Plasma etch rate measurements of thin PMMA films and correlation with the glass transition temperature

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Abstract. Plasma etch rate (ER) measurements (via in situ spectroscopic ellipsometry) of thin PMMA (poly methyl-methacrylate) films, in an Inductively Coupled Plasma (ICP) reactor are presented. It is shown that plasma ER decreases as the initial polymeric thickness decreases, indicating an increased plasma etch resistance of thin PMMA films. An ER-T_g (glass transition temperature) correlation, reveals a clear inverse relation, namely that the ER decreases when the T_g increases.

1. Introduction
Thin and ultra-thin polymeric films have attracted much scientific attention due to the increased demand in micro- and nano-technology. Until now it has been clearly demonstrated that thin film properties are in general different from those of the bulk material: Keddie et al [1] showed that for polystyrene (PS) and PMMA films on silicon there was a substantial change in T_g for thicknesses lower than 100nm, while the importance of process conditions has been illustrated by Raptis et al [2]. Lin et al and Frank et al [3],[4] showed that diffusion and other transport properties of polymers are also strongly affected by the film thickness. Van der Lee et al [5] have shown that the density of thin PMMA films is increasing in the vicinity of the SiO_x/PMMA interface.

These changes in the physicochemical properties greatly affect many industrial processes, such as lithography. For example baking cycles in lithography may be affected due to T_g changes [2]. Burns et al [6] have already shown that the dissolution rate of ultra-thin phenolic films decreased significantly from the bulk rate, which is consistent with the decrease of diffusion coefficient in other polymeric systems, i.e. PMMA and PS [3],[4].

Here, we explore the so-called thin film effects on the plasma etching of PMMA, by measuring the plasma ER, as a function of polymer film thickness.

2. Experimental procedure
2.1 Sample preparation
PMMA films of two different number average molecular weight (M_n=120k and M_n=15k) were prepared by spin coating on bare silicon wafers, and then baked (annealing) at 160°C for 30min. They were left to cool down to room temperature.
2.2 Glass transition temperature measurements

The measurement is based on the discontinuous transition of optical parameters and thermal expansion coefficient of the polymeric film at T_g [1]. T_g is determined where the curve of the ellipsometric angles Ψ and Δ vs. the temperature of the film changes its slope. A J.A. Woollam spectroscopic ellipsometer was utilized, equipped with a programmable-PID hot-plate. The incident angle was set to 75°. Ψ and Δ, were recorded during the heating of the sample; heating rate is 20°C/min. The precision of the measured T_g is better than ±5°C.

2.3 Plasma etch rate measurements

Etch resistance studies were performed in an inductively coupled (ICP) etcher (MET) from Alcatel. In all cases, the process conditions were kept identical: source power 600W, bias voltage -100V, O_2 pressure 1.33Torr, O_2 flow 100sccm, and constant electrode temperature 15°C. The substrate temperature was controlled with He-backside cooling.

The thickness of the sample during etching was monitored via in situ spectroscopic ellipsometry. A two-layer model, consisting of Si substrate and a Cauchy layer (Si/Cauchy layer), was used for the analysis of the ellipsometric data. Then the dispersion parameters and the thickness of the Cauchy dispersion model were fitted to match the experimental data. The ER value was calculated by linear fitting to the thickness-process time raw data; such data for PMMA (M_n=15k) are shown in figure 1. In all cases the value of R^2 was higher than 0.98, indicating a reliable fitting of the linear model. The ER measurements were reproducible and no difference over 5nm/min was recorded. A straightforward manipulation of the data shown in figure 1 reveals that the smaller the initial thickness of the film, the smaller the etching rate, i.e., the ratio of the thickness variation over the etching time.

![Figure 1. Thickness variation of PMMA (M_n=15k) films during plasma treatment (raw data). The slope of each curve (i.e ER) remains constant throughout the process. Although the slopes seem to be (visually) identical for every initial thickness, the linear fitting procedure reveals a variation (see figure 2).](image)

3. Results and discussion

In figure 2 we present the plasma ER measurements of PMMA (M_n=120k) and PMMA (M_n=15k) vs. their initial thickness. There is a clear dependence of plasma ER on the initial polymer thickness for both M_n PMMA films. The plasma ER is decreasing as the initial polymer thickness is decreasing, indicating an increased etch resistance of the thinner polymeric films, which corresponds to a relative difference between the ER for films of ~600nm and ~50nm of about 20%.

Moreover figure 2 shows that the ER of PMMA (M_n=120k) is lower than the ER of PMMA (M_n=15k) throughout the studied range of initial polymer thickness.
Figure 2. Plasma ER variation vs. initial thickness of PMMA (M_n=120k) and PMMA (M_n=15k). (Lines on the graph are only to guide the eye). Notice that ER is decreased by 20% as thickness is reduced from 500nm to 50nm.

Figure 3. T_g of PMMA (M_n=120k) and PMMA (M_n=15k) vs. film thickness. (Lines on the graph are only to guide the eye)

The first approach to explain differences in ER of different polymeric systems is via the use of the structural identity of the macromolecule of each system. The carbon-atom-density (Ohnishi) parameter and the Ring parameter are widely used to provide a basic prediction of the ER based on structural characteristic of the macromolecules [7],[8]. In our case Ohnishi and Ring parameter remain the same for the films of different initial thicknesses, since the chemical compositions of the film are identical.

Thus, the measured differences must be attributed to changes in physicochemical properties that affect ER, such as density, diffusion coefficients, void fraction etc. At the interfaces these properties are different from the bulk material [3]-[5]. Even though these parameters are known to affect the etch kinetics and their effects have been modeled [9]-[10], the relevant experimental measurement cannot be readily performed.

In order to explain our results we employ a correlation of the plasma ER to the T_g of the film, in each initial polymer thickness. This correlation demonstrates some unique advantages; (a) T_g can be readily measured even with non-destructive testing methods (e.g. spectroscopic ellipsometry), and (b) T_g, although it is not a pure thermodynamic property, it contains thermo-physical information that is related to the plasma etch kinetics (e.g. diffusional motion, void fraction etc).

Figure 3 shows the measured T_g values of the film vs. polymer thickness for both PMMA (M_n=120k) and PMMA (M_n=15k). The T_g of the thick films are consistent with the Fox-Flory equation that predicts the dependence of T_g on the M_n [11]. With regard to the thinner films, T_g increases as the polymer thickness decreases for thicknesses lower than ~200nm. In this thin-film region, the differences in the T_g between PMMA (M_n=120k) and PMMA (M_n=15k) – if any – become weaker, as it has been already shown by Keddie et al [1].

By correlating data on figure 2 and on figure 3 a clear, inverse relation is revealed in that ER decreases where T_g increases for both M_n PMMA. This correlation is also present for the thick films, where PMMA (M_n=120k) has higher T_g and lower plasma ER compared to the PMMA (M_n=15k).

4. Conclusions
We presented plasma etch rate measurements of thin PMMA films, and shown a clear dependence of ER on the initial polymer thickness: ER decreases as the initial polymer thickness decreases, in both PMMA (M_n=120k) and PMMA (M_n=15k).

In order to explain these results we correlated the ER profile to the T_g profile vs. polymer thickness. Differences in T_g indicate differences in structural and physical properties (conformation,
orientation, density etc) that are reflected as different behavior during plasma treatment and subsequently as different ER.

The above results are not unique to PMMA, as we have demonstrated similar behavior for other polymers and commercial photoresists [12].

![Diagram showing different film effects on plasma ER]

Figure 4 illustrates schematically this proposed thin-film effects on plasma ER.

These findings, i.e. increased etch resistance of thin films, slightly alleviate the demands for etch resistance of ultra thin photoresist films of the next generation lithography (NGL).

Finally, these results suggest that ER of thin films should be referred to specific film thickness.

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