# Positive Photoresists - Exposure

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There are a large number of materials, both organic and inorganic, which are sensitive to light (see, for example, Ref. 1).  However, over the years one specific class of photosensitive materials has been dominate in the application of integrated circuit manufacturing -- the diazonaphthoquinone/novolak system found in conventional g-line and i-line positive photoresists.    Rather than present a comprehensive review of photoresist materials here, I will limit my discussion to this one material, though the general principles will often apply to any photoresist.  (For an excellent in-depth text on these materials, consult Ref. 2).

The purpose of a photoresist is given by its name:  it must be sensitive to light so that patterns can be formed in it and it must resist subsequent etching or other steps so that the pattern can be transferred into the underlying substrate.  It would be difficult to find one chemical substance which adequately performs both of these functions, as well as other important functions such as adhesion and coatability.  Thus, most high performance photoresists "divide the labor" by using specific components which perform or enhance one of the necessary functions.  The conventional positive photoresist has three major components:  a photosensitive component called the *photoactive compound* (PAC), a *novolak resin* to provide structural stability and etch resistance, and a *solvent* which puts the solid photoresist into liquid form for the purpose of coating a substrate.

The PAC used in conventional positive photoresists is a diazonaphthoquinone (DNQ), an imposing sounding name for the non-chemist.  A nitrogen group (the diazo-) provides the chemical bond which is sensitive to light.  Absorption of ultraviolet or near ultraviolet light excites the molecule which can then undergo a chemical reaction by taking in water and releasing nitrogen gas to produce a compound known as a carboxylic acid.
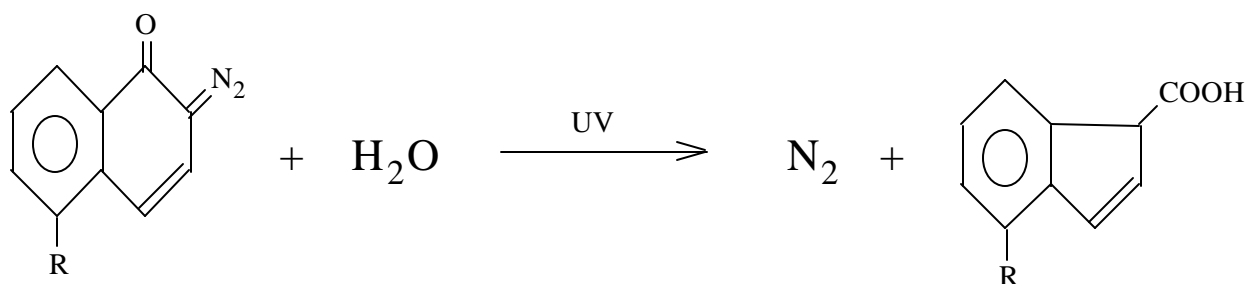
The DNQ is a fairly nonpolar organic molecule which is soluble in many organic solvents but not very soluble in water. The carboxylic acid photoproduct, on the other hand, is quite polar and is thus soluble in polar solvents such as water. In fact, since acids react quite well with bases, the carboxylic acid is very soluble in a solution of aqueous base. Thus, using an aqueous base as the developer, the exposed PAC is soluble but the unexposed PAC is not, creating a solubility differential with exposure that forms the basis of resist image formation.

It is not sufficient to simply change the solubility of the PAC upon exposure; the entire photoresist mixture must change its solubility. Thus, the interaction of the PAC with the novolak resin is crucial. Novolak by itself is moderately soluble in the aqueous base developer. However, upon addition of the DNQ, the solubility of the mixture is dramatically reduced. The DNQ strongly interacts with the novolak (usually through hydrogen bonding) and inhibits dissolution of the resin, typically by a factor of 10 to 100. For this reason, the DNQ is often called a *dissolution inhibitor*. The acid photoproduct, on the other hand, enhances the solubility of the resin. The acid continues to interact with the resin, resulting in a 10 to 100 fold increase in its dissolution rate. This inhibition/enhancement effect is optimized by careful construction of both the PAC and the resin.

Although the discussion above describes what happens to photoresist upon exposure to light, it fails to quantify the *amount* of chemical conversion for a given amount of exposure energy. The answer to this question is obtained by a *kinetic* analysis of the reaction. Kinetics is the study of how fast a reaction proceeds and is based on the statistical probability that all of the reacting species will be at the right place at the right time to react. In order to determine the kinetics of a chemical reaction, one must know not only the overall reaction, but also the mechanism, i.e., the intermediate chemical steps that lead to the final product. Determining the mechanism of a reaction is often extremely difficult. Fortunately, DNQ exposure has been extensively studied and the mechanism is well established.

Let $M$ represent the concentration of unexposed PAC at any time during exposure, where $M_O$ is the initial PAC concentration (before exposure). If $P$ represents the concentration of the photoproduct (the carboxylic acid), then the stoichiometry of the reaction says that

$$P \ = \ M_O - M \tag{1}$$

Kinetics will tell us the rate at which the PAC disappears during exposure with the following result:

$$\frac{dM}{dt} \ = \ -CMI \tag{2}$$

where $C$ is a rate constant and $I$ is the intensity of light acting on the photoresist for an exposure time $t$. This equation, called the kinetic rate equation for this reaction, says that the rate at which the PAC disappears (is exposed) is proportional to the concentration of the PAC to the first power, and is called *first order* for this reason. Equation (2) can easily be integrated (assuming $I$ is independent of $M$) to solve for the remaining PAC concentration after exposure.

$$M \;=\; M_o e^{-CE} \tag{3}$$

where

$$E \;=\; \int_0^t I\,dt \tag{4}$$

is the exposure dose.  It is very important to note that the exposure dose used in these equations is the actual exposure dose that is seen at some given point in the photoresist and is a function of, but quite different from, the nominal incident dose that is generally set with the exposure tool.

An understanding of the kinetics of the exposure of our DNQ resist has lead to an equation which quantifies the amount of PAC left after exposure as a function of the exposure dose.  But as I mentioned, the dose of importance to the photoresist is the actual dose at the point of interest in the resist, not the nominal incident dose.  The dose within the resist differs from the incident dose due to the reflections, absorption, and interference of the light as it passes through the resist and other films present on the wafer.  Thus, an optical analysis of the film stack and wafer is required to relate incident dose to the actual dose at some point in the resist.

One of the important processes which causes the light intensity to change within the photoresist is absorption.  The amount of absorption can be quantified with the *Lambert Law of Absorption*, which states that within a homogeneous material the relative change in intensity with distance traveled is constant.  In equation form,

$$\frac{dI}{dz} \;=\; -aI \tag{5}$$

where $z$ is the distance traveled and $a$ is a constant called the *absorption coefficient*.  For a material which is a mixture of several components (such as photoresist), the absorption coefficient is a function of the concentration of the absorbing species.  As one might expect, increasing the concentration of a highly absorbing component of the resist would increase the overall absorption coefficient of the resist.  This relationship is quantified by *Beer's Law*, an empirical law which states that the absorption coefficient of a mixture is directly proportional to the concentration of each absorbing species.  The proportionality constant for each component is called the molar absorptivity of the component and is a fundamental property of the material.

For example, a photoresist may be made up of a resin $R$, a solvent $S$, a photoactive compound $M$, and, after some exposure, a photoproduct $P$.  The absorption coefficient for the photoresist would be given by

$$a \;=\; a_M M + a_P P + a_R R + a_S S \tag{6}$$

where $a_i$ is the molar absorptivity of component $i$. Note that both $M$ and $P$ are a function of exposure. Thus, in general, exposure will change the value of the absorption coefficient of the photoresist! It is convenient to rearrange equation (6) to group the exposure dependent and exposure independent terms. Recalling that $M$ and $P$ are related by the stoichiometry of the reaction (equation (1)), equation (6) can be simplified to read

$$\boldsymbol{a} \quad = \quad Am + B \tag{7}$$

where $m = M/M_o$ is the relative PAC concentration and $A$ and $B$ are constants for a given photoresist material. Note that $m$ initially is 1 (no exposure) and goes to 0 (complete exposure).

For a conventional DNQ/novolak resist, $A$ is a positive number. Thus, exposure (which decreases $m$) will decrease the absorption coefficient making the resist more transparent. We say that these resists *bleach* upon exposure and the change is noticeable to the eye. For this reason $A$ is often called the *bleachable absorption coefficient* and, by analogy, $B$ is called the *nonbleachable absorption coefficient*. Together with the kinetic rate constant of equation (2), these parameters are known as the ABC parameters of a photoresist and are extremely important in describing the optical properties of a photoresist. The ABC parameters are also called the Dill parameters, after Rick Dill of IBM who first described them [3].

Exposure kinetics entails a knowledge of the chemical effects of exposure of photoresist to light and allows us to quantify the lithographic effects of various exposure doses. However, it is not sufficient to know the dose *incident* on the resist, we must know the dose *within* the resist. Absorption is one important process which affects the dose within the resist. Another extremely important phenomenon is the multiple reflections and interference of light as it passes through the thin photoresist film and possibly other films on the wafer. These *thin film interference effects* give rise to standing waves and swing curves, two topics for the next edition of this column.

## References

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3. F. H. Dill, et al., "Characterization of Positive Photoresist," *IEEE Trans. Electron Dev.*, ED-22, No. 7, (1975) pp. 445-452, and *Kodak Microelectronics Seminar Interface '74* (1974) pp. 44-54.