Optical Lithography

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Abstract—This is the first in a series of papers describing a theoretical process model for positive photoresist. This model, based upon a set of measurable parameters, can be used to calculate the response of photoresist to exposure and development in terms of image surface profiles. The model and its parameters are useful in many ways, from measuring quantitative differences between different resist materials to establishment of process sensitivities and optimization of the resist process within a manufacturing system.

In this paper, the concepts of photoresist modeling are introduced by following the exposure and development of a photoresist film on silicon exposed by a uniform monochromatic light flux. This very simple example provides insight into the complex nature of the photoresist process for reflective substrates.

The accompanying paper, "Characterization of Positive Photoresists," gives detail about measurement of the new photoresist parameters. It is supported by "*In-Situ* Measurement of Dielectric Thickness During Etching or Developing Processes" which discusses automated experimental techniques needed to establish photoresist development rates. These resist parameters provide a complete quantitative specification of the exposure and development properties of the resist. They also allow quantitative comparisons: lot to lot, material to material, and processing condition to processing condition.

The fourth paper, "Modeling Projection Printing of Positive Photoresists," applies the process model to one technique of photoresist exposure. This paper contains the detailed mathematics of the model. The model is then used to calculate line-edge profiles for developed resist images.

INTRODUCTION

OPTICAL lithography has become the dominant pattern delineation process in microelectronics. It is used for semiconductor devices, integrated circuits, magnetic elements and circuits, thin- and thick-film passive components, interconnections, and packaging. Additionally, it is used to create chrome masks for itself and patterns for other technologies such as silk screen printing and mask-delineated evaporation. It has contributed in a major way to the vast increases in productivity in electronics over the past decade.

Optical lithography as applied in microelectronics uses photoresists—light-sensitive paints which can be applied as thin-film coatings on surfaces where a pattern is to be delineated. The photoresist film is then exposed to an optical pattern using blue or ultraviolet light, creating exposed and unexposed areas. Development selectively removes the resist according to its exposure state. The remaining pattern of photoresist on the surface is used to delineate etching, plating, sputtering, evaporation, or other processes commonly used in microelectronics.

Even though competing techniques for exposure of resist materials using X-rays or electrons are being explored [1], [2], optical exposure remains by far the dominant technology. In integrated circuit manufacture, photoresists are now commonly used to delineate patterns with smallest dimensions of a few micrometers. However, in 1966, Scheutze and Hennings showed 0.4-μm patterns produced by projection printing [3]. For microwave acoustic transducers, Smith has made 0.4-μm patterns over broad areas by contact printing with thin conformable masks [1]. Holographic exposure has been used for gratings and optical couplers with patterns having under 0.1-μm periodicities [4]. Thus, although X-ray and electron exposure potentially have greater resolution than optical exposure, we are not yet pushing the limits of the optical lithographic technology in manufacture.

Photoresists have their roots in the beginnings of photography, and their chief usage today is still in the printing industry rather than in microelectronics. This usage varies from making patterns for halftone prints to creation of plates for offset lithography. It is from this latter application that microelectronics engineers have come to refer to the usage of photoresist to delineate patterns as lithography even though it bears little relationship to the ancient lithographic process of printing with wax patterned stone.

Optical lithography is similar to conventional photography in that a light-sensitive thin film is chemically altered by light so that an image can be produced by a subsequent development process. However, both the chemical processes and the resulting images are very different. Photography involves multiphoton absorption by silver compounds, whereas optical lithography for positive photoresists involves destruction of an organic compound by single photon absorption. The photographic image is one of optical density; the lithographic one is one of surface profile. Development in photography involves plating silver crystals on latent image specks; development of positive photoresists is an etching process. The differences are sufficient enough that an entirely new mathematical basis must be built for understanding optical lithography.

Photoresists are available for both positive and negative processes, i.e., development causes removal where the photoresist was exposed or unexposed. In this paper, we introduce a quantitative theoretical basis for the lithographic process as applied to positive photoresists. These are the materials with which most of the very high resolu-

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tion results have been obtained. They are being used increasingly in semiconductor manufacture. Significant differences between the behavior of the positive and negative resists make the mathematical treatment of exposure and development for one inapplicable to the other.

Positive photoresists are typically three-component materials consisting of a base resin which gives the resist its film-making properties, a photoactive compound, and volatile solvents to make the material liquid for application. In a dried film (typically 0.3–2 μm thick), the photoactive compound serves to inhibit dissolution of the photoresist in an alkaline aqueous developer solution. We refer to this compound as an inhibitor to emphasize this role. Destruction of the inhibitor by light creates by-product compounds which allow dissolution of the resist, resulting in increased rate of removal of the resist by the developer.

Lithography can be better understood if we consider the exposure and development process separately. Exposure modifies the photoresist chemically due to destruction of the inhibitor by the light in a suitable wavelength range. The effect of chemical modification is highly localized around the point where the photon is absorbed, and exposure level can vary widely within the resist film. Development is an etching process which selectively removes the photoresist at a rate related to the amount of inhibitor destroyed. The link between these two processes is the inhibitor distribution after exposure.

PHOTORESIST EXPOSURE

It would be convenient if we could consider thin films of photoresist to be uniformly exposed from the surface to the substrate. Two factors prevent this: the strong optical absorption of the material associated with its photosensitivity, and reflection from the substrate which causes coherent interference effects within the thin photoresist film [5]. Unlike photography, we have no antihallation coating for photoresist and the thin-film nature of the process itself causes exposure to be nonuniform. Unless we pay careful attention to these nonuniformities, there is no hope of understanding photoresist exposure.

The inhibitor compound typically represents about 30 percent of a dried photoresist film. The strong absorption associated with its photosensitivity contributes significantly to the optical absorption of the material at exposing wavelengths. As the inhibitor is destroyed, this absorption is removed as well. This can be described in terms of a relative inhibitor term $M(z,t)$ which is the fraction of the inhibitor remaining (at any position, z, and exposure time, t) as compared to the inhibitor concentration before exposure. There is little scattering in most photoresist films, so that the absorption constant, α, is given by

$$\alpha = AM(z,t) + B \tag{1}$$

where A and B are measurable materials parameters which describe the exposure dependent and exposure independent absorption.

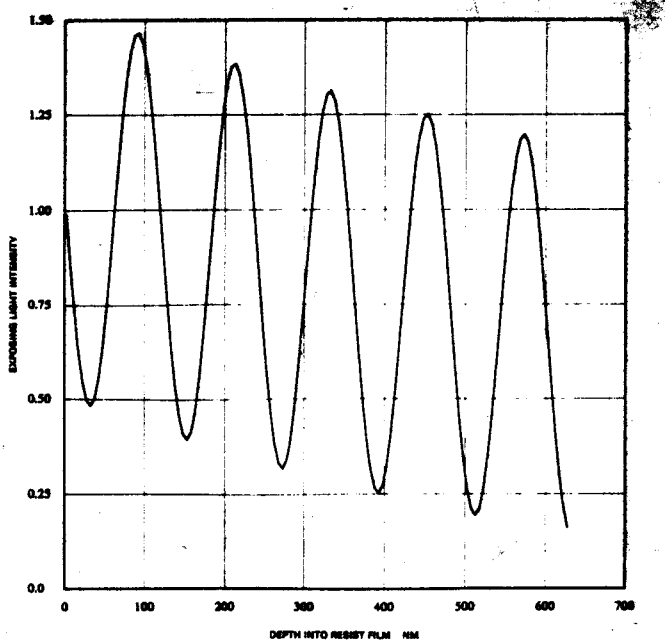

Fig. 1. Plot of intensity of exposing light within a 630-nm AZ1350J photoresist film on bare silicon at the beginning of exposure at a 404.7-nm wavelength.

The rate of destruction of the inhibitor is dependent on the local optical intensity $I(z,t)$, the local inhibitor concentration, and a measurable optical sensitivity term, C, as given by

$$\frac{\partial M}{\partial t} = -I(z,t)M(z,t)C. \tag{2}$$

A, B, and C depend upon the photoresist material and exposure wavelength. For Shipley Chemical Company's AZ1350J® photoresist, one of the commonly used high-resolution resist materials, $A = 0.86\ \mu m^{-1}$, $B = 0.07\ \mu m^{-1}$, and $C = 0.018\ cm^2/mJ$ for a 404.7-nm exposure wavelength. The accompanying paper "Characterization of Positive Photoresist" describes the measurements of these parameters in detail.

Photoresists are used for a variety of applications on a variety of substrates. These range from simple metal, semiconductor, or glass surfaces to complex multilayer structures of dielectrics, metals, and semiconductors. One common attribute of these substrates is that they reflect some of the exposing light back into the photoresist. As long as the substrate is smooth with specular (mirror-like) reflection, thin-film optical techniques can be used to calculate the intensity distribution within the resist film during exposure.

To understand the problems associated with resist exposure, we will consider in this paper a resist film (630 nm of AZ1350J photoresist) on bare silicon exposed to a uniform incident light flux of 15.7 mJ/cm² at a wavelength of 404.7 nm. The calculation techniques used in "Modeling Projection Printing of Positive Photoresists" allow us to calculate the optical intensity within the photoresist film. This is shown for the beginning of exposure in Fig. 1.

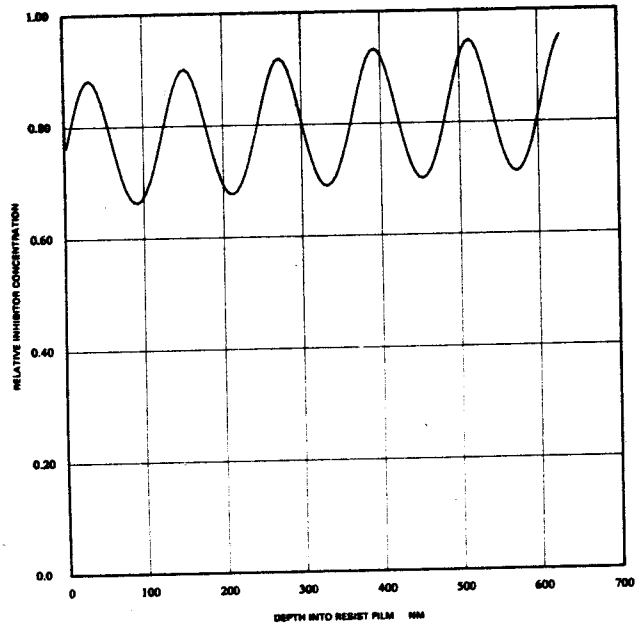

Fig. 2. Inhibitor concentration as a function of depth into an AZ1350J photoresist film on bare silicon exposed with 15.7 mJ/cm² at a wavelength of 404.7 nm.

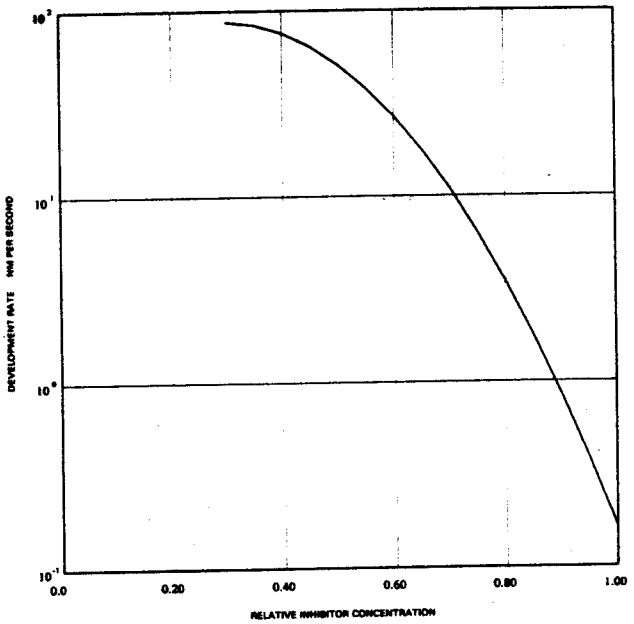

Fig. 3. Development rate curve for AZ1350J photoresist in 1:1 AZ developer:water at 20°C.

Optical interference causes the large close-spaced variation in intensity. Absorption causes the decrease in average intensity from the surface to the substrate. This intensity pattern changes in magnitude as the resist exposes due to a change in absorption, but the positions of the interference maxima and minima do not move.

Exposure of photoresist under this condition destroys more inhibitor at the intensity maxima than at the minima. The distribution of inhibitor within the film after exposure to 15.7 mJ/cm² is shown in Fig. 2. Although these variations appear small, it should be remembered that for unexposed photoresist $M = 1$, so that a value of $M = 0.7$ after exposure corresponds to six times the change seen with a value of $M = 0.95$.

PHOTORESIST DEVELOPMENT

Development of positive photoresist can be considered a surface-rate limited etching reaction. The parameters that control this rate are resist and developer chemistry (held constant) and the inhibitor concentration of the photoresist at the surface exposed to the developer. An experimentally determined curve relating development rate R to inhibitor concentration M, provides the link between exposure and development. "Characterization of Positive Photoresists" discusses the measurement of this $R(M)$ relationship.

Fig. 3 shows a typical development rate curve for AZ1350J photoresist in 1:1 AZ developer: H_2O at 20°C. The range of development rates shown by this curve is large. Unexposed photoresist is removed at a rate of under 0.2 nm/s whereas heavily exposed films are removed at nearly 100 nm/s. Even small variations in inhibitor concentration can cause significant change in development rate.

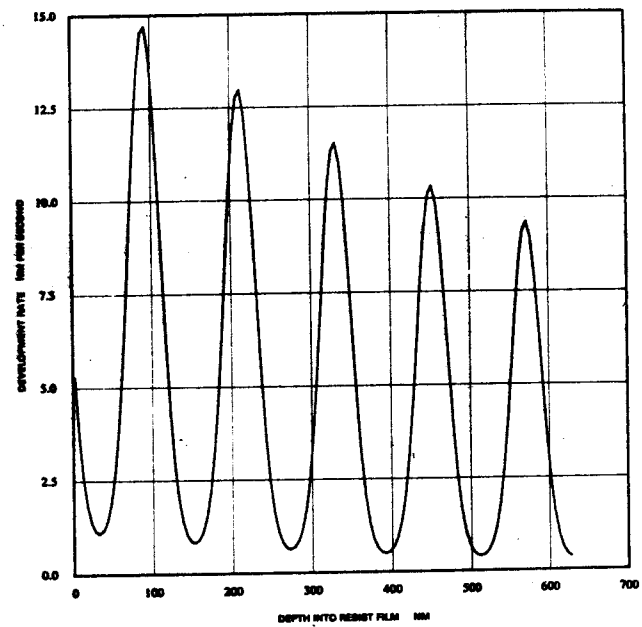

Fig. 4. Development rate profile for a 630-nm AZ1350J photoresist film on bare silicon exposed to 15.7 mJ/cm² at a wavelength of 404.7 nm.

We can use the $R(M)$ curve of Fig. 3 to obtain a development rate profile for the inhibitor distribution shown in Fig. 2. This is shown in Fig. 4. The development rate within our "uniformly exposed" photoresist film varies from under 1 nm/s at the lower interference minima to nearly 15 nm/s at the higher maxima. It is obvious that it will take a relatively long time to etch through the

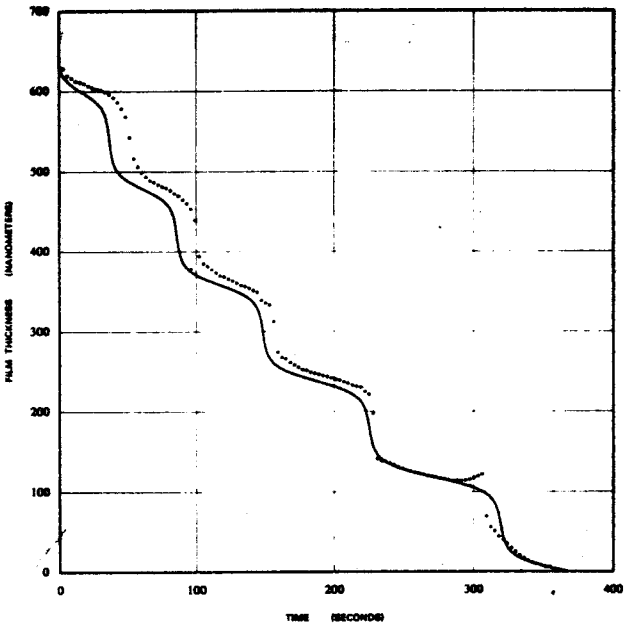

Fig. 5. Experimental and theoretical plot of AZ1350J photoresist film thickness during development.

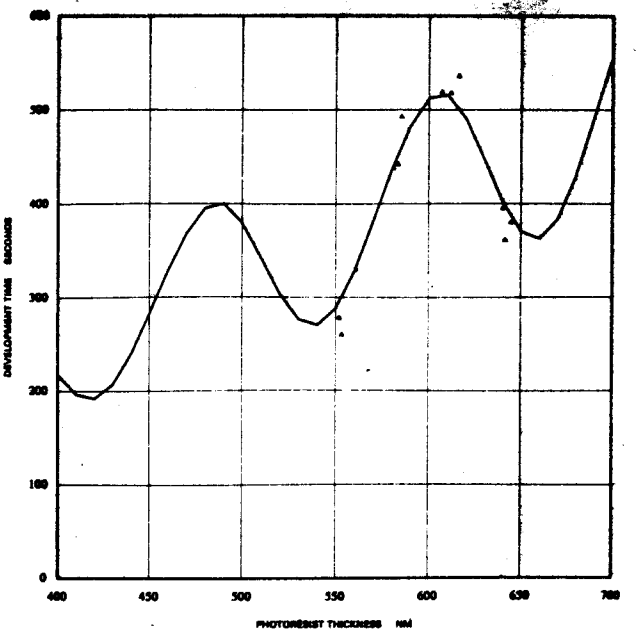

Fig. 6. Time to develop through photoresist films on bare silicon as a function of film thickness for constant exposure of 18 mJ/cm² at 404.7-nm wavelength showing calculated and experimental results.

regions of low-development rate compared to those with a high-development rate. This often causes problems developing through the exposure minimum nearest the substrate.

The time to develop from the surface ($z = 0$) to any depth, w, in a "uniformly exposed" resist film can be calculated from

$$t(w) = \int_0^w \frac{dz}{R(z)} \tag{3}$$

where $R(z)$ is a rate profile like that shown in Fig. 4.

This result is shown plotted as the thickness of a developing photoresist film as a function of development time in Fig. 5. Also in this figure is a measured curve of thickness versus development time for a 630-nm thick resist film exposed to 15.7 mJ/cm² at 404.7 nm and developed in 1:1 AZ developer: H_2O at 20°C. The measurement was made using the automated IOTA spectrophotometer discussed in the accompanying paper "*In-Situ* Measurement of Dielectric Thickness During Etching or Developing Processes."

The stair-step shape of Fig. 5 is evidence of the influence of interference effects in photoresist exposure. The excellent agreement between the experimentally determined curve and the calculated one gives assurance that we understand the photoresist exposure and development process quantitatively. This agreement between experiment and theory even holds down to the scale of the interference effects which are only 60 nm from an exposure maximum to the adjacent minimum.

Because we have photoresist as a thin film on a reflecting substrate, we expect the overall reflectivity of the resist–substrate combination should vary as we change the resist thickness. Reflectivity maximizes for even quarter-wavelength multiples of resist thickness which lowers the energy coupled into the resist; reflectivity minimizes for odd quarter-wavelength multiples where energy coupling maximizes. This makes the time necessary to develop through a photoresist film periodic with resist thickness for a fixed exposure flux. Fig. 6 shows a calculation of the time to develop through films of AZ1350J resist on bare silicon exposed to 15.7 mJ/cm² at 404.7 nm and developed in 1:1 AZ developer: H_2O at 20°C as a function of resist thickness. The experimental points show good agreement with the calculated curve. Without theory and careful thickness measurement, their spread would have been interpreted as scatter.

CONCLUSIONS

The photoresist modeling concepts presented here have many uses. Even the simple one-dimensional example described previously has been useful for studies of different resists, developers, resist thicknesses, substrates, and exposure wavelengths. The availability of *in-situ* measurement tools for determining resist thickness during development provides a convenient verification of modeled results.

The resist parameters A, B, C, and $R(M)$ are a complete description of the exposure and development properties of the resist since they are sufficient for the analytic model. Quantitative comparisons of resist materials or process conditions can be expressed in terms of these parameters. For example, prebake of AZ1350J photoresist at 100°C for 1 h has been found to thermally decompose nearly half of the inhibitor, resulting in a significant reduction

in the exposure dependent absorption term A and the development rate curve $R(M)$. This, of course, is also evident in modeled results.

The model has been used to predict contours of coherent optically produced diffraction gratings and to investigate the effect of dye additions to the resist in an attempt to reduce interference effect [6]. The nonlinearity of resist response, easily seen with the model, has clearly been responsible for failure of efforts to use positive photoresist to make phase holograms. With help from the model to find linear response regions, one could hope for greater success.

The changes in resist parameters and processing conditions can be studied in terms of image profiles and profile sensitivities. With the model, one can see detail unobservable by any experimental techniques. Even where results can be studied experimentally, difficulty in controlling experimental conditions often obscures the results.

This new model represents a starting point. With the ability to predict what to expect for photoresist response, we can now look for discrepancies between theory and experiment and improve the model. For example, high prebake temperatures, in addition to changing the resist parameters, alter the resist surface with relation to the bulk so that the film can no longer be treated as isotropic. Surface initiation parameters for development can be introduced to improve the accuracy of the model.

We are just beginning to make optical lithography a quantitative engineering science. More materials and processing conditions need to be evaluated. Contact and near-contact exposure environments need to be modeled. The projection exposure model needs to be applied to the new polychromatic exposure systems. Although the newer X-ray and electron-beam systems potentially have higher resolution capability, optical lithography will be the main-line technology for many years. The process is not yet being practiced at its demonstrated limits; considerable gains in density, performance, and yield are still available.

The photoresist materials we have to work with are varied, and they perform well. They have been easy enough to use that remarkable progress has been made in spite of the absence of a quantitative process theory describing how they work. The patterns are becoming smaller and smaller, giving greater productivity to the technology. This is making the control of the pattern-making technologies more critical. The metallurgical microscope has been the commonly used process control tool, but as the patterns get smaller, the capability of optical microscopy to study detail becomes limited. New tools are needed, and a process model is one of them.

Optical lithography using photoresists is playing an important role in the revolution of microelectronics. We now interconnect thousands of transistors into complex integrated circuits on a tiny chip of semiconductor not much larger than was used for a single transistor only a few years ago. Magnetic bubble devices, Josephson tunneling cryotron switches, circuit boards, packages, color-TV tubes, display devices, and evaporation masks are among the many elements manufactured using photoresists. If silicon is to be the new steel, perhaps photoresists are the new coal, necessary for the manufacture of the steel.

REFERENCES

[1] H. I. Smith, "Fabrication techniques for surface acoustic wave and thin film optical devices," *Proc. IEEE*, pp. 1361–1387, Oct. 1974.
[2] D. R. Herriott, R. J. Collier, D. S. Alles, and J. W. Stafford, "EBES, a practical electron lithographic system," *IEDM Tech. Dig.*, Washington, D. C., Dec. 1974, pp. 21–22.
[3] J. H. Scheutze and K. E. Hennings, "Large-area masking with patterns of micron and submicron element size," *Solid-State Technol.*, vol. 9, pp. 31–35, July 1966.
[4] C. V. Shank and R. V. Schmidt, "Optical technique for producing 0.1-μm periodic surface structures," *Appl. Phys. Lett.*, vol. 23, pp. 154–155, Aug. 1973.
[5] S. Middelhoek, "Projection masking, thin photoresist layers, and interference effects," *IBM J. Res. Develop.*, vol. 14, pp. 117–124, Mar. 1970.
[6] A. R. Neureuther and F. H. Dill, "Photoresist modeling and device fabrication applications," Proc. Microwave Research Institute Symposium XVIII, New York, N. Y., Apr. 1974.