This paper describes discrete metal compounds that are soluble in commonly known ester and alcohol organic solvents such as PGMEA and PGME. These metal-containing compositions (RX4) can form homogeneous films in varying film thickness in the range of nanometers to micrometers with excellent film thickness uniformity of less than 300 Å. RX4 films are photosensitive and can form negative tone patterns under multiple exposure conditions. RX4 films demonstrate tunable optical and electrical properties. Furthermore, such films act as useful patternable hard mask due to their excellent etch selectivity against organic layers and silicon oxide. High density of RX4 films renders them exceptionally resistant to high power ion beams in applications involving ion implantation.

Keywords: refractive index, dielectric, etch selectivity, ion implantation

1. Introduction

Use of metal-containing, film-forming materials and their applications is well known. Most of conventional methods of generating patterned metal-containing films involve pattern transfer via multiple layers of photoresist, metal-based hardmask and organic layers. Formation of fine patterns into metal-containing layers is achieved by multiple steps of imaging of photoresist and multiple steps of pattern transfer via etching into hardmask to organic antireflective layer to substrate. Metal-based hardmasks can be deposited by CVD or sputtering processes which are cumbersome and expensive but also are limited in their capability to print patterns with high resolution.

A more pragmatic approach is spin-on metals or metal oxides of interest are commonly generated by a sol-gel process, where the precursor solution is applied by spin-coating and heated to high temperatures [1,2]. The sol-gel process is terminated with ligands to provide metal oxide nanoparticles [3,4]. Solubility in limited range of solvents and long-term stability restricts commercial viability of this approach.

Photosensitive metal complexes can be used for patterning as such complexes undergo a low-temperature reaction in the presence of light of particular wavelength [5-7]. When exposed through a mask, the unexposed portion of the film can be dissolved in a suitable developer. One issue of utilizing such metal complexes is that their low native absorption to UV light, requiring high amounts of exposure dose.

This paper describes discrete photosensitive metal-containing compounds in compositions (RX4) that can be spin-coated and reworked like a typical organic photoresist material. High resolution patterns can be achieved under multiple exposure conditions. RX4 films demonstrate tunable optical and electrical properties. Furthermore, such films act as useful patternable hard mask due to their excellent etch selectivity against organic layers and silicon oxide. High density of these RX4 films renders them exceptionally resistant to high power ion beams in applications involving ion implantation.

2. Experimental

2.1. Materials and Processing

All materials were commercially obtained from Sigma Aldrich. RX4 compositions were prepared in industry-accepted initiators and organic solvents in concentrations from 3 to 45 wt%.

RX4 films were prepared using industry-standard equipment such as spin coaters, hotplates and mask aligners. Bulk films of RX4 were flood
exposed or baked. High temperature bake was performed in furnace. Conditions are described in the results section.

2.2 Analysis

Etching of RX4 films was performed in an Oxford Plasmalab 100 ICP Etcher. Implantation was performed with a Varian 350D Ion Implanter. E-beam exposure performed on Raith e-Beam writer using 10 keV and a dose of 0.22 pC. Conditions are described in the results section.

2.3. Characterization

Refractive index at 633 nm was measured using Metricon Gadolinium Garnet Prism Coupler. Refractive index over multiple wavelengths and Reflectance measured with n&k Analyzer. Dielectric constant was measured using a 4Dimensions Mercury Probe CVmap instrument. EDX analysis was performed with Oxford 6587 Microanalysis X-Ray Detector.

3. Results and Discussion

3.1. Film-forming Properties

RX4 compositions of this study were prepared in combination of PGMEA and PGME as solvents. Film thickness vs. spin speed in Fig. 1 shows RX4 compositions form resist-like coating after spin-coating and post application bake (PAB) of 120°C for 120 s. Transparent RX4 films of thicknesses ranging from 30 nm to 2.5 μm have been formed. RX4 composition was spin-coated, baked at 120°C for 120 s and i-line exposed to form a 1.7 μm thick film. The film was defect-free as confirmed by KLA Surfscan data in Table 1. Surface defect count of less than 0.3/cm² indicates no aggregation of particles as is commonly observed in films containing nanoparticles. Lack of surface aggregation of particles was also confirmed by surface scanning electron micrograph (SEM) as shown in Fig. 2.

3.1.1. Filling and Planarization Properties

Data in Fig. 3 was generated by coating a 2.8 μm RX4 film over trenches that are etched 0.9 μm into silicon oxide layer (PAB of RX4 film 130°C/120 s, i-line exposure). The cross-sectional SEM picture show excellent filling properties of the RX4 film as confirmed by lack of any voids. The average film thickness variation across 300 mm wafer is less than 300Å suggesting good cross-wafer uniformity.

![Fig. 1. Film thickness variation of RX4 Composition spin-coated at typical spin speeds and post-application baked at 120°C for 120 s.](image1)

Table 1. Surfscan particle analysis of RX4 film (1.7 μm thickness, i-line exposed).

| Particle Size, μm | 0.3 | 0.2 |
|-------------------|-----|-----|
| Particle Count/cm² | 0.22 | 0.26 |

![Fig. 2. Scanning electron micrograph (SEM) of RX4 film surface (1.7μm thickness, i-line exposed).](image2)

![Fig. 3. Cross-section SEM of RX4 film as planarizing layer on silicon oxide trenches (RX4 PAB 130°C/120 s, i-line exposed).](image3)
3.1.2. Etch Properties

RX4 films were evaluated for dry etch pattern transfer capabilities. Figure 4 shows etch selectivity of RX4 film compared to other materials in typical pattern transfer RIE processes. In Figure 4 (a) a RX4 film was spin-coated on silicon oxide with a film thickness of 380 nm. After PAB at 110°C for 120 s, a film thickness of 200 nm was achieved. The RX4 film was then exposed with a negative tone trench mask using a Suss MA6 mask aligner and a trench pattern was developed using PGME. When the pattern was transferred using C₄F₈ in ICP conditions the etch resistance RX4 film is four times more than silicon oxide (etching conditions C₄F₈ 45 sccm, O₂ 5 sccm, 10 mTorr, RF 29 W, ICP 3500 W, 3 min). The etch resistance of the RX4 film is increased even further when baked at 250°C for 5 minutes (Film thickness 95 nm).

Good etch selectivity of RX4 has a useful application as a hard mask for effectively transferring patterns into semiconducting substrates. One example is use of RX4 film as a hardmask in a trilayer process. In this scheme, the bottom most layer was an organic layer of film thickness 130 nm coated on silicon oxide with film thickness of 200 nm. A RX4 hardmask composition was coated on top of organic layer. After baking at 225°C for 120 s, a film thickness of 30 nm was achieved. Finally, the topmost layer was a patterned styrenic-DUV photoresist (Film thickness 75 nm).

As shown in Fig. 4 (b), CHF₃ etching conditions provide etch selectivity of RX4 film for pattern transfer (etching conditions CHF₃ 45 sccm, O₂ 5 sccm, 40 mTorr, RF 150 W, 3 min).

Next in Fig. 4 (c) organic layer is etched selectively with O₂ plasma as well as removing any remaining photoresist (etching conditions O₂ 10 sccm, 10 mTorr, RF 50 W, 20 min).

The third step involves pattern transfer to silicon oxide layer by ICP etch in C₄F₈ (etching conditions same as above). Simulation in Fig. 5 indicates RX4 film thickness should be between 25-45 nm to keep reflection control. SEM image in Fig. 6 shows patterns can be transferred to silicon oxide even when RX4 film is 30 nm thick.

![Fig. 4. Etch rate measurements: (a) C₄F₈ ICP etch rates of silicon oxide (380 nm thickness) and RX4 film (PAB 110°C /120 s, broadband exposed, 200 nm thickness) before and after a 250°C/ 5 minute bake (95 nm thickness); (b) CHF₃ RIE etch rates of styrenic-DUV photoresist (75 nm thickness) and RX4 film hardmask (bake 225°C /5 min, 30 nm thickness); (c) O₂ plasma etch rates of RX4 film hardmask, styrenic-DUV photoresist and organic layer (130 nm thickness).](image)

![Fig. 5. Reflection simulation for RX4 film as hard mask (Thickness Layer 2) with organic layer (130 nm thickness) and Styrenic-DUV photoresist (85-105 nm thickness range).](image)
Good etch selectivity of RX4 film can be explained by the metal content as well as higher film density in comparison to an organic film. Data in Table 2 show that the film density of RX4 film after soft bake is twice as much as PMMA film.

### Table 2. Film density of RX4 film before and after high temperature bake compared to PMMA film.

| Material | Processing conditions | Film Density (g/cm³) |
|----------|-----------------------|---------------------|
| RX4 PAB 120 C/120 s | 2.01 |
| RX4 PAB 120 C/120 s & 300 C/ 20 min. | 2.61 |
| PMMA PAB 120 C/120 s | 1.16 |

### 3.1.3. Ion Masking Properties

Data in Table 3 shows ion masking properties of RX4 film under two different conditions. The RX4 film was intact after standard doping conditions with $^{31}\text{P}^+$ as well as after implanting $^{27}\text{Al}^+$ at 650°C. After implantation, the RX4 film was removed with buffered oxide etch to expose the substrate underneath. Masking efficiency of the film was determined by EDX probing the now unmasked substrate. Absence of doped ions confirms ion masking power of RX4 film. Good ion stopping power of RX4 films is also attributed to high density of the film.

### Table 3. Ion implant conditions and EDX analysis after RX4 film removal.

| RX4 Film Thickness | Ion | Implant Dose (ions/cm²) | Implant Energy (keV)* | Implant Current (mA) | Stage Temp. (°C) | Substrate Analysis by EDX |
|--------------------|-----|------------------------|-----------------------|----------------------|------------------|---------------------------|
| 440 nm $^{31}\text{P}$ | 5.00 x 10¹⁵ | 190 | 150 | No heat | P Ion Undetectable |
| 580 nm $^{27}\text{Al}$ | 5.00 x 10¹⁶ | 150 | 250 | 650 | Al Ion Undetectable |

*Singly ionized, Tilt Angle 7 degrees

### 3.2. Lithographic Properties

RX4 compositions can be combined with a wide variety of photo initiators for patterning under different exposure conditions from Broadband to DUV to E-beam. Negative tone patterns are formed, where unexposed area is developed using commonly used solvent-based developers like PGMEA and PGME. In one example, RX4 film was prepared by baking at 90°C for 120 s to form a 150 nm thick film. This RX4 film was exposed by a Raith E-beam writer at 10 keV at exposure dose 0.22 pC. Figure 7 shows 500 nm posts at dense and 1:1 pitch after development with PGME.

### Table 4. Refractive index of RX4 film at increasing bake temperatures.

| Temp (°C) | Time (min) | n at 633nm |
|-----------|------------|------------|
| 120       | 2          | 1.55       |
| 250       | 20         | 1.59       |
| 300       | 10         | 1.75       |
| 400       | 10         | 1.88       |
| 600       | 10         | 1.94       |
Table 5. Refractive index and absorbance of RX4 film at different wavelengths.

| λ (nm) | 120°C 2 min | 250°C 20 min |
|--------|-------------|--------------|
|        | n | k | n | k  |
| 193    | 1.73 | 0.02 | 1.68 | 0.015 |
| 248    | 1.6  | 0.002 | 1.63 | 0.002 |
| 365    | 1.55 | 0.003 | 1.59 | 0 |

Tunable refractive index of RX4 films can be exploited for the control of light reflective properties. Figure 8 shows examples of reflectance decreasing with increasing temperature. RX4 films also shows excellent antireflective properties in the visible region compared to other substrates such as SiN as shown in Fig. 9.

![Fig. 8. Reflectance of RX4 film at increasing bake temperatures.](image)

Fig. 8. Reflectance of RX4 film compared to SiN and Bare Si.

RX4 films are transparent even after baking at high temperature. Table 5 shows k values at different wavelengths. Figure 10 shows that transparency of the RX4 film on quartz does not change in the visible range after baking at 350°C.

![Fig. 10. Transmittance of RX4 film on quartz before and after high temperature bake at 350°C for 10 minutes.](image)

3.4. Electrical properties

RX4 films display high dielectric properties that can be tuned as well. Table 6 shows the dielectric constant values for RX4 film which was broadband exposed with Suss MA6 mask aligner and baked at three temperatures. The dielectric constant increases dramatically with high bake temperature, as film acquires more of chemical characteristics typical of metal oxide.

Table 6. Dielectric constant of RX4 film at increasing bake temperatures.

| Temp (°C) | Time (min) | Dielectric at 10kHz series | Dielectric at 10kHz parallel |
|-----------|------------|----------------------------|-----------------------------|
| 120       | 2          | 6.37                       | 6.42                        |
| 250       | 20         | 12.31                      | 12.28                       |
| 600       | 10         | 42.47                      | 32.37                       |

The leakage current of RX4 film is low. Figure 11 shows that leakage current for RX4 film baked at 250°C for 30 minutes is less than 10⁻⁶ over negative and positive voltage range.

![Fig. 11. Leakage current at both negative and positive voltage of RX4 film baked at 250°C/ 30 minutes.](image)
4. Conclusion

A metal-containing film with broad range of applications is demonstrated. Such films can be patterned under different exposure conditions. Optical properties of these films can be utilized in applications for light management due to their effective antireflective coatings with tunable refractive index. High film density and variable metal content imparts excellent etch selectivity against organic and inorganic films of interest in pattern transfer into semiconducting substrates. These films show excellent ion-stopping powers under extreme conditions of ion implantation.

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