All Dry Lithography: Applications of Plasma Polymerized Methylsilane as a Single Layer Resist and Silicon Dioxide Precursor

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Introduction

Silicon dioxide is the primary dielectric fabric of silicon integrated circuits, and the need to pattern it accounts for a large percentage of all photolithographic operations.¹ Sub half-micron device processing schemes find yet additional applications for patterned oxide as "hard masks".² For example, critical level polysilicon gate structures may be etched with greater selectivity and linewidth control through an intermediate thin oxide layer, which is deposited over the gate stack and patterned using organic photoresists. A new direct approach for patterning thin oxide layers with sub-0.25 μm resolution could provide a valuable alternative, as well as an important new approach to integrated micro-optical elements and dielectric device features.

We have previously described the use of a new deep UV resist material, plasma polymerized methylsilane (PPMS), which is deposited from a low power RF plasma discharge in Methylsilane at room temperature.³ This material possesses an amorphous organosilicon hydride network structure illustrated in Figure 1. While initially opaque in the deep UV (i.e. 248 nm), a typical 0.25 micron thick film undergoes efficient photo-oxidation with bleaching to form glasslike siloxane network material. Patterns may be developed using chlorine plasma etching to give negative tone patterns, or by wet HF based development to give positive tone patterns, in both cases with sub-0.25 micron resolution.⁴ In previous papers we have demonstrated the use of thin PPMS imaging layers over both plasma deposited or spun-on organic underlayers to provide a general bilevel process.^{3,4,5} Using 248 nm exposure tools, such schemes afford sub-0.25 μm design rule capabilities over difficult device topography. Here we describe the discovery and development of a fundamentally different application unique to PPMS: a new direct approach to patterned silicon dioxide.

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Figure 1. Basic chemistry of the deposition and patterning of plasma polymerized methylsilane PPMS.

Figure 2. Basic PPMS negative tone bilevel process used to measure general lithographic performance. Full details including experiments over device topography have been described elsewhere.

Figure 3. Measured linewidth vs. exposure dose for coded 0.25, 0.35, and 0.50 micron equal l/s patterns printed using the negative tone PPMS bilevel process as previously described elsewhere.⁵

Figure 4. Equal 0.20 micron L/S patterns printed using our standard negative tone bilevel process with a 1800 Å thick PPMS imaging layer over 7000 Å of hard baked novolak resin. Exposure dose was 85 mJ/cm².

Materials and Methods

Plasma polymerized methylsilane (PPMS) resist films employed in this work were deposited using a PlasmaTherm SL-700 parallel plate deposition-etch system containing an 11" D showerhead. Wafers were centered on a removable aluminum substrate platen which is shuttled between a vacuum loadlock position and the deposition chamber. Methylsilane (99.9 % purity, Voltaix) was delivered at a flow rate of 50 sccm, and the deposition pressure was controlled at either 200, 300, or 400 mTorr (± 20 mTorr) with a net RF power between 10 and 20 W at 13.56 MHz. The exact selection of deposition parameters within this range can be used to fine tune the photo-sensitivity, but was found to have little effect on the conversion of patterned films to oxide. All deep UV exposures were performed on a GCA XLS 248 nm deep UV stepper in air. When wafers were stored for more than an hour between deposition and development, they were transferred to a nitrogen purged box. Chlorine plasma development was performed using a high density plasma etch platform incorporating either a helical resonator or Helicon high density plasma source operating at 13.56 MHz. Typical source power was 2500 W with 25 W applied to the wafer chuck. Chlorine pressure and flow rates were 2 mTorr and 80 sccm, respectively, and etch time to endpoint (the removal of all material in unexposed areas) was ca. 30 seconds for a 0.25 micron thick film.

Wafer processing tools ordinarily used for the dry oxygen plasma stripping of organic photoresists offer a particularly convenient method for converting PPMSO films to low density oxide. A GaSonics ® Aura Model 1000 was used to convert photo-oxidatively patterned and developed (or simply blanket exposed) PPMS films to oxide using a standard 90 second process cycle used to strip tough, hard-baked resist layers. Wafers are processed (one at a time) immediately downstream of a 1000 W RF plasma discharge in 2.2 Torr of oxygen, while simultaneously being heated to ca. 220 °C by quartz IR lamps. Changes in film composition were determined by RBS and XPS (using depth profiling), and thickness and refractive index changes were measured using ellipsometry, profilometry, or with a Nanometrics system.

Results and Discussion

The similarity in composition and structure between PPMSO and SiO₂, together with the established reactivity of Si-Me and Si-H moieties with oxygen suggest that the conversion shown in Figure 2 should occur with minimal shrinkage. However, since the conversion consumes oxygen and liberates water and carbon dioxide, efficient mass transfer (i.e.

gaseous diffusion) must occur throughout the thickness of the film being converted. Such diffusion was found to be sufficient to allow complete oxidation of films up to 2500 Å thick using a single pass through a standard oxygen plasma organic resist stripping module. XPS depth profile results (using argon ion sputtering) indicated the elimination of carbon, and an increase in O:Si ratios to between 2.05 and 2.20 (see Figure 6). Refractive indices measured on 1000 Å thick films following the carbon stripping process fall to between 1.42 and 1.43. Subsequent annealing over 400 °C results in water desorption and consolidation to material with a O:Si ratio of $2.00 \pm .05$. Thicker films require increasingly aggressive conditions and/or retain a substantial amount of carbon near the silicon interface. It is informative to compare the carbon stripping process used to convert films to oxide with that used to transfer PPMSO patterns anisotropically through an organic material with oxygen.^{3,4,5} Working at low (2 mTorr) pressure with a high density plasma etcher, complete oxidation is limited to the film surface, with underlying material retaining a 0.6 -0.7 C:Si ratio.

Figure 7 indicates the changes in film thickness occurring in the conversion of blanket photo-oxidized PPMS films to oxide. As might be predicted from the basic chemical transformations involved, the up to 15% expansion on photo-oxidation is nearly balanced by the contraction during carbon stripping and annealing. The factor most important in determining the thickness of oxide resulting from a patterned film is the selectivity achieved during the chlorine plasma development step. The low pressure, high density plasma etch systems used in most of our work reproducibly gave selectivities of ca. 3 for unexposed vs. exposed regions. These conditions provide large process latitudes with excellent linewidth control for bilevel and some single level processes. However, applications involving the use of PPMS as a photodefinable dielectric (or whenever film thickness is as important as linewidth) may be more readily accomplished using more conventional plasma etching tools. For example, the selectivity obtained for Chlorine plasma development at 20 mTorr, 100 sccm, and 200 W RF using a PlasmaTherm SL-700 system was typically 10 or greater for a 248 nm exposure dose of 50 mJ/cm² using a 0.25 µm thick film of PPMS.

PPMS derived oxide films on highly doped silicon were coated with aluminum to produce thin film capacitor structures which were used in preliminary measurements of dielectric properties. Dielectric constants on freshly annealed samples ranged between 2.8 and 3.0, but were found to show modest increases of up to 0.2 when exposed to ambient humidity. This behavior is typical of low density oxides prepared by other methods and does not necessarily preclude its use as a dielectric layer, so long as subsequent encapsulation prevents moisture uptake. PPMS derived oxide films were also investigated using thermally programmed desorption spectroscopy employing mass spectroscopic identification of

Figure 5. Changes in surface composition by XPS after each process step.(expressed as C:Si or O:Si atomic ratio). Depth profile analysis using argon ion sputtering of 2000 Å thick films after step D indicated a relatively uniform composition with complete removal of carbon.

Figure 6. Changes in film thickness during the conversion of thin PPMS films to oxide.

Figure 7. Changes in refractive index during the stepwise conversion of PPMS to silicon dioxide.

evolved gases. Following the GaSonics process, the only significant peaks detected were those for water at $m/e = 18$ and 17 , with the onset of desorption appearing at around 200°C and largely complete after a few minutes at 400°C . However, such consolidation was still not complete, and refractive indices typical of fused silica ($1.45 - 1.46$) were obtained only after heating over 1000°C in a wafer tube furnace.

Additional studies employing thinner films provided a preliminary assessment of dielectric strength and breakdown behavior, as well as an indication of pinhole defect density. For example, an array of aluminum contact pads covering ca. one half the area of a 5" Si wafer were patterned over a $916 \text{ \AA}$ thick PPMS derived oxide layer. Current vs. voltage measurements were performed to obtain values for the breakdown voltage. Only one device fell more than two standard deviations below the mean, and the average dielectric strength (calculated for values of V measured just below the onset of exponential C-V behavior) was over $5.0 \times 10^6 \text{ V/cm}$, typical of a conventional plasma oxide.

In order to demonstrate the utility of PPMSO derived oxide layers as hard masks, $2000 \text{ \AA}$ thick PPMS films were deposited and patterned over two bare silicon wafers. After conversion to oxide using the GaSonics module, one wafer was annealed at 450°C and both patterns were etched into the substrate with Chlorine plasma. As illustrated by the SEM photos of $0.25 \mu\text{m}$ L/S features in Figure 9, mask erosion and tapered profiles are evident on the first wafer, but after the anneal step etch selectivity was similar to that obtained using a PECVD oxide hard mask. A more practical demonstration involved the patterning of a $3000 \text{ \AA}$ TiN/polysilicon gate stack. After conversion of PPMSO to oxide, the TiN/polysilicon stack was etched using a recipe developed for use with a standard PECVD deposited oxide "hard mask" (normally patterned using a chemically amplified deep UV resist formulation).⁶ PPMS films were photo-oxidatively patterned with 45 mJ/cm^2 of 248 nm light, dry developed, and converted to oxide using the process described above and illustrated in Figure 8. This left behind a $900 \text{ \AA}$ thick oxide layer. Pattern transfer directly into the gate stack (even without an anneal step) provided well resolved 0.25 L/S features, albeit with some mask erosion and tapered profiles. This is just one application in which all dry PPMS based processing can be accomplished in fewer steps employing standard wafer processing tools but with this fundamentally different resist process.

Conclusion

The use of plasma polymerized methylsilane as a photodefinable oxide precursor offers a step-saving alternative to current procedures for the deposition and photolithographic patterning of oxide hard masks. Thin conformal films are deposited, patterned and developed in an entirely dry process which can be readily integrated in vacuum cluster

Figure 8. Comparison of conventional vs. new all dry PPMS based approach to thin patterned oxide.

Figure 9. SEM of nominally 0.25 μ m L/S etched into a silicon wafer using an all dry PPMS derived hard mask process without (a) and with (b) a 450 °C anneal step between the conversion of patterned PPMS to oxide and chlorine plasma pattern transfer into the silicon.

Figure 10. SEM of 0.25 μ m L/S pattern etched into a 3000 Å TiN/Polysilicon gate stack using an all dry PPMS derived hard mask process. Approximately 200 Å of PPMS derived oxide remains of the initially 2000 Å thick PPMS layer.

processing tools. The complete conversion of patterned films to SiO₂ was established by a variety of techniques, and its dielectric constant and breakdown behavior was demonstrated by the fabrication of thin film capacitor test devices. Recent and ongoing studies have demonstrated the direct extension of both positive and negative tone single and bilevel PPMS based process to use with 193 nm exposure tools. At both wavelengths, PPMS process schemes can provide a step saving, high resolution approach to thin oxide layers.

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