

Plasma etching of thin and ultra-thin polymeric films probed with in situ spectroscopic ellipsometry

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In situ plasma ER measurements of different polymers probed with spectroscopic ellipsometry (SE), in high density Oxygen plasma discharge are presented. It is demonstrated that ER is not a constant value throughout the process but it is a function of thickness or process time. Initially ER exhibits a variation which can attain 20% increase. For remaining film thickness less than ~100 nm ER decreases gradually and finally ER reduces until the complete etch of the polymer. This final region correlates with surface roughness developed until then and strongly depends on the process time. Based on these measurements ER depends on initial thickness for films with initial thickness thinner than 150 nm.

Introduction

In most cases of plasma processing of polymers, plasma etch rate (ER) is treated as being a constant value throughout the plasma process. However some studies have demonstrated that ER is actually a function of film thickness [1,2], process time [3,4] or both. Similar observations have been recorded for the dissolution (development) rate (DR) of polymers, revealing a DR variation vs. film thickness.

In this work we present plasma ER measurements via in situ spectroscopic ellipsometry (SE) of atactic (a-), isotactic (iso-) and syndiotactic (syndio-) poly(methyl methacrylate)-(PMMA) and poly(styrene)-(PS) films on Si and SiO₂ under high density O₂ plasma discharges, and observe variations of ER vs. time and thickness. Based on these findings along with data obtained from the literature we try to identify the reasons for these variations and deduce the key mechanisms controlling the plasma etching performance of thin and ultra thin polymeric films.

Experimental

For the plasma processing we used a Helicon (RF source at 13.56 MHz) reactor by Alcatel (MET system). Process gases, namely O₂ (99.95% pure) from AirLiquide-Hellas. Unless otherwise stated the etching step was conducted under 600 W, 1.33 Pa, 100 sccm O₂, -100 V, 15 °C, 9 V coil voltage. The substrate temperature was controlled with He-backside cooling.

All polymers were used as received with no further purification. Films were prepared by spin coating. Film thickness was controlled by changing the polymer solution and the speed of spin-coating. Films were baked above T_g for 30 min (annealing) to remove the solvent from the polymeric film; this, of course, does not completely preclude the presence of entrapped solvent within the polymeric layer. They were left to cool down to room temperature.

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 (Psi and Delta).

Results and discussion

Fig.1 illustrates a typical example of ER variation vs. remaining film thickness for the case of PMMA (M_n=120k) films on Si. Films with various initial thicknesses were studied.

Three kinds of ER variations are recorded: (a) ER increase (~8%) within the first stages of etching (~first 10 sec), followed by a gradual increase of ~20% until ~120 nm remaining film, (b) ~25% ER decrease after ~120 nm remaining film, and finally (c) ER drastic decrease at the final stages of etching (completion of etching) until ER=0.

Variations (a) and (b) occur regardless the initial thickness, while the variation (c) strongly depends on process time. Its starting point is a function of initial thickness or process time as indicated in Fig. 1. Actually it

correlates with the surface roughness amplitude, and indicates means to control surface roughness of polymers, in that maximum surface roughness is attained in exactly this point. Roughness evolution modeling is employed to interpret this behavior; in this region the remaining roughness is the only material left, and the underlying Si wafer is un-etchable.

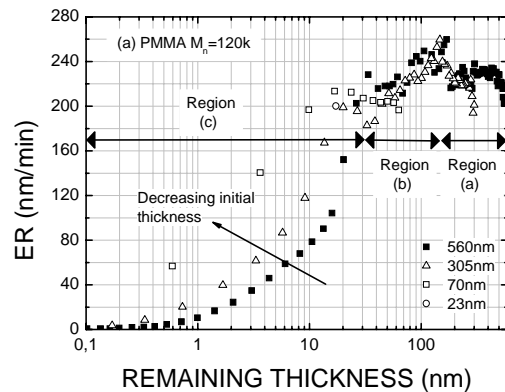


Fig. 1 ER vs remaining film thickness of PMMA ($M_n=120k$) films on Si.

For ultra thin polymer films (less than ~ 100 nm) ER increase (region a) is not recorded; we attribute this to thin-film effects, namely the change of material properties due to interfacial phenomena, which may be followed by glass transition temperature measurements (T_g^{film}).

Based on these measurements average ER depends on initial thickness for films with initial thickness thinner than ~ 150 nm (see Fig. 2).

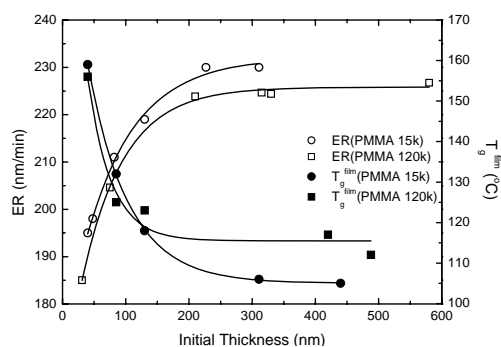


Fig. 2 Average ER of PMMA ($M_n=15k$ and $M_n=120k$) films on Si, vs. initial film thickness. T_g^{film} values are also plotted.

This ER variation does not depend on the model used to analyze the ellipsometric data. In Fig. 3 data of thickness and ER against process time are depicted when a surface roughness layer (srough) is implemented, along with the Cauchy layer, in the ellipsometry analysis. No significant

differences are recorded in ER and in average ER.

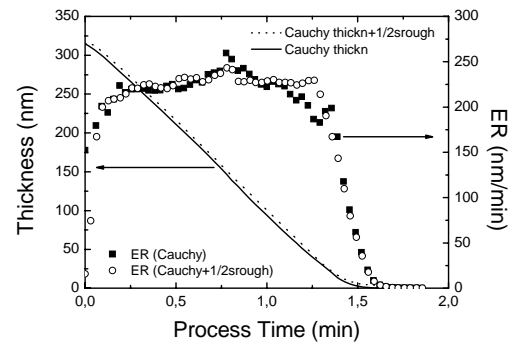


Fig. 3 ER profile when a roughness layer is also used to fit the ellipsometric data.

Conclusions

In situ thickness variation measurements during Oxygen plasma etching of polymers indicate that actual ER is not a constant value throughout the etching process. ER variations both at the first stages but also at the final stages of the etching reveal that the average ER depends on film thickness or etching duration.

The ER profile at the final stage of etching (until $ER=0$) strongly depends on the process time and the surface roughness developed until then.

These results are of interest both when ultra-thin polymers are used e.g. EUV lithography, chemical nano-patterning etc, or when high surface roughness is needed, e.g. antireflective coatings, super-hydrophobic coating fabrication etc.

References

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