Photosensitive Titania Polymers

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A metal containing negative working photoresist is derived from crosslinkable organotitanium polymer which upon exposure to an oxygen plasma or baking in air, is converted to titanium dioxide (titania) or to a mixed, titanium-organic containing metal oxide. The metal oxide formed *in situ* imparts etch resistance, depending on the post applied bake process, to a bilayer lithographic process. The composition may also be directly deposited and patterned into permanent metal oxide device feature by a photolithographic process, or can be applied as dielectric bottom antireflective coating.

Keywords: organotitanium, negative tone, photodefinable

1. Introduction

Semiconductor devices such as integrated circuits, solid state sensors and flat panel displays are produced by microlithographic processes in which a photoresist is used to form a desired feature pattern on a device substrate. Light is passed through a patterned mask onto the photoresist layer which has been coated onto the device substrate. The resulting pattern serves as a mask for selectively modifying those regions that are not protected by the pattern. These modifications may include, ion implantation, etching, or deposition of a dissimilar material.

Plasma etching processes are being used increasingly to transfer photoresist patterns into device substrates or underlying layers. If the photoresist is removed by the etching process before the underlying layer has been fully etched, then the feature size will begin to increase as the etching process proceeds since the photoresist is no longer protecting the area of the substrate which it once covered. Over etching is disadvantageous because of the precision required in pattern transfer.

Plasma etching processes for organic layers such as color filters used in solid state color sensors and flat panel displays require photoresist materials with exceptional resistance to oxygen plasma etching. Conventional photoresist cannot be used effectively since they are primarily mixtures of organic

compounds and resins which are etched more rapidly than the color layers.

Many products have been developed to provide greater etch selectivity when patterning organic layers by oxygen plasma etching. These include organic-inorganic hybrids [1], surface silylation [2], nanoparticle loaded photoresist [3], and others [4]. During the process, the silicon components in the photoresist are rapidly converted to silicon dioxide which resists further etching. The *in-situ* formed silicon dioxide layer then becomes the mask for etching the underlying organic layer.

Although oxygen is normally the principal plasma etchant for organic layers, it may be admixed with various fluorinated gases such as NF_3 , C_2F_6 , HCF_3 , and CF_4 to aid in the removal of inorganic residues arising from metallic species. The inorganic residues are often present, for example, in color filter layers. Since, silicon dioxide is readily etched by fluorine-containing plasma etchants, silicon-containing photoresists cannot be used effectively in plasma etching processes where fluorine-containing gases are present.

In some applications, it might be desirable to leave the plasma etch resistant photoresist in place as permanent component of device structure. In display applications, this layer must have optical clarity. Silicon containing photoresists often

exhibit poor optical clarity after plasma etching or high temperature thermal treatments which are usually applied to color filter layers. Other applications of interest for metal containing photoresist are ferroelectric materials, and high dielectric constant layers. Current technology for depositing the latter two applications required chemical vapor deposition, patterning and calcination processes to obtain complex metal oxides.

In this paper we describe a novel photosensitive titania polymer with good plasma etch resistance to oxygen or fluorinated gases, convertible to metal oxide with adjustable optical properties controlled by precursor composition and process. The described photoresist composition is also easily integrated into modern microlithographic processing schemes.

2. Method

2.1 Polymer synthesis

n-Butyltitane (BT) was purchased from Geleste and used as received. BT can be reacted with a number of β -diketones, β -ketoesters, α -carboxylic acids, acid salts or esters containing acrylate functionalities. In the example provided, BT was reacted with 2-(methacryloyloxy)ethyl acetoacetate (MEAA) purchased from Aldrich (Scheme 1). In a flask under N_2 atmosphere, 20 grams of BT were mixed with 44.8 grams of MEAA. The mixture was stirred at ambient temperature for 2 minutes until a semisolid formed. The flask was then heated to 70 °C for 12 hours. The residual n-butanol can be distilled from the reaction mixture or left in the polymer resin.

2.2 Photoresist formulation

Above Ti-MEAA complex (26 grams) was formulated into a negative working photoresist with

an i-line sensitive free radical initiator to induce photocrosslinking isopropyl thioxanthone (ITX, 1%), a synergist 2-octyl-p-dimethylamino benzoate (ODAB, 3%), and propylene glycol methyl ether (PGME) solvent (71%). The solution was stirred at room temperature for 1 hour and passed through a 0.2 μm endpoint filter.

2.3 Processing

Silicon substrates were coated with formulated resist at 3000 rpm/1 min, and post applied bake at 120 °C/1 min. The coated film was exposed using a broadband UV source (100-300 mJ/cm²), developed with 0.237N TMAH, rinsed with DI water and spun dried. Photolithography, in a bilayer mode, was evaluated using a polyester underlayer on silicon. Plasma etch was carried out in O_2 and O_2/CF_4 90/10 at 400-600 Torr and 100-150 Watts at various film post applied bake temperatures.

3. Results and Discussion

3.1 Polymer stability.

Accelerated aging studies were evaluated by measuring solution kinematic viscosity and FT-IR at 50 °C over a period of several days. Table 1 shows that the photoresist formulation remains stable with only a slight decrease in viscosity after 38 days. Normally, side reactions, crosslinking, or water hydrolysis causes metal containing complexes of this type to gel over short time resulting in a drastic increase in viscosity. FT-IR of the Ti-MEAA complex over time showed no change in carbonyl absorption bands. A change in this band would indicate a thermally induced decomposition mechanism. This phenomena was observed with other less sterically hindered ligands.

Polymer solution stability was dependant on the solvent used. For example, non coordinating solvents, such as PGMEA, provide better stability

Scheme 1. Synthesis of photosensitive titania polymer.

than coordinating solvents such as ethyl lactate or PGME.

Table 1. Solution stability of titania photoresist at 50 °C.

Days	Viscosity (cst)
0	19.6
14	18.2
38	17

3.2 Photolithography

We evaluated the patterning properties of the organotitanium polymers under broadband and i-line (365 nm) exposure.

A broadband source was used to demonstrate a lithographic bilayer process using the Ti-MEAA complex. The photosensitive titania resist and polyester underlayer were coated on silicon as shown in Figure 2a. After exposure and alkaline development, the resist was removed from the unexposed areas (Figure 2b). The resist image served as a hard mask during the subsequent O₂ plasma etch of the underlayer (Figure 2c). The mask pattern shown in Figure 2c shows resolution slightly less than 2 microns. After underlayer etch, the plasma gas was changed to CF₄ to etch the Si substrate down to a depth of ~260 nm. This last etch process was allowed to run until the titania oxide layer was removed from the polyester underlayer. A final O₂ plasma etch step removed the underlayer leaving the etched silicon substrate behind (Figure 2d).

Titania resist – 85 nm
Underlayer – 225 nm
Silicon

(a) Bilayer resist stack.

(b) After resist exposure and development.

(c) After underlayer O₂ plasma etch.

(d) After silicon etch and resist removal.

Figure 2. Bilayer process using Ti-MEAA photoresist.

Interestingly, while small features could be patterned sharply and clearly, large features (>1 μm) had distorted edges and show some residue in the open areas. This problem was linked to the thermal properties of the polymer. The polymer seemed too soft (tacky) at low post-applied and post-exposure bake temperatures. At these temperatures, diffusive and flow effects were magnified in larger structures, leading to the observed distortion and residue problems. These were minimized in sub-micron structures.

Sub-micron patterns can be obtained when using i-line lithography. The sensitivity-contrast curve obtained for i-line exposure (6300C DSW, NA 0.42, σ 0.50) is shown in Figure 3.

Figure 3. Sensitivity contrast curve for titania resist under i-line exposure (90 °C soft-bake/no PEB).

The curve indicates that the resist had respectable sensitivity judging from its D50 [5] value of 60-70 mJ/cm². The contrast value was less than acceptable (<1), but it could be increased to a value of about 1 by applying a post-exposure bake at 100-110 °C (60 sec) prior to development.

In order to overcome the above problem, other more thermally stable (glassy) titania polymers were prepared as potential positive working resists. Exposure followed by development in aqueous TMAH produced clean submicron features in both normal and reverse image modes (Figure 4). A sensitivity-contrast curve obtained for one positive working composition is shown in Figure 5.

Figure 4. SEM photos of negative tone titania resist. 0.47 μm isolated and 1:1 dense lines.

Figure 5. Sensitivity-contrast curve for positive working titania resist under i-line exposure.

The dosage threshold for image formation was very high ($>1000 \text{ mJ/cm}^2$), but it may still be practical for some applications. Contrast was about 1.25, which is modest for a positive resist. Nevertheless, submicron features could be generated reproducibly with the materials because of the thin resist thickness ($<150 \text{ nm}$).

3.3 Bake and Etch studies

Film thickness and etch resistance were correlated to the post applied bake process. Table 2 summarizes the results.

Table 2. Variations of photoresist etching resistance with baking conditions.

Bake process	Film thickness ($\text{\AA}$)	Etch gas	Etch time (min)	Film lost during etch (%)
120 °C hotplate 2min	1531	O_2	5	2.6
"	1495	O_2/CF_4	2	21.7
"	1495	O_2/CF_4	4	100
175 °C hotplate 5min	983	O_2	5	8.6
"	983	O_2/CF_4	2	24.0
"	983	O_2/CF_4	4	62.2

Increasing bake temperature decreases the film thickness. As expected, this phenomenon is attributed to the outgassing of carbonaceous components and formation of a more dense titania oxide film. A thinner film however, does not increase etch resistance to O_2 . We suspect that during the etch process in O_2 , an oxide layer is quickly formed which prevents further film loss.

In O_2/CF_4 , the opposite phenomena is observed. As film thickness is reduced by high temperature bake, resistance to etch increases. It appears that the loss of organic components in the titania resist makes the film less susceptible to CF_4 plasma.

3.4 Other application: Bottom antireflective coating (BARC)

The complexation of titanate polymers with other light absorbing non-acrylic organic molecules produces films with interesting optical properties. For example, when the starting BT is complexed with an i-line absorbing chromophore a wet developable film with antireflective properties is produced. Figure 6 shows performance of PFi34A8 commercially available photoresist on the titanate bottom antireflective coating composition.

Figure 6. PFi34A8 i-line photoresist on a titanate BARC composition. 0.40 μm lines and spaces.

The BARC composition is applied, baked and coated with the photoresist. After exposure, the BARC is removed during the same step as photoresist development.

4.0 Conclusions

A versatile photosensitive titania polymer has been described. The titania photoresist has good solution stability, and excellent etch resistance to plasma O₂ and O₂/CF₄ plasma etch. The use of this novel photosensitive polymer system in a bilayer process, broadband, and negative and positive tone i-line lithography was demonstrated. In addition, this polymer system can be applied as wet developable BARC. Studies are on-going to further explore the resolution limits and applications of photosensitive titania polymers in various microlithographic processes.

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5. D50 value is the dose required to retain 50% of the starting film thickness during development.