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The influence of the intensity of an electric field on properties of P(VDF-TeFE) thin films during the annealing process

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Introduction

In various energy harvesting technologies, we have focused on human voice to extend the operating life-time of portable electronic devices. Since a human voice has irregular frequency and energy as an acoustic wave, we have studied about the fabrication of a membrane-type micro-generator which has low resonant frequency using a piezoelectric polymer. Thus, we have selected P(VDF -TeFE) (Poly vinylidene fluoride and tetrafluoroethylene) (supported by Daikin Co.Ltd.) to combine with MEMS technology. This polymer is the same with PVDF as a copolymer in all aspects.[1] Fig. 1 shows β-phase structure of PVDF and P(VDF-TeFE) (80/20). Since a stretching method is impossible to apply to MEMS process, selection of casting solvents and processing method are very important. For this reason, we have carried out the annealing process at a temperature higher than the melting point. As a result, a polarity of the film is lowered seriously.[2]

In this study, for the application of an electric field, we have investigated the variation of the film properties as a function of an electric field during the annealing process.

Experiment

A Pt/Ta deposited Si substrate was prepared to coat the film. Methyl-ethyl-ketone (MEK) and N,N-dimethylacetamide (DMA) were used as a solvent to cast the polymer granule. Single and mixed solutions were prepared as a coating solution; single solution of 4% concentration was made up only MEK and mixed solution was made up MEK (73%) and DMA (27%). A mixing ratio of the mixed solution and a temperature of the annealing process were determined by the previous study.[3]

To reduce influences of moisture in atmosphere during the coating process, N_2 gas was filled in the spin-coating chamber before the process. The annealing process was carried out at 195 °C. The electric field was applied by 0.5, 1 and 2 MV/m for 2 mm distance between electrodes during the annealing process as shown in Fig.2.

Results and discussion

Fig. 3 shows XPS spectra of C 1s for variation of the electric field. At the region of 283.5 ~ 288 eV in Fig. 3-(a) and (b), CH_n bond and C-O-C bond are detected except for the film annealed with 1 MV/m. CH_n bond is a fragment which is come off the chain structure of the polymer. C-O-C bond is possible to be formed by an invasion of O atom into the chain structure.[3] Fig. 4 shows XPS spectra of O 1s for variation of the electric field. In Fig. 4-(a), C-O-C bond and -OH bond are detected. With intensities of the bonds, the volume of O atom which interfered in the chain structure is considerable, and the atoms affect a remanent polarization of the film. In Fig. 4-(b), C-O-C bond is not observed. However, -OH bond and O atoms are detected, and a little H_2O bond is also detected at about 533 eV.

Fig. 5 shows a quantitative comparison of ratio with each bond in single and mixed solution. In Fig. 5-(a), a detection of CH_n, CC and -CO- bonds means broken or deformed monomer chain as an abnormality of a chain structure in the polymer. On increasing an electric field, a ratio of these bonds is reduced. In a case of 2 MV/m, however, the ratio is increased than a case of 1 MV/m. $-CF_2-\underline{C}H_2-CF_2-$ and $-CF_2-\underline{C}F_2-CF_2-$ bonds which are shown in Fig. 5-(b) are the main frame of a P(VDF-TeFE) chain structure. In case of 1 MV/m, a ratio of the bonds is same as the film formed without an electric field. In a case of 0.5 and 2 MV/m, contrarily, the ratio is lower than the others. As a result, there is a suitable range for an electric field which is applied during the annealing process.

Table 1 shows the variation of remanent polarization at the condition of 100 V and 0.1 Hz. A remanent polarization of the film annealed with an electric field of 1 MV/m is two times higher than that of the film annealed without an electric field. However, for the electric field of 0.5 and 2 MV/m, a state of the film is changed to a paraelectric state.

Conclusion

It is found that the electric field affects the properties of the film during an annealing process. In the electric field lower than suitable intensity, the electric field cannot affect the properties. Otherwise, the electric field disturbs the formation of the film. In our result, we found that there is a suitable intensity of an electric field to have a decisive effect on the properties of the film.

Acknowledgements

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References

[1] Jian Xun Wen, Polymer journal, Vol.17, No. 2, pp 399-407 (1985)
[2] J.-H. Jeong, C. Kimura, H. Aoki, M. Okuyama and T. Sugino, ECS Trans., **19**, pp. 59 (2009)
[3] J.-H. Jeong, C. Kimura, H. Aoki and T.Sugino, Jpn. J. Appl. Phys. **49** 04DK23 (2010)

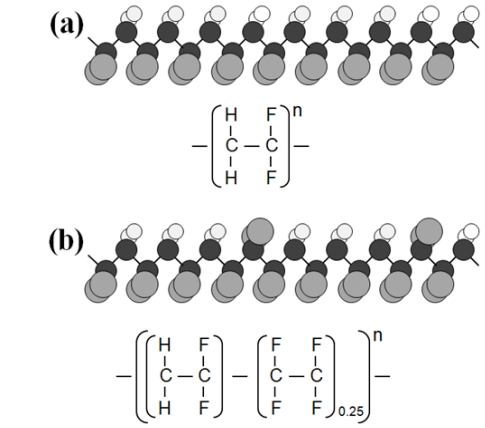

Fig.1. Molecular structures of
(a) PVDF and (b) P(VDF-TeFE)

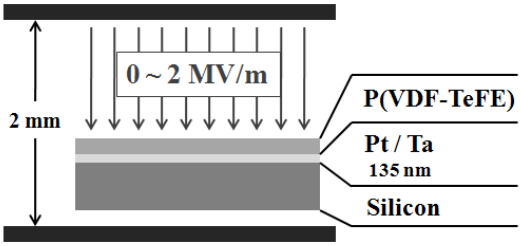

Fig.2. Schematic of a thermal treatment
using an electric-field application

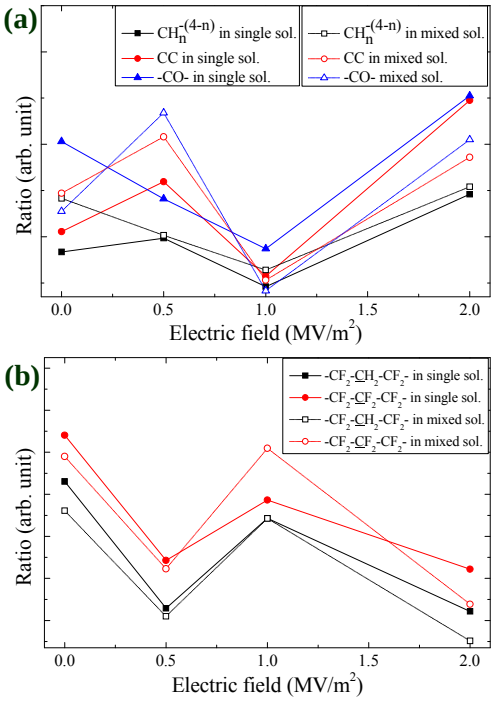

Fig.5. Quantitative comparison of each bond in;
(a) single solution and (b) mixed solution

Table 1. Variations of permanent polarization for frequency of bias voltage

Bias field (MV/m)	Single solution (mC/m^2)	Mixed solution (mC/m^2)
0	30.9	18.2
0.5	Break (paraelectric)	
1	33.1	25.8
2	Break (paraelectric)	

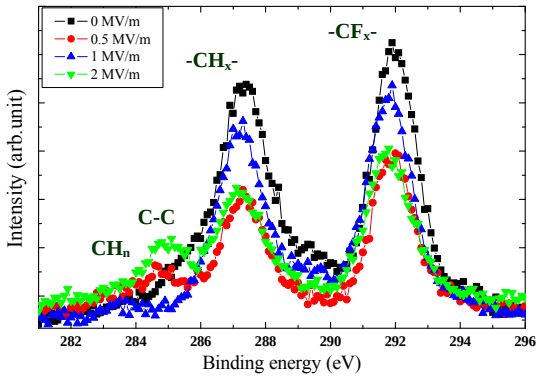

Fig.3-(a). XPS Spectra of C 1s for 4% single solution with various electric fields

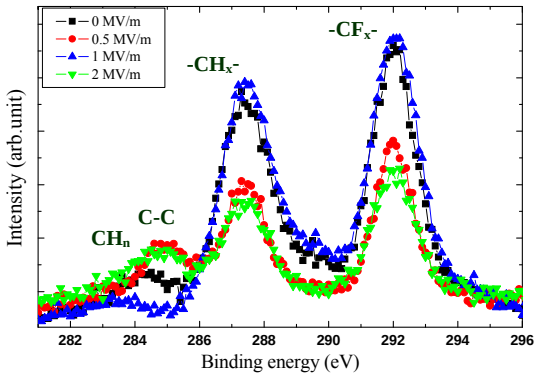

Fig.3-(b). XPS Spectra of C 1s for 4% mixed solution with various electric fields

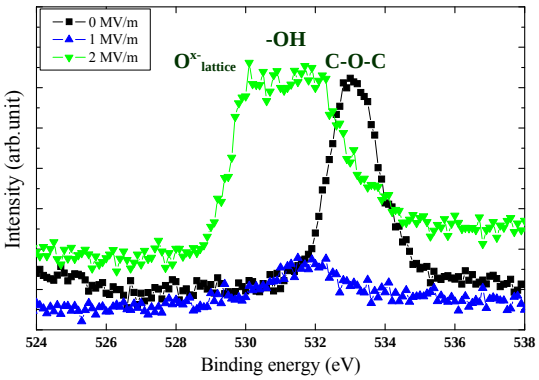

Fig.4-(a). XPS Spectra of O 1s for 4% single solution with various electric fields

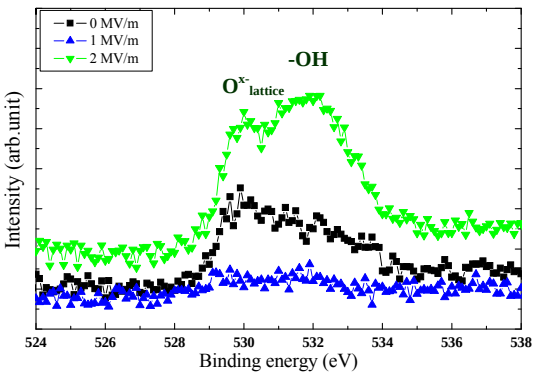

Fig.4-(b). XPS Spectra of O 1s for 4% mixed solution with and without electric field