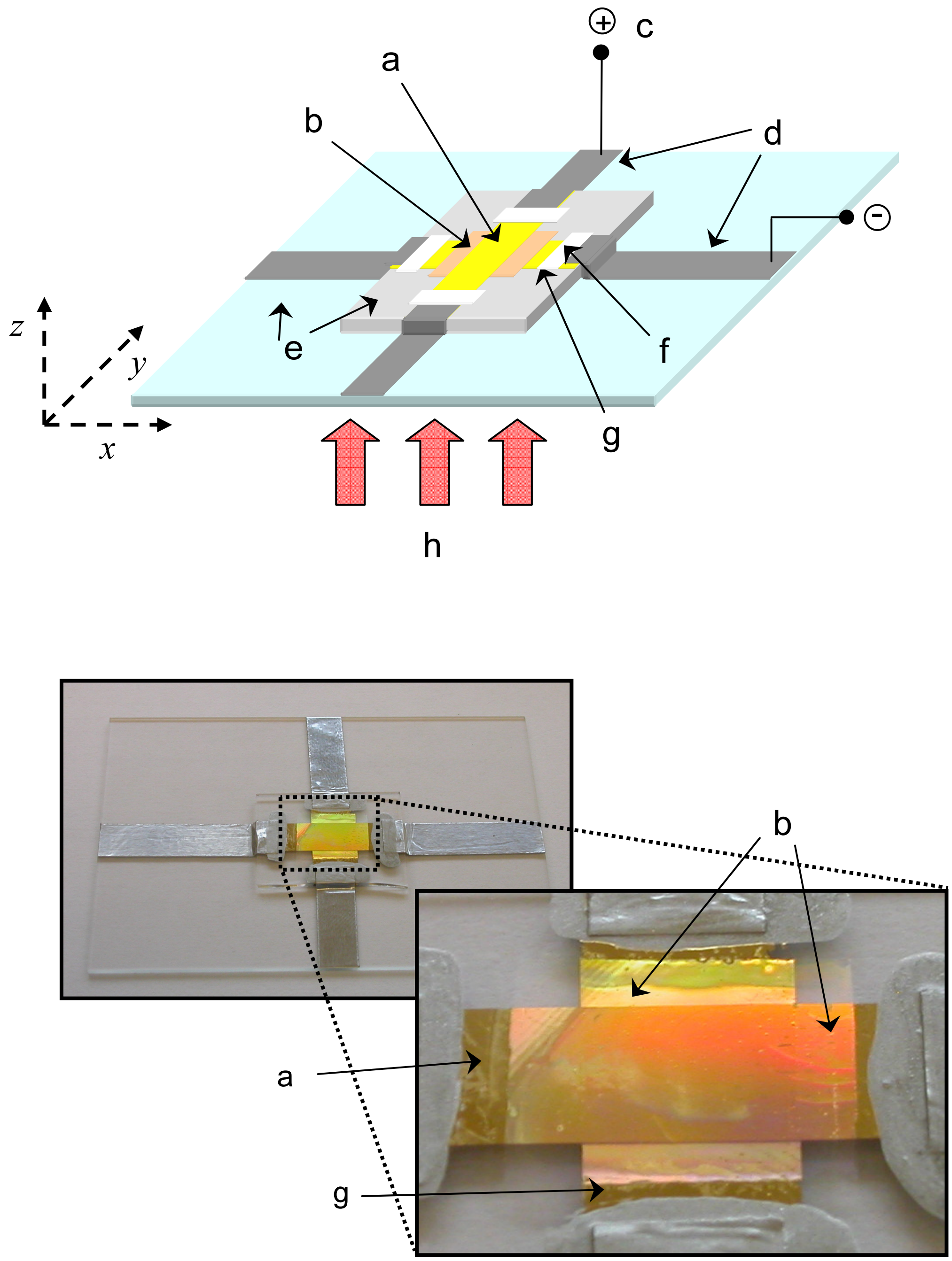
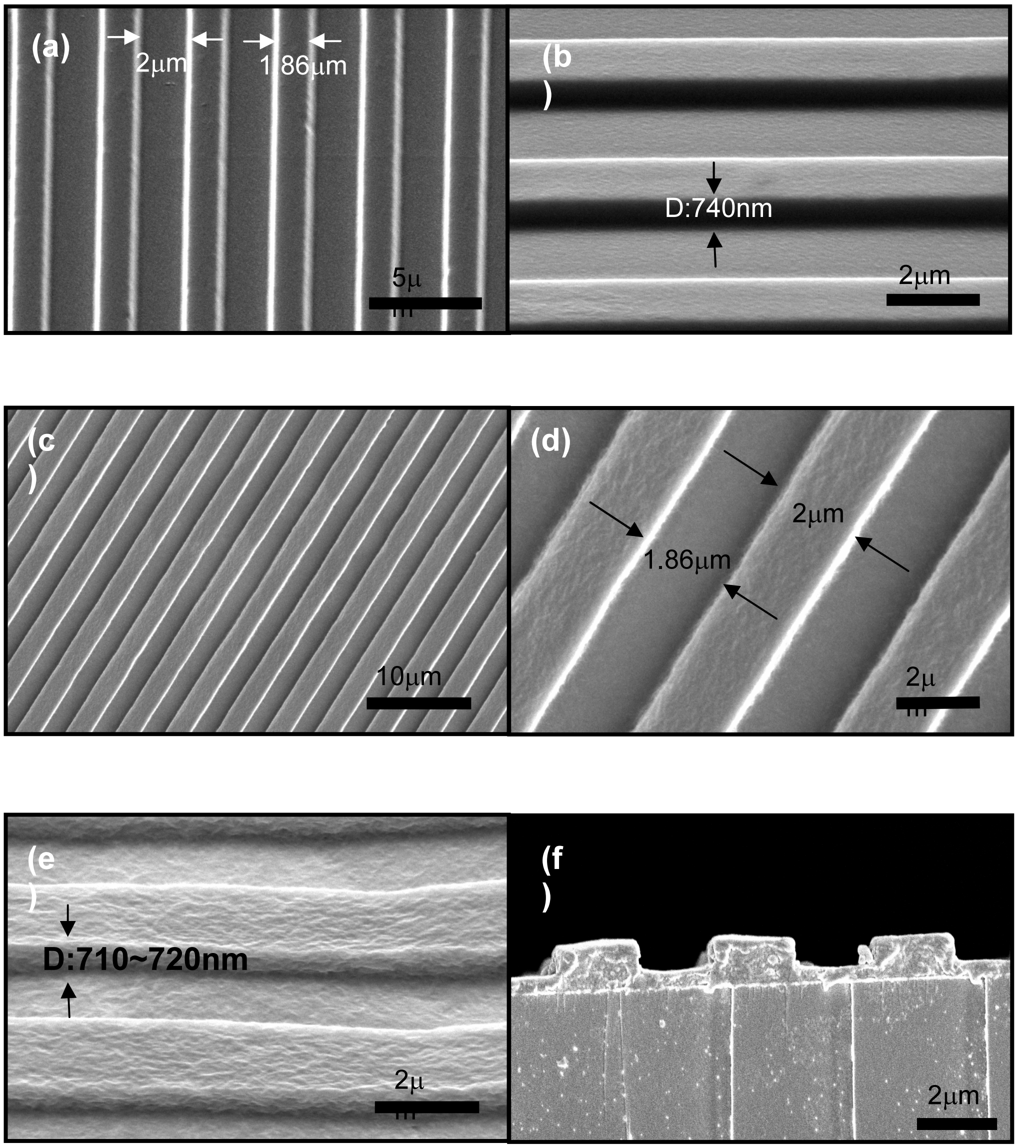


Figure 2. (Top) Schematic structure and poling process of PVDF line grating sample and (Bottom) Its low resolution real image



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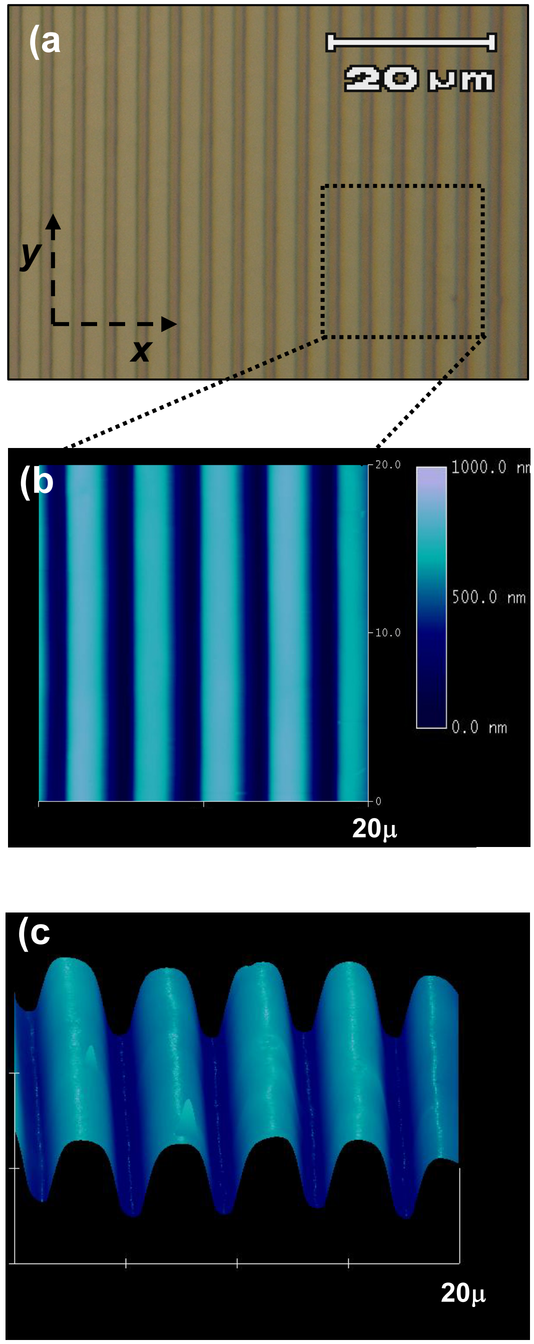
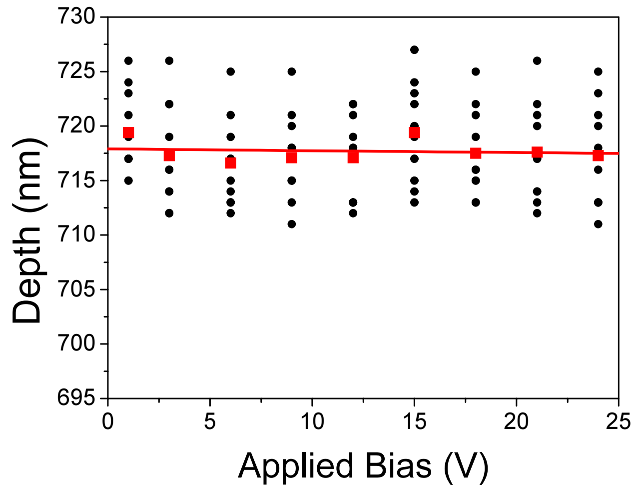
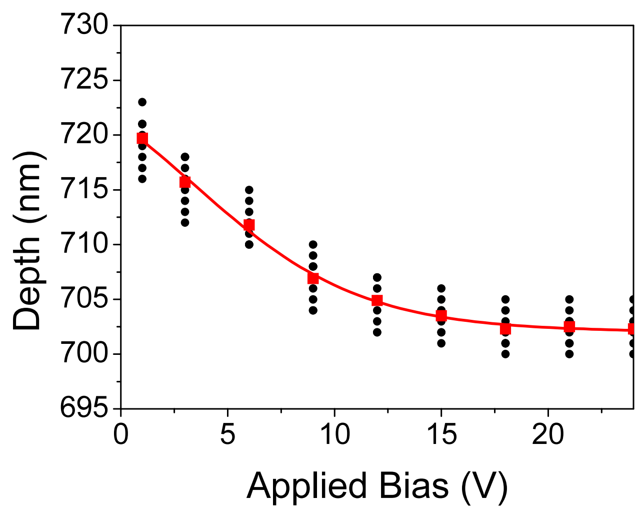


Figure 4. (a) Optical microscope image and 20mm scan size AFM images of PVDF replica: (b) top view, and (c) 3D view.1



(a)



(b)

Figure 5. Average depth changes of (a) unpoled and (b) poled PVDF line grating sample under external bias from 0 to 24V obtained from AFM observation

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