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MODELING THE EFFECTS OF PREBAKE ON POSITIVE RESIST PROCESSING

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INTRODUCTION

The purpose of a positive photoresist prebake is to dry the resist by removing solvent from the film. However, as with most thermal processing steps, the bake has other effects on the photoresist. When heated to temperatures above 70°C, the photoactive compound (PAC) of a diazo-type positive photoresist begins to decompose to a non-photosensitive product. The reaction mechanism is thought to be identical to that of the PAC reaction during ultraviolet exposure.[1-4] The identity of the product X will be discussed in a following section.

To determine the concentration of PAC as a function of prebake time and temperature, consider the first order decomposition reaction,

$$M \xrightarrow{UV} P \qquad (2)$$

where M is the photoactive compound. If we let M_0' be the concentration of PAC before prebake and M_0 the concentration of PAC after prebake, simple kinetics tells us that

$$\frac{dM_o}{dt} = -K_T M_o$$

$$M_o = M_o' e^{-K_T t_b} \qquad (3)$$

$$m' = e^{-K_T t_b}$$

where t_b = bake time
K_T = rate constant at temperature T
$m' = M_0/M_0'$.

The dependence of K_T upon temperature is given by the Arrhenius equation.

$$K_T = A_r e^{-E_a/RT} \qquad (4)$$

where A_r = Arrhenius coefficient
E_a = activation energy
R = universal gas constant

Thus, the two parameters E_a and A_r allow us to know m' as a function of the prebake conditions.

The effect of this decomposition is a change in the chemical makeup of the photoresist. Thus, any parameters which are dependent upon the quantitative composition of the resist are also dependent upon prebake. The most important of these parameters fall into two categories: 1) optical (exposure) parameters such as the resist absorption coefficient, and 2) development parameters such as the development rates of unexposed and completely exposed resist. A technique will be described to measure E_a and A_r and thus quantify these effects of prebake.

EXPOSURE PARAMETERS

In the model proposed by Dill, et. al.,[5] the exposure of a positive photoresist can be characterized by the three parameters A, B, and C. A and B are related to the optical absorption coefficient of the photoresist, α, and C is the overall rate constant of the exposure reaction. More specifically,

$$\alpha = A\,m + B$$
$$A = (a_M - a_P)M_0 \qquad (5)$$
$$B = a_P M_0 + a_R R + a_S S$$

where a_M = molar absorption coefficient of the photoactive compound M
a_P = molar absorption coefficient of the exposure product P
a_S = molar absorption coefficient of the solvent S
a_R = molar absorption coefficient of the resin R
M_0 = the PAC concentration at the start of the exposure (i.e., after prebake)
m = M/M_0, the relative PAC concentration as a result of exposure.

These expressions do not take into account the effects of prebake on the resist composition. To do so, we can modify equation (5) to include absorption by the component X.

$$B = a_P M_0 + a_R R + a_X X \qquad (6)$$

where a_x is the molar absorption coefficient of the decomposition product X and the absorption term for the solvent has been neglected. If we let M_0' be the PAC concentration before prebake,

$$X = M_0' - M_0. \qquad (7)$$

Thus,

$$B = a_P M_0 + a_R R + a_X(M_0' - M_0). \quad (8)$$

Let us consider two cases of interest, no bake and full bake. When there is no prebake, $M_0' = M_0$ and

$$A_{NB} = (a_M - a_M)M_0'$$
$$B_{NB} = a_P M_0' + a_R R. \quad (9)$$

We shall define full bake as a prebake which decomposes all PAC. Thus $M_0 = 0$ and

$$A_{FB} = 0$$
$$B_{FB} = a_X M_0' + a_R R \quad (10)$$

Using these special cases in our general expressions for A and B,

$$A = A_{NB} m'$$
$$B = B_{FB} - (B_{FB} - B_{NB})m'. \quad (11)$$

DEVELOPMENT PARAMETERS

The development rate is, of course, dependent on the concentration of PAC in the photoresist. An analytical expression for this dependence has been given by Mack.[6]

$$r = r_{max}\frac{(a+1)(1-m)^n}{a+(1-m)^n} + r_{min} \quad (12)$$

where r = development rate (nm/sec)

r_{max} = development rate of fully exposed resist

$$r_{max} = -\frac{k_D D}{k_D/k_R M_0^n + 1}$$

r_{min} = development rate of unexposed resist

n = developer selectivity (an experimentally determined constant)

$a = k_D/k_R M_0^n$

$$a = \frac{(n+1)}{(n-1)}(1-m_{TH})^n$$

m_{TH} = the threshold relative PAC concentration.

Thus, knowing m' one can modify the values for r_{max} and a (or n) accordingly. This procedure assumes, however, that the product X does not effect development rate. Of course, the validity of this assumption depends on the identity of compound X.

Several studies have been performed to determine the composition of the product X[2-4]. The results indicate that there are two possible products and the most common outcome of a prebake decomposition is a mixture of the two. The first product is formed via the reaction (13) and is identical to the product of UV exposure.

As can be seen, this reaction requires the presence of water. A second reaction, which does not require water, is the esterification of the ketene with the resin (14).

Both possible products have a dramatic effect on dissolution rates. The carboxylic acid (III) is very soluble in developer and enhances dissolution. In terms of the parameters of equation (12), the formation of product (III) can be modeled as a blanket exposure of the resist. The dissolution rate of unexposed resist (r_{min}) will increase due to the presence of the carboxylic acid. The dissolution rate of fully exposed resist (r_{max}), however, will not be affected. Since the chemistry of the dissolution process is unchanged, the values of n and m_{TH} will also remain unchanged.

The ester (IV), on the other hand, is very difficult to dissolve in aqueous solutions and thus retards the dissolution process. It will have the effect of decreasing r_{max}. The affects of ester formation on the parameters n and m_{TH} are less obvious. Analysis of development rate data for AZ1350J at prebake temperatures of 70°C and 100°C shows that the value of n is smaller at the higher temperature and m_{TH} remains unchanged.[6]

If the two mechanisms given in equations (13) and (14) are taken into account, the rate equation (3) will become

$$\frac{dM_0}{dt} = -K_1 M_0 - K_2[H_2O]M_0 \quad (15)$$

where K_1 and K_2 are the rate constants of equations (13) and (14), respectively. For a given concentration of water in the resist film this reverts to equation (3) where

$$K_T = K_1 + K_2[H_2O]. \quad (16)$$

Thus, the relative importance of the two reactions will depend not only on the ratio of the rate constants but on the amount of water in the resist film. The concentration of water is a function of atmospheric conditions and the past history of the resist-coated wafer. Further experimental measurements of development rate as a function of prebake temperature are needed to quantify these effects.

Table I
Prebake Model Parameters for Various Resists

Resist	A_{NB} (μm^{-1})	B_{NB} (μm^{-1})	B_{FB} (μm^{-1})	E_a (Kcal/mol-K)	ln (A_r) (A_r in min^{-1})
Kodak 820 (365 nm)	1.00	0.10	0.19	30.3	35.3
OFPR-800 (436 nm)	0.44	0.055	0.14	30.8	36.5
Acculith 6010 (405 nm)	0.54	0.06	0.09	52.3	64.4

EXPERIMENT

Examining equation (11), one can see that the parameter A can be used as a means of measuring m', the fraction of PAC remaining after prebake. Thus, by measuring A as a function of prebake time and temperature, one can determine the activation energy and the corresponding Arrhenius coefficient for the proposed decomposition reaction. Using the technique given by Dill, et al,[5] A, B and C can be easily determined by measuring the optical transmittance of a thin photoresist film on a glass substrate while the resist is being exposed. The positive photoresists used were KODAK Micro Positive Resist 820, OFPR-800 and Acculith 6010.

Examples of the measured transmittance curves are given in Figure 1, where transmittance is plotted versus exposure time. The different curves represent different

prebake temperatures. For every curve, A, B, and C can be calculated.[5] Figure 2 shows the variation of the resist parameter A with prebake conditions. According to equations (3) and (11), this variation should take the form

$$\frac{A}{A_{NB}} = e^{-K_T t_b}$$

$$\ln\left(\frac{A}{A_{NB}}\right) = -K_T t_b. \quad (17)$$

Thus, a plot of ln(A) versus bake time should give a straight line with a slope equal to $-K_T$. This plot is shown in Figure 3. Knowing K_T as a function of temperature, one can determine the activation energy and Arrhenius coefficient from equation (4). The results are given in Table I for the resists studied. One should note that the parameters A_{NB}, B_{NB} and B_{FB} are wavelength dependent, but Ea and Ar are not.

CONCLUSIONS

Figure 2 shows an anomaly in which there is a lag time before decomposition occurs. This lag time is the time it took the wafer and wafer carrier to reach the temperature of the convection oven. Equation (3) can be modified to accommodate this phenomena,

$$m' = e^{-K_T(t_b - t_{wup})} \quad (18)$$

where t_{wup} is the warm-up time. A lag time of about 11 minutes was observed when baking a ¼" thick glass substrate in a wafer carrier. When a 60 mil glass wafer was used without a carrier, the warm-up time was under 5 minutes and could not be measured accurately.

Figure 4 shows and interesting phenomenon that occurred during convection oven prebake of Acculith 6010 at temperatures of 130°C or higher. The data shows two distinct linear regions, the first being the decomposition of PAC, the second depicting the decomposition of the resin due to the high temperatures. The same phenomenon was observed for OFPR-800 at 130°C.

Although all the data presented thus far has been for convection oven prebake, the above method of evaluating the effects of prebake can also be applied to hot-plate prebaking. An initial study into hot-plate prebaking seems to indicate that the activation energy is not affected by the method of prebake, but the Arrhenius coefficient will be significantly different.

Finally, the effects of prebake on the exposure parameters A and B have been incorporated into the lithography model PROLITH (the Positive Resist Optical Lithography model)[6]. As of yet, the effects of prebake on development have not been included in this model pending further experimental studies.

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REFERENCES

1. F. H. Dill and J. M. Shaw, "Thermal Effects on the Photoresist AZ1350J," *IBM Jour. Res. Dev.*, Vol. 21, No. 3, (May, 1977) pp. 210-218.
2. J. M. Shaw, M. A. Frisch and F. H. Dill, "Thermal Analysis of Positive Photoresist Films by Mass Spectrometry," *IBM Jour. Res. Dev.*, Vol. 21, No. 3, (May, 1977) pp. 219-226.
3. J. M. Koyler, F. Z. Custode and R. L. Ruddell, "Thermal Properties of Positive Photoresist and their relationship to VLSI Processing," *Kodak Interface '79*, (Nov. 1979) pp. 150-165.
4. D. W. Johnson, "Thermolysis of Positive Photoresists," *Adv. Resist Tech., Proc.*, SPIE Vol. 469, (1984) pp. 72-79.
5. F. H. Dill, et. al., "Characterization of Positive Photoresists," *Trans. Electron Dev.*, Vol. ED-22, No. 7, (July, 1975) pp. 445-452.
6. C. A. Mack, "PROLITH: A Comprehensive Optical Lithography Model," *Optical Microlith. IV, Proc.*, SPIE Vol. 538, (1985) pp. 207-220.

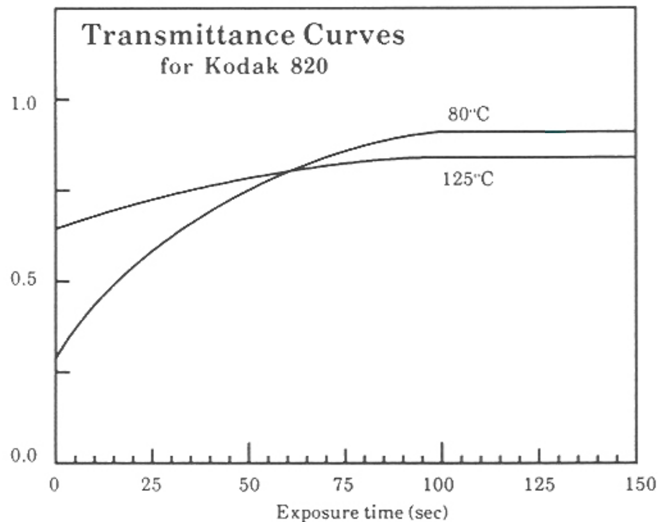

FIGURE 1: Two transmittance curves for Kodak 820 at 365 nm. The curves are for a prebake of 30 minutes at the temperature shown.

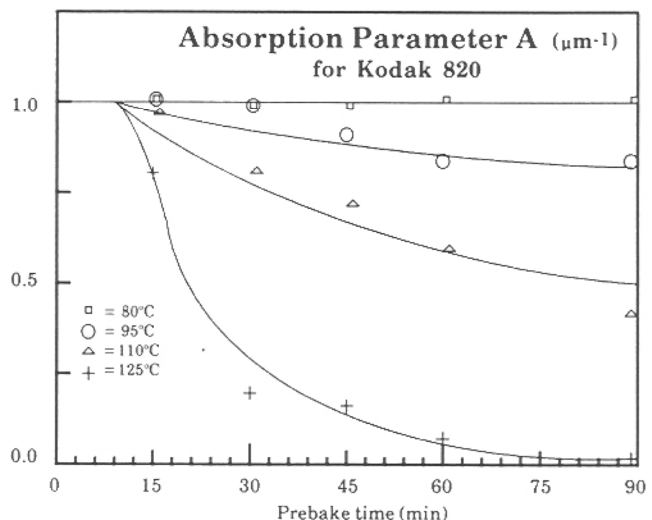

FIGURE 2: The variation of the resist absorption parameter A with prebake time and temperature for Kodak 820 at 365 nm.

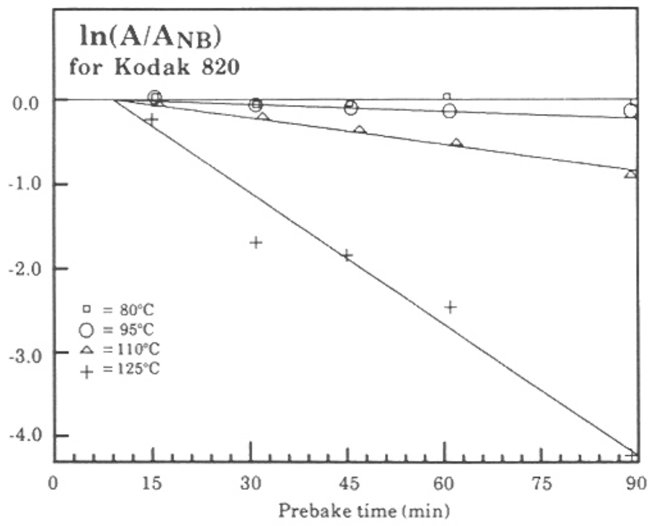

FIGURE 3: Log plot of the resist absorption parameter A with prebake time and temperature for Kodak 820 at 365 nm.

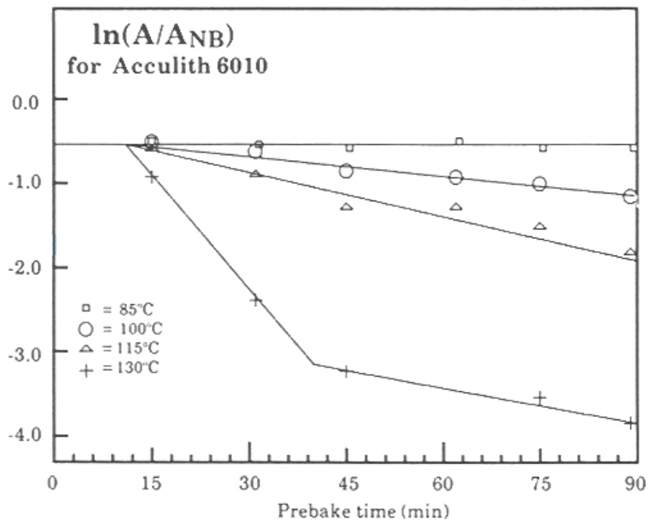

FIGURE 4: Log plot of the resist absorption parameter A with prebake time and temperature for Acculith 6010 at 405 nm.