Capabilities and Limitations of Plasma Polymerized Methylsilane (PPMS) All-Dry Lithography

Gary Dabbagh, Richard S. Hutton, Raymond A. Cirelli, Anthony E. Novembre, Elsa Reichmanis, and Omkaram Nalamasu

*Bell Labs – Lucent Technologies
600 Mountain Avenue, Murray Hill, New Jersey 07974 USA*

In this paper we report the results of a feasibility study of manufacturability of processes using plasma polymerized methylsilane (PPMS) as both a single-layer and a bilayer resist in both negative and positive tone development modes. PPMS has shown great promise as the basis for an all dry lithographic process. The photosensitive polymer is deposited in a low power plasma of methylsilane gas and is comprised of a Si-Si bonded network. PPMS undergoes efficient photo-oxidative crosslinking upon exposure to 248 or 193 nm light in air to form an oxide-like material (PPMSO). We have identified several structural differences of films deposited at different temperatures and have correlated those differences to the air stability and the photosensitivity of PPMS films. We have also examined the effect of laser pulse power and repetition rate on the efficiency of exposure and conclude that the rate of oxygen diffusion into the film limits the effectiveness of high laser power for increasing the throughput of an exposure tool. We have concluded that positive tone PPMS processing is not practical because of the slow diffusion of oxygen through the film, required for effective photo-oxidation of PPMS to occur.

Keywords: PPMS, CVD resist, all-dry lithography

1 INTRODUCTION

The extension of optical lithography to the production of the next generation of semiconductor devices has been enabled by the recent progress in the field of 193 nm lithography utilizing ArF excimer lasers. Among the most important of these developments has been the design of innovative resist technologies to overcome the high absorbance at 193 nm of the deep-UV resists currently in use.¹⁻³ One technology employing plasma polymerized methylsilane (PPMS) as the photosensitive material,⁴⁻⁶ is a novel all-dry photolithographic process. PPMS provides a flexible resist platform in that it is sensitive at both 248 and 193 nm. It can be developed to yield either positive or negative tone images, and it can be used as a single layer resist or as the imaging layer in a bilayer process. It has the added advantage that it is an all-dry process and consequently reduces the volume of liquid waste requiring disposal.

Figure 1. Bilayer process schemes for bilayer PPMS.

As illustrated in Scheme 1, PPMS is deposited in a low power plasma of methylsilane gas and is easily photo-oxidized in the presence of air to a glass-like material we denote as PPMSO. As depicted in Figure 1, exposed PPMS films may be developed in either a positive tone mode using vapor HF or aqueous buffered oxide etchant (BOE) to remove the PPMSO or in the negative tone mode using a Cl_2 based plasma to remove PPMS with a selectivity of 3 *versus* PPMSO.

Scheme 1. Plasma polymerization of methylsilane and its subsequent photo-oxidation to PPMSO.

2 EXPERIMENTAL

2.1 Silicon

PPMS films were deposited on 150 mm p-type Silicon (100) wafers. The wafers were designated as "device quality" and were coated with silicon nitride on the backside. Wafers had a single flat and were laser scribed with unique identification numbers. Wafers were cleaned at our facility by first undergoing a front and backside scrub using an automated DNS scrubber. Wafers were then cleaned in the following sequence: NH_4OH and H_2O_2 , DI water rinse, HCl and O_3 , DI water and finally an IPA dry. These were all carried out on a Submicron Systems (SMS) wet chemical cleaning bench. Some wafers were inspected for light point defects by a Tencor Surfscan laser light scattering instrument both before and after PPMS deposition.

2.2 Methylsilane

Methylsilane (UHP grade) was obtained from Voltaix, Inc. of North Branch, NJ and was analyzed by gas chromatography using a thermocouple detector and also by mass spectroscopy of the separated eluents. The technique was denoted by Voltaix as GC-TCD/MS. The results of the analyses are shown in Table 1.

Table 1. Analysis of impurities found in methylsilane gas. (Lot #2341.1, Voltaix Inc.)

Component	Analysis
N_2	2 ppm
$\text{Ar} + \text{O}_2$	ND (< 2 ppm)
CH_4	ND (< 2 ppm)
CO_2	1 ppm
SiH_4	2 ppm
$\text{CH}_3\text{SiH}_2\text{Cl}$	ND (< 2 ppm)
$(\text{CH}_3)_2\text{SiH}_2$	5 ppm

2.3 Plasma Deposition

The plasma deposition of methylsilane was accomplished in an Applied Materials (AMAT) DxZ chamber which was retrofitted onto an AMAT Precision AM 5000 platform. The DxZ chamber is a parallel plate reactor which was configured with a 150 mm process kit. The AM 5000 can accommodate eight wafers in the inert atmosphere of the storage elevator while processing each lot. Due to the air sensitivity of the PPMS films, wafers were only processed in batches of eight or less. The distance between the substrate and the electrode was set to 575 mil. Film deposition on the AM5000 platform in the DxZ process chamber provided several easily adjustable parameters, such as gas flow rates and pressures, plasma power and electrode-to-wafer distance. The temperature of the wafer stage was controlled by resistive heaters and was easy to adjust upward. With no active cooling however, reducing the stage temperature was an hours-long process. The chamber wall temperature, heated by a circulating fluid in series with three other chambers on the AM5000 was not adjusted because of the critical processing needs of the other chambers for other Lucent Technologies projects.

The 13.56 MHz radio frequency (RF) generator (adjustable up to 800 W) had a fixed matching network. The chamber was fitted with four gasses: methylsilane, He, freon-14, and N_2O .

Cassettes containing up to 8 wafers were placed in the AM 5000 robot handler and were then transferred to a nitrogen purged storage elevator. Wafers were introduced into the processing chamber and placed upon the resistively heated pedestal. After deposition, each PPMS coated wafer was removed from the process chamber and held in the storage elevator until all of the eight wafers were processed. After the eighth wafer was processed, all eight were removed from the storage elevator to the air ambient of the processing cassette by robotic manipulation. Wafers which were not processed or characterized immediately were placed in a modified Plexiglas dessicator with rapidly purging nitrogen gas. A chamber cleaning operation was run after every group of 8 wafers. The specifications of the deposition and cleaning processing steps are summarized in Table 2.

3 Film Characterization

3.1 Ellipsometric Measurement

PPMS film thickness and refractive index (n) were determined with a Rudolph Research AutoEL-II ellipsometer or with a Thermawave Model 2600 Opti-Probe. The Rudolph AutoEL-II was used for manual single point readings and operated with 632 nm light at a 70° angle of incidence from the wafer plane normal. The Opti-Probe 2600 DUV was used for automated multipoint measurements and was used for mapping the film surfaces. Infrared spectra were obtained with a Nicolet Magna-IR 560 FTIR spectrometer. X-ray photoelectron spectra were obtained on a Physical Electronics Model 5600 XPS system.

Table 2. PPMS Deposition and Chamber Cleaning Process Steps for the AMAT DxZ Plasma Chamber on the AMAT Precision 5000 Platform**Deposition***Pressure Stabilization:*

Helium	200 sccm
Pressure	1.4 Torr
Time	20 s

Methylsilane Flow Stabilization:

Methylsilane	100 sccm
Pressure	1.4 Torr
Time	12 s

Plasma Deposition: 1000Å thick film

Methylsilane	100 sccm
Pressure	1.4 Torr
Time	45 s
RF Power	60 W

Chamber clean*Pressure Stabilization:*

Freon 14	1500 sccm
N ₂ O	500 sccm
Pressure	4.5 Torr
Time	5 s

Plasma Clean:

Freon 14	1500 sccm
N ₂ O	500 sccm
Pressure	4.5 Torr
Time	240 s
RF Power	800 W

3.2 UV Exposure

PPMS films were exposed on a converted Lambda Physik KrF laser coupled to a Karl Suss projection printer. Although the optics were designed for use with 125 mm wafers, we used exposure data from the wafer centers only. The power output was estimated to be 1 mJ/s with the laser pulse rate at 50 Hz. Regions of the wafer were masked from the 193 nm light by covering with pieces of silicon wafer to control exposure dose. Wafers were exposed while in ambient clean room air. Lithographic exposures were carried out at 248 nm using a GCA XLS 248 stepper (0.53 NA) while clean dry air was purged through the optical system for a minimum of 30 minutes prior to exposure. At 193 nm, either an ISI 9300 Microstepper (0.6 NA) or the SVGL Micrascan II (0.5 NA) located at MIT Lincoln Laboratory was used. 193 nm exposures on the ISI Microstepper required clean dry air be blown through a protective nosecone above the wafer plane. The

Table 3. PPMS etching conditions on the Lucas high density helicon source etcher.

Cl₂ Etching conditions	
Source power	2500 W
Chuck power	25 W
Cl ₂ gas flow	80 sccm
Pressure	2.0 mTorr
Temperature	-10° C

nosecone was normally purged with nitrogen as was the rest of the stepper cabinet. A minimum of 30 minutes of air flow was carried out before exposure. The SVGL stepper normally keeps the wafer chuck in an air ambient, so no additional air purge was necessary.

3.3 Negative Tone Cl₂ Plasma Development

Films were developed using a Lucas - Signatone Inc. Vortex model 5410 helicon source etcher. For the negative tone process, the wafers were etched with Cl₂ for a length of time determined by the refractive index of an unexposed area of PPMS and also by the thickness of the PPMS films to be removed. The etch rates were roughly 30–35 Å/s for films exhibiting refractive indices of 1.65–1.69 respectively. We eventually introduced optical emission endpoint detection at 388 nm. The conditions for Cl₂ etching are summarized in Table 3. Development was also accomplished using an Applied Materials 5000 MERIE system with optical emission endpoint detection at 281 nm.

3.4 Positive Tone HF Development

Development was performed on an FSI Excalibur HF vapor etching tool. Some of the positive tone results were obtained using either immersion development in 7:1 buffered oxide etch (BOE) or in concentrated aqueous HF.

3.5 Pattern Transfer

Either an O₂ plasma etch on the Lucas helicon etcher or a CO₂ plasma etch on the Applied Materials MERIE etcher was used to accomplish pattern transfer of the imaged PPMS layer into the underlying organic resists used in the bilayer systems.

3.6 Analysis

Feature dimensions were determined from top-down measurements on a Hitachi 4160 scanning electron microscope (SEM). Cross sectional imaging was performed on a Hitachi 2500 SEM. Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet Magna-IR 560 FTIR spectrometer. X-ray photoelectron spectra (XPS) were obtained on a Physical Electronics Model 5600 XPS system

Figure 2. The refractive index (n , 633nm at $\phi=70^\circ$) for 1000Å PPMS films deposited at 100, 150 and 200 °C as a function of time in ambient clean-room air.

Figure 3. The effect of rf power and chamber pressure on 150°C PPMS Baseline Conditions: 1.3 Torr, 70 Watts.

4 Results and Discussion

4.1 PPMS Deposition

The air stability of the PPMS films (as measured by the drop in the refractive index) varied with deposition temperature. Figure 2 shows a plot of the refractive index (n) vs time in air for a 1000Å thick films deposited at 100°C, 150°C and at 200°C.

Within a particular temperature regime, individually altering the pressure or rf power did not change the general shape of the refractive-index vs time-in-air curves. Figures 3 and 4 show series of depositions at 150°C and 200°C respectively. Raising the deposition pressure or lowering the plasma rf power tended to lower the refractive index or stability curve. Likewise, lowering the pressure or raising the power increased the refractive index curve.

The 150°C depositions produced films that show a rapid initial drop in n from 1.74 to 1.70 during the first 30 min. followed by a slower decrease over many hours. Clearly, there are two decay processes occurring, each with its own characteristic decay time (t_1, t_2). The time constant t is the time in which the value for n diminishes to $1/e$ of the total drop observed for t . The rapid decay for the baseline curves of Fig. 3 occurs with an approximate time constant, t_1 of 0.2 h. The slower decay exhibits a t_2 of 9.6 h.

We attempted to eliminate the initial rapid drop by depositing films at higher temperatures. Films deposited at 200°C show a more uniform decrease in n over the same time period, however, they initially show values of n that are too high to be useful sensitive resists. Although the 200°C films eventually exhibited values of refractive index in the range we expected for sensitive films ($n = 1.74$), these high temperature films showed little sensitivity to 193 nm light. Clearing doses for such films were in excess of 150 mJ/cm².

We attempted to deposit films which exhibited rapid initial drops in n followed by periods of slow uniform decreases in n . Films deposited at 100°C showed a rapid drop in refractive index to $n \approx 0.15$ in only 2 to 3 hours.

Figure 4. The effect of rf power and chamber pressure on 200°C PPMS Baseline Conditions: 1.3 Torr, 70 Watts.

No leveling off at any useful refractive index range was observed (see the 100°C curve in Fig. 2).

We were able to prepare films at temperatures below 150°C which exhibited air stability's similar to films produced at 150°C. These were achieved by depositing from plasmas at low rf power and low pressure. At 45°C, a plasma at 0.6 Torr and 20 W deposited a 1000Å PPMS film that had a stability profile virtually identical to films deposited using the POR but at a slow deposition rate of only 320 Å/min. This indicated that there was probably a continuum of satisfactory conditions that span the parameter space between 45°C and 150°C but this area was not fully explored.

In light of processing control and latitude considerations, it was deemed necessary that 150°C deposited PPMS films sit in air for 30 to 60 minutes in order to allow the rapid drop in n to occur after which either N₂ storage or processing should commence. Total time in air should not exceed 3 hours before exposure and that the exposure should be carried out on films exhibiting an $n = 1.70$ to 1.65.

In order to approximate the relative photosensitivity

Figure 5. Refractive index (n) of 1000Å POR PPMS as a function of 193 nm exposure time (1s $\approx$ 1mJ/cm²).

Figure 6. Cl_2 etch selectivity of 1000Å POR PPMS as a function of 193 nm exposure time ($1\text{s} \approx 1\text{mJ}/\text{cm}^2$).

of these different PPMS films, we measured the refractive index and film thickness of exposed (193 nm light) and non-exposed sections of the coated Si wafers. Measurements were made before and after exposure and also after development in a Cl_2 plasma. Cl_2 development selectivity was targeted at unexposed / exposed > 3 . The results are shown in Figures 5 and 6 for PPMS films deposited at 150°C .

The results shown in Figure 5 indicate that films as old as 20 h in air show some photosensitivity. However, the results shown in Figure 6 indicate that the required process latitude for exposure and subsequent development may restrict the sit time in air to under 3 hours. Films with values of $n \approx 1.65$ are still sensitive enough to show a development selectivity of 3. The problem is significantly worse for films deposited at 100°C shown in Figure 7, where the data suggests that film sensitivity, *vis a vis* etching selectivity, drops to an unacceptable level within 30 min of exposure to air.

The fourier transform infrared spectroscopy (FTIR) of 3000 Å thick PPMS films provided some insight into the refractive index based stability results that we observed. Spectra were collected at 10 min. after deposition and also after an exhaustive 193 nm exposure ($2\text{ J}/\text{cm}^2$) in the presence of air and are shown in Figure

Figure 7. Cl_2 etch selectivity of 100°C PPMS as a function of 193 nm exposure time ($1\text{s} \approx 1\text{mJ}/\text{cm}^2$).

8. The results of the IR spectroscopy show that the absorption attributed to Si-H increases as the deposition temperature drops. The 100°C PPMS film shows an Si-H peak that is nearly twice that shown by the 200°C film.

The spectra obtained from unexposed films show that the absorbances attributed to Si- CH_2 -Si (2900 and 800 cm^{-1}) increase with increasing deposition temperatures. The more photolytically stable Si-C bond, (relative to an analogous Si-Si bond) would tend to decrease the lithographic photosensitivity of the higher temperature PPMS films. Spectra obtained from the exposed PPMS films show absorbances that indicate substantial oxidation occurs in the 100 and 150°C films but not in the 200°C film. PPMS films deposited at 100°C have significantly greater lithographic sensitivity than films deposited at 150 and 200°C , but are much less stable in air. One contribution to the observed stability trend may be the density of the films (Table 4). The low density of the 100°C PPMS film allows for increased diffusion of oxygen into the films. The intensities of the SiO_2 and SiO peak ($\sim 1100\text{ cm}^{-1}$) and the OH peak ($\sim 3300\text{ cm}^{-1}$) are roughly three times greater for the low density 100°C film than for the 200°C film after photo-oxidation.

Figure 8. The FTIR spectra of 3000Å thick PPMS films deposited at 200 (top), 150 (middle) and 100°C (bottom). The spectra labeled unexposed and exposed, were from films that sat in air for 10 min before acquisition of the FTIR data, and from films that were exposed to $2\text{ J}/\text{cm}^2$ 193 nm UV light delivered at 50 Hz, respectively.

4.2 248 nm Lithography

In order to evaluate the 248 nm lithographic performance of PPMS we employed a timed Cl_2 plasma etch development of the exposed PPMS coated wafers on the Lucas helicon etcher. PPMS films (2000Å) were deposited over a 7000Å layer of hardbaked novolac resin which acts as a planarizing layer. The combined use of a thick PPMS layer (2000Å vs. 1000Å), and the underlying organic layer was necessary to increase the contrast of the SEM images of the PPMS derived imaging layer for metrology purposes. The results listed below were obtained from top-down SEM measurements.

We found the 248 nm dose to print equal 0.25µm line and space features in a 2000Å PPMS film on top of a 7000Å film of (HBR) was 110 mJ/cm². The exposure latitude (Figure 9) for 0.25µm ± 10 % features was 114 mJ/cm² to 119 mJ/cm² (13.6% with respect to a nominal dose of 110 mJ/cm²). Focus latitude was 0.75 µm and 0.85 µm for 0.25 µm and 0.35 µm equal L/S features, respectively (Figure 10). The linearity at the nominal dose of 110 mJ/cm² for both isolated and equal line and space features was within 5% of coded dimensions of

Table 4. Characteristics of nominally 3000Å thick PPMS films deposited at various temperatures.

Deposition Temp. (°C)	<i>n</i> (+/-0.02)	Dep. Rate (Å/s)	Density (g/cm ³)	Photo-sensitivity
200	1.82	14	1.14	low
150	1.72	22	1.10	medium
100	1.69	34	1.00	high
65	1.67	65	-	very high

0.25 µm to 1.0 µm. The iso-dense bias was less than 6% (Figure 11).

4.3 193 nm Lithography

PPMS films were evaluated for use as a negative-tone single-layer mode photoresist in 193nm light. We have found a strong correlation between the dose delivery method and the extent to which the PPMS film becomes photooxidized.

PPMS films (1000 Å) were deposited on 6 inch substrates (either bare Si or 0.7 µm of a hard baked novolac resin on Si). Exposures at 193 nm were obtained on an ISI stepper operating nominally at 400 Hz laser pulse rate with the output locked at roughly 0.89 mJ/cm²/pulse, when measured at the wafer plane. We were able to adjust the laser repetition rate to as low as 5 Hz and we also had the ability to insert a diffuser in the beam line to attenuate the output power to 1% of its nominal value.

Bulk clearing doses (E_0) were determined as that dose required to provide an etch selectivity of 3 (unexposed / exposed) when developed in a Cl_2 plasma in an Applied Materials etch chamber controlled by an optical emission end point detector.

Figure 9. Measured linewidths of a 0.25 µm L/S coded dimension as a function of dose.

Figure 10. Measured normalized linewidths as a function of GCA stepper focus offset.

Figure 11. Printed CD as a function of coded CD for equal line and space and isolated line geometries.

Figure 12. Plot of etch response of a 1000Å PPMS film as a function of 193 nm laser-dose and repetition rate.

Figure 12 shows a plot of PPMSO thickness remaining from an initial 0.1µm thick film of PPMS as a function of 193 nm UV dose delivered at three different rates. The horizontal line at $y = 666$ marks the level at which an etch selectivity of 3 is reached. At a flux of 356 mJ/cm²/s, a selectivity of 3 is reached only after 85 mJ/cm². When the UV dose is delivered at a flux of 0.45 mJ/cm²/s (*i.e.*, $\sim 1/80$) an etch selectivity of 3 is achieved at only 20 mJ/cm².

Figure 13 shows that the dose required to obtain a selectivity of 3 drops from 85 mJ/cm² to only 16 mJ/cm² when the light is attenuated by 1/100 at 400 Hz. Similarly, Figure 14 shows that at 50 Hz, the dose required for a selectivity of 3 is reduced from 50 mJ/cm² to only 15 mJ/cm² when the 193 nm beam is attenuated by 1/100.

The preceding results indicate that the contrast and the E_0 bulk clearing dose in PPMS films using our ISI 193 nm stepper are significantly improved by using a rapid pulse rate (400 Hz) and an attenuated beam (100×).

4.4 Reciprocity Failure

The conversion efficiency of the photo-induced oxidation of PPMS to PPMSO is reduced if the photon flux is delivered above some optimum rate. The photo-oxidative conversion involves the photo-induced bond

Figure 13. Plot of etch response of a 1000Å PPMS film as a function of 193 nm laser-dose delivered at a repetition rate of 400 Hz and two different beam intensities.

Figure 14. Plot of etch response of a 1000Å PPMS film as a function of 193 nm laser-dose delivered at a repetition rate of 50 Hz and two different beam intensities.

breaking of the PPMS polymer. Oxygen diffusion to the site of the broken bond is required to trap the nascent radical. The rate determining factor for the photo-oxidation of PPMS is the availability of oxygen. Because of constraints by the stepper manufacturer

Table 5. A comparison of the deposition processes for the POR film and the more reactive 100° C film.

DepTemperature	150° C	100° C
RF Power	60 Watts	95 Watts
Methylsilane Flow	100 sccm	120 sccm
Chamber Pressure	1.4 Torr	1.8 Torr
Substrate-Electrode distance	525 mil	425 mil

concerning issues related to lens damage and focus control, exposures could not be carried out in an O₂-rich environment.

Reciprocity failures observed when patterned in the negative tone are not accurately gauged since only a thin photo-oxidized PPMSO layer is needed to supply the etch resistance necessary to define an image. In the positive tone, where PPMSO is etched away using HF-based chemistries, photo-oxidation needs to occur

Figure 15. Change in refractive index with time for PPMS films prepared at 100°C in air and N₂, respectively.

Figure 16. Remaining PPMS-derived film as a function of dose after aqueous vapor-HF development.

through the full thickness of PPMS in order to selectively remove the exposed areas. Therefore positive tone PPMS processing is affected more adversely by reciprocity failures than is negative tone processing.

One method available to us to increase air diffusion into the PPMS films during 193 nm exposure is the use of films that are less dense and presumably offer less of a diffusion barrier. We knew early on that PPMS films could be deposited which were inherently more reactive than those PPMS films deposited at 150 °C. These films however, were too reactive with ambient air to be of any use to us in the initially defined feasibility project. We prepared films at 100 °C and compared them with films deposited at 150 °C. Table 5 highlights the differences between these two deposition processes. Storage of the reactive 100 °C films was accomplished by using a dessicator flushed with a rapid stream of N₂ gas. Film stability, as determined by the change in refractive index is plotted in Figure 15.

A crude vapor-HF-development method was used to assess the exposure dose required to clear an area of a patterned PPMS film in positive tone: the wafer was suspended for 5 minutes, latent-image side down, approximately 1 cm above a bath of 49% aqueous hydrofluoric acid. The remaining film thickness in the optically exposed areas was measured on a Thermawave

Figure 17. Cl₂ plasma development of negative-tone PPMS resist as a function of dose and the effects of attenuation (1/100) of the laser beam on 100 °C- and 150 °C deposited PPMS.

Figure 18. Remaining PPMS derived film thickness vs. exposure dose for HF vapor developed PPMS. The upper curve was obtained using full laser power output ($\sim 360 \mu\text{W}/\text{cm}^2/\text{pulse}$ delivered at 350 Hz) and the lower curve with the beam attenuated to 2.5% of full power.

OptiProbe 2600. The results of exposing the 100 °C PPMS films at three respective laser repetition rates are shown in Figure 16. Each data point is the average of three similarly exposed dies on each wafer.

It is evident that the films deposited at the lower temperature of 100 °C, show a reciprocity failure. Doses of 24 to 26 mJ/cm² were found to leave 400 Å of the original 1000 Å of the PPMS film when imaged with the high throughput rate of 400 Hz; but when imaged at either a 40 or 4 Hz, the remaining film thickness was 150 and 60 Å, respectively.

Similarly conducted experiments in the negative tone showed the reciprocity failure was mitigated by the use of the more reactive, 100 °C films. Figure 17 shows the normalized thickness remaining of the exposed region of a 1000 Å thick PPMS film after Cl₂ plasma etching as a function of the 193 nm dose for two types of films: the 150 °C and the 100 °C films, respectively.

It was found that increasing the exposure time for imaging PPMS films by either decreasing the laser-pulse rate or by attenuating the laser-beam intensity improved the apparent photospeed for imaging PPMS films.

In summary, the use of PPMS films that are more

Figure 19. Contrast curves obtained by the exposure of nominally 1000 Å thick 100 °C PPMS films. The intensity of the 193 nm source was 0.9 mJ/cm²/pulse measured at the wafer plane.

Figure 20. Contrast curves obtained for very photosensitive PPMS films deposited at 100, 65 and 45 °C. The 193 nm light was delivered at 36 mJ/cm²/s.

reactive toward oxidation mitigate the effect of reciprocity failure in a negative tone process but do not alleviate the problem for positive-tone PPMS processing.

4.5 Single Layer PPMS

Following aqueous HF vapor development of oxidized PPMSO films deposited at 150 °C and photo-oxidized on the SVGL Micrascan 193 scanner at MIT – Lincoln Labs, it was observed that even at high doses the PPMSO was only partially developed. Increasing the development time or the HF concentration in the FSI Excalibur process chamber did not effect further removal of the film.

Exposures were also carried out with the laser attenuated to 2.5% of its nominal value. The results of this experiment are shown in Figure 18. There is a clear increase in the efficiency of photo-oxidative exposure resulting in the removal of more material at lower doses, but at the expense of increased exposure time. In addition, a non-developable residue of ~200Å remained which we speculate to be a material that is more carbodic in nature, *i.e.* more intervening, bridged methylene groups in the polymeric backbone chain.

In addition to laser pulse power, the photo-oxidative efficiency of the exposure is also affected by the laser pulse repetition rate. In order to assess the extent of this effect in the positive tone processing of PPMS, sensitive 100 °C films were exposed on the ISI Microstepper using several combinations of laser power and repetition rate. The films were exposed at laser repetition rates of 400, 40 and 10 Hz using 900 μJ/cm² pulses. For this experiment, positive tone development was accomplished by immersion in a room temperature bath of concentrated HF for 5 minutes. The results illustrated in Figure 19 show a marked increase in contrast by reducing the laser repetition rate by one order of magnitude from 400 to 40 Hz.

In order to increase the ease with which oxygen could diffuse into PPMS films (presumably because of lower film density), depositions were carried out at temperatures of 65 and 45 °C. The photo-oxidative

efficiency of these very reactive films was compared to that of 100 °C films. The results of 40 Hz exposures (36 mJ/cm²/s) and development by immersion in 7:1 BOE are shown in Figure 20.

The very reactive 65 and 45 °C films exhibit a diminished contrast and also suffer from significant dark erosion because of the rapid oxidation that occurs in the normal handling of these films in ambient air. There appears to be no compelling reason to deposit extremely reactive films due to thermal oxidation concerns.

4.6 Bilayer PPMS

We have deposited PPMS films on various organic substrates in order to assess the imaging capabilities of positive tone lithography. Generally, PPMS was deposited on 4500Å of hard baked organic photoresists. We found that HF based development (immersion in an aqueous HF solution, or treatment in a process chamber containing gaseous HF, water and nitrogen), always left a residue which prevented the pattern transfer of the PPMS image into the underlying organic film by an oxygen plasma etch. The use of a chlorine plasma based

Table 6. The results of XPS analysis of the surface composition of PPMS after each process step.

Atomic Ratio	As deposited ⁴ (1 Hr in air)	Photo-oxidized ⁴ (100 mJ/cm ²)	Post HF Vapor development
C/Si	0.82	0.79	0.86
O/Si	0.30	0.98	0.80

descum step prior to the oxygen etch resulted in uneven breakthrough and produced a grassy residue on the patterned wafer.

Anhydrous HF diluted with nitrogen in the HF vapor chamber was ineffective at developing the latent image defined in the PPMS films. The addition of small amounts of water vapor were necessary for development to occur. However, in all cases, aqueous HF vapor development in the FSI chamber caused the PPMS films to blister or delaminate when used in a bilayer format (Figure 21A). On careful inspection of developed single layer PPMS systems, we observed many small star cracks on the surface as well (Figure 21B).

Low sensitivity 200 °C PPMS films underwent severe delamination and were not investigated any further. The highly photosensitive 100 °C PPMS films did not show any qualitative improvement over the 150 °C films. The type of blistering observed on MXP-7 organic resist (Figure 21A) was observed to some degree on all organic underlayers tested, which included Hoechst AZ1024, Shipley 1808, Microlithography Chem. Co. MXP-7. Several experimental formulations of spin-on low-K dielectric materials, PAE-2, FLARE 2.0, FPI-136, BCB and SiLK, obtained from various sources, showed similar results. With the exception of the Shipley 1808, all the above mentioned organic films were not affected when treated to the same HF vapor etch process used to develop the PPMS derived oxide.

Figure 21. Optical micrographs displaying blistering on both exposed and unexposed regions of an HF vapor developed image exposed onto a 750Å, 150 °C PPMS on 3700Å hardbaked MXP-7 resist (A), and surface cracks on an developed image from a 750Å, 150 °C PPMS film deposited over bare silicon (B).

A 100 – 300 Å thick residue that remained after HF development appeared regardless of the PPMS deposition conditions used. The residue was not removed by going to as high as 200% over etch conditions in the FSI HF vapor chamber or by immersion in concentrated HF solutions, indicating that the residue was not a simple oxide of PPMS. The results of X-ray photoelectron spectroscopy (XPS) on the PPMS derived residue was performed and the results were compared to the C/Si and O/Si ratios obtained at different prior processing steps. The results shown in Table 6, indicate that the C/Si ratio of the residue is significantly higher than in PPMS or PPMSO supporting the carbidic nature of the residue. Similarly the low O/Si ratio of the residue also points to a carbide-like film. The XPS results also indicated that there was ~ 4% fluorine in the post HF developed PPMS derived residue.

Image transfer through underlying organic resists was normally carried out using an O₂ or a CO₂ plasma etch. However, the PPMS derived residue does not etch in either O₂ or CO₂ plasma and a halogen based descum step was employed to break through the residue before subsequent pattern transfer. Both Cl₂ and C₂F₆ based etch chemistries were tested. Figure 22A shows a scanning electron micrograph (SEM) of an exposed 750 Å thick 150 °C PPMS film on silicon after development in the HF vapor etch chamber and a 20 s Cl₂ plasma descum step. Figure 22B shows the porous surface that remains after an exposure of 40 mJ/cm² on a bilayer

system comprised of 750 Å of 150 °C PPMS over 0.7µm of a low-K dielectric, PAE-2.

The porous texture of the residue shown in Figure 22 did not lend itself to uniform etching and uneven breakthrough resulted in the pattern transfer step. Figure 23 shows SEM's of patterns obtained using 1000Å thick 100 °C PPMS on 4500Å of hard-baked AZ1024 resist. They were shot at a dose of 28 mJ/cm² delivered at 40 Hz laser repetition rate. Development was carried out by immersion in 7:1 BOE for 5 minutes. A timed CO₂ etch was carried out after a 10 s Cl₂ descum step. A significant amount of grassy residue remains in the exposed areas which are due to the uneven breakthrough caused by the porous nature of the PPMS derived residue.

The positive tone processing of PPMS in either a single or a bilayer mode is hampered by the presence of a porous PPMS derived residue which causes the uneven breakthrough in subsequent pattern transfer steps. The photo-oxidation of PPMS which is highly dependent on oxygen concentration and the permeability of the PPMS film to oxygen, does not completely oxidize at the fluence of current or anticipated 193 nm exposure tools. Reactive, less dense PPMS films deposited at lower temperatures do not sufficiently compensate for the rate limiting diffusion of oxygen into the film as it is being exposed. In addition, the reactive films exhibit poor performance during HF development as demonstrated by cracking, blistering and loss of adhesion.

Figure 22. Scanning electron micrographs of the surface of positive tone HF vapor developed PPMS images on silicon substrate after a 20 s Cl₂ plasma descum step (A), and on an organic low-K dielectric film (B).

Figure 23. SEM's of 0.18 μm line and space patterns (from above at 40° (A) and in cross-section (B)) obtained using PPMS in a bilayer positive tone mode. The images were developed in aqueous 7:1 BOE and pattern transfer was accomplished using a CO_2 plasma etch after a Cl_2 descum stem to break through the PPMS derived residue.

5 Conclusions

5.1 Deposition

The two desirable attributes of PPMS films, low rate of thermal air-oxidation and a high rate of photo-oxidation, were found to be coupled and diametrically opposed. A deposition process which afforded a useful level of photosensitivity and etch selectivity, resulted in films with poor air stability. Films deposited at 150 °C were found to benefit from sitting between 30 and 60 minutes in air before either storage in N_2 or processing was begun. The refractive index of these films should be in the range of 1.65 – 1.70 at the time of exposure. Films treated in this way exhibited a clearing dose at 193 nm of 5 – 10 mJ/cm^2 and an etch selectivity of 3.

5.2 Exposure

The results indicate that the contrast and the bulk clearing dose, E_0 , required to achieve an etch selectivity of 3 are greatly improved by using a rapid pulse rate of 400 Hz and an attenuated beam (1/100) on the ISI 193-nm stepper. At a high laser power of 0.9 $\text{mJ}/\text{cm}^2/\text{pulse}$, films exposed at 400 Hz required over 4 times the clearing dose to effect the same Cl_2 -plasma etch selectivity as a PPMS film exposed at 50 Hz. It was evident that the most efficient way to convert PPMS to PPMSO was to deliver the photons slowly by either by attenuating the laser fluence or by reducing the laser-pulse repetition rate. Either of these actions reduces the throughput in the exposure tool.

5.3 Positive-tone Processing

Processing positive-tone PPMS in either a single or a bilayer system was hampered by the presence of a porous PPMS-derived residue that caused an uneven breakthrough in subsequent pattern-transfer steps. The photo-oxidation of PPMS, which is highly dependent on oxygen concentration and the permeability of the PPMS film to oxygen, does not completely oxidize at the fluence of current or anticipated 193 nm exposure tools. Reactive, less-dense PPMS films deposited at lower temperatures do not compensate sufficiently for the rate-limiting diffusion of oxygen into the film during optical exposure. Additionally, more-reactive films exhibit poor performance during HF development as

demonstrated by cracking, blistering, and loss of adhesion.

5.4 Negative-tone Processing

PPMS films deposited for us in negative tone Cl_2 based plasma development do not suffer from the same processing concerns as in positive-tone processing since only a PPMSO film, sufficient in thickness to provide etch resistance for pattern definition. PPMS film speed can be adjusted over a wide range based upon the deposition temperature of the PPMS film and its post-deposition and post-exposure handling.

6 Acknowledgements

We thank SEMATECH and in particular, Gerald Smolinsky, for their support in this project. We also thank Anthony Forte and Scott Doran of MIT/Lincoln Labs for their help with experiments carried out at the Massachusetts facility.

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