Etching Efficiency of Polymethacrylates for Monochromatic Low Energy Ion Beams

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1. Introduction
Polymethacrylates with aliphatic side chains has been focused on as the candidates of organic photo-resist materials in the photo-lithography processes using ArF excimer lasers or the other light sources in the shorter wavelength region. Dry etching resistance of the organic resist materials is one of the most important key features in the lithography processes, and the molecular design of the organic resists have been extensively studied in view of the materialization of polymers bearing the higher dry etching resistance for RIE processes. Recently organic polymer materials have also been the leading candidates of low-k dielectrics in the semiconductor fabrication processes. However the objectives of the use of organic layer are standing on the completely different basis in the two applications: dry etching resistance/plasma ashing and plasma processing/utilization as insulating layers. For future molecular design of polymers in micro- and nano-electronic processes, it is necessary to understand sufficiently dry etching mechanisms of organic polymers with well-defined structures as the model of not only resists but also low-k dielectric materials.

2. Method
Polymethacrylates: (CH₂C(CH₃)COOR)ₙ were synthesized by radical polymerization using AIBN as the radical initiator from corresponding distilled monomers purchased from Wako Chemical Co. LTD. or Aldrich Chemical Inc. The substituents (R) were methyl (PMMA), t-butyl (PBUrMA), benzyl (PBMA), cyclohexyl (PCHMA), tricyclodecany (PCDMA), isopropyl (PIPMA), n-propyl (PnPMA), n-buthyl (PnBuMA), n-dodecyl (PLMA), phenyl (PPMA), and octadecyl (PODMA), respectively. After the characterizations of molecular weight, density, Tg, and FT-IR spectroscopy, the polymers were spin coated on Si wafers at 200-400 nm thick, followed by pre-baking at 120 °C for 2 min. Low energy ion beam irradiation was performed by an Elionix EIS-200ER ECR ion source with the terminal voltage of 50-300 V, and the thickness of the film was measured by ULVAC Dektak 3st surface profiler and/or JEOL JSM-6335F scanning

![Graph showing relative etching rate as a function of terminal voltage](image)

Figure 1. Relative etching rate of a variety of polymethacrylate as a function of the empirical parameter derived from equation 1. The terminal voltage was changed from 50 to 300 V.

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electron microscope. The etching rate of the polymer films was also determined by SAMCO RIE-10 plasma etching system.

3. Results

Etching rate of organic layers had been investigated for a variety of plasma sources and organic materials to predict dry etching resistance. Several studies had reported some effective empirical relationship between the chemical structures of the organic materials and their etching rate ($E_R$) for plasma sources.\textsuperscript{1,3} The well-known relationships are;

\begin{equation}
E_R \propto \frac{N_T}{(N_C - N_O)}
\end{equation}

\begin{equation}
E_R \propto \frac{M_{CR}}{M_{TOT}}
\end{equation}

\begin{equation}
E_R \propto K_S N_T \left( \frac{N_C - N_O}{N_C} \right)
\end{equation}

where $N_{C}, N_{O}$, and $N_T$ are the number of consisting atoms,\textsuperscript{1,3} $M_{TOT}$ and $M_{CR}$ are the mass of the monomer unit and carbon atoms in the ring structures,\textsuperscript{2} and $K_S$ is an empirical constant depending on the ring structures.\textsuperscript{3,5} Based on these empirical relationship, we discussed the relative etching rate of the polymers used in the present study.

Figure 1 shows the relative etching rate of the polymers for $N_2$ ion beams as a function of the parameter determined by equation (1). The values of $E_R$ observed at the terminal voltage of 300 V are clearly proportional to the empirical parameter. This is consistent with the previous reports on the etching processes using high energy (> 300 eV)O$_2$, Ar, or the other halogenated gases based plasma ion beams, suggesting that the simple atomic sputtering model gives a good interpretation to the etching mechanism of the higher energy $N_2$ ion irradiation than 300 eV. However the clear relationship shows a considerable deformation with a decrease in the energy of incident ion beams, and the empirical parameter is no longer effective to represent the value of $E_R$ observed by using the lower energy ion beams than 100 eV. The other empirical parameters, determined by equations (2) or (3), also indicate inadequate fittings for the observed $E_R$. Thus the threshold energy of the validity of the sputtering model is concluded to be ~300 eV for $N_2$ based ion beams. The large differences in the $E_R$ of isomeric polymers: PnPMA and PrBuMA, etc., at the lower energy of incident ion beams than 100 eV also suggests that the etching mechanism strongly depends not only on the chemical reaction between the polymers and the incident ions, but also the polymer backbone configurations. The higher etching rate was observed for PIPMA than that for PPMA which was the isomer of PIPMA. The density of these polymers is consistent with each other, and the value of $T_m$ is higher in case of polymethacrylate with the branching side chains ($T_m = 392$ K for PrBuMA, 298 K for PrBuMA, 304 K for PrPMA, and 356 K for PIPMA). In spite of the higher thermal stability of the polymethacrylate with branching side chains, the etching rates of the polymers were higher apparently in comparison with those of the straight chain isomers.

The plausible mechanism of the radiation induced degradation of polymethacrylate is as follows,

1) Side chain ester group dissociation
2) Disproportionation reaction giving a chain end radical and a double bond.

The relative yields of the ester removal reaction (G(est)) and the total main chain dissociation reaction (G(s)) were determined for PrBuMA and PrBuMA, suggesting almost consistent yield of G(s) (G(s)$_{PrBuMA}$/G(s)$_{PnPMA}$ = 1.3) and large difference in the yield of G(est) (G(est)$_{PrBuMA}$/G(est)$_{PnPMA}$ = 3.7), respectively.\textsuperscript{4,5} Thus the higher yield of G(est) contributes predominantly in the large value of the etching efficiency in case of polymethacrylate with branching side chains. This was also confirmed by the relatively larger decrease of the IR peaks attributed to carbonyl groups after the ion beam irradiation to PrBuMA and PIPMA. However the ratio of the yields: G(s)/G(est) > 1 for all the polymers indicates that the predominant reaction in the polymethacrylate is always main chain dissociation reactions, and the similar values of G(s) in PnPMA and PrBuMA are inconsistent with the far higher value of $E_R$ in PrBuMA. Molecular configuration of the polymers has shown a dramatic increase in molecular stiffness by the substitution from $n$-butyl to t-butoyl groups.\textsuperscript{6} This may be the case giving rise in the value of $E_R$. Radiation induced chemical reactions and the molecular configuration will be important to optimize the reactive ion etching yield, particularly for ion beams containing the lower energy ions than 100 eV.

References