Titanium Cluster Polymers as Reactive Ion Etch Barriers

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Titanium oxide films are barriers to the reactive oxygen etching of photoresists in silicon device fabrication. Medium-sized clusters of Ti oxide–alkoxide have been isolated by Klemperer et al. as intermediates in the formation of sol–gels from Ti tetraalkoxides and water. We report that one of the clusters, $Ti_{11}O_{13}(OiPr)_{18}$, reacts with diols in hydrocarbon solvents to form network cluster polymers. These polymers form thin films of Ti-rich material that can be pyrolyzed to the anatase form of TiO_2. Chemisorption of these cluster polymers onto the surfaces of poly(vinylbenzylphosphonic acid) copolymers (*Macromolecules* **1995**, *28*, 110) gives thin coatings with significant etch resistance. A sequence of three depositions is sufficient to create an etch mask with 300:1 selectivity vs the untreated copolymers. Prospects for using this chemistry in microlithographic patterning via surface imaging will be discussed.

Surface imaging may be required for the implementation of 193 nm and extreme UV (14 nm) lithography.[1] With surface imaging, as opposed to bulk imaging, high-resolution exposure need only be carried out at a shallow depth of the polymer film or at the polymer surface, thus improving depth of focus and minimizing difficulties associated with radiation absorption by the resist. Following the exposure, the exposed and unexposed surface regions must be differentiated by a chemical treatment that confers etch resistance preferentially to one of the regions so that dry development can be carried out. This may be accomplished by the application of a refractory element[2] such as Ni, Si, Zr, or Ti to the resist.

Three approaches that have been considered for forming the required etch-resistant surface layer are the selective deposition of electroless nickel,[3] the buildup of chemisorbed, self-assembled films of zirconium phosphate/phosphonates;[4] and treatment with etch-resistant small molecules (containing one refractory atom per molecule) such as silanes[5] and titanium tetrachloride[6] by permeation through the surface or condensation at the surface. The first method has been described by researchers at the Naval Research Laboratories[3] and Shipley and has been extended by us to vinyl benzylphosphonate copolymers.[12] The main advantages of electroless nickel are the integrity of the etch mask and the high inherent etch resistance associated with nickel metal. The main disadvantages are the uneven growth of the films and the amplification of defects associated with initiation of metal deposition on unwanted areas of the resist. If a "defect" originates as the deposition of a miniscule amount of electroless nickel catalyst in an area not intended to be metallized, the defect may grow to a substantial metal island during the subsequent process. The second method provides a highly etch resistant film as well, though not as resistant as a native metal, and does not greatly amplify defects; however, it requires numerous deposition cycles to build a thick and continuous film. The absorption of small molecules such as titanium tetrachloride onto hydrophilic polymers (the third method described above), which, while forming an etch barrier by reaction with sorbed surface water, also retarded the etching of unexposed areas because of the propensity of the small titanium compound to penetrate into a variety of hydrophobic films.

If clusters or polymers rich in etch-resistant elements were chemisorbed instead of small molecules or ions as in method 2, the number of deposition cycles could be greatly reduced, and a more continuous film could result. Use of very large species as the adsorbants offers the additional advantage of confining the adsorption to the near-surface region because of the difficulty of clusters penetrating into a high molecular weight resist. Even the very largest known clusters (>100 metal atoms), however, are still too small to deliver sufficient etch-resistant material to a surface in just a few treatments.[6] Where small-molecule treatments have shown promise, such as in recent silylation experiments, the Si must penetrate at least 2000 Å into the bulk of the resist film if enough of it is to be incorporated, in which case swelling becomes a serious issue.

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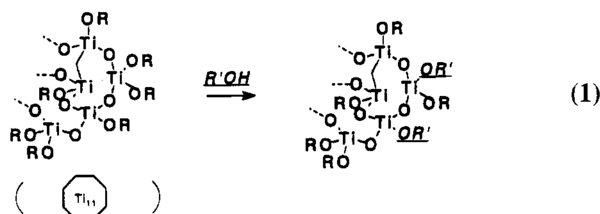
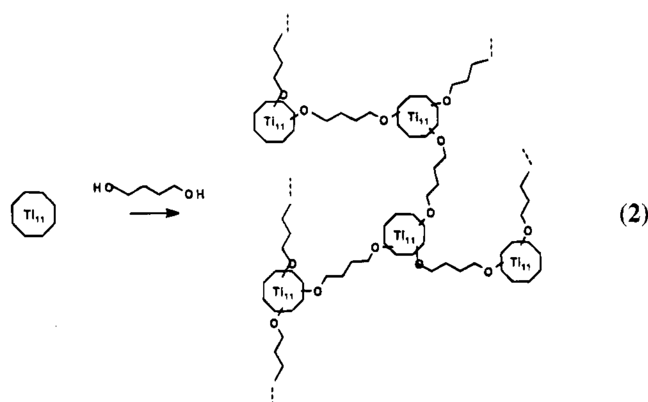
The synthesis of titanium oxide-alkoxide clusters containing 7−16 Ti atoms has recently been reported.[7] These discrete compounds have been isolated as intermediates in the partial hydrolysis of Ti tetraalkoxides under sol−gel-forming conditions. The nonhydrolyzed alkoxide groups can be exchanged for different alkoxides with some selectivity via nucleophilic substitution reactions, as generically illustrated in eq 1. It therefore





seemed possible to synthesize large-network polymers from these clusters by carrying out the exchange reaction with simple diols (eq 2). In this manner, clusters with modest amounts of a refractory element per molecule could be converted into cluster polymers that would deliver a much larger amount of metal element with each covalently linked molecular unit, enough to be significant on the scale needed for etch resistance, even in one deposition.

In this paper, a procedure is given for synthesizing a network polymer of one of the more stable of these clusters, $Ti_{11}O_{13}(OiPr)_{18}$ (**1**).[8] Evidence for polymer formation is derived from ^{13}C NMR and dynamic light scattering (DLS). The cluster polymer forms spun films that are rich in Ti and highly etch resistant. Application of this polymer from solution onto the surfaces of polar organic polymers, especially vinyl benzylphosphonic acid copolymers, greatly enriches the copolymer surfaces in Ti, as judged by XPS and X-ray fluorescence, and confers substantial etch resistance after a single coating, yielding a barrier with 300:1 selectivity vs untreated polymer after only three applications. Prospects for utilizing this procedure in the fabrication of electronic devices are discussed.

Results

Synthesis and Properties of the Cluster Polymers. Compound **1** was synthesized by the partial hydrolysis of $Ti(OiPr)_4$ as previously described,[8] except trituration with acetonitrile was omitted and two crystallizations were carried out. Although crude (singly crystallized) product could be polymerized, all cluster polymers described here were made from doubly crystallized material. The strongly proton-decoupled ^{13}C NMR spectrum we obtained for **1** exactly matched the literature spectrum.[9]

Polymerization of **1** was carried out by the azeotropic distillation of 2-propanol from toluene solutions of **1** and 5−20 wt % vs **1** of diols. Generally, the diol was 1,4-butanediol, giving the cluster polymer product **1-but**. Carbon NMR spectra of **1-but** showed a shifting of the envelope of peaks to lower field and coalescence of the individual peaks into broad humps as more equivalents of diol were used. Dynamic light scattering observation of solutions of the cluster polymer filtered through 0.45 μm disks indicated a very high degree of polymerization, with particle sizes in the range 100−1000 Å, and with larger particles associated with a larger amount of diol in the polymerization mixture. However, even the highest molecular weight cluster polymer solutions were not viscous, except at >40 wt % in toluene. Evidence for large particles combined with low solution viscosity is characteristic of colloid behavior, where material is suspended in large assemblies but where attractive or entangling forces are weak. Considering the nonpolar media involved in the cluster polymerization and the neutral reagents, ionic species would not be expected. However, hydrogen bonding through dangling OH groups cannot be ruled out as contributing to the association of cluster polymers. Attempted determination of molecular weight by gel permeation chromatography was unsuccessful, because of the reaction of the cluster polymer with the column.

A sample of **1-but** from 16 wt % diol was spin-coated onto a fused silica plate, forming a clear, insoluble film. The absorbance of this film at 190 nm was 5/μm, and at its absorbance maximum of 235 nm, 10/μm. On baking the film at 600 °C for 20 min, the film became rough but remained continuous. X-ray diffraction of this film showed a peak characteristic of the anatase form of titanium dioxide.[10] Use of the cluster polymer from 10% butanediol gave a film that was initially redissolvable in toluene. However, this film did not remain continuous on baking, and the baked film gave a poorly defined XRD peak. At the conclusion of this work, another example of anatase formation from a precursor film, chemisorbed on a self-assembled monolayer, appeared in print.[15]

In addition to butanediol, cluster polymers were synthesized from 1,4-butynediol and 3-hexyne-2,5-diol. The cluster polymer from the latter is potentially imageable because of the acid lability of the propargylic C−O bond, as proposed in eq 3. The use of cyclohexanediol to cross-link **1** gave a gel that was partially soluble at best.

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(9) However, with weak proton−carbon decoupling, we observed splitting of the three downfieldmost methine carbons at 79.42, 79.20, and 79.13 ppm into clean doublets and minor discrepancies in a few of the peaks in the 78−79 ppm range (78.99, 78.86, 78.77, 78.40, 78.12, 78.01). Nine of the peaks (76.37, 76.40, 76.50, 77.15, 77.42, 77.57, 78.15, 78.46, 78.63) were identical to those reported previously even under weak decoupling conditions.

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Table 1

Ti species	substrate polymer	Ti surface concn by XPS (20° takeoff angle, atom % Ti)	Ti concn by XRF (atoms/cm^2) × 10^{-15}	etching rate (Å/s)
$Ti_{16}O_{16}(OEt)_{32}$	A	11.1	19	>200
	D	11.8	18	>200
	E	13.1	19	>200
1-but (5)[b]	none[c]	19.4		<3
	A	10.0		60
	D	8.8		150
	E	12.6		280
none	B[d]	0		230
1-but (10)[b]	B[d]	8.7	1.1	100
	C[d]	9.1	2	80
	F[e]	13.9	4.0	>200
	G	10.1	3.1	low but uneven
1-but (19)[b]	B[d]		5	50
	C[d,j]	7.0	4	20
	F[e]		4	>190
1-but (16)[b]	C[d,f,j]		6.6	9
	C[d,g,j]		15	0.7
	C[d,h,j]	5.0[i]	3.1	30
$Ti(OiPr)_4$	C[d,j]	9.8	6.4	30
Ti_{11}–butynediol(5)	C[d]		6.9	30
	H[f]			very low, very rough

[a] 20–60 s of etching time. [b] Percent diol in the cluster polymerization mixture. [c] Cluster polymer spin coated on a wafer. [d] With triphenylsulfonium hexafluoroarsenate, baked to deprotect. [e] With diphenyliodonium triflate, irradiated and baked to deprotect. [f] Two depositions, water-saturated toluene equlilbration between depositions. [g] Three depositions, as in f. [h] Immersion in 1% stearylamine in toluene before deposition of Ti. [i] 90° XPS was 6.6 atom % Ti. [j] Used in Figure 2.

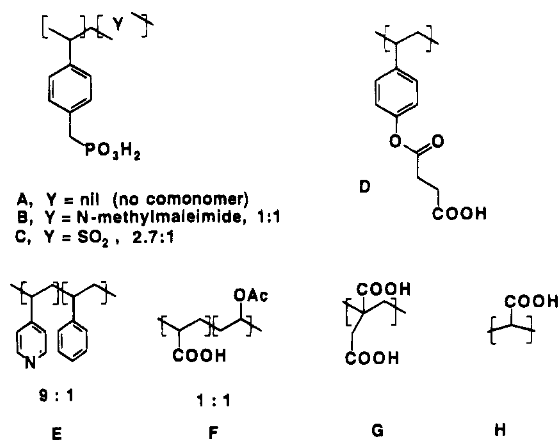
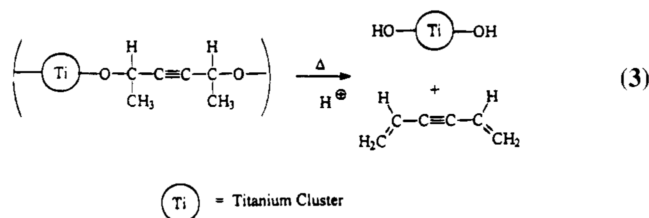


Figure 1. Structures of substrate polymers to which Ti species were adsorbed.



(3)

Chemisorption and Etch-Barrier Formation. Dilute toluene solutions of Ti species were applied to spun films of a variety of polar organic polymers whose structures are illustrated in Figure 1. The Ti-coated films were then characterized by XPS, XRF, and determination of reactive ion etch rates. Detailed procedures are given in the Experimental Section, and the data are presented in Table 1. Every sample retained a significant amount of surface Ti as judged by XPS. The maximum attainable value is that of a spun cluster polymer film, which had 20 atom % Ti. The rest of the samples, prepared by surface treatment, had 6–14 atom % Ti, indicating substantial coverage, but with open areas which gave rise to the substrate polymer XPS signals. Characterized in this way, the amount of surface Ti deposited varied little with the dryness of the toluene used to preequilibrate the samples, the deposition time (1–15 min), or the nature of the organic substrates and the Ti species being adsorbed. The phosphonate polymers, in particular, are polar enough that swelling of the substrate films by the toluene is insignificant, <1% as measured by Nanospec thickness monitoring seconds after film soaking. Ti concentrations using XPS at 90° takeoff angles were 60–90% of those at 20°, suggesting that the Ti deposit is the equivalent of at least several monolayers of TiO_2. Poly(vinylpyridine) bound Ti particularly well; however, it is not clear why the pyridine ring should have such a great attraction for the Ti clusters.

In contrast to XPS, XRF measures total Ti incorporation in the samples, whether at the surface or in the bulk. By this measure, the nonpolymerized (but highly reactive) Ti_{16} cluster[7] was more effective at depositing (or doping) Ti into the polymers than was **1-but**. Both carboxylic acid and phosphonic acid polymers incorporated substantial amounts of Ti from **1-but**, in the 10-monolayer range. However, *only the phosphonic acid polymers treated with cluster polymer* (or the parent alkoxide) *retained Ti with sufficient continuity for significant etch resistance in one application.* In one case, a treated carboxylic acid polymer (G) displayed etch resistance as well, but the sample was so rough that a definite etch rate could not be determined. For a series where the substrate polymer (C) and reagent (**1-but**) were kept the same, a correlation between total Ti incorporation and etching rate was meaningful, as shown in Figure 2. Outside this series, the correlation was weaker, and for the many samples which showed no etch resistance at all, Ti incorporation was obviously ineffective.

Single depositions of polymers of **1** decreased the etching rate of the underlying substrate polymer by an order of magnitude. *This is the first demonstration of significant etch resistance from a single adsorption from solution.* However, much greater etch selectivity would

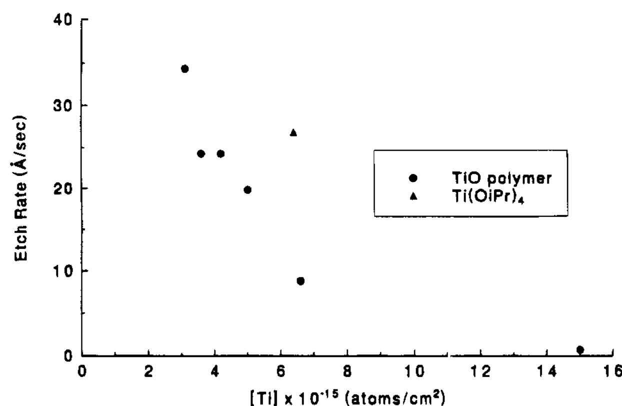


Figure 2. Etch rate vs Ti content for samples indicated in Table 1 with the appropriate footnote.

be needed for a real process. Treatment of a singly coated sample of polymer C with water-saturated toluene followed by **1-but** in toluene, twice in turn, lowered the etching rate to a barely measurable value, indicating an etch selectivity of >300:1. This level of selectivity is in a useful range for dry etch resist development with ultrathin masking layers and is equivalent to that for the etch barrier formed by the neat cluster polymer. Polyfumaric acid[11] also attracted sufficient Ti in two treatments to form an etch mask, but again the COOH-substituted polymer showed a rougher morphology.

To reverse the tone of dry etch development, it might be desirable to chemisorb a "blocking" reagent onto exposed regions to prevent Ti cluster polymer adsorption and have it bind to unexposed, or subsequently flood-exposed, regions of a substrate film. Stearylamine was tested as such a blocker and had a small effect in lessening the etch resistance of the adsorbed cluster polymer. Ti isopropoxide conferred etch resistance to polymer C, but the etch resistance per Ti atom was much less than for the cluster polymers. More of the Ti from the small molecule source may have been ineffectively dispersed into the bulk of the substrate.

Discussion

Titanium alkoxides, as small molecules, clusters, and cluster polymers, are bound to the surfaces of a variety of polar polymers from toluene solutions. The mechanism of binding may be a combination of acid–base interactions, hydrogen bonding, titanium ester formation, reaction with polymer-bound water, and dipolar interactions. In terms of the quantity of Ti bound, pyridine, carboxylic acid, and phosphonic acid functional groups were roughly equivalent; if anything, the pyridine polymer bound the most titanium. However, only the phosphonic acid polymers bound the Ti in a form that consistently gave a smooth, effective etch barrier. The phosphonic acid group would be strongly involved in all the likely interactions with Ti alkoxides, but the special effect that phosphonic acid seems to have on the morphology of the Ti film cannot be definitively explained. However, if anionic species are required for binding and assembling the Ti alkoxides, then phosphonic acid polymers would be especially suitable since this functional group would be substantially ionized relative to COOH and pyridyl groups. The Ti is intercepted at the polymer surface by a high density of near-surface bonds. The surface becomes effectively cross-linked, and the cluster polymer is not dispersed into the bulk polymer below the surface.

Etch selectivity among different polymers treated with Ti under similar conditions suggests that it would be possible to distinguish different regions of a photopatterned film by etch development after treatment with Ti reagents. However, we have not actually demonstrated this phenomenon. Doing so would require the photocreation or photodestruction of phosphonic acid groups. The latter has never been demonstrated, although the former has been accomplished using photoacid catalysis of phosphonate ester dealkylation. If this reaction were done on a polymer that was insoluble in toluene, most likely a cross-linked polymer, patterned deposition of the Ti reagents could be explored. For the patterns to be etchable in a useful way, the Ti deposits would have to be smoother than they are now, and additional care would have to be taken to ensure that the toluene deposition solutions remained particle free. The solutions can be handled on the time scale of minutes to hours in the air, and measures to prevent exposure to humidity would improve the shelf life of the reagent solutions.

One additional possibility for using these Ti cluster polymers would be incorporating them into films that would be directly imaged. Considering the etch selectivity of **1-but**, the absorbance at 190 nm is fairly low, so cluster polymers related to **1-but** could be considered as candidate components of 193-nm lithographic materials, provided that they are sufficiently hydrolytically stable.

Experimental Section

Synthesis of 1. A modification of the previously described procedure[8] was employed. Titanium tetraisopropoxide (106 g) was dissolved in 100 mL of dry 2-propanol. A solution of 4.3 g of water in 100 mL of 2-propanol was added dropwise under nitrogen with stirring over 2 h. After stirring for >1 additional hour, the mixture was concentrated on a rotary evaporator to remove all the 2-propanol. The residue was dissolved in 50 mL of freshly opened toluene and reprecipitated by adding 200 mL of anhydrous acetonitrile and cooling below 0 °C. The precipitate was recrystallized from 100 mL of toluene by the slow addition of 75 mL of acetonitrile and cooling. Yield 21 g (63% based on H_2O); ^{13}C NMR discussed in the Results.

Synthesis of 1-but. Cluster **1** was dissolved in 10 times its weight of freshly opened toluene. A solution of 5–20 wt % vs **1** of 1,4-butanediol dissolved in a few milliliters of dry THF or dioxane was added. Most of the solvent (80%) was distilled into a Dean–Stark trap, and a second comparable portion of toluene was added. The distillation was continued until about 3 times the original cluster weight remained. This solution was stored and concentrated or diluted as needed for further experiments. The ^{13}C NMR spectrum showed a broad hump from 75 to 81 ppm for the methine carbons of high molecular weight **1-but**. The identical procedure was also used to prepare samples of **1** polymerized with 2-butyne-1,4-diol and 3-hexyne-2,5-diol.

Adsorption Experiments. Films of organic polymers were spun onto silicon wafers and dried or thermally deprotected as needed. The samples were preequilibrated in either dry or water-saturated toluene for several minutes and then immersed in 1% solutions of Ti reagent in toluene for 1–15 min. The treated samples were vigorously rinsed in fresh dry toluene and characterized by XPS, XRF, and etching.

Substrate Polymers. Phosphonic acid polymers were prepared and spin-coated as previously described.[12]

Poly(itaconic acid) (structure G), was purchased from Polysciences. Poly(carboxylpropanoyloxystyrene) (structure D) was prepared by a standard styrene polymerization procedure.

Poly (*tert*-butyl fumarate) (precursor to structure H) was prepared according to a literature procedure.[13] The resist solution was formulated with 10 wt % of polymer and 10 wt % (versus polymer) of diphenyliodonium triflate in tetrahydrofuran.

The copolymer of crotonic acid and vinyl acetate (structure F) was prepared according to a literature procedure.[14] The resist solution was formulated with 10 wt % of the polymer and 10 wt % (versus polymer) of diphenyliodonium triflate in cyclohexanone.

Films of the carboxylic acid polymers were prepared by spin-coating silicon wafers at 2000 rpm followed by postapplication bake at 120 °C for 1 min. Exposures were done with a Lambda Physik Model 103G 248-nm excimer laser in a Karl Süss contact printer using a dose of 100 mJ/cm^2.

Sample Analysis. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer (Physical Electronics) Model 5600 ESCA system equipped with an Al Kα monochromatic X-ray source. The spectra were acquired at 400 W power and the chamber pressure during acquisition was 5×10^{-10} Torr. Charging of the insulating surfaces was compensated using a low-energy electron flood gun. The spectra were shifted as necessary by setting the C 1s hydrocarbon peak at 248.8 eV. Determinations were made at 20° and 90° takeoff angles where the mean escape depths for phosphorus are 6 and 18 Å, respectively.

X-ray fluorescence (XRF) spectra were recorded on a Kevex Omicron XRF spectrometer equipped with a Rh target. The spectra were acquired at 50 keV and 0.1 mA under vacuum at a fixed 45° angle relative to the detector. All samples were compared to standard reference samples.

Plasma etching was carried out using a Lucas-Signatone Inc. Vortex Model 5410 helicon source etcher with an oxygen pressure of 2.5 mTorr and a flow of 100 sccm. The source power was 2000 W and the chuck power 75 W. The wafer temperature was 25 °C.

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