Advanced measurements for photoresist fundamentals

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ABSTRACT

Advances in optical lithography, using chemically amplified photoresists, have continued to meet ITRS [1] goals. However, line-edge roughness (LER) and critical dimension (CD) control remain technical challenges for upcoming 65-nm and 45-nm nodes because both the image resolution and the thickness of the imaging layer now approach the macromolecular dimensions characteristic of the polymers used in the photoresist film. With accompanying decreases in film thickness, the photoresist/substrate and photoresist/air interfacial properties, and component distribution increasingly affect the overall performance of a photoresist. New measurement methods are needed to address fundamental issues that may limit the development of future photoresists.

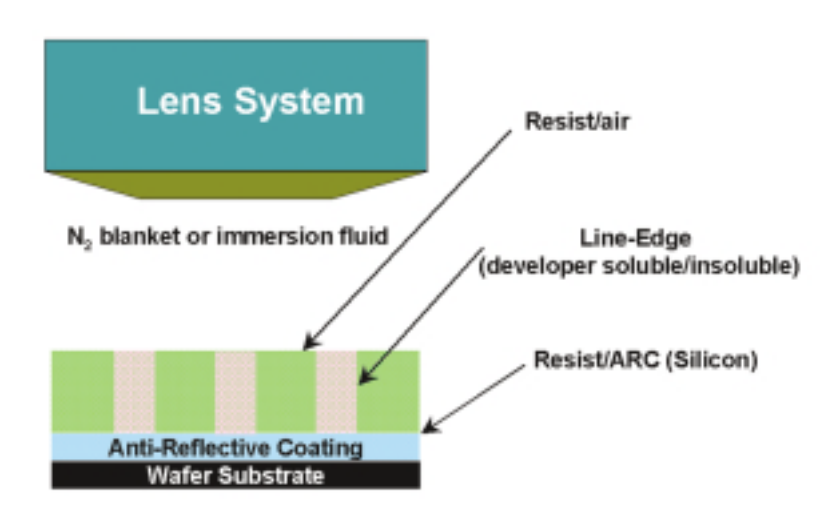

Figure 1. Schematic of lithographic interfaces. The highlighted interfaces include the resist/air, resist/substrate, and the developed latent image line-edge. Current exposure conditions utilize an inert nitrogen blanket, however, next-generation tools include immersion conditions leading to photoresist/liquid interfaces.

Introduction

Photolithography remains the driving and enabling technology in the semiconductor industry to fabricate integrated circuits with ever-decreasing feature size [1]. Current fabrication facilities use chemically amplified photoresists; complex and highly tuned formulations of polymer thin films loaded with photoacid generators (PAGs) and other additives. In a positive tone photoresist, a designed pattern is transferred to the silicon substrate by altering the solubility of areas of a polymer-based photoresist thin film through an acid-catalyzed deprotection reaction after exposure to radiation through a mask and a post-exposure bake. The material in the exposed areas is removed by an aqueous base developer, typically 0.26 M [2] tetramethylammonium hydroxide (TMAH). The reaction-diffusion and development processes must be controlled to achieve LER less than 1.5 nm at the 65-nm node for 2007 approaching the macromolecular dimensions of the polymer in the photoresist. The continued decrease in photoresist thickness has increased the influence of interfacial effects on lithographic performance.

Unique high-spatial resolution measurements are needed to investigate the limits on materials and processes that challenge the development of photoresists for next-generation lithography. In particular, we discuss three interfacial problems where information from new measurements provides insight into photoresist performance; characterization of water in the bulk and at the photoresist/substrate interface, component segregation at the photoresist/air interface, and the role of developer at the line-edge. Figure 1 highlights the interfaces of interest in a schematic of the predeveloped line:space pattern in a thin photoresist film upon an antireflective coating (ARC).

National research facilities provide a sophisticated experimental platform to rapidly expand the understanding of current materials and technical problems, as well as new tools typically unavailable at industrial or university laboratories. The use of synchrotron radiation at the National Synchrotron Light Source at Brookhaven National Laboratory (BNL) and the neutron source at the National Institute of Standards and Technology's (NIST) Center for Neutron Research provides an infrastructure to develop and extend materials and process development, providing complementary data to experimental results from on-line exposure tools.

Interfacial challenges for next-generation lithography

Due to the multiple stages in the photolithography process, routes to solving problems with CD or LER control must carefully consider contributions from each process step in addition to effects due to inherent material properties. Several studies were initiated to provide high-resolution measurements of components at the surface and interfaces that affect photoresist performance. Highlights include water profiling under immersion, photoresist component segregation at surfaces and interfaces, and developer fundamentals at model line-edges. The details of the experimentation are omitted, and only discussion of the results and their implications are presented. All the work has recently been presented or is available from the recent published literature such as the proceedings of the International Society for Optical Engineering (SPIE).

Immersion lithography: water profilometry

With the emergence of immersion lithography as a means to extend the 193-nm wavelength to the 45-nm node, the role of liquids in contact with photoresist films is important, not only for component leaching and contamination, but also due to the detrimental influence of trace levels of water (or other immersion fluid) on the reaction and diffusion of photoacid generators. In addition a nonuniform water profile within thin films can also lead to incorrect assumptions regarding the antireflective properties at the ARC/photoresist.

The distribution of deuterium oxide (D_2O) within model photoresist films in direct contact with a liquid was measured using neutron reflectivity. Neutron reflectivity is a powerful measurement method that provides detailed information about the through-plane profile of thin films. The water distribution within photoresist films can be measured because of the large neutron scattering contrast between hydrogen and deuterium. Data are collected from photoresist films immersed in D_2O. This method provides Å resolution in film thickness as well as a direct measure of the isotopic composition information.

Figure 2 shows the volume fraction of water at the photoresist/substrate interface [3]. We observe a region near the buried interface where the water concentration deviates from the bulk. Increases and decreases in the relative water concentration at the interface have been observed depending upon the specific polymer and substrate. For immersed poly(4-tert-butoxy-carbonlyoxystyrene) (PBOCSt), a model 248-nm photoresist [4], supported on a hexamethyldisilazane (HMDS)-treated silicon wafer, an excess concentration of water was observed where the maximum concentration at the interface was 17% by volume. In contrast, a depletion of water was observed for poly(4-hydroxystyrene) (PHOSt), a developer soluble resist, on HMDS-treated wafers. In the bulk of the film, the PHOSt absorbs almost 25% water by volume; depletion indicates that the interface cannot accommodate this amount. As the resist films become thinner, the interfacial water concentration dominates the resist swelling – the swelling for the PBOCSt and PHOSt films become similar for ultrathin films with thickness less than 200 Å as shown in the inset of Figure 2 for the fraction of film expansion $(h - h_o)/h_o$ versus the initial dry film thickness (h_o). This implies that the interfacial concentration is strongly dependent upon the surface chemistry, but relatively independent of the photoresist itself. The structure of the interfacial fluid is an important consideration for ARC/photoresist selection or surface preparation, even though bulk immersion fluid absorption values may be acceptable within process limits.

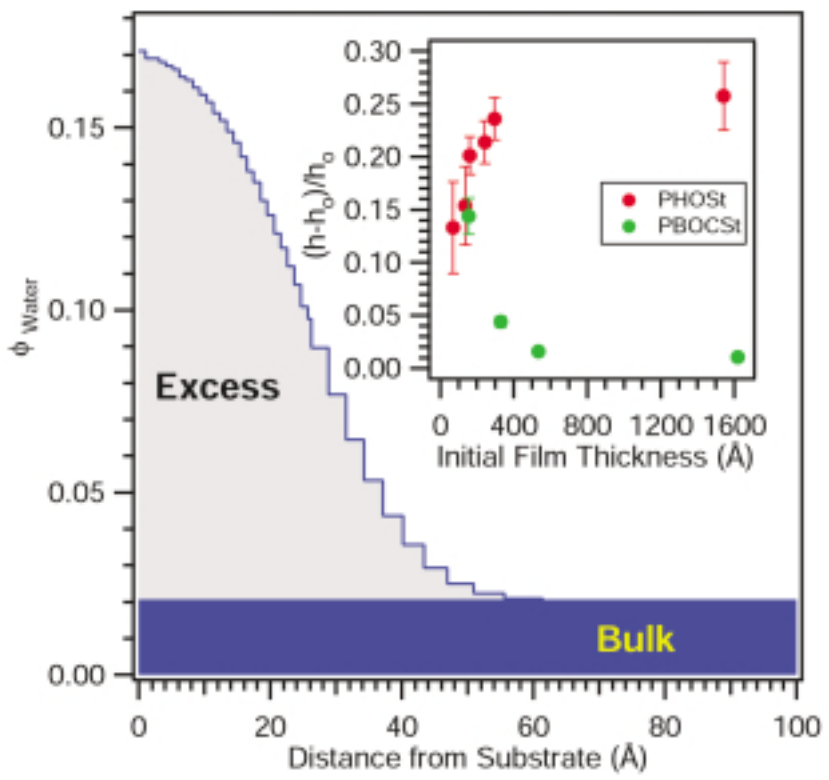

Figure 2. Volume fraction of water distributed near the PBOCSt/HMDS treated substrate as determined by neutron reflectivity. The excess of water at the substrate reaches a maximum concentration of 17% by volume. (inset) Dependence of film thickness on the total film swelling for two model photoresists in thin and ultrathin films. Adapted from [3].

Interfacial component segregation: surface versus bulk

As photoresist film thickness decreases, the presence of surfaces and interfaces can also control the distribution of critical photoresist components such as the photoacid generator. This nonuniform composition distribution can influence the resist chemistry and cause process or formulation-specific problems. Methods such as X-ray photoelectron spectroscopy (XPS), Rutherford back-scattering (RBS), and contact-angle measurements are typically used to provide surface chemistry information. More recently, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy at the NIST-DOW U7A beam-line at BNL was developed as a novel spectroscopic tool to provide depth profiling of the surface chemistry of organic films with nanometer resolution, while simultaneously measuring the bulk composition. The ability to measure the absorption edges of carbon, fluorine, nitrogen, and oxygen allows distinctions to be made between photoresist polymers, photoacid generator, and base additives. When acquiring NEXAFS spectra, soft X-rays are preferentially absorbed by the sample when the incident radiation is at the appropriate energy to excite a core-shell electron to an unoccupied molecular orbital. Auger electrons and photons are emitted when the excited core electron from the irradiated sample relaxes. Electrons emitted from deep within the film cannot escape; only electrons from the near surface of the film have enough kinetic energy to escape the surface potential. The bulk chemistry of the sample is measured by detecting photons emitted from up to ≈200 nm into the film by a fluorescence yield detector.

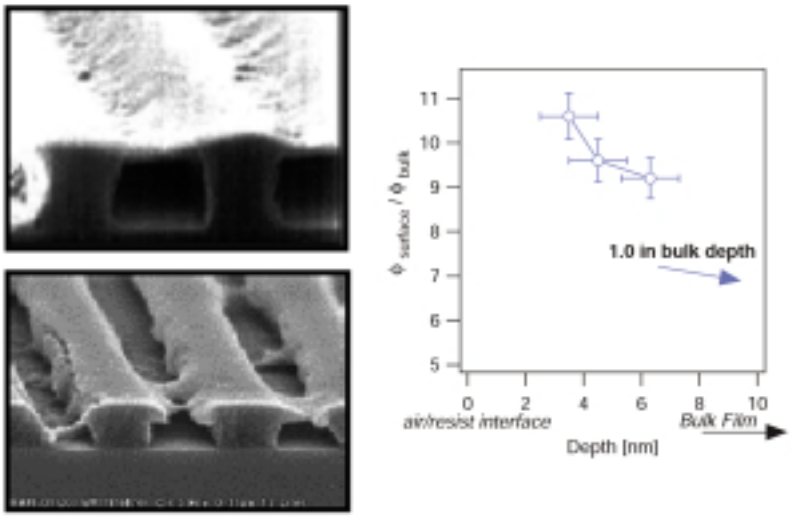

Figure 3. Schematic of the surface-related problems observed with patterned photoresists. Quantification of photoacid generator segregation in model 248-nm resist system. The surface exhibits an enriched PAG concentration over the top 6 nm when compared to the bulk as determined by NEXAFS. Adapted from [7].

Photoresist formulations employing polymer blends of fluorinated homopolymers and copolymers were recently [5] proposed for 157-nm exposure. The protected copolymer was designed as a dissolution inhibitor to the homopolymer to enhance its lithographic performance. However, the more hydrophobic or lower surface tension species will wet the blend film surface when heated in air. Preferential wetting [6] of the components to the thin-film/air interface was measured by comparing the chemical properties up to 6 nm into the surface to the bulk properties of the film using NEXAFS. Three blend film thickness were examined (80 ±2) nm, (60 ±2) nm, and (35 ±2) nm as summarized in Table 1 as a function of homopolymer (PNBHFA) and copolymer (P(NBHFA-co-MCPTFMA) blend content [7]. From the NEXAFS results, the surface composition changes little with thickness. For example, the 25:75 (mass ratio) blend films (PNBHFA:P(NBHFA-MCPTFMA)) have surface compositions between (47 and 51)%, hence independent of film thickness. This has implications for next-generation lithography due to decreasing thickness of photoresist films. In contrast to thicker films, a surface-rich component will be depleted from the rest of the film for ultrathin films (< 100 nm) and alter the expected performance of the photoresist. Additionally for thin films, a significant fraction of the film thickness will be enhanced in one component, influencing subsequent imaging, development, and etch processes.

TABLE 1: COMPOSITIONS OF THE LINEAR COMBINATIONS OF COMPONENT SPECTRA USED TO FIT THE SURFACE SPECTRA OF VARIOUS PNBHFA:P(MCPTFMA-NBHFA) MASS RATIO BLEND FILMS. FITS ARE ±≈5%

Film thickness	Initial blend composition PNBHFA:P(MCPTFMA-NBHFA)	Surface composition PNBHFA
80 nm	75:25	0.78
	50:50	0.57
	25:75	0.47
60 nm	75:25	0.82
	50:50	0.63
	25:75	0.51
35 nm	75:25	0.80
	50:50	0.62
	25:75	0.48

Similarly, PAG component segregation is observed by the NEXAFS technique by measuring spectra at the fluorine absorption edge. The PAG chemistry could be monitored with 2 nm precision at the surface and through the bulk to depths of 200 nm. The segregation of the PAG can lead to problems similar to those discussed in photoresist segregation. For example, if a PAG is designed to be present at 5% by mass in the overall film, but is enhanced by 10 times in a surface layer approximately 10 nm thick, the effective PAG concentration in the remaining film will be reduced, potentially leading to processing problems. The depth profile of the PAG is shown in Figure 3 for a model 248-nm resist system. The combination of NEXAFS and resist performance can identify mechanisms for solving process related problems such as T-topping or closure as shown in Figure 3.

Developer fundamentals: model line-edge

At the 65-nm node, line-edge roughness must be less than 1.5 nm [1]. With these stringent design criteria, it is increasingly important to determine the sources of LER and to provide solutions to reduce LER. The complexity of this problem comes from the enormous number of variables that can affect or tune the observed LER. Contributions to LER range from the exposure optic conditions, shot noise, material incompatibility, photoacid miscibility, and developer-resist interactions. Intense interest has now focused on the role of developer type and additives on LER because strategies for this final process may solve problems occurring at the exposure-tool scale. We have developed a strategy to highlight the material contributions to critical dimension control and line-edge roughness minimization by quantifying the developer influence on the photoresist [8,9]. A model photoresist bilayer geometry was constructed to simplify this problem using standard processing conditions and blanket ultra-violet (UV) light exposure as shown in Figure 4a. The method leads to a well-defined deprotection gradient between

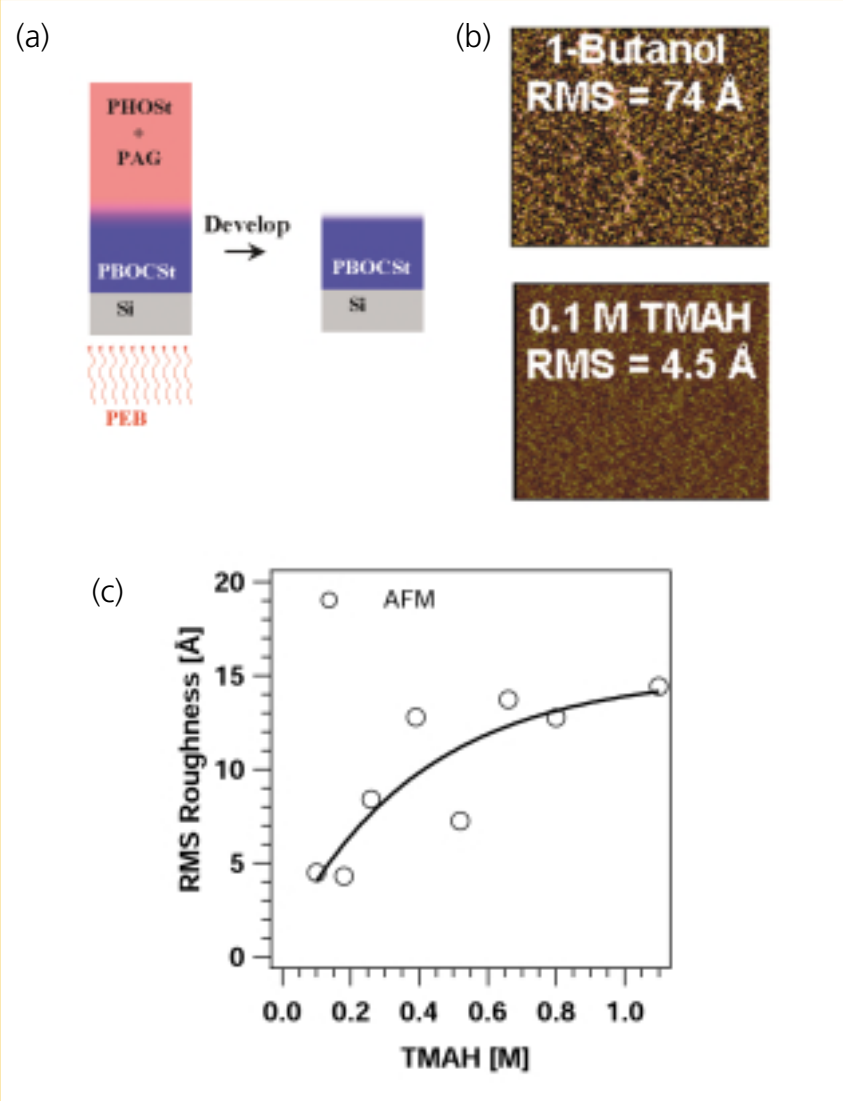

Figure 4 (a) model 248-nm materials comprise the bilayer experimentation serving as the model line-edge subject to development. (b) Development using either a polar solvent developer such as 1-butanol or 0.10 M TMAH developer illustrating the importance of developer choice on the surface features. Image sizes corresponds to 5 μm × 5 μm. (c) Developer strength dependence on the model line-edge roughness. Model studies will guide exposure-tool experimentation. Adapted from [10].

a photoacid feeder layer and a bottom-protected photoresist. This model line-edge width is dependent on the post-exposure bake processing, providing a method for examining material contributions to LER under varying conditions. We use this platform to investigate the influence of developer strength, additives, swelling and reaction front width effects on the final CD and model LER [10].

The ability to selectively dissolve areas in a patterned photoresist arises from the solubility of one of the components in an aqueous base solution. However, the interaction between the photoresist and developer is a function of developer strength, type of developer such as polar solvent versus aqueous base, and developer additives. Parameters such as developer strength and polar solvent are process variables that could affect LER. Figure 4b shows that development by 1-butanol compared to 0.10 M TMAH aqueous base leads to an increased surface roughness of 73 Å compared to 4.5 Å, as measured by atomic force microscopy (AFM). The source of the roughness difference in this system arises from swelling induced by a polar solvent (1-butanol). The aqueous base does not swell the photoresist film during development. The type of developer affects the solubility and mechanism of surface restructuring during the development and drying steps both of which contribute significantly to LER. Hence, the elimination of resist swelling, in the presence of a protection gradient, may be a viable strategy to reduce roughness and control critical dimensions. Using a weaker developer leads to lower LER, whereas a stronger developer strength, as shown in Figure 4c leads to an increase in LER. These model experimental methods provide a platform for systematic investigation of contributions to LER that are associated with the development process.

Summary

Model photoresists and sophisticated new measurement methods can provide a wealth of complementary information to exposure-tool experimentation to improve performance of photoresists as the industry enters the 65-nm node. These tools are especially needed because of the complexity of photoresist formulations and process steps in the preparation of nanostructured features. Here, three interfaces were highlighted that will become more important as feature size and film thickness shrink. The solid/photoresist interface was highlighted with regards to the nonuniform distribution of water for a model 248-nm material using neutron reflectivity. The segregation of photoresist components was discussed illustrating both photoresist blend and photoacid segregation. Lastly, the role of developer type and strength on model photoresist line-edges was presented to provide detailed insight into the origins of line-edge roughness from the development process. High-resolution experiments with nanometer resolution are needed and are being developed to help solve photoresist problems for upcoming nodes.

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