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The effects of an electric-field application on properties of P(VDF-TeFE) thin film

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Abstract

In the processes to form a P(VDF-TeFE) thin film, we have studied about the thin film formation with various conditions of a spin-coat speed, a concentration and a type of solvents, and annealing temperature. As a molecular structure of the film is changed by concentrations or types of solvent, the annealing in electric field is carried out to prevent the changes. We have investigated the film formed by annealing with and without electric field, also confirmed the rising of permanent polarization.

Introduction

The conventional energy storage techniques based on chemicals have demerits such as finite lifetime and large scale. We have studied the fabrication of a micro-generator as shown Fig.1 which is activated by acoustic wave on a level with human voices. Because of the nature of the source wave, the material of a membrane should have low density and elasticity and be compatible with LSI processes to apply to MEMS processes.

P(VDF-TeFE) (Poly-vinylidene fluoride and tetrafluoroethylene) (supported by Daikin Co.Ltd.) closely resembles PVDF in a molecular structure as shown Fig.2 [1]. According to Table 1, For average mechanical parameters of P(VDF-TeFE) and PVDF film, a resonant frequency of PVDF film is almost double compared with P(VDF-TeFE) film because elastic modulus of PVDF is higher than that of P(VDF-TeFE). For example, if a thickness of membrane is 1um and a radius is 500um, a resonant frequency of the membrane will be 1610.25Hz [2].

Experiment

Using the 3-types of solvents such as Methyl-Ethyl-Ketone (MEK), Dimethylacetoamide (DMA) and mixed solvent with MEK and DMA, the P(VDF-TeFE) thin film was formed by spin-coating method on a surface of a Pt/Ta-deposited silicon substrate. In a case of casting in only DMA, the adhesion of the film is very bad. Moreover the roughness of film surface was changed by annealing temperature, and the roughness affects an electric performance [3].

For this reason, the experiments were achieved by concentrations of 4% and 10%, annealing temperature of 195C° and electric field of 1 MV/m in all of conditions as shown Fig. 3.

Results and discussion

Fig.4 shows that XPS spectra and FTIR spectra of the samples formed with single solution (MEK 100%) and mixed solution (MEK:DMA=3:1) by 10% concentration. In Fig.4-(a), the cases of annealing in electric field are very different from the cases of annealing in none field. In the region of 284 ~ 286 eV, particularly, C-C bonds and C-H bonds didn't appear in a case of annealing in electric field. In Fig.4-(b), since there is not a change of bond structure for all of conditions, the molecules seem to be arranged by electric field as a charge-up state. Fig.5 shows the case of 4% concentration. As shown Fig.4, there are not big changes of molecule structure. However, the quantity of C-C bonds and C-F bonds is very different from the spectra of Fig.4. Contrary to a case of 10% solvent, the absorption of C-C bonds is low, and it will be expected that the chain of C-C bonds is cut. Fig.5 shows the change of permanent polarization (Pr) for a frequency of bias input. Pr is decreased by an increase of bias frequency over all. The decrease of Pr means that the molecules in a film cannot react to the frequency of bias voltage. In a case of 4% single solvents, the results show a simple difference of polarization. In a case of mixed solvents, however, the quantity of polarization is changed largely by a frequency of bias voltages.

Conclusion

In order to apply the P(VDF-TeFE) film to a piezoelectric membrane of a micro generator, we have achieved a film forming process for various conditions and also achieved the improvement of film characteristics with annealing method in electric field and types of solvents.

Acknowledgements

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References

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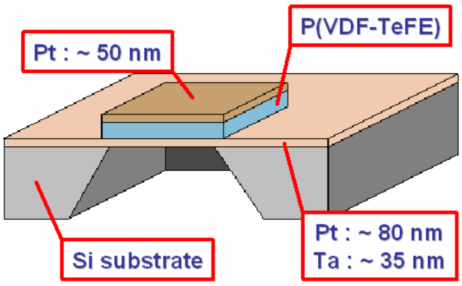

Fig.1. Schematic of micro-generator using P(VDF-TeFE) membrane

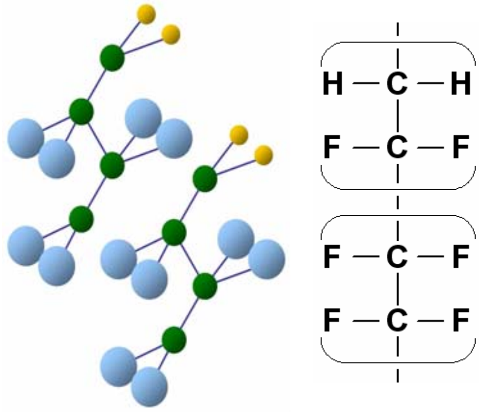

Fig.2. Molecular structure of P(VDF-TeFE)

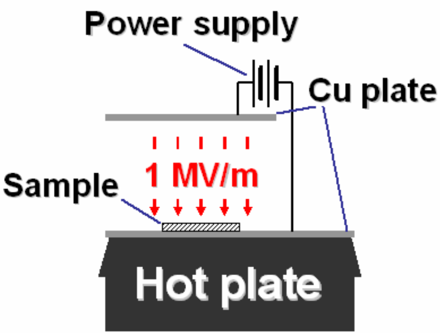

Fig.3. Schematic of annealing process in electric field

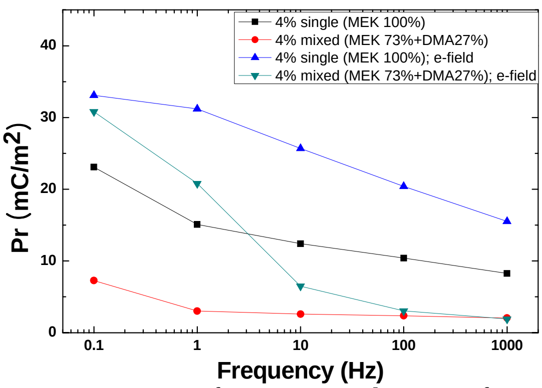

Fig.6. Variations of permanent polarization for frequency of bias voltage

Table 1. Comparison with piezoelectric material

Parameter	Unit	PZT	PVDF Stretched	P(VDF-TeFE) Unstretched
Density	10^3 kg/m^3	7.5	1.8	1.9
Elastic Modulus	10^9 N/m^2	110	3.0	1.2
Electromechanical Coupling Coefficient		0.51	0.2	0.21

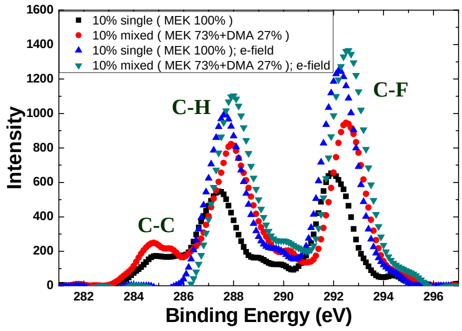

Fig.4-(a). XPS Spectra for 10% solution with and without electric field

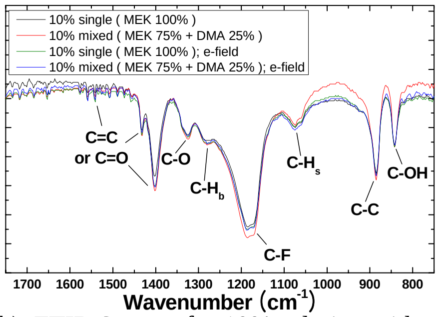

Fig.4-(b). FTIR Spectra for 10% solution with and without electric field

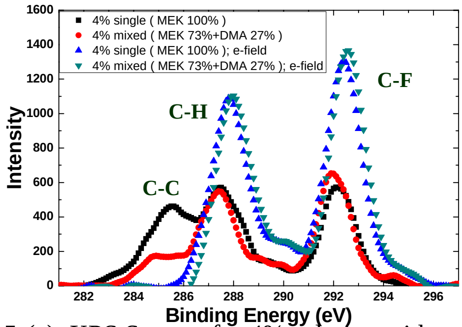

Fig.5-(a). XPS Spectra for 4% solution with and without electric field

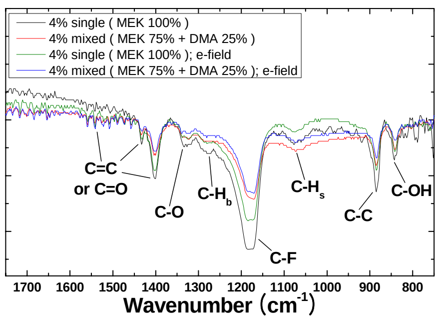

Fig.5-(b). FTIR Spectra for 4% solution with and without electric field