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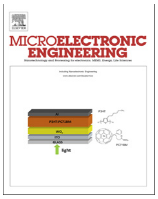

Photolithographic properties of tin-oxo clusters using extreme ultraviolet light (13.5 nm)

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ABSTRACT

We have studied the photolysis of tin clusters of the type $[(RSn)_{12}O_{14}(OH)_6]$ X_2 using extreme ultraviolet (EUV, 13.5 nm) light, and developed these clusters into novel high-resolution photoresists. A thin film of $[(BuSn)_{12}O_{14}(OH)_6]$[*p*-toluenesulfonate]$_2$ (***1***) was prepared by spin coating a solution of (***1***) in 2-butanone onto a silicon wafer. Exposure to EUV light caused the compound (***1***) to be converted into a substance that was markedly less soluble in aqueous isopropanol. To optimize the EUV lithographic performance of resists using tin-oxo clusters, and to gain insight into the mechanism of their photochemical reactions, we prepared several compounds based on $[(RSn)_{12}O_{14}(OH)_6]$ X_2. The sensitivity of tin-oxide films to EUV light were studied as a function of variations in the structure of the counter-anions (**X**, primarily carboxylates) and organic ligands bound to tin (**R**). Correlations were sought between the EUV sensitivity of these complexes *vs.* the strength of the carbon–carboxylate bonds in the counter-anions and *vs.* the strength of the carbon–tin bonds. No correlation was observed between the strength of the carbon–carboxylate bonds in the counter-anions (**X**) and the EUV photosensitivity. However, the EUV sensitivity of the tin-oxide films appears to be well-correlated with the strength of the carbon–tin bonds. We hypothesize this correlation indicates a mechanism of carbon–tin bond homolysis during exposure. Using these tin clusters, 18-nm lines were printed showcasing the high resolution capabilities of these materials as photoresists for EUV lithography.

1. Introduction

As the microelectronics industry continues to follow Moore's law [1], photoresist designers face ever-growing challenges associated with resolving increasingly smaller patterns. With 22-nm gate-lengths currently in production, many chip manufacturers are looking for ways to implement the 16 and 10-nm lithography nodes. Chip manufacturers currently use 193-nm scanners for printing these features, however, these systems have already surpassed their resolution capabilities and imaging is made possible only by multiple patterning. Extreme ultraviolet (EUV, 13.5-nm wavelength) lithography is thought to be the next imaging technology for fabricating microelectronic devices, however, there are still many obstacles that must be overcome. The traditional, chemically-amplified photoresist systems which have been successful in lithography since the 1960s are finally encountering extremely challenging hurdles: (1) poor photon absorption in thin-films; (2) moderate etch selectivity [2,3] and; (3) limited gains in resolution [4,5].

Recently, two completely new resists have been developed based on hafnium-oxide nanoparticles [6–9]. Researchers at Inpria Co., have developed one of the highest resolution EUV photoresists ever created [6]. This resist has demonstrated resolution of 8 nm dense line and space patterns at 200 mJ/cm^2 [6]. Christopher Ober's group at Cornell has also developed resists which utilize hafnium-oxide nanoparticles with equally remarkable performance [7–9]. Although the Cornell resists (36-nm lines) do not have the high resolution capability of the Inpria resist, they are capable of excellent sensitivity (12 mJ/cm^2). The very notion of preparing photoresists using inorganic or organometallic compounds is still extremely new, but this pioneering work has demonstrated the great potential of inorganic systems as photoresists.

Here we describe the synthesis and lithographic evaluation of thin films of tin-oxo clusters ($[(RSn)_{12}O_{14}(OH)_6]X_2$, Fig. 1A) using

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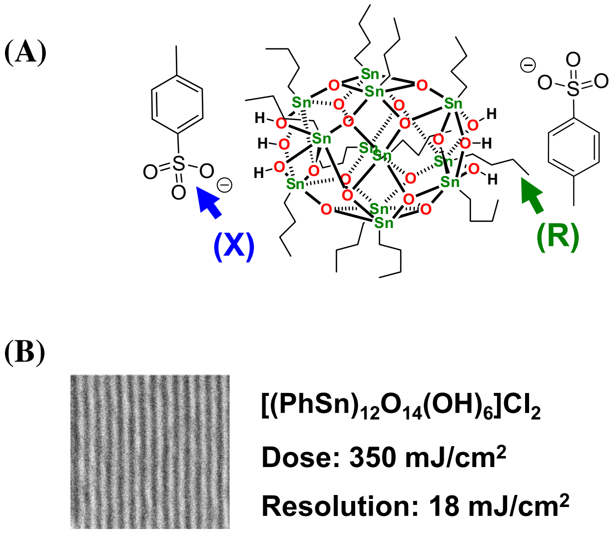


Fig. 1. The mechanism of photolysis for Tin clusters of the type $[(RSn)_{12}O_{14}(OH)_6]X_2$ was explored through structural variation. (A) Clusters were made varying the bond energies of both the counter-ions (**X**) and the organic ligands (**R**) and tested for EUV lithographic performance. (B) Highest-resolution results for tin clusters. The best imaging was achieved by the clusters containing the phenyl organic ligands (**R**), which was capable of 18-nm resolutions.

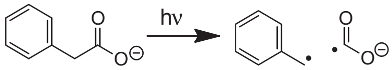


Fig. 2. Photo-induced homolytic cleavage of phenylacetate. Phenylacetate is known to undergo a photochemical decarboxylation where generation of benzyl radical has been detected suggesting a homolytic cleavage mechanism [51,55–58].

extreme ultraviolet light (EUV, 13.5 nm). These types of tin clusters have been known for over 20 years [10–46]. They consist of spherical tin-oxo cages in which each of the twelve tin atoms is covalently bound to one organic (**R**) group. The clusters have a +2 charge and are typically precipitated with pairs of anions (X^-). These materials have been investigated as self-assembled monolayer dopants [10], as esterification catalysts [11] and as organometallic hybrid materials [12], but until now their photoreactivity has never been evaluated.

This investigation into the use of tin-oxide clusters as EUV photoresists has been motivated by three conclusions. (1) The work by Inpria and Cornell provided an excellent demonstration that metal-oxide nanoparticles/clusters could provide exceptional lithographic properties. (2) Both tin and oxygen readily absorb EUV photons with optical densities that are 10.5 and 1.7 times greater than carbon [47]. We proposed that these higher optical densities should allow resists based on these tin-oxo clusters to better utilize the EUV photons that are used in EUV lithography to provide superior lithographic performance based on more efficient utilization of the EUV photons to give better sensitivity and lower shot noise [48]. (3) The tin-oxo clusters are smaller and more uniformly sized than the HfO_2 nanoparticles and should, therefore, be capable of excellent resolution and LER.

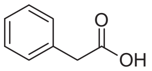
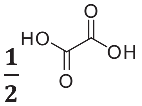
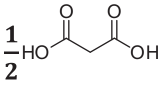
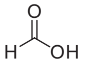
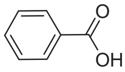
In addition to preparing tin-oxo clusters that are known in the literature, we have made six new compounds. The lithographic performance of eight tin-oxo clusters were then evaluated lithographically using the EUV interference lithography tool at Paul Scherrer Institute (PSI) and the results were analysed.

2. Results and discussion

In an initial study, the tin-oxo cluster $[(n\text{-}BuSn)_{12}O_{14}(OH)_6](p\text{-}CH_3C_6H_4SO_3)_2$ (***1***) was prepared as previously described in the literature [13]. The tin cluster (***1***) was dissolved in 2-butanone and spin-coated into a thin film. The film was exposed to EUV light in an open field pattern using the Berkeley direct contrast tool (DCT) and developed in 66% aqueous isopropanol solvent for 30 s [49]. Upon exposure to 20 mJ/cm^2 EUV light, the film became less soluble in developer – thereby exhibiting the properties of a negative-tone photoresist. In a related experiment, we were able to print 18-nm dense lines by exposing a film of $[(n\text{-}BuSn)_{12}O_{14}(OH)_6]Cl_2$ using the interference lithographic tool at PSI (Fig. 1B).

Since these clusters exhibit photoreactivity and are capable of printing high resolution lines, we designed a set of experiments to explore their lithographic properties as a function of structure. Specifically, we prepared a series of compounds with variation in the carboxylate counter-anion and the alkyl group bound to tin with the hope of identifying which of these structural features participates in the exposure mechanism. Since the resolution capabilities of these clusters varies, yet all capable of printing 50-nm

Table 1
Five tin clusters were synthesized by combining the appropriate acid (**HX**) with the tin cluster hydroxide (***2***). The relative bond energy for each acid is also included and, if decomposition occurs, should correspond with the relative sensitivity [59].

Acid (HX)	Structure	Bond dissociation energy (kcal/mol)
	**(3)** $[(BuSn)_{12}O_{14}(OH)_6][C_6H_5CH_2COO]_2$	67
	**(4)** $[(BuSn)_{12}O_{14}(OH)_6][OCOCOO]$	80
	**(5)** $[(BuSn)_{12}O_{14}(OH)_6][OCOCH_2COO]$	85*
	**(6)** $[(BuSn)_{12}O_{14}(OH)_6][HCOO]_2$	97
	**(7)** $[(BuSn)_{12}O_{14}(OH)_6][C_6H_5COO]_2$	103

[*] Bond energy estimated from bond energy of acetic acid α-proton.