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The dry etching process for patterning P(VDF-TeFE) thin film with various conditions

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1. Introduction

We have used P(VDF-TeFE) thin film to fabricate membrane-type micro-generator in which electricity is generated by human voice vibration. Increasing the surface area of the film, the film was etched by dry etching processes as well as it will be easy to receive the vibration. In this study, dry etching conditions for P(VDF-TeFE) thin film are changed and its variation is observed.

Energy harvesting technology is an advanced concept by which so many energy sources in our life can be converted into usable electrical power. Among them, we have focused on human voice energy to extend for operating portable devices. It is known that the voice is composed of acoustic waves with low frequency. For practical use of human voice as an energy sources, a patterned-type piezoelectric polymer was fabricated in order to receive a minute aerial vibration by the voice as shown Fig.1 [1].

P(VDF-TeFE) means the mixture of (Poly-vinylidene fluoride and tetrafluoroethylene). Fig.2 shows the β-phase structure when the ratio of P(VDF-TeFE) is (80/20). This copolymer has a lower elastic modulus than PVDF only. Therefore, it is easy to fabricate a piezoelectric film with low resonant frequency.

In this study, we investigate the influence of the ratio of the solvent (0 to 100 %) on the film. As a new method, the film is etched to increase the surface area so that even a minute pressure of fluctuation of air by sound wave will able to receive and will convert into energy. Therefore, the film was etched by an inductive coupled plasma-reactive ion etching (ICP-RIE) equipment to increase the surface area of membrane.

2. Experimental procedure

The 3-types of solvents such as Methyl-ethyle-ketone (MEK), N,N-dimethylacetamide (DMA) and mixed solvent with MEK and DMA was used to cast P(VDF-TeFE) thin film. The film was formed by a spin-coating method on a surface of a Pt/Ta deposited silicon substrate. After spin-coating, the film was annealed at 195 °C to decrease the surface roughness [2].

A method of dry etching for this film was not reported earlier. The dry etching conditions are shown in Table.1. To investigate etching process, the temperature and RF bias power are used as parameter to find out the best condition of etching. CF_4 and O_2 gases are used for dry etching and the gas combination is changed.

3. Results and discussion

Fig.3 shows XPS spectra of the samples formed with mixed solutions in which the ratio varies from 0 to 100 %. Broad peaks of $-CF_2-\underline{C}F_2-CF_2-$ and $-CF_2-\underline{C}H_2-CF_2-$ bonds are observed for MEK 75 % and 50 % solutions. In cases of high DMA i.e. when MEK ratio is 25 % or 0 %, an adhesion of the film was very bad. As DMA has a higher solubility than MEK, the $-CF_2-\underline{C}F_2-CF_2-$ and $-CF_2-\underline{C}H_2-CF_2-$ bonds are increased in the case of a little mixing DMA with MEK solvent.

Fig.4 shows hysteresis loop of the measured polari -zation as a function of applied electrical field for MEK 75 % solvent. The remnant polarization of the film is 0.4 $\mu C/cm^2$. The remnant polarization becomes much higher in the case of annealed with electric field application [2].

Fig.5 shows the etching rate of P(VDF-TeFE) film for MEK 100 % and 75 % solvents ratio as a function of etching gas combinations. In a case of only CF_4 gas, etching of the film didn't almost progress. For both the mixture of solvents, the etching rate increases with the addition of O_2 but at $O_2 / (O_2+CF_4) = 0.6$ the etching rate was maximum. Above that point, the etching rate falls again sharply. Hence, it is understood that the etching of the film progresses mainly due to O_2 gas presence as well as at the ratio of 0.6 (etching gas combination of $O_2 / (O_2+CF_4)$), and the etching rate is good enough to fabricate the film. Fig.6 shows the SEM image of the etched film when MEK solvent and the etching gas combination were 75 % and 0.6, respectively. It is observed that the roughness of the etched surface mainly didn't change before and after a dry etching process.

Fig.7 shows the etching rate with changing the temperature and RF bias power conditions. It is found that the etching of the film didn't progress at low temperature and without RF power conditions. But with increasing temperature i.e. above 0 °C the etching rate increases. In addition, etching rate is observed more sharply when the RF bias power is increased from 0 to 100 W. Hence, it is understood that the O_2 radical reactions mainly progress the etching of the film.

4. Conclusion

In order to pattern P(VDF-TeFE) thin film precisely for a membrane-type micro-generator, we have curried out the dry etching process using ICP-RIE equipment. The etching of the film was affected by a ratio of O_2+CF_4 mixture gas. As a result, we understood the etching of the film is mainly progressed by the O_2 radical reactions. Moreover, it is thought that the etching rate at the gas ratio of 0.6 is good enough to fabricate the film.

Acknowledgements

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References

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[2] J.H. Jeong, C. Kimura, H. Aoki, M.Okuyama and T. Sugino, ECS Trans., 19, pp. 59 (2009)

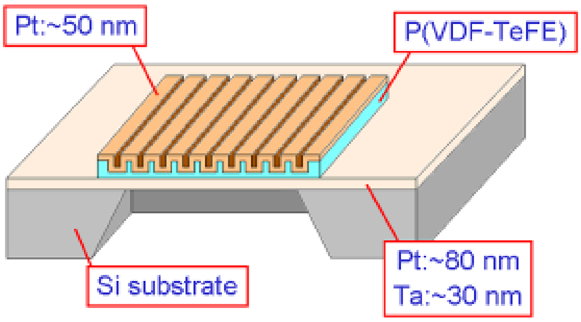

Fig.1 Schematic of micro-generator using patterned P(VDF-TeFE) thin film as a membrane

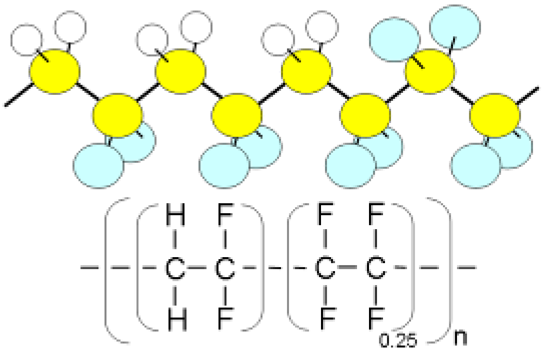

Fig.2 Molecular structure of P(VDF-TeFE)

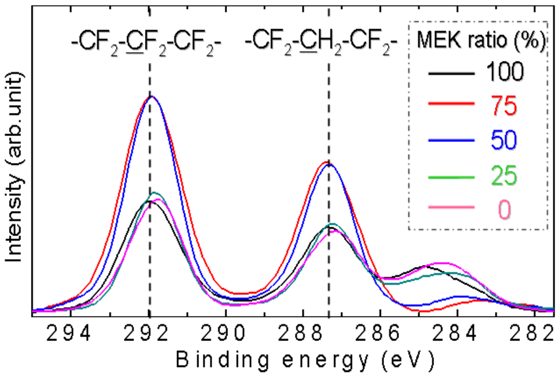

Fig.3 XPS spectra (C1s) of P(VDF-TeFE) film for MEK ratio

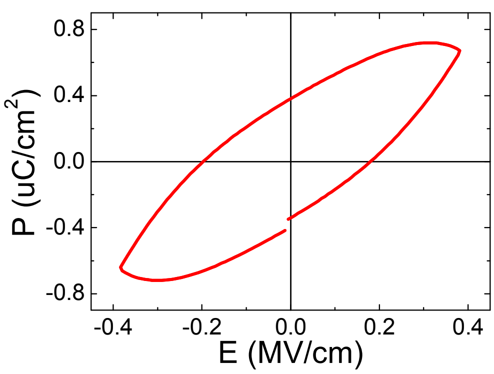

Fig.4 Polarization versus electric field hysteresis loop of P(VDF-TeFE) film with MEK 75% solvent

Table.1 Condition of the etching process

CF_4 flow rate	0~15 sccm
O_2 flow rate	0~15 sccm
ICP power	400 W
RF bias	0, 100 W
Pressure	6 Pa
Temperature	RT, 0 ,-25 ˚C

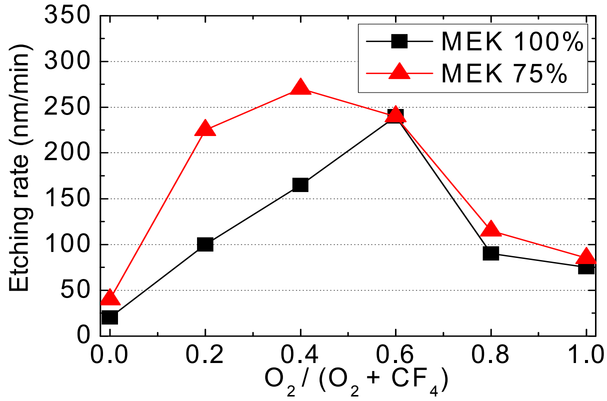

Fig.5 Etching rate for changing the gas combinations

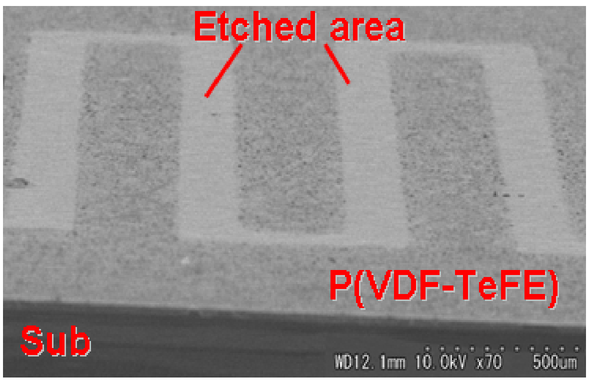

Fig.6 SEM image of the film which was etched with gas combination O_2 / (O_2+ CF_4) = 0.6

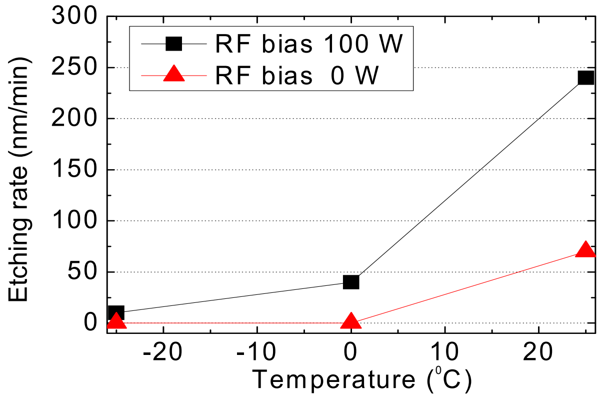

Fig.7 Etching rate of P(VDF-TeFE) film for changing temperature and RF bias power conditions