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Reactive ion etching of poly(vinylidene fluoride-trifluoroethylene) copolymer for flexible piezoelectric devices

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A microfabrication process for poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) based flexible piezoelectric devices is proposed using heat controlled spin coating and reactive ion etching (RIE) techniques. Dry etching of P(VDF-TrFE) in CF_4+O_2 plasma is found to be more effective than that using SF_6+O_2 or Ar+O_2 feed gas with the same radiofrequency power and pressure conditions. A maximum etching rate of 400 nm/min is obtained using the CF_4+O_2 plasma with an oxygen concentration of 60% at an antenna power of 200 W and a platen power of 20 W. The oxygen atoms and fluorine atoms are found to be responsible for the chemical etching process. Microstructuring of P(VDF-TrFE) with a feature size of 10 μm is achieved and the patterned films show a high remanent polarization of 63.6 mC/m^2.

reactive ion etching, P(VDF-TrFE), piezoelectric polymer, spin coating, flexible sensor

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Flexible microdevices varying from plastic solar cells, patchable body sensors and organic light-emitting diode (OLED) devices have been developed and are greatly improving the quality of life [1–3]. Piezoelectric flexible materials such as polyvinylidene fluoride (PVDF) and poly (vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) have attracted great attention for flexible device applications. The piezoelectricity of PVDF was discovered by Kawai in 1969 [4], and there are at least four crystalline phases of PVDF, among which the polar phase I (β) shows a very high piezoelectric voltage coefficient. P(VDF-TrFE), a copolymer of VDF and TrFE, shows a significant piezoelectricity with proper compositions. Due to their remarkable piezoelectric, mechanical and chemical properties, PVDF and P(VDF-TrFE) are widely used for developing nanogenerators [5], metal-ferroelectric-metal capacitors [6], and heart beat sensors [7]. Cantilever shaped P(VDF-TrFE) actuators were also fabricated for mini-robots application, in which a multilayered P(VDF-TrFE) structure was proposed to achieve a large displacement with a low driving voltage [8].

Most of the PVDF based devices were fabricated using commercial PVDF films and traditional fabrication techniques such as scissoring, laser machining, and lamination [9,10]. With the aim of integrating piezoelectric polymers into microdevices, ionized evaporation, electrospray, electrospun, Langmuir-Blodgett deposition, and heat controlled spin coating methods were developed. Ionized evaporation and electrospray processes were reported to deposit PVDF films for pyroelectric infrared sensors in 1990s [11,12]. An electrospun method was employed to fabricate PVDF nanofibers for sensors and energy harvesters [5,13]. For fabrication of nonvolatile memory devices, low-temperature fabrication approaches including Langmuir-Blodgett deposition [14,15] and spin coating methods [16] were developed. The spin coated P(VDF-TrFE) films, intrinsically tending to form phase I crystal with a high remanent polarization, are

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*Corresponding author (email: jiangyg@buaa.edu.cn) widely used in recent researches [6,17,18].

Microstructuring of the P(VDF-TrFE) films is a critical process for fabrication of flexible piezoelectric devices. A modified Bosch process using C_4F_8, SF_6 and O_2 gases were applied to P(VDF-TrFE) etching with a commercial ion coupled plasma (ICP) reactive ion etching (RIE) equipment [8]. However, the RIE mechanism of P(VDF-TrFE) using fluorine or oxygen based gas has not been intensively studied. In this paper, we report the experimental study on the reactive ion etching mechanism of P(VDF-TrFE) films for fabrication of P(VDF-TrFE) based flexible microdevices.

1 Experimental

Figure 1 illustrates a schematic structure of P(VDF-TrFE) based flexible devices, which comprises of a P(VDF-TrFE) layer sandwiched by double electrode layers on a flexible polydimethylsiloxane (PDMS) substrate. It can be fabricated using a metal deposition, P(VDF-TrFE) spin coating and patterning process. Microfabrication of P(VDF-TrFE) on the flexible PDMS substrate is a critical process for the batch fabrication of the P(VDF-TrFE) based devices.

The experiment on RIE of P(VDF-TrFE) is done with a procedure shown in Figure 2. A flexible PDMS substrate with a thickness of 300 μm is used as the starting material. The surface of the PDMS substrate is modified by oxygen plasma to improve the adhesive strength between the PDMS substrate and the metal layer (Figure 2(a)). The adhesive strength is affected both by the chemical state of bonding and the morphology of the surface [20]. A layer of Cr-Au with a thickness of 300 nm is deposited by sputtering as the bottom electrodes on the PDMS substrate. The P(VDF-TrFE) layer is formed by the heat controlled spin-coat method (Figure 2(b)). As the composition of VDF and TrFE is very effective to achieve a high piezoelectric coefficient and a low current leakage, an optimized P(VDF-TrFE) copolymer powder (KF W#2200) with a composition of VDF/TrFE=75/25 mol% from KUREHA Corporation is used in our experiments. The P(VDF-TrFE) powder is dissolved in methylethyl ketone with mechanical stirring at a temperature of 60°C to obtain a solution of 10 wt%. After naturally cooling to room temperature, the solution is spin coated on the substrate at 1700 r/min. The 2-μm-thick P(VDF-TrFE) film is annealed at 140°C in nitrogen gas ambient for 2 h to enhance the crystallinity [21]. Aluminum is deposited by sputtering with a thickness of 300 nm as the upper electrodes, and subsequently patterned by photolithography and wet etching processes (Figure 2(c)). Using the patterned aluminum as the mask, the P(VDF-TrFE) is patterned by a home-made ICP-RIE system (Figure 2(d)).

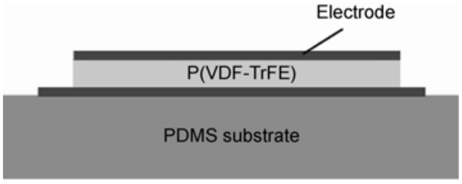

Figure 1 Schematic structure of P(VDF-TrFE) based flexible sensing devices.

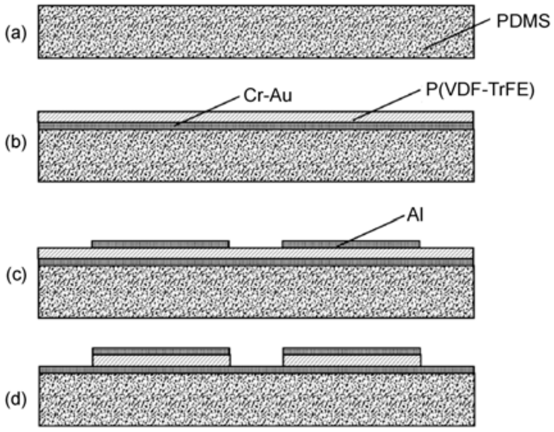

Figure 2 Experimental procedure for micromachining of P(VDF-TrFE).

2 Results and discussion

The X-ray diffraction (XRD) pattern is used to analyze the crystallinity of the P(VDF-TrFE) film prepared by the heat controlled spin coating method as shown in Figure 3. The diffraction peak appeared at 20°(2θ) is assigned to β-phase of the P(VDF-TrFE) copolymer film. Dry etching experiments are carried out using the home-made RIE system. Antenna power refers to the radiofrequency (RF) power applied to the ICP antenna which is a conical coil, and platen power means the RF power applied to the cathode. Antenna power and gas composition are the most important factors that influence the etching results. As the result, we first investigate the antenna power dependence of the etching rates. In the experiment, pure oxygen is utilized as the feed gas with a flow rate of 50 sccm at a process pressure of 5 Pa and a constant platen power of 20 W. The etching rate

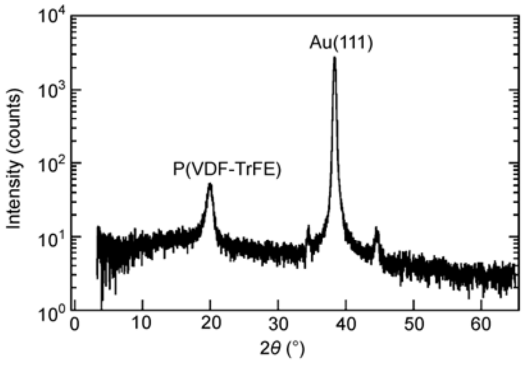

Figure 3 X-ray diffraction pattern of the P(VDF-TrFE) film prepared by the heat controlled spin coating method.

monotonously increases by improving the antenna power as shown in Figure 4. The high antenna power increases the density of reactive species, improving the etching rate of P(VDF-TrFE).

In order to characterize the gas composition dependence of the etching rate, the RIE system is fed with CF_4+O_2, SF_6+O_2 and Ar+O_2 gas mixtures, respectively. The oxygen concentration varies from 0 to 100 vol%. The experiment is done at a constant antenna power of 200 W, a platen power of 20 W, and a process pressure of 5 Pa. With a total flow rate of 50 sccm, the etching rate variation with the gas composition is plotted in Figure 5. The etching rate using SF_6+O_2, or Ar+O_2 gas mixtures is monotonously increases by increasing the O_2 concentration. As a result, it can be concluded that the oxygen is one of most effective species in the plasma responsible for the etching of P(VDF-TrFE). However, there is an optimized composition of the CF_4+O_2 gas mixture to achieve the highest etching rate. It is well known that CF_4 molecules are decomposed to CF_2^+ ions, CF_3^* radicals, and fluorine atoms in the plasma, whilst oxygen exists in the form of oxygen atoms. Among the excited species such as CF_3^* radicals, CF_2^+ ions, and fluorine atoms, fluorine atom is responsible for reactive etching of P(VDF-TrFE), as the etching rate is maximum when the density of fluorine atoms presents a maximum for P(VDF-TrFE) [22]. The following mechanism is suggested for the RIE process by fluorine and oxygen atoms.

$$\left[\left(C_2H_2F_2\right)C_2HF_3\right]_n + F + e \rightarrow CF_2^+ + HF + e \tag{1}$$

$$\begin{aligned}\left[\left(C_2H_2F_2\right)C_2HF_3\right]_n &+ O + e \rightarrow CF_2O + CO \\ &+ CO_2 + HF + e\end{aligned} \tag{2}$$

$$CF_2O \rightarrow CO + 2F \tag{3}$$

From above equations, it can be seen that the concentration of fluorine atoms can be improved by the addition of oxygen. The relative concentration of oxygen and fluorine atoms is responsible for the etching rate of P(VDF-TrFE) when CF_4+O_2 feed gas mixture is utilized.

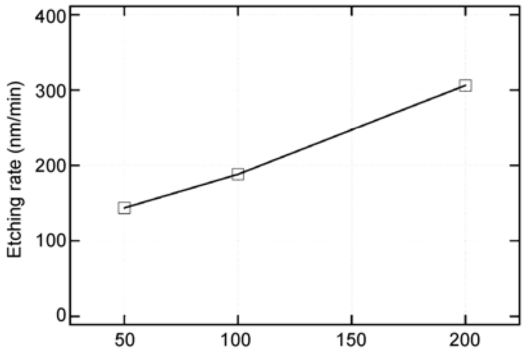

Figure 4 Etching rates of the P(VDF-TrFE) film as a function of antenna power using pure oxygen as the feed gas with a flow rate of 50 sccm at a process pressure of 5 Pa and a constant platen power of 20 W.

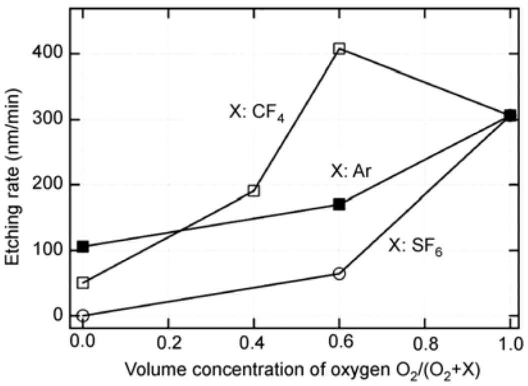

Figure 5 Etching rates variation with the feed gas compositions varying from CF_4+O_2, Ar +O_2, and SF_6+O_2 with a total flow rate of 50 sccm at a process pressure of 5 Pa, a constant platen power of 20 W and an antenna power of 200 W.

SF_6 is a well known reactive gas for plasma etching of silicon with an ultra low etching rate for polymers. The etching mechanism of P(VDF-TrFE) is much different from that of PDMS. As there is silicon element in PDMS, plasma etching using the SF_6+O_2 gas mixture shows a higher etching rate than that using the CF_4+O_2 gas mixture, and the highest etching rate is obtained at a high SF_6 percentage of 75 vol% [19,23]. In order to realize the final piezoelectric flexible device, the specimen and concentration of feed gases should be optimized for selective etching of P(VDF-TrFE) and PDMS.

Figure 6 illustrates the scanning electron microscope (SEM) image of the etching results. The P(VDF-TrFE) strips with a feature size of 10 μm have been successfully fabricated. In order to characterize the piezoelectric response of the P(VDF-TrFE) films after being patterned by RIE, P-E hysteresis measurement is employed as shown in Figure 7. The remanent polarization and coercive electric field are found to be as high as 63.6 mC/m^2 and 82.4 MV/m, respectively. The successful etching of P(VDF-TrFE) with excellent piezoelectricity using RIE can greatly contribute to the batch fabrication of P(VDF-TrFE) based flexible devices.

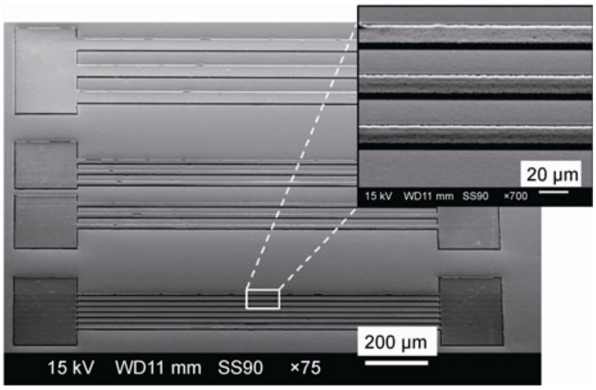

Figure 6 Scanning electron microscope (SEM) images of patterned P(VDF-TrFE) microstructures.

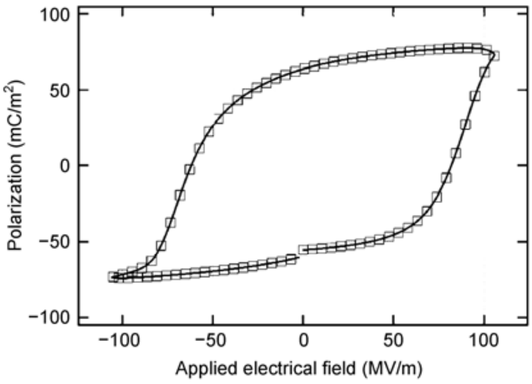

Figure 7 Measured P-E hysteresis curve of the patterned P(VDF-TrFE) film with a thickness of 2 μm.

3 Conclusions

Batch fabrication of P(VDF-TrFE) based flexible devices was proposed. Micromachining of P(VDF-TrFE) films with an excellent piezoelectric coefficient was achieved via the heat controlled spin coating and reactive ion etching methods. Gas mixtures of CF_4+O_2, Ar +O_2, and SF_6+O_2 were investigated to optimize the etching conditions. With an antenna power of 200 W, a platen power of 20 W, and a pressure 5 Pa, a very high etching rate of 400 nm/min was achieved with a mixture of 40% CF_4/60% O_2. It can be concluded that the excited fluorine and oxygen atoms are responsible for the reactive ion etching of P(VDF-TrFE) and the etching rate is related to their relative concentrations. The successful dry etching of P(VDF-TrFE) will significantly contribute to batch fabrication of flexible piezoelectric devices.

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