

Molecular weight and processing effects on the dissolution properties of thin poly(methyl methacrylate) films

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Abstract

An experimental set-up based on multiwavelength interferometry, is applied in order to study *in-situ* the dissolution process of thin resist films. The interference function was the basis for a fitting algorithm, which analyses the experimental data and evaluates the progress of the resist thickness with time. The dissolution of various PMMA molecular weights (15 K, 350 K, 996 K) and resist thicknesses (20–300 nm), in various developers, consisting of mixtures of methyl iso butyl ketone (MIBK), iso propanol (IPA), H₂O at various relative concentrations, was studied. Surface dissolution inhibition was shown in unexposed resists with high molecular weights and increased thickness in the case of MIBK–IPA 1-1 and IPA–H₂O 7-3 developers. After that the whole dissolution process evolved at a steady rate. Dissolution of thick films proved to be unpredictable showing complex dissolution curves. Low molecular weight resists presented a smooth dissolution curve without dissolution inhibition. Samples exposed with small DUV doses, exhibited dissolution behavior similar to the unexposed cases, whereas high exposure doses, within the lithographically useful range, led to smooth dissolution behavior. In the case of MIBK–IPA 1-3 developer significant swelling was observed.

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1. Introduction

During the last 10–15 years significant research effort has been devoted worldwide, to the understanding of thin polymeric film properties (e.g. [1–5]). In such thin polymeric films, several parameters appear totally different from the ones at thicker films. From the point of view of patterning the two most important properties that undergo significant change from the transition of relatively thick to thin films are physicochemical properties such as the glass transition temperature (T_g^{film}) (e.g. [6–8]) and the dissolution rate (e.g.

[9,10]). A polymeric film supported on a substrate could be considered as a 3-layer stack; the top layer (resist/environment interface) and the bottom layer (resist/substrate interface) having a thickness of a few radii of gyration and the middle layer having the properties of the bulk film. As total film thickness decreases below a certain value, the contribution of the interfacial layers increase and thus the physicochemical properties start to deviate from the bulk ones. The established methods for the characterization of polymeric films and in particular resists, provide information attributed to the average properties, and sometimes are not applicable to thin films. For example the differential scanning calorimetry (DSC) tools, which are used for the measurement of glass transition temperature of bulk poly-

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mers, are improper for films. In addition, it is desirable for thin films to employ *in-situ* characterization methodologies that provide detailed information vs. depth. In this context, the majority of the experimental studies use a single wavelength interferometric set-up, (e.g. [10–12]) to evaluate the dissolution characteristics of polymeric films several hundred nanometers thick. However, multiwavelength reflectance [13,14] set-ups and quartz crystal balance [15] tools have been applied recently for the monitoring of the dissolution process in the case of thin polymeric films. In addition, significant research effort is devoted for the simulation of the dissolution process (e.g. [16]). Multiwavelength interferometry has been successfully employed for a variety of applications necessitating the monitoring of film thickness changes of optically transparent films. Such typical applications are: glass transition temperature [17], swelling due to gas absorption [18], monitoring of thermal processing steps (Post Apply Bake (PAB), Post Exposure Bake (PEB)) [19].

PMMA resist is still the mostly used positive resist for high resolution lithography applications and its application has been extended from the classical electron beam lithography (e.g. [20]), to proton beam lithography [21], nanoimprint lithography [22] and Extreme Ultra Violet (EUV) lithography [23]. Significant research effort has been devoted for the understanding of the PMMA's lithographic mechanism and further improvement of its performance. The main topics covered so far were the development step (ultrasonic agitation, developer concentration, developer composition, molecular weight distribution of irradiated areas) (e.g. [24,25]), the molecular weight [26,27] and the role of casting solvent [28]. From the dissolution studies it was revealed that the implementation of a *co-solvent* developer consisting of iso propanol (IPA) and H₂O at a specific relative concentration range improves the sensitivity and the lithographic performance [29]. On the other hand, from a molecular weight study [7] it was revealed that the average molecular weight (M_w) has a systematic effect upon resist performance, especially in the case of dense patterns. The lithographic performance of high molecular weight PMMA is found to be superior to the low molecular weight.

The aim of the present work is to present a methodology based on multiwavelength (in the visible range) interferometry for the *in-situ* characterization of dissolution of thin resist films, and its application on the study of film thickness and processing conditions effects on the dissolution properties of poly(methyl methacrylate) (PMMA) films for a wide molecular weight range.

2. Experimental

2.1. Experimental set-up and materials

The dissolution study was performed on a home-made set-up, shown in Fig. 1. A transparent vessel is filled with the developer. A sample holder outside the vessel is manip-

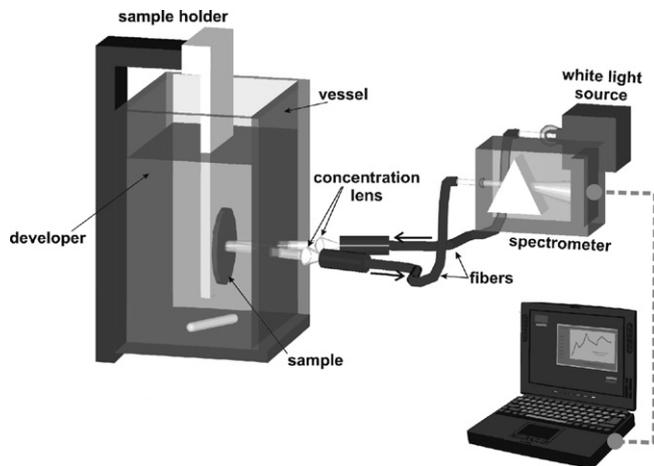


Fig. 1. Dissolution rate monitoring set-up based on multiwavelength interferometry.

ulated in a sliding fashion in order to insert the sample (wafer coated with the polymer under study) in the developer solution. Opposite to the holder and outside of the vessel two other holders (each one accommodating an optical fiber and a lens) are mounted in a position such as to guide the light almost normal to the sample, receive the reflected light from the sample and guide it back to a spectrometer connected to a PC. Magnetic stirring assists the dissolution, while the rotation speed is adjusted to the point where no bubbles are created by the excessive stirring. The sliding approach offers very high repetitive results and allows a significant number of experiments to be conducted without any need of realignment.

Overall, the set-up developed, offers high flexibility, reproducibility and limited need for re-adjustment between successive samples. The latter feature is very important, given the fine adjustment required for the optimum reflectance signal and fitting with the interference equation.

For the measurement part a white light source (Avalight, Avantes) which emits light in the visible–near infrared range (>470 nm) is used. Its lower spectral boundary is safely higher than the lower limit at which the incident light can cause any resist exposure. The light is guided onto the sample wafer surface via one of the optical fibers and then reflected back to the spectrometer via the second one.

The spectrometer used for the data acquisition (Ocean Optics) is a single channel card and the data acquisition rate of 1 full spectrum/sec was used. The duration of the experiments was set to 20 min. Normally the developing times are much shorter but our choice allowed for the revelation of the behavior of some resist/solvent pairs in particular in the case of unexposed samples. Here, we would like to point out the presence of a time delay corresponding to the time between the start of the application and that of the beginning of data acquisition. Such a delay may reflect surface inhibition phenomena. Another related point of concern is that for solvents attacking rather quickly certain resists an erroneous estimate of initial thickness may result.

Due to such concerns, the procedure followed was to insert the wafer in the solvent few seconds afterwards the start of data acquisition.

The substrates used for the present study were $2 \times 2 \text{ cm}^2$ pieces from Si wafer with an approximately 1000 nm thick silicon dioxide layer thermally grown (1100 °C, 200 min wet oxidation) on top of it. On top of the SiO_2 layer, the resist to be studied is applied. Certainly other optically transparent films could be used, such as silicon nitride, however SiO_2 was selected due to the easiness of its growth.

The resists used, were prepared from PMMA polymer in propyl glycol mether ether acetate (PGMEA) purchased from Sigma-Aldrich. The preparation of the resist involved 96 hours stirring and then filtering. Various concentrations were used in order to be able to cover a wide resist thickness range (20–300 nm). Three molecular weights, 15 K, 350 K, 996 K were used in order to study the effect of molecular weight on the dissolution rate. The resist films were obtained after spin coating at proper speeds and Post Apply Bake (PAB). The developers used in the present study are mixtures of Methyl Iso Butyl Ketone (MIBK), Iso PropAnol (IPA) and deionized water (H_2O). The optical Cauchy constants of the resists, the SiO_2 and the Si substrate, were measured with a spectroscopic ellipsometer (J.A. Woollam M2000F rotating compensator ellipsometer) within the 300–1000 nm spectrum, at an angle of incidence of 75.14°. Primary data collection and subsequent data processing was accomplished with the commercial WVASE32 software [5].

2.2. Thickness calculation and software

The primary light passing through the developer solution, incident on the developer/resist interface, and after partial reflection is transmitted through the resist layer, where, after a partial reflection on the resist/substrate interface continues inside the SiO_2 layer where the absorbance in the VIS/NIR spectrum is negligible. Finally the light is totally reflected at the SiO_2/Si interface. The three beams (Fig. 2) emerging from the sample cause a final interference signal which is directed through the optical fiber to the spectrometer with a total energy E , approximated by the

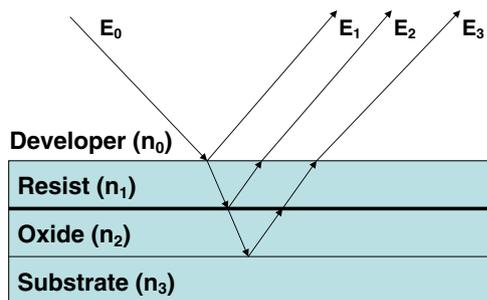


Fig. 2. Propagation of the light into the stack of PMMA/ SiO_2 /Si sample. Partial reflectance occurs at the PMMA surface, PMMA/ SiO_2 interface and total reflection at the SiO_2/Si interface. The incidence angle in the figure is exaggerated for illustration purposes.

interference equation as it is described in detail in Refs. [17,18].

The application of the interference equation on the whole spectrum (1 full spectrum/sec) allows the calculation of the resist thickness during the dissolution process. In Fig. 3 the experimental reflectance spectrum and the according fitted one after the application of the interference equation are compared and presented for a PMMA/ SiO_2 /Si sample. It is clear that the extrema are observed at the same wavelengths for both the experimental and the fitting data, showing a very high fitting accuracy. The observed differences on the intensity of the extrema between the experimental and fitting spectra could be attributed on reflections on the vessel and also energy losses as the reflected signal is guided to the optical fiber connected to the spectrometer. On the other hand the observed intensity differences of the maxima are due to the emission spectrum of the light source used and the response curve of the particular grating used in the spectrometer.

The existence of the SiO_2 layer is necessary for effective application of this methodology for thin films by providing an adequate number of extrema in the spectrum [30]. The use of the intermediate SiO_2 layer may be understood by considering that its presence increases the optical path of the traveling light and the number of interference fringes in the recorded spectrum, resulting in significantly improved fitting accuracy. In Fig. 4 the effect of the grown thermal oxide on the calculated film thickness during the dissolution is presented. When there is no the silicon dioxide layer, no extrema can be detected in the reflectance spectrum and for that reason the fitting with the interference equation is wrong.

The post processing of the acquired data is carried out by software written in Matlab[®]. The idea behind the software is to find the correct thickness of the remaining resist at each sampling instance by fitting the intensity graph produced by the theoretical calculation (Eqs. (1) and (2)) to the

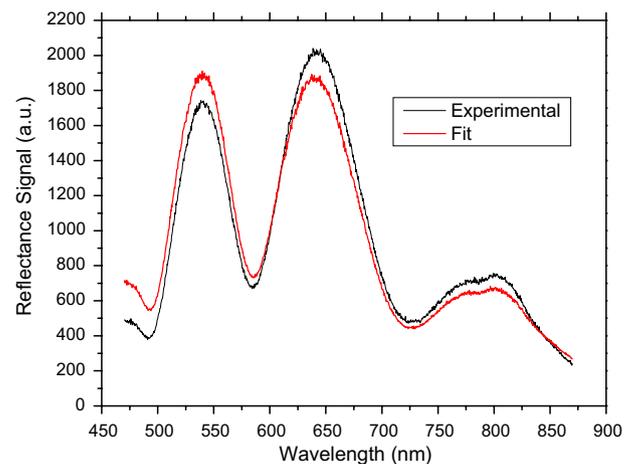


Fig. 3. Experimental spectrum in the case of PMMA/ SiO_2 /Si sample into the developer solution, and the spectrum obtained after fitting with equation 1. The extrema are observed on the same wavelength, evidence of high fitting accuracy.

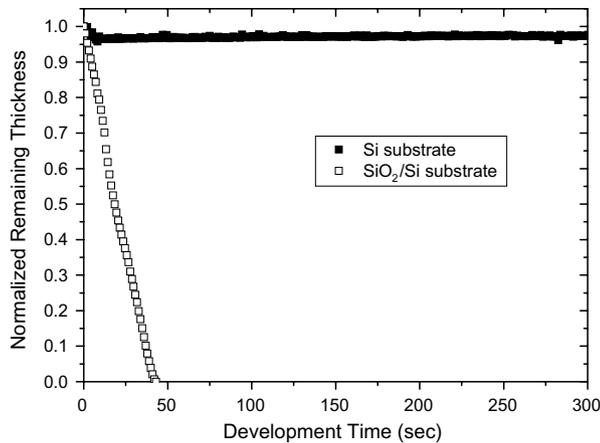


Fig. 4. The effectiveness of the fitting algorithm depends heavily on the presence of an intermediate SiO_2 layer. The absence of the thick SiO_2 layer drives to absolutely wrong results about the dissolution process.

experimental reflectance spectrum. At each instance the correct thickness will be the one that, for all wavelengths (from the configured range) gives the best matching. The refractive indices are considered constant during the experiment but the dependence of the refractive index from the wavelength is taken into account.

The algorithm developed is based on a path traversal on a 2D array having as indices thicknesses, and multipliers. The traversal starts at the center of the thickness and multiplier range and is executed following the minimum difference between the experimental and calculated spectra. The position at which the minimum difference was found is the candidate as the next center for which the above procedure is repeated. The algorithm finishes when at the chosen center the best fitting is achieved.

3. Results

Due to the resolution capabilities of PMMA resist [31], significant research effort is applied on the further process optimization (PAB, exposure strategy, development) of resolution, sensitivity and process latitude [29,32]. However, limited work has been devoted in the study of PMMA dissolution in the case of ultra thin films. The most common developer for PMMA is a mixture of MIBK and IPA. MIBK is a good solvent for PMMA (can be used for the preparation of PMMA solution also) and dissolves, with a different rate, both exposed and unexposed areas, providing a very high sensitivity value but also significant thickness loss in the unexposed regions. In order to improve the dissolution selectivity between exposed and unexposed regions, and thus the lithographic performance, the development strength of the developer should be decreased which is achieved by the IPA. Traditionally, the MIBK–IPA 1–3 mixture is preferred which provides almost negligible thickness loss in the unexposed regions, higher contrast, high resolution and moderate sensitivity.

Several years ago, a co-solvent (IPA, H_2O mixture) has been proposed for the PMMA development step [33] and

recently successfully applied for high resolution applications (e.g. [34]). When pure IPA or H_2O are used for the PMMA development, they provide very low sensitivity and contrast values. The dissolution of PMMA in the IPA– H_2O mixture has not been totally understood so far. A possible explanation is that H_2O molecules due to their small size diffuse slightly in the exposed PMMA areas causing surface swelling, and then IPA removes the swollen areas. Main chain scission in PMMA is initiated by cleavage of the main chain carbon to carbonyl carbon bond causing small molecule volatile products such as CO , CO_2 , CH_3O and radical species [35]. Due to this volatilization the free volume in the polymeric film increases in the exposed regions. Thus it is relatively easy for the highly polar H_2O molecules to diffuse in the exposed regions due to their small size and cause slight swelling allowing the removal of these areas from the IPA. The removal of swollen regions is instant and the dissolution proceeds smoothly and is H_2O diffusion controlled. In the unexposed regions, the free volume of PMMA matrix is small and the diffusion rate of water molecules in these regions is very low thus the dissolution rate of unexposed areas is very small. Therefore low thickness loss in the unexposed areas occurs and high contrast and resolution are observed.

In the present study, the effect of MIBK–IPA 1–1, MIBK–IPA 1–3, and IPA– H_2O 7–3 developers on the dissolution of various molecular weights of PMMA for a wide lithographically useful thickness (20–300 nm) range is examined. This dissolution study is applied in the case of exposed and unexposed samples and in all cases the temperature was 23 ± 1 °C. Because of the wide resist thickness range used in the present study, the PMMA thickness values are plotted as normalized to the initial thickness; this form of presentation allows for better visualization and also aids comparisons.

3.1. Dissolution studies on unexposed films

As all three developers present limited or negligible dissolution rate in the case of unexposed PMMA films, the dissolution is monitored for 20 min, which is a time considerably longer than the usual dissolution time in the case of high resolution lithography. In Fig. 5, the dissolution of unexposed 350 K PMMA films, for film thickness in the 20–200 nm range, in the case of IPA– H_2O 7–3 developer is depicted. The dissolution behavior is the same for all film thicknesses exhibiting dissolution inhibition (DI) at the beginning of the dissolution and changes afterwards depending strongly on the initial thickness. The DI period lasts approximately 70 sec for thicknesses of 20, 40 nm and ~100, 150 sec for the 100, 200 nm respectively. This dissolution inhibition is desirable, in particular in the high resolution and high aspect ratio patterning applications e.g. magnetic head fabrication for 100 Gbit/in.² aerial density [36]. In the latter application for example, the desired aspect ratio is at least 8:1 and requires the patterning of PMMA films with thickness >1 μm while the development

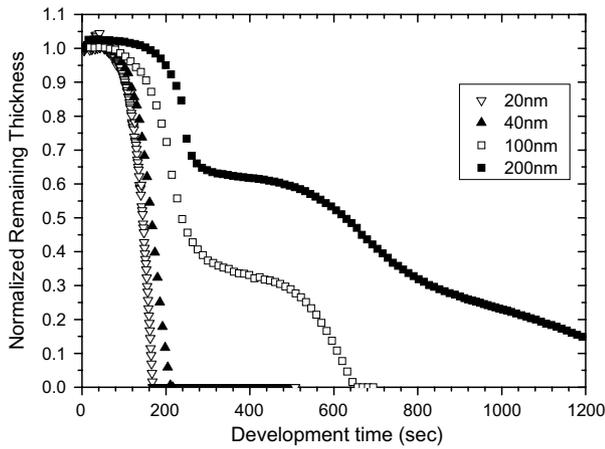


Fig. 5. Normalized remaining thickness vs. development time in the case of PMMA ($M_w = 350$ K) for a wide thickness range and for IPA–H₂O 7-3.

step lasts several minutes. For thicknesses <100 nm the dissolution (Fig. 5) proceeds smoothly after that DI period while for thicker films intermediate dissolution inhibition plateaus are observed. The observed DI period at the beginning of the dissolution is common for higher molecular weights. This is shown in Fig. 6 where the dissolution behavior of the three molecular weights in the case of thin films is illustrated. The 15 K molecular weight PMMA film, does not show any DI period throughout the whole dissolution period, while the heavier ones (350 K, 996 K) clearly show an initial DI period. However, afterwards the DI period the dissolution proceeds quite smoothly. This DI period, causes a significant increase of the required time for the total removal of poly(methyl methacrylate) films in the cases of 350 K, 996 K molecular weight. From those two last figures it is obvious that the initial DI period depends on the molecular weight and the initial thickness of the resist. As the thickness and the molecular weight increases the dissolution inhibition is expected in the initial as well as in the intermediate stages of the dissolution per-

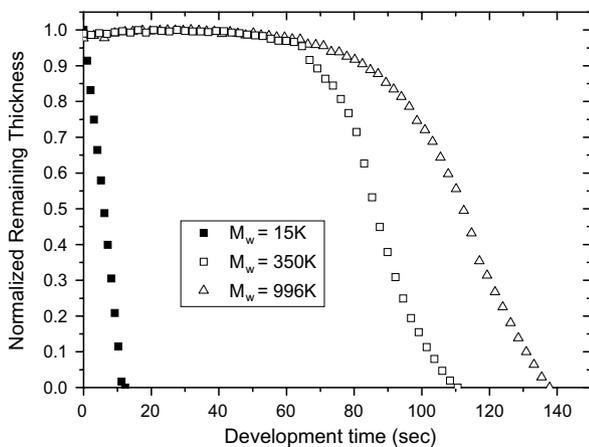


Fig. 6. Effect of molecular weight on the dissolution of thin PMMA films (~ 57 nm) in MIBK–IPA 1-1 developer.

iod. This dissolution inhibition period is desirable for high resolution lithography results; thus the small molecular weight (15 K) is considered as inappropriate and can not be used in such applications. The poorer lithographic performance of low molecular poly(methyl methacrylate) thin films, has also inferred in the past, for the case of high resolution electron beam exposure [29,37].

In the case of the conventional MIBK–IPA 1-3 developer, the unexposed PMMA ($M_w = 350$ K) film did not dissolve; however it clearly swelled as shown in Fig. 7; indications for such an effect, upon employment of the particular developer, have been reported by us previously [29]. Three different initial thicknesses were chosen to show the effect of the resist's thickness on the dissolution of this particular developer. As shown, in Fig. 7, the thicker resist films (185 nm, 280 nm) do not dissolve but slowly swell throughout the whole duration of the experiment. The final calculated film thickness is approximately 20% higher for a dissolution time of 1200 sec for both films which is an indication that at a thickness of at least 185 nm the film presents bulk properties. On the other hand, the 45 nm film swells in a rather uncontrollable manner and the calculated film thickness exceeds 100% the initial thickness. Despite the fact that the swelling percentage is different for thick and thin films, the absolute swelling thickness value is 40–50 nm in all cases. The swelling front propagates in the polymeric film with time for both thin and thick films. For the developing time employed, the swelling front covers the whole film in the case of thin films, while this is not the case for thick films. This significantly increased swollen film thickness could be attributed to the very good adhesion of the PMMA film to the SiO₂ surface. The attachment takes place through multiple hydrogen bonding between the carbonyl groups of the chains and the hydroxyl groups of the silicon dioxide surface [35]. This attachment reduces the mobility of chains having immediate access to the substrate surface and, possibly, also the mobility of chains immediately entangled to the first layer

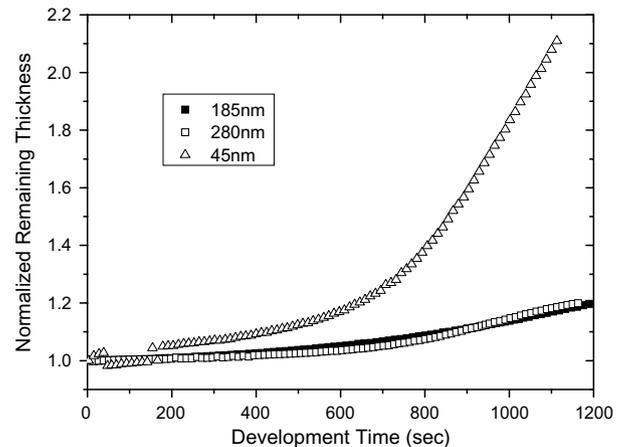


Fig. 7. Swelling of unexposed PMMA ($M_w = 350$ K) films in the case of MIBK–IPA 1-3 developer. Swelling depends strongly on the initial thickness.

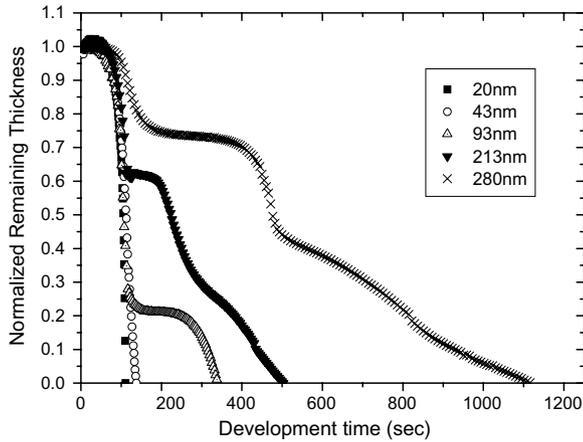


Fig. 8. Dissolution of PMMA 350 K in the case of MIBK-IPA 1-1 developer for a wide thickness range.

of chains. Therefore this solvent is not appropriate for the highest possible resolution.

In Fig. 8, the dissolution process in the case of 350 K PMMA in MIBK-IPA 1-1 solution for a wide thickness range is shown. The dissolution proceeds in a way similar to the one observed for IPA-H₂O developer. In all cases, a dissolution inhibition period is observed which is significantly smaller than the one observed in the co-solvent case.

3.2. Dissolution studies on exposed films

Since PMMA is a positive tone resist it is very interesting to study the dissolution behavior of exposed regions and, in particular, to identify the developer contrast i.e. the ratio of the dissolution rate between exposed and unexposed regions. For this part of the study, exposure areas with different exposure dose are required. Since PMMA is sensitive to irradiation below 220 nm, the necessary exposures were carried out with a broad band DUV Hg-Xe lamp (Oriel) (emission window 190–250 nm). In order to identify the useful exposure dose range, a contrast curve experiment was carried out first (Fig. 9) and the exposure doses for the initiation of the thickness loss (~500 sec) and the complete removal of PMMA (~2500 sec), for a development time of 60 sec, were determined. Exposed samples at these two doses as well as one more, corresponding to the middle of the contrast curve, were studied using the dissolution apparatus. In Fig. 10, the dissolution behavior of the samples in MIBK-IPA 1-1, are presented. For the unexposed and exposed with small dose samples, the dissolution does not proceed smoothly and dissolution inhibition phenomena are observed. On the contrary when the exposure dose is high, the dissolution proceeds smoothly. Similar phenomena observed in the case of IPA-H₂O 7-3 developer. In Fig. 11, the mean dissolution rates as they were calculated from the beginning and total resist removal points are presented for the two developers. The fact that the dissolution rate of the unexposed regions is considerably lower in the IPA-H₂O 7-3 case provides with higher process latitude [29].

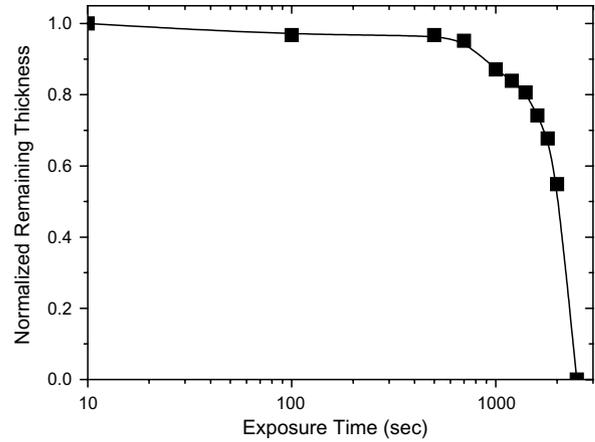


Fig. 9. Contrast curve for PMMA ($M_w = 996$ K) for MIBK-IPA 1-1 developer. The development time used was 60 sec. The substrate was 1000 nm SiO₂ over Si.

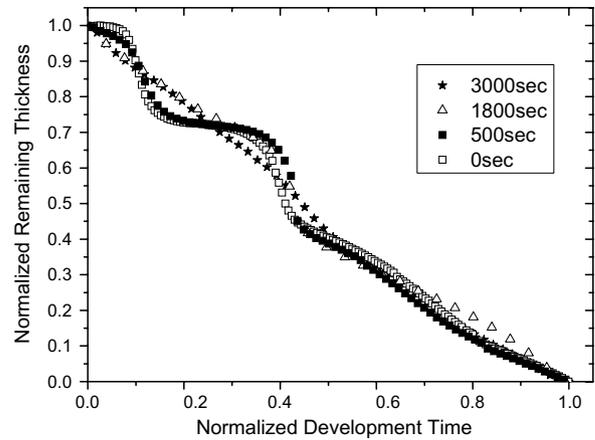


Fig. 10. Normalized remaining thickness vs. normalized development time for PMMA ($M_w = 996$ K) in the case of MIBK-IPA 1-1 developer. The initial film thickness was 310 nm. The normalized development time for each exposure dose is calculated as the ratio of the development time (t) over the time required for total dissolution of the polymeric film (t_0). The t_0 values are 928 sec (exp. time 0 sec), 488 sec (exp. time 500 sec), 102 sec (exp. time 1800 sec) and 41 sec (exp. time 3000 sec). The use of normalized development time allows the comparison of the development process for samples exposed with considerably different exposure dose.

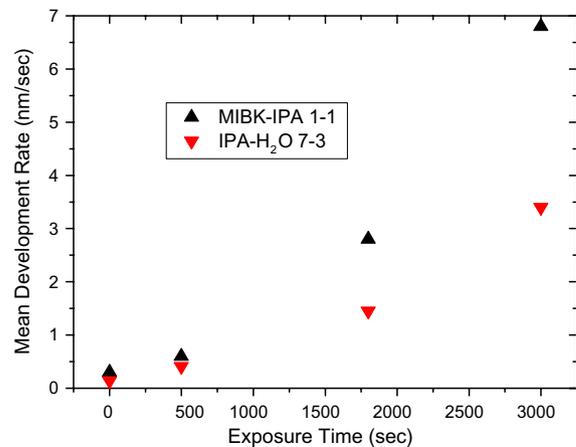


Fig. 11. Mean development rate for PMMA ($M_w = 996$ K) for a wide exposure dose range.

4. Conclusions

An effective multiwavelength interferometry methodology was developed and was applied for the monitoring of film thickness changes during the dissolution of PMMA films in various developers. The set-up developed consists mainly of the vessel where the dissolution takes place, optical fibers to guide the white light, from an appropriate source, on the sample wafers and back to a spectrometer where real time recording of the reflectance spectra was performed.

Using that apparatus, the dissolution process of PMMA resist films of various molecular weights 996 K, 350 K, 15 K and thicknesses 20–300 nm in different solvents, was studied. In the case of MIBK–IPA 1-1 and IPA–H₂O 7-3 developers, the obtained results are similar. An initial dissolution inhibition (DI) period was observed in the case of unexposed high molecular weights, 996 K, 350 K, regardless of the initial film thickness resists. In the case of low molecular weight (15 K) the surface inhibition period is negligible and the dissolution proceeds smoothly throughout the whole dissolution period. On the other hand, intermediate DI plateau were observed for high initial resist thicknesses regardless of the molecular weight. When MIBK–IPA 1-3 is used, swelling is observed with an increased percentage in favor of thin resist films, thus proving improper as a developer for ultimate resolution lithography. In the case of exposed samples, when the exposure dose is small (inadequate for thickness loss in the contrast curve) the dissolution behavior is similar to the one observed for the unexposed samples. However when the exposure dose is high, corresponding to the dose required for total resist removal in the contrast curve, the dissolution proceeds smoothly without any dissolution inhibition plateau due to the significant decrease of the molecular weight caused by the chain scission.

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