Study on the surface characteristics of parylene-C films in inductively coupled O_2/CF_4 gas plasma

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Abstract

In this article, we reported the results of etching poly-monochloro-para-xylylene (parylene-C) thin films using inductively coupled plasma and CF_4/O_2 gas mixture. The CF_4 gas fraction increased up to the approximately 16 %, the polymer etch rate increased in the range of 277 – 373 nm/min. It confirmed that the etch rate of the parylene-C mainly depended on the O radical density in the plasma. Using a contact angle measurement, the contact angle increased with increasing the CF_4 fraction. Moreover, the contact angle was highly related a CF_x functional group on parylene films.

1. Introduction

Organic Thin Film Transistors (OTFTs) have been investigated for possible use in low-cost, large area, flexible electronic applications during many years.[1] Simultaneously, OTFT devices have been required to be scaled down.

Parylene-C (poly-monochloro-para-xylylene) is more suitable organic material for gate dielectric in OTFTs. A patterning process for the organic film is required in order to apply it to OTFTs. Specifically, the patterning of organic semiconductors is necessary for eliminating parasitic leakage, reducing cross talk in order to achieve high on/off ratios, and removing material from the optical path.[2] Patterning process of organic films has been widely carried out by O_2 plasma. However, it is well known that an oxygen plasma can cause damage the semiconductor and dielectric layer due to the interaction between the oxygen radials and polymer resulting in the formation of several functional groups on the polymer surface.[3] These functional groups can rotate into the bulk of the material and move away from the polymer surface.[4] As a result, functional groups lead to degradation of transistor performance. Hence, preventing the functional groups is essential to improve the OTFTs' performance. Research in this field has been so far studied by many researching groups. However, various gas chemistries have not been widely examined to reduce the formation of the functional groups, even though the reaction of the polymer with the plasma-created species makes a large effect on the formation of the functional groups.

In this work, in order to obtain more information about the effect of CF_4 gas addition to oxygen plasma, we investigated the plasma treated surface of parylene-C films and the plasma characteristics in inductively coupled O_2/CF_4 mixing gas plasma.

2. Experimental

The 300-nm thick parylene-C films were deposited on Si (100) substrates by chemical vapor deposition. The wafers were then plasma-treated with a radio-frequency (RF) etching system.

Etching experiments were performed in a planar Inductively Coupled Plasma (ICP) reactor, which was described detail in our previous work. [5] A Quadrupole Mass Spectrometry (QMS) (HPR-30, Hiden Analytical) was performed in Residual Gas Analysis (RGA) mode, delivering data on the neutral species only. The etching conditions were: a total gas flow rate of 60 sccm; an operating pressure of 4 mTorr; an input ICP power of 300 W and; a bias power of 30 W. The gas mixing ratios were varied by adjusting the partial flow rate of the mixture components and were set in the range of 0 – 50 % CF_4 in the CF_4/O_2 mixture. The parylene-C film samples used in this study were 2 × 2

cm^2 in area. In order to determine the etch rate, the etched depths of the parylene-C film were measured using a surface profiler (Alpha-step 500, Tencor). X-ray Photoelectron Spectra (XPS) were extracted using a VG Scientific ESCALAB 200R XPS system with Al (Kα) (1486.6 eV) radiation operating at 260 W. The binding energy was calibrated using C 1s peak at 284.5 eV. Static contact angles for water and diiodomethane were measured using a sessile drop method with a contact angle goniometer (SEO Phoenix 300) at room temperature.

3. Results and discussion

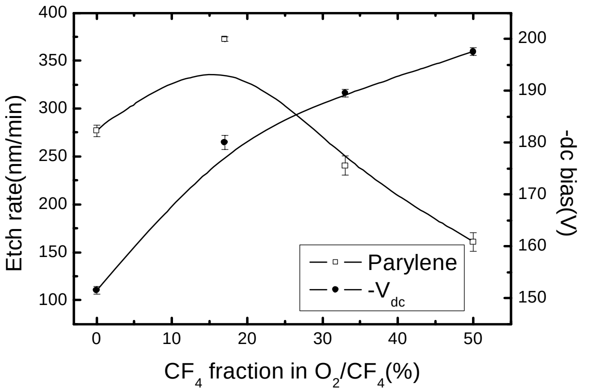


Fig. 1 Parylene-C etch rate and negative dc bias as functions of the CF_4 gas fraction in the CF_4/O_2 plasma

Figure 1 shows the parylene-C etch rate and negative dc bias as a function of the CF_4 gas fraction in the CF_4/O_2 plasma. From Fig. 1, it can be seen that, as the CF_4 gas fraction increases up to the approximately 16 %, the polymer etch rate increases from 277 to 373 nm/min.

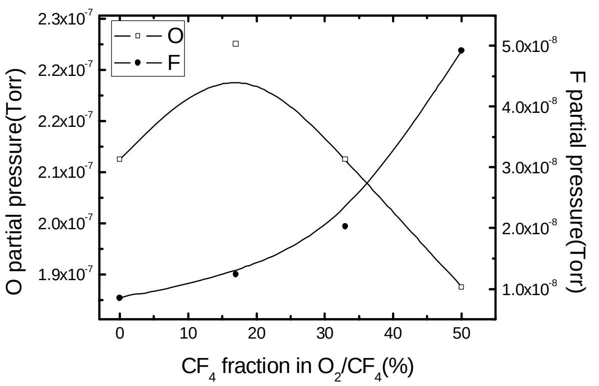


Fig. 2 O and F partial pressures as a function of the CF_4 gas fraction

As the CF_4 fraction of over 16%, the etch rate of the parylene-C rapidly decreases. However, the negative dc bias increases monotonically up to 50% of CF_4 fraction and was -197 V in 50 % CF_4 mixture.

Figure 2 shows the variation of partial pressure for each neutral species of O and F in the CF_4/O_2 plasmas which were obtained by the QMS. From Fig. 2, we can observe that the change of O radical density shows a very similar trend as that of polymer etch rates in the CF_4/O_2 plasma. Accordingly, the polymer etch rate is closely dependent on the O radical density in the CF_4/O_2 plasma.

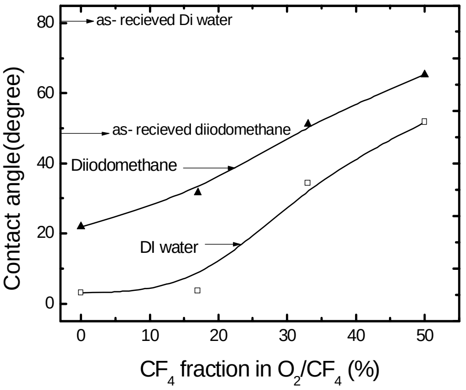
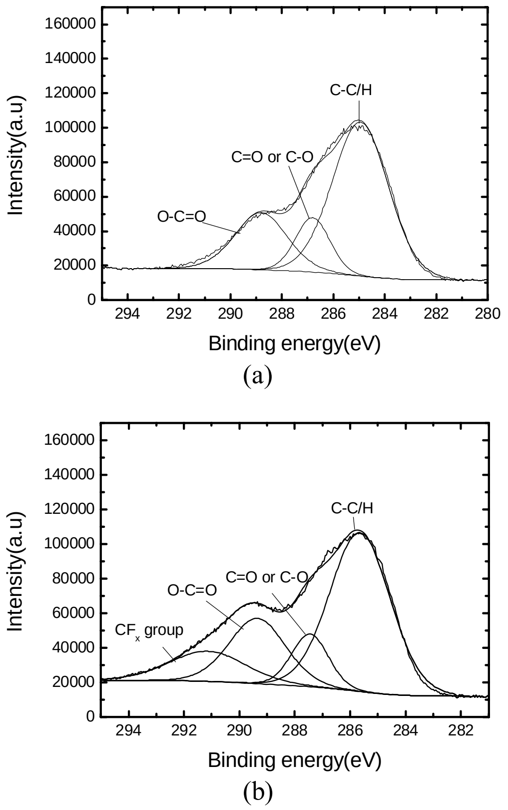


Fig. 3 Contact angles as a function of the CF_4 gas fraction

Figure 3 shows the contact angle and the surface energy with increasing CF_4 fraction. In Fig. 3, we can confirm that the contact angle increases with CF_4 fraction. For D.I. water, the contact angle increases from 3.1 to 51.8° with CF_4 fraction in the range of 0 to 50%, respectively. At the same time, for diiodomethane solution, the contact angle increases from 21.9 to 65.3 °, respectively.

Figure 4 represents the deconvolution of C 1s spectrum. As shown in Fig. 4(a), we can observe that the carbon peak is composed of three different carbon species in pure O_2 plasma treatment. Each peak basically corresponds to C-C/H, C=O (or C-O), and O-C=O bonds which are observed at 284.5, 286.3, and 288.2 eV, respectively. [6] At the O_2/CF_4 plasma, new peak was observed at the binding energy of approximately 291 eV in Fig. 4(b). In generally, the fluorine atom was formed to CF_x group on organic materials. So, peak of 291 eV is surely related to CF_4 gas addition to the O_2 plasma which corresponds to CF_x group.



(a)

(b)

Fig. 4 Deconvolution of a C 1s spectrum at (a) pure-O_2 and (b) 50% CF_4 fraction

It is also known that the contact angle for CF_x groups is higher than that of the functional groups such as O-C=O and C=O (or C-O) bonds. Therefore, we can found that the formation of CF_x functional group is surely influenced to the contact angle in Fig. 3.

4. Summary

In this article, the results were obtained from the etch of poly-monochloro-para-xylylene (parylene-C) thin film, which was carried out in ICP etch system using CF_4/O_2 gas mixture. The effects of CF_4 addition to O_2 plasma on etch rates were investigated. The CF_4 gas fraction increased up to the approximately 16 %, the polymer etch rate increased in the range of 277 – 373 nm/sec. In contrast, the etch rate rapidly decreased with increasing the CF_4 fraction over 16 %. Based on the QMS data, it was confirmed that the etch rate of the parylene-C mainly depended on the O radical density in CF_4/O_2 plasma.

By a contact angle measurement, the contact angle increased with increasing the CF_4 fraction. It is related to the generation of a CF_x functional group on parylene film after CF_4 addition in CF_4/O_2 plasma.

Acknowledgement

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5. References

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