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Surface characteristics of etched parylene-C films for low-damaged patterning process using inductively-coupled O_2/CHF_3 gas plasma

Yong-Hyun Ham [a], Dmitriy Alexandrovich Shutov [b], Kwang-Ho Kwon [a,*]

[a] Department of Control and Instrumentation Engineering, Korea University, Chungnam 339-700, Republic of Korea
[b] Department of Electronic Devices and Materials Technology, Ivanovo State University of Chemistry and Technology, 153000 Ivanovo, Russia

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ABSTRACT

We investigated the effectiveness of CHF_3 admixture in O_2 plasma for a low damage patterning process. We used inductively-coupled plasma (ICP) etching of parylene-C thin films with O_2/CHF_3 gas mixtures. Plasma diagnostics were performed by using a double Langmuir probe. Also in order to examine the relationship between the plasma and surface energy, we attempted to conduct a simplified model-based analysis of the CHF_3/O_2 plasma.

The surface energy decreased as the admixture fraction increased with fluorocarbon containing gas. The decreased surface energy is related to the functional groups of CF_x polymer at binding energy of around 290 eV and low ion physical damage. We observed that a small addition of CHF_3 to O_2 plasma produced a high etch rate, low surface energy, and low roughness compared to pure oxygen plasma.

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1. Introduction

Organic thin film transistors (OTFTs) have been studied extensively and are expected to play a key role in flexible display with organic electronics [1,2]. Poly(monochloro-para-xylylene) (parylene-C) is widely used as a gate dielectric in OTFTs because of its low leakage current and low energetic disorder at the semiconductor–insulator interface, due to its low polarity [3,4].

In the fabrication of OTFTs, a patterning process for organic semiconductor and gate dielectric material is necessary to eliminate parasitic leakage, reduce cross talk to achieve high on/off ratios, and remove the material from the optical path [5].

In general, O_2 plasma has been widely used for the patterning process of organic materials [6]. However, oxygen plasma can cause damage to the dielectric during the patterning process [6,7], and this damage leads to degradation of transistor performance. The interaction between the oxygen plasma and polymer results in the formation of several polar groups on the polymer surface [8]. These polar groups can rotate to the bulk of the material and subsequently move away from the polymer surface. The increase in insulator polarity leads to an increased leakage current. Accordingly, the suppression of the formation of polar functional groups during the plasma etching process is an urgent problem.

To prevent the formation of oxygen-related polar functional groups during O_2 plasma patterning, etching processes using new gas mixtures should be considered for the pattering of organic materials. However, studies on the effects of additive CHF_3 gas on etched polymer film are not available in the literature.

Accordingly, we investigated effectiveness of adding CHF_3 to O_2 plasma for use in low damage pattering processes. In addition, the plasma characteristics, etched surface characteristics were examined and model-based analysis of the plasma was conducted. Finally, the correlation between the plasma characteristics and the surface properties of the etched substrate is described in detail.

2. Experiment and modeling details

2.1. Sample preparation and plasma etching

300 nm-thick parylene-C films were deposited on Si (1 0 0) substrates by chemical vapor deposition. Etching experiments were performed in a planar inductively-coupled plasma (ICP) reactor, as described in our previous work [9]. The plasma was excited in the cylindrical quartz chamber using the five-turn copper coil connected to the 13.56 MHz power supply. The coil was located on the top side of the chamber and was separated from the plasma region by a 10 mm thick horizontal quartz window. The bottom electrode was also connected to another 13.56 MHz power supply to control the negative dc bias voltage. During the etching process, the temperature of the substrate holder was held at 18 ± 2 °C by the circulation of de-ionized water.

The etching conditions were as follows: a total gas flow rate of 60 sccm, an operating pressure of 4 mTorr, an input ICP power

* Corresponding author. Tel.: +82 41 860 1447; fax: +82 41 865 1820.
E-mail address: kwonkh@korea.ac.kr (K.-H. Kwon).

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of 300 W, and a bias power of 30 W. High quality gases consisting of ultra-pure O_2 (99.999%) and CHF_3 (99.999%) were used in this process. The gas mixing ratio was varied by adjusting the partial flow rate of the mixture components, and was set in the range of 0–50% CHF_3 in the O_2/CHF_3 mixture.

Plasma diagnostics has been enabled with double probes (DLP2000, Plasmart Inc.), which were installed through the chamber wall-side view port. The probes were placed at 4 cm above the bottom electrode and centered in the radial direction. Similarly with our previous work [9], the electron temperature (T_e) and the total positive ion density (n^+) were derived from the original I–V traces using the software supplied by the equipment manufacturer.

2.2. Analysis of surface characteristics

To determine the etch rate, the etched depths of the parylene-C film were measured using a surface profiler (Alpha-Step 500, KLA-Tencor). The nano-scale surface profile was examined using an atomic force microscope (XE-150, PSIA). The roughness of the films was obtained using images with a scan size of 10 μm × 10 μm.

The 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 narrow scan spectra of all regions of interest were recorded with a pass energy of 20 eV to quantify the surface composition and identify the chemical binding states. The binding energy was calibrated using the C 1s peak at 284.5 eV [10].The static contact angles for deionized (DI) water and diiodomethane were measured using the sessile drop method with an SEO Phoenix 300 contact angle goniometer at room temperature. The measurements were carried out immediately after the plasma treatment (they typically took about 5 min). The surface energy was derived from the contact angle using software supplied by the equipment manufacturer. The Fowkes's theory was used to calculate the surface free energy [11,12].

2.3. Model description

To obtain data on the densities and fluxes of plasma active species, we used a simplified global (0-dimensional) model with a Maxwellian electron energy distribution function (EEDF) and with a quasi-stationary approximation for the volume kinetics [13]. The applicability of the Maxwellian approximation for EEDFs in CHF_3/O_2 inductive discharges at low pressures was demonstrated by Klopovsky et al. [14] by an outstanding agreement between plasma diagnostics data and modeling results.

The modeling algorithm was based on the simultaneous solution of the balance equations for neutral and charged species in a steady-state approximation and the quasi-neutrality conditions for the volume densities of charged particles The list of processes taken into account by the model was composed using [13,15–23] and is shown in Table 1. The reaction set for the charged balance equation are shown in the Table 2. In more detail the model described by Kim et al. [24].

As the input parameters for modeling, we used the experimental data on electron temperature (T_e) and total positive ion density (n^+) extracted from the Langmuir probe measurements.

3. Results and discussion

Fig. 1 shows the changes in plasma characteristics as function of the CHF_3 fraction in O_2. This figure shows that while the positive ion densities decrease with increasing the CHF_3 fraction, the electron temperatures increase. At the same time, this figure indicates that the decrease in the ion density has an influence on the decrease in the etch rate with increasing the CHF_3 fraction (Fig. 2).

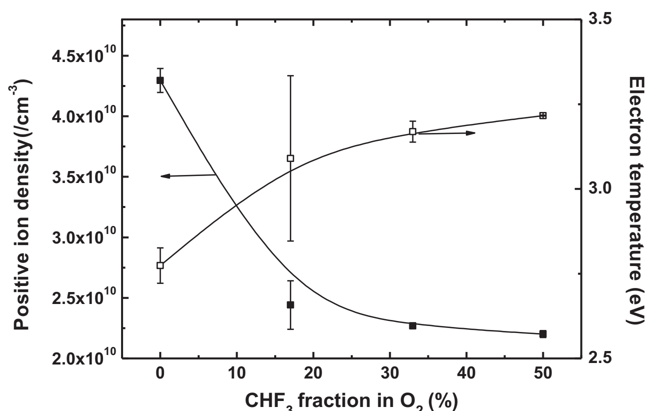

Fig. 1. Measured electron temperature and positive ion density as functions of the CHF_3 fraction in O_2.

Fig. 2 shows the parylene-C etch rate as a function of the CHF_3 fraction in O_2. We note that as the CHF_3 fraction increases to 17%, the parylene-C etch rate increases in the range of 277–318 nm/min, while the etch rate rapidly decreases as the CHF_3 fraction increases above 17%. This result is in agreement with a previous report [25,26]. Liao et al. indicated that the maximum etch rates of photoresist and benzocyclobutene were achieved at a CF_4 fraction of 30% [25]. Same result was shown by Ham et al., [26] for the parylene-C films in the CF_4/O_2 mixtures.

At first, it can be explained that for a high concentration of the fluorocarbon gas, fluorocarbon film might be formed on the polymer surface by direct deposition from the plasma, and that this fluorocarbon layer would function as a diffusion barrier for the reactive species, thereby causing the etch rate of the polymer to decrease as the fluorinated gas concentration increased beyond a critical value. At second, the decrease of the main oxidative plasma-polymer etching agent, oxygen atoms flux on the surface as the result of the oxygen dilution may lead to the decrease of the etch rate. Really, modeling shows (Fig. 3) the increase of the fluorocarbon-containing radicals and decrease of the $O(^3P)$ atoms with the increase of the CHF_3 concentration in the CHF_3/O_2 mixtures.

Fig. 4 shows the variation in contact angle (the diiodomethane data are not shown) and surface energy as functions of the CHF_3 fraction in O_2. For DI water, the contact angle increased with increasing CHF_3 fraction. The surface energy was calculated on the basis of DI water and diiodomethane contact angles. We found that

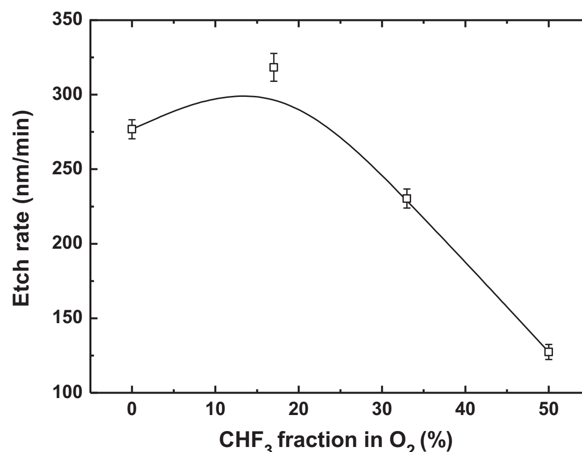

Fig. 2. Etch rate of Parylene-C as a function of the CHF_3 fraction in O_2.

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