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Basic Issues Associated With Four Potential EUV Resist Schemes

Trilayer, Organometallic Bilayer, or Plasma Deposited-Plasma & Developed Bilayer, and Silylated Resists

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Abstract:

Four of the better developed resist schemes that are out growths of DUV (248 and 193 nm) resist development are considered as candidates for EUV. They are as follows: trilayer, a thin imaging layer on top of a refractory masking/pattern transfer layer on top of a planarizing and processing layer (PPL); solution-developed, organometallic bilayer where the imaging and masking layer have been combined into one material on top of a PPL; plasma deposited, photo-definable plasma developed organo-refractory material on top of a PPL; and finally silylated resists. They are examined in a very general form without regard to the specifics of chemistry or the variations within each group, but rather as to what is common to each group and how that affects their effectiveness as candidates for a near term EUV resist. In particular they are examined with respect to sensitivity, potential resolution, optical density, etching selectivity during pattern transfer, and any issues associated with pattern fidelity such as swelling.

Key Words: Photoresist, Silylation, Surface-Imaging,

Introduction:

The 0.13 μm generation is expected to enter production in the year 2004. EUV lithography has demonstrated the ability to print sub 0.1 μm features in thin photoresist films (1). Subsequently, it is considered to have an excellent likelihood of being the exposure wavelength used in production. While the technological hurdles associated with the design and fabrication of a prototype EUV stepper are being undertaken, a program to develop a photoresist capable of imaging in the EUV environment must be achieved. This EUV environment is distinctly different from what current steppers employ. The three most important differences associated with exposure tools utilizing 13.5 nm radiation are exposure in vacuum, low photon flux, and absorption. Since absorption of 13.5 nm photons is atomic in nature, direct excitation of core electrons results from absorption of EUV radiation. Consequently, almost all materials absorb strongly at 13.5 nm, even air. This mandates that the exposures must be undertaken in vacuum. Even thin films show sloping sidewalls due to the effect of dose gradation through the film. The requirements for a final resist thickness in excess of the exposure depth of the film mandate surface imaging (2).

The requirements for an EUV resist are fairly easy to guess based on what has been required in the past and what is known about what the first pilot production exposure tools will be like. The photoresist must certainly be capable of resolution of at least 0.1 μm and probably less, depending on exactly when EUV is employed in the manufacturing process. The film thickness will probably not be less than 0.3 μm nor greater than 0.6 μm. Sidewalls must be very steep, probably 88°. Linearity must be between ±5-10% for features ranging in size from 0.1 to 1 μm. Line edge roughness and cd control will be at most 5 nm. Calculations (3) at Lawrence Livermore National Laboratories suggest that for economic viability based on throughput issues and likely source power and incident flux, the photoresist will need to have a sensitivity below 5 mJ/cm^2. While it is desirable to have both resist tones available, if this is not possible, positive tone is required. Positive tone allows definition of smaller vias than allowed by a negative tone resist.

In this paper we will attempt to qualitatively examine a few of the more mature potential resist schemes for EUV. Comparison of the different

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schemes is difficult at best given the variation in processing and materials used. For example, there are dozens of different silylation schemes that operate on entirely different chemistries and physics yet are lumped together by virtue of relying on diffusion of silylation agents into an exposed resist. Despite differences, there are many common factors that allow the various schemes to be examined together without regard to the numerous differences in materials and processing within a group.

The four groups to be discussed are solution developed thin film conventional resists used in a trilayer resist processes, bilayer resist schemes using solution developed resists that contain inorganic materials for enhanced etch resistance, plasma deposited organometallic films, and finally silylated resists. This list is by no means complete and there are many innovative ideas that may provide a solution to EUV resist needs. Some examples of these ideas are self-developing resists, photo-deposition, and the NRL approach of selective electroless metallization on substrates or a PPL. However, since industrial perception and experience with a given technology are critical for acceptance, trilayer, silylation, plasma deposited resist, and organometallic bilayer resist rise to the top in terms of likelihood for production.

Each of these four categories will be examined as to the applicability of the scheme to address some of the critical issues of EUV resists. All the issues can not be addressed for each scheme, however, a few of the critical issues can. Hopefully, several strategies for EUV resists will become apparent. Critical to the success of each is sensitivity and whether or not the resists must or can employ chemical amplification, CA. CA is provides increased sensitivity, but at the cost of resolution. It remains to be determined whether or not a CA resist will be able to provide the resolution required.

Since all schemes require at least one pattern transfer step into an underlying resist, the etch resistance of the masking layer must be addressed. Independent of the method of generation of the masking layer, it must have etch resistance adequate to pattern the underlying planarizing/processing layer. Ideally, the masking layer will allow a great deal of latitude in the etch step and provide for adequate overetch as required by topography. Closely related to this issue of etch latitude is the optical density of the resist employed. The intimate nature of this relationship will become more apparent as various schemes are examined. The optical density of the resist will determine the optimal resist thickness that can be employed. Additionally, the thickness of the film used will undoubtedly have an influence on defect density associated with flaws in the coverage of the resist. Lastly, the changes that occur in the resist during imaging will affect the suitability of the resist processing for EUV. In particular, volume changes during and after exposure will be examined as these are very likely to cause problems with CD and pattern fidelity.

Routes:

Perhaps the most mature resist scheme for EUV is a trilayer scheme using thin e-beam resists on top of a refractory material, either a sputtered refractory oxide, a metal or a spin-on glass (4). Trilayer is shown schematically in Figure 1. The refractory material (masking layer in Figure 1) would be on top of a thicker organic planarizing and processing layer. There are numerous advantages to this scheme, but also a few concerns. The clear advantage is that each of the layers serves only one purpose thus decoupling the roles of the imaging, pattern transfer and processing & planarizing layers. In theory, each layer should function optimally. The clear drawbacks to employing a trilayer scheme for every level of device manufacture are expense, lowered throughput, and increased defect density associated with the thin imaging layer.

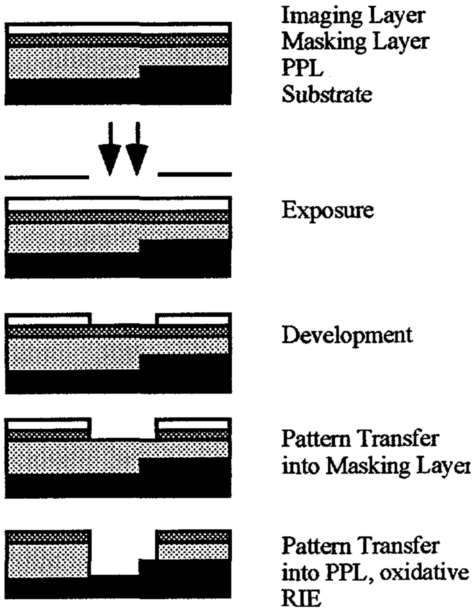

Figure 1. Schematic of a trilayer lithographic process.

The probability of achieving the desired sensitivity for a trilayer scheme is good. Chemically amplified resists such as Ray-PN have demonstrated excellent imaging with sensitivity <10 mJ/cm^2. High resolution and high contrast resists such as PMMA are insensitive and require doses of 60 mJ/cm^2. The more sensitive e-beam resists such as EBR-9 are significantly more optically dense and probably would need to be used in a film that is too thin for adequate pattern transfer.

Since oxygen is a much greater absorber than carbon or hydrogen, (5) resists that are phenolic based rather than acrylate based or carboxylic acid based are likely to be more transparent and consequently can be used in thicker imaging films. Increasing the film thickness is attractive for two main reasons. Spin coating <1000Å thickness defect-free films is difficult. Second increasing the film thickness makes pattern transfer into the hard mask easier since it relaxes the selectivity needed in the etch step.

The use of photoresists that are free of oxygen and other elements (nitrogen, sulfur, etc.) that have high extinction coefficients at 13.5 nm is attractive, but the unstated requirement for photoresists to be developed in 0.26M TMAH makes this unlikely. Most acidic functionalities that provide solubility in TMAH are oxygen based-carboxylic acids or phenols.

Overall, a trilayer scheme may be feasible for EUV. Trilayer schemes are less prone to edge roughness than other schemes. This combined with existence of both positive and negative tone CA resists makes trilayer attractive. However, they are unlikely to succeed in production due to the defect density associated with extremely thin imaging layers and the difficulty in pattern transfer using thin films.

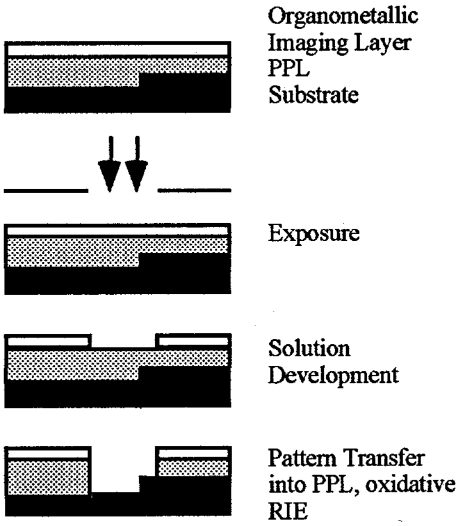

Figure 2. A schematic of a positive tone organometallic bilayer process.

Similar to trilayer are organometallic bilayer resists. A positive tone organometallic bilayer scheme is shown in Figure 2. Unlike trilayer where the imaging layer and the masking layer are different, in an organometallic bilayer scheme the imaging layer is used as a mask for patterning the underlying PPL. This is usually achieved by using an imaging layer that contains significant amounts of a refractory element such as silicon to confer etch resistance during an oxidative plasma development step. The imaging etch mask layer can take on many forms, such as photodefinable spin-on glasses (6), polysilanes (7), or refractory containing classical e-beam type resists such as silicon containing polyolefin sulfones (8) or silicon containing acrylates and α-halomethylstyrenes (9). All of these techniques require a wet development step prior to pattern transfer into the PPL.

Again, if TMAH is to be used as the developer, then the resists must contain significant oxygen for the acid functionalities. This decreases the exposure depths. The thinness of the resist places significant constraints on what the etching selectivity of the resist must be. If the resist does not contain an adequate amount of refractory material then the latitude for processing during the oxidative pattern transfer step becomes very narrow, and in particular, overetch latitude suffers. If image quality, resolution and sidewall considerations mandate a 60 nm thick imaging layer to transfer patterns into a 500 nm PPL, then the etch selectivity must be at least a minimum of 17 for a 100% overetch. It will be almost impossible to achieve this since refractory element content increases at the expense of solubility controlling functionality.

Sensitivity of organometallic bilayer schemes should be similar to that of other resists since one can imagine a number of different chemistries that employ chemical amplification schemes. More problematic is the volume change associated with some of these different schemes. Stresses introduced into very thin film resists due to the loss of material during processing may cause problems with pattern fidelity.

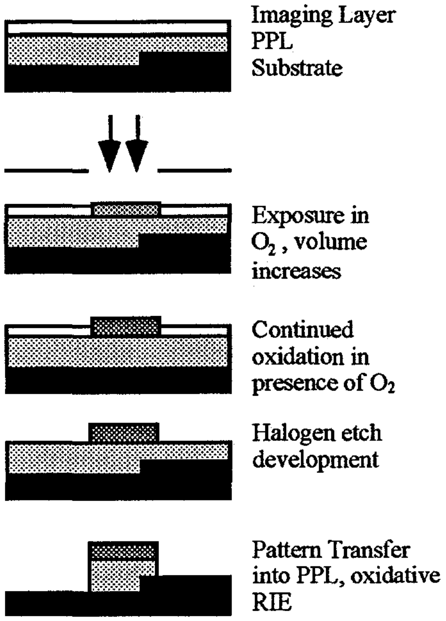

Figure 3. Negative tone polysilyne resist scheme.

An extension of the organometallic resist used in a bilayer form is a plasma deposited and plasma developed resist, shown in Figure 3. An example of this class of resist would be the plasma deposited polymethylsilynes (10). In theory, all steps including coating the wafer, exposure and development could be carried out in vacuum using a cluster tool. However, this is not the case. During imaging and possibly after as shown in Figure 3, the wafer must be exposed to significant amounts of oxygen or air to allow the photo-catalyzed oxidation of the silicon atoms to occur.

Polysilynes have not been extensively examined for suitability in EUV let alone optimized. Since oxygen is required in the imaging, some pressure of oxygen must be present in the EUV tool during exposure. It is not known what effect this will have on exposure and to what degree it will attenuate the radiation need for exposure. Undoubtedly there will be trade off between increased oxygen pressure and improved sensitivity and decreased radiation intensity at the wafer. Surprisingly, polymethylsilynes examined to date demonstrated an absorption similar to that of PMMA which is very absorbing. While they should be very transparent to EUV since they are composed of only carbon, hydrogen and silicon, it is likely that there is a thin layer of highly oxygenated polysilynes at the surface which raises the absorption coefficient. It may be impossible to eliminate this passivation layer since oxygen is required during exposure. If this passivation layer forms in the dark and if oxygen is required during exposure then the transparency gains of using a resist composed of just carbon, hydrogen and silicon are lost even with the use of a cluster type tool.

The sensitivity of polysilynes exposed in EUV under a slight pressure of oxygen was approximately 10-15 mJ/cm^2, between that of PMMA (40-60 mJ/cm^2) and SAL 601 (6-7 mJ/cm^2). Results with deep UV exposure suggest resolution of 0.2 μm features is readily achievable. The trade off between oxygen diffusion and dose and the type of "chemical amplification" that occurs during exposure to oxygen during and after imaging will need to be controlled to make a viable EUV process. Determinations of edge roughness, optimized sensitivity, and ultimate resolution are still waiting for thorough examination. Additionally, the effect of the swelling due to oxygen uptake (in some ways similar to the swelling associated with silylation) remains to be determined, especially with respect to its effect on pattern fidelity. One last consideration is that the absorbance of the film is increasing as oxygen diffuses into the film during exposure. This is the exact opposite of photo-bleaching and will affect the sidewall profile and subsequently may degrade resolution.

In deep UV exposures, the polysilynes provided excellent etch resistance during the pattern transfer into the organic processing layer. However, the etch selectivity during the chlorine plasma development step was significantly lower. The etching selectivity between the exposed and unexposed regions was approximately 3. While this is very low, excellent patterns were achieved. It again remains to be determined whether this will be adequate for the development of a robust processing scheme.

The final option for an EUV resist to be examined here is a silylated bilayer (11). Figure 4 shows a bilayer scheme similar to the SAHR (12) process. Silylation has been a potential resist scheme for I line and deep UV lithography for nearly a decade. Consequently, much is known about silylation, and there are numerous silylation schemes. However, many of the issues of sensitivity and volume changes are applicable to all gaseous silylation schemes.

Achieving the needed sensitivity with silylation is conceptually fairly easy given that CA deep UV resists have sensitivities of <5 mJ/cm^2. Whether the kinetics that allow one to image solution developed resists at low dose will also allow one to achieve adequate silicon contrast at the same dose remains to be determined.

Like solution developed resists used for the *trilayer scheme or the organometallic bilayer*, attenuation of radiation in the resist is a significant problem. Reaction of aminosilanes with resists requires acidic functionalities such as carboxylic acids or phenols. This requires oxygen in the resist which leads to decreased absorption depth. Imaging depths will probably not be more than 2000Å at the most and probably significantly less. This in turn places constraints on the pattern transfer step.

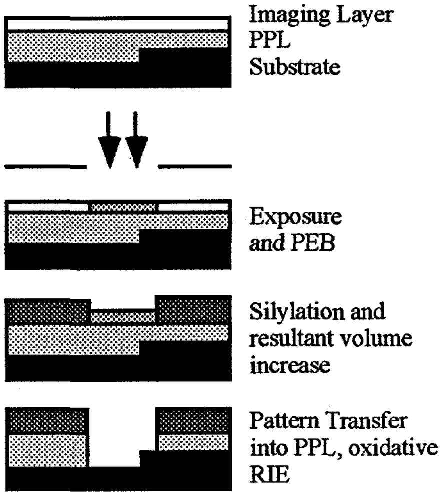

Figure 4. A positive tone bilayer silylation process.

Perhaps the most significant challenge faced by silylation is associated with the swelling that occurs during silylation. Numerous schemes have been devised to address this. They range from the use of crosslinkers before (13) and during (14) silylation, to partial solution development prior to silylation (15). Swelling and subsequent flow of the resist often necessitates the use of a descumming step (16) prior to the pattern transfer step. This descum step wherein a thin layer of photoresist is removed from the surface uniformly, can be either solution or plasma based. In either case, it adds complexity and cost. It would be more desirable to improve the chemistry to the point where a descum step is not required.

Despite these problems, silylation type processes have demonstrated very good resolution. In recent EUV exposures using our positive tone bilayer process we have recently demonstrated sub 0.13 resolution with doses approaching the goal of 5 mJ/cm^2. High quality 0.15 µm line and space patterns using our disilane silylation, bilayer process are shown in Figure 5. Figure 6 shows a high magnification of view of 0.13 l/s patterns. The edge roughness is very clearly visable in both sets of images. The wealth of information and experience present with silylation schemes makes silylation clearly a promising candidate for a near term resist for EUV.

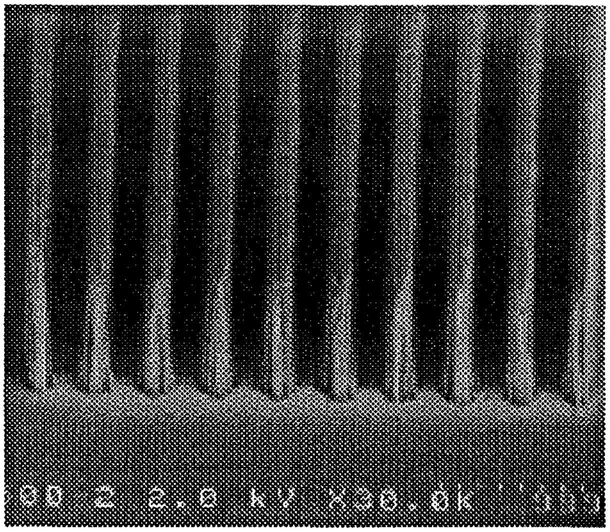

Figure 5. 0.15 µm line and space patterns from EUV.

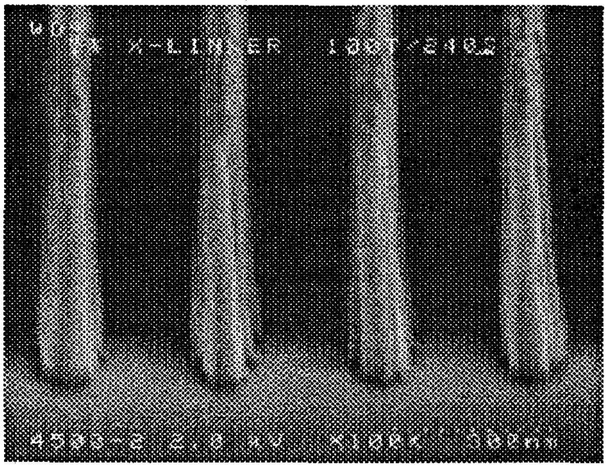

Figure 6. 0.13 µm line and space patterns from EUV.

Conclusions:

None of the schemes addressed are clearly a final solution in the search for a EUV resist scheme. They all have some advantages, yet none is without significant problems. Increased work needs to be undertaken to examine each of these schemes more thoroughly before it can be claimed to be the answer to the resist needs at 13 nm. Additionally, there is potential for some other photoresist scheme or technique to have a significant impact at 13.5 nm.

Despite these uncertainties and unknowns few unifying observations can be made. Most significant are those related to attenuation. The requirements for a TMAH developable resist and a silylation based resist ensure a significant concentration of oxygen in the photoresist. Since oxygen is a strong absorber, the usable imaging thickness decreases. This in turn places increased demands on the etch selectivity of the masking layer. Silylating agents must confer exceptionally good etch resistance if the silylation depth is matched to the imaging depth.

The use of non aqueous developable resists could have the biggest impact on the range of polymers that one could consider for an organometallic bilayer resist. The 1/e depth for a cresol novolac resist is 2000 Å. Based on trilayer results, and thin film imaging experiments, 70 nm is a workable resist thickness. A theoretical imaging material composed of just carbon and silicon (polypropylmethylsilane for instance) would have a 1/e depth of 4000Å, twice as transparent as a cresol novolac. However, if the ratio of 1/e to practical imaging thickness holds from a cresol novolac to a polycarbosilane, then the practical thickness would be 140 nm. This is certainly better than 70 nm, but is still probably too thin to be practical. Unfortunately, most of the schemes for an organic developable resist are negative tone. Also an issue is whether or not an organic developable resist can be made immune to solvent swelling and the resulting problems.

Finally, at the current time, one has the two different paths or situations to choose from in the EUV resist game. They are thicker more transparent films with reasonable etching selectivity or thin films that image better and have exceptional etching selectivity. The organometallic bilayer and silylation schemes falls into the former category while plasma deposited polysilynes or trilayer schemes are in the latter. The defect density of thin films may be problematic while thicker films image slightly more poorly due to absorption. Neither situation is ideal. Silylation has the distinct advantage of offering imaging in a thin film that then is swollen with the refractory containing materials. Provided that the swelling does not introduce problems with image fidelity and provided that the swelling can be controlled, then silylation offers the best compromise.

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