

## **Analysis of Deprotection Reaction for Chemically Amplified Resists by Using FT-IR Spectrometer with Exposure Tool**

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### **ABSTRACT**

A Fourier transform infrared (FT-IR) spectrometer with built-in exposure tool (248 nm) is used to perform *in situ* observations of the decomposition of protective groups (deprotection reactions) in chemically amplified resists during exposure, with the exposure ambient temperature varied. In addition, the activation energy and the prefactor of deprotection reaction necessary for lithography simulation are determined. Resist polymers used in this experiment are poly (*p*-hydroxystyrene) (PHS) protected by Ethoxyethyl (EOE) or by *tert*-Butoxycarbonyl (t-BOC), and its copolymers. The activation energy is compared at room temperature (23 °C). As a result, the activation energy for EOE deprotection reaction is 8.90 kcal/mol, while for t-BOC deprotection reaction is 23.65 kcal/mol. The activation energy for EOE resist is much lower than for t-BOC resist. Progress of the deprotection reaction in EOE resist during exposure at room temperature can be explained in terms of differences in activation energies. In the copolymer resist, introduction of EOE into PHS protected by t-BOC resulted in a decrease in the activation energy required for the t-BOC deprotection reaction. From this it is found that in a resist composed of PHS copolymer with heterogeneous protection groups attached, the interaction affect between protection groups deprotection reactions. Lithography simulations of resist profiles are performed with the activation energy and the prefactor varied, and the effect of the activation energy on the resist profile is investigated. The results indicate that patterning is possible for an exposure ambient temperature of 20 °C or higher for EOE resist, and that of 70 °C or higher for t-BOC resist.

### **1. INTRODUCTION**

Beginning with the research by Ito and colleagues in 1987<sup>[1]</sup>, chemically amplified (CA) resists using acid-catalyzed reactions have become indispensable for the manufacture of sub-half-micron semiconductor devices. During this period, diverse researches have been conducted to improve the resolution of CA resists and to enhance environmental stability<sup>[2]-[5]</sup>. In positive-type CA resists, acid is produced in photochemical reactions as a catalyst and protection groups are dissociated

in the heating process that follows exposure (PEB: post-exposure bake). Therefore the acid generation efficiency by exposure, acid diffusion, the type of protection groups and the protection ratios are closely related to CA resist performance. An accurate understanding of deprotection reactions is essential for the development of resists and the evaluation of processing technologies. In recent years appropriate models for deprotection reactions during PEB have been proposed<sup>[6]~[8]</sup>. However there have been few reports of analysis of deprotection reactions during exposure<sup>[9]</sup>. Therefore we develop an FT-IR spectrometer equipped with a UV light source, analyze and model of deprotection reactions during exposure in positive-type CA resists. In addition, we determine the parameters for lithography simulation and simulate the resist profile.

## **2. EXPERIMENTAL**

The analysis system used in these experiments is MODEL PAGA-100 by Litho Tech Japan (Fig. 1). This system is based on MODEL-135 by BIO-RAD, but equipped with a 248 nm exposure tool, a bake plate, and a wafer transport shuttle (Fig. 2). The exposure tool uses a dielectric film filter to narrow the spectral width of the ultraviolet light emitted from a Xe-Hg lamp to 248 nm before incidence on the wafer via an optical fiber. Exposure dose in wafer surface is 3 mW/cm<sup>2</sup>. A bake plate is used to control the ambient temperature during exposure between room temperature and 150 °C. In order to enable observations of IR light transmitted through a Si wafer, a 10 mm diameter hole is opened in the center of the bake plate. In process of measurements, first, a sample are transported in a wafer transport shuttle, into the FT-IR sample chamber, and next began exposure and IR measurement as soon as it reaches the prescribed temperature by the bake plate.

The resists used in this experiments are composed of PHS resin protected by EOE or by t-BOC, and its copolymers (Fig. 3). Resist compositions are shown in Table 1. A homopolymer resist is protected by 45 % EOE (hereafter the notation H450055, where numbers are the protection ratios of EOE, t-BOC, and OH), a homopolymer resist is protected by 35 % t-BOC (H003565), a copolymer resist is protected by 26 % EOE and by 9 % t-BOC (C260955), and a copolymer resist is protected by 12 % EOE and by 23 % t-BOC (C122355). Triphenyl sulphonium triflate (TPS) is used as a photoacid generator (PAG). Resists are contained PAG at 3 wt%.

The resist thickness is 1 μm for all samples. The prebaking is carried out for 90 s at 90 °C. These samples are exposed in an IR sample chamber with the ambient temperature during exposure varied, and *in situ* observations of the IR spectra are performed. The variation in protection group absorption with exposure obtained during *in situ* measurements are converted into deprotection reaction rates, exponential functions are fitted to obtain exposure-induced deprotection reaction curves. A deprotection simulator by Litho Tech Japan is used for the analysis. It is used to obtain the deprotection reaction constant  $C_2$  from these deprotection reaction curves. From an Arrhenius plot of  $C_2$  obtained for

various exposures ambient temperatures, the activation energy  $E_a$  (kcal/mol) and the prefactor ( $s^{-1}$ ) are calculated and compared.

A development rate measurement system RDA-790 by Litho Tech Japan is used to determine the development parameters required for simulations<sup>[10]</sup>. The activation energies, the prefactors, the development parameters and the ABC parameters are used to simulate resist profiles.

### **3. RESULTS**

#### **3.1 Deprotection Reaction Model**

Fig. 5 shows deprotection of EOE and t-BOC during exposure at 68 °C as obtained from the *in situ* IR spectra. Exposure generates acids in the EOE resist, and a heat-induced acid-catalyzed reaction causes dissociation of EOE groups and production of PHS; the dissociated EOE groups are thought to undergo hydrolysis and be decomposed into ethanol and aldehydes (Fig. 4-a)<sup>[11]</sup>. In the t-BOC resist, exposure causes production of acid, and another heat-induced acid-catalyzed reaction causes dissociation of t-BOC groups and production of PHS; the dissociated t-BOC groups are thought to decompose into carbon dioxide and isobutene (Fig. 4-b)<sup>[1, 12]</sup>. In terms of the IR spectrum, as the exposure dose is increased, absorption of ether groups at 947  $cm^{-1}$  decreased in the EOE resists, and absorption of ester carbonyl groups at 1760  $cm^{-1}$  decreased in the t-BOC resists, indicating that dissociation of protection groups occurred (Fig. 5). These peaks are plotted as PHS protection ratio versus exposure dose in Fig. 6. Deprotection occurs with increase in the exposure ambient temperature, and an exponential function can be fitted to the deprotection reaction data (eq. (1)).

$$[P]_{\text{exp}} = \exp(-C_2 E) \quad (1)$$

Here  $[P]_{\text{exp}}$  is the protection ratio,  $C_2$  is the deprotection reaction constant, and  $E$  is the exposure dose.

An Arrhenius plot of deprotection reaction constant  $C_2$ , calculated from eq. (1) for the several samples with the exposure ambient temperature varied, is shown in Fig. 7. The Arrhenius plots is expressed by eq. (2).

$$C_2 = A_r \exp(-E_a / RT) \quad (2)$$

Here  $C_2$  is the deprotection reaction constant,  $A_r$  is the prefactor, and  $E_a$  is the activation energy.  $R$  is the universal gas constant, and  $T$  is the absolute temperature. The activation energies calculated from the Arrhenius plots are found different two regions: a region at low temperatures where the reaction rate is controlled by the deprotection reaction ( $K_{\text{amp}}$ ), a region at high temperatures where the reaction rate is controlled by acid diffusion ( $K_{\text{diff}}$ ). The existence of two regions in the activation energy agrees with the model proposed by Byers and Petersen<sup>[13, 14]</sup>.

### 3.2 Measurement Results

The activation energies at room temperature are compared. The activation energy for EOE deprotection reaction is 8.90 kcal/mol, while for t-BOC deprotection reaction is 23.65 kcal/mol. The activation energy for EOE resist is much lower than for t-BOC resist. Progress of the deprotection reaction in EOE resist during exposure at room temperature can be explained in terms of differences in activation energies. In the copolymer resist, introduction of EOE into PHS protected by t-BOC resulted in a decrease in the activation energy required for the t-BOC deprotection reaction (Table 2, Figs. 8 ~ 11). From this it is found that existence of heterogeneous protection groups affect the action of acid on deprotection reactions.

### 3.3 Simulation Results

Using the activation energies and the prefactors obtained in section 3.2, simulations of resist profiles are performed with the exposure ambient temperature varied (Figs. 12 and 13). The parameters used in simulations are shown in Table 3. The simulations are performed focusing on the activation energies and prefactors for each protection groups.

In the case of PHS protected by EOE, 250 nm L/S patterns are possible at an exposure ambient temperature of 20 °C. However, as the activation energy and the prefactor increased on introduction of t-BOC, the optimum exposure dose and the exposure ambient temperature increase. In the case of PHS protected by t-BOC, 250 nm L/S patterns are possible at an exposure ambient temperature of 70 °C. However, as the activation energy and the prefactor decreased on introduction of EOE, the optimum exposure dose and the exposure ambient temperature decrease.

From this, it is confirmed that existence of heterogeneous protection groups affect the action of acid on deprotection reactions.

## **4. CONCLUSION**

The analysis of deprotection reaction is hitherto performed by only the changes of IR absorption of protection groups in PEB. However it is difficult to accurately analyze deprotection reactions at the protection groups like EOE dissociated at room temperatures. By using this system for the in situ analysis of deprotection reactions during exposure with the exposure ambient temperature varied, it is possible to get valuable insights for deprotection reactions in resists having protection groups which undergo deprotection at room temperatures. In order to clarify changes in resist profiles by deprotection reactions during exposure, lithography simulation studies will be needed which take into consideration the activation energies of heterogeneous protection groups.

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Table 1 Resists composition

	EOE	t-BOC	OH
H450055	45%	0%	55%
C260965	26%	9%	65%
C122365	12%	23%	65%
H003565	0%	35%	65%

Table 2 Activation energies and Prefactors

	H450055	C260965	C122365	H003565
EOE $K_{amp}E_a$ [kcal/mol]	8.90	10.30	10.86	-
EOE $K_{amp}\ln(Ar)$ [ $s^{-1}$ ]	11.26	13.34	14.06	-
EOE $K_{diff}E_a$ [kcal/mol]	2.48	3.77	4.31	-
EOE $K_{diff}\ln(Ar)$ [ $s^{-1}$ ]	1.10	3.07	3.76	-
t-BOC $K_{amp}E_a$ [kcal/mol]	-	12.30	16.07	23.65
t-BOC $K_{amp}\ln(Ar)$ [ $s^{-1}$ ]	-	14.31	19.53	30.80
t-BOC $K_{diff}E_a$ [kcal/mol]	-	6.72	8.29	10.55
t-BOC $K_{diff}\ln(Ar)$ [ $s^{-1}$ ]	-	6.72	8.69	11.94

Table 3 ABC parameters and Development parameters

Parameters	Values
Resist Thickness	700 nm
Prebake	90 °C / 90 s
A	-0.03 $\mu m^{-1}$
B	0.24 $\mu m^{-1}$
C	0.04 $cm^2/mJ$
Development Time	60 s
Development Model	Mack
Development $R_{max}$	308.00 nm/s
Development $R_{min}$	0.11 nm/s
Development $M_{th}$	0.01
Development n	8.00
Exposure Wavelength	248 nm
Feature Width	250 nm L/S



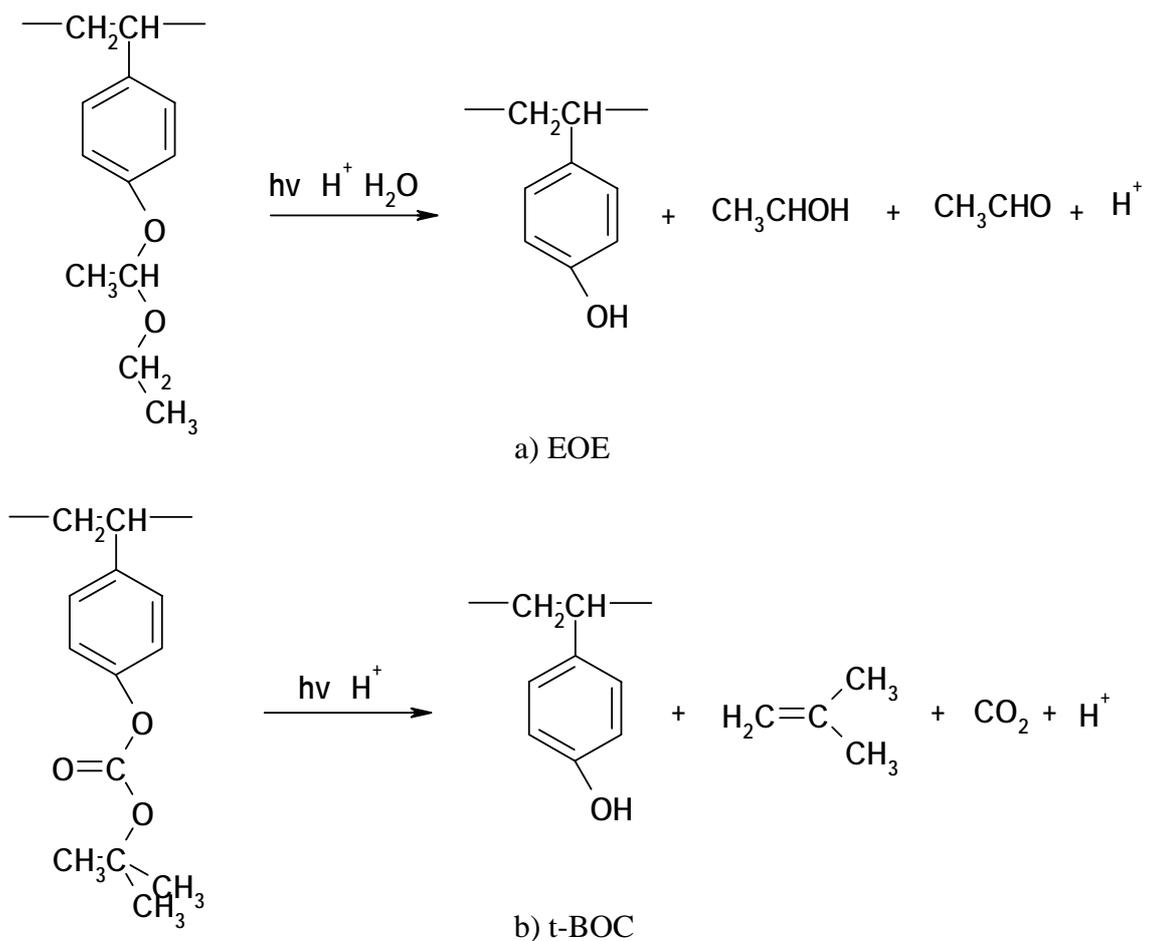


Fig. 4 Deprotection reaction mechanism

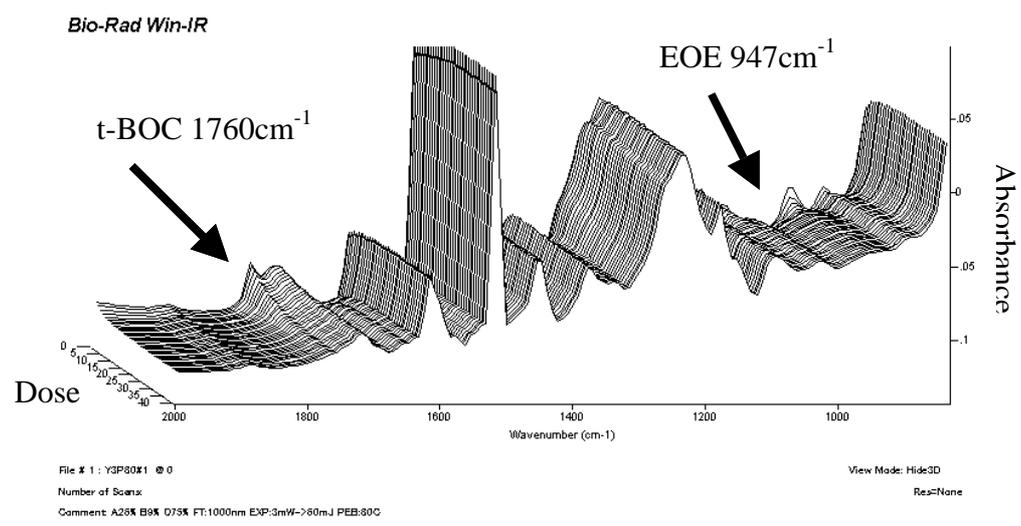


Fig. 5 IR absorption spectra of deprotection reaction

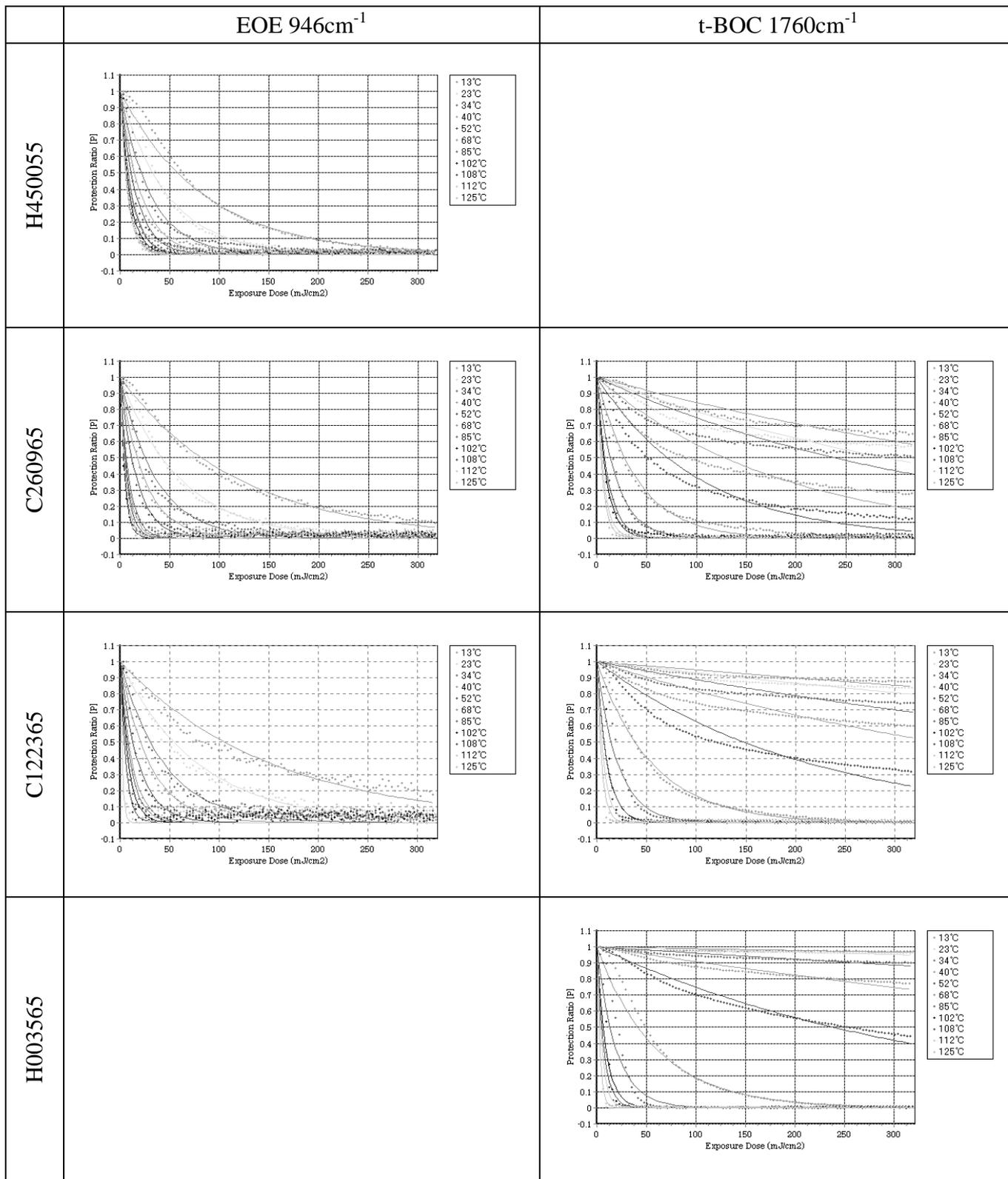


Fig. 6 PHS protection ratio versus exposure dose

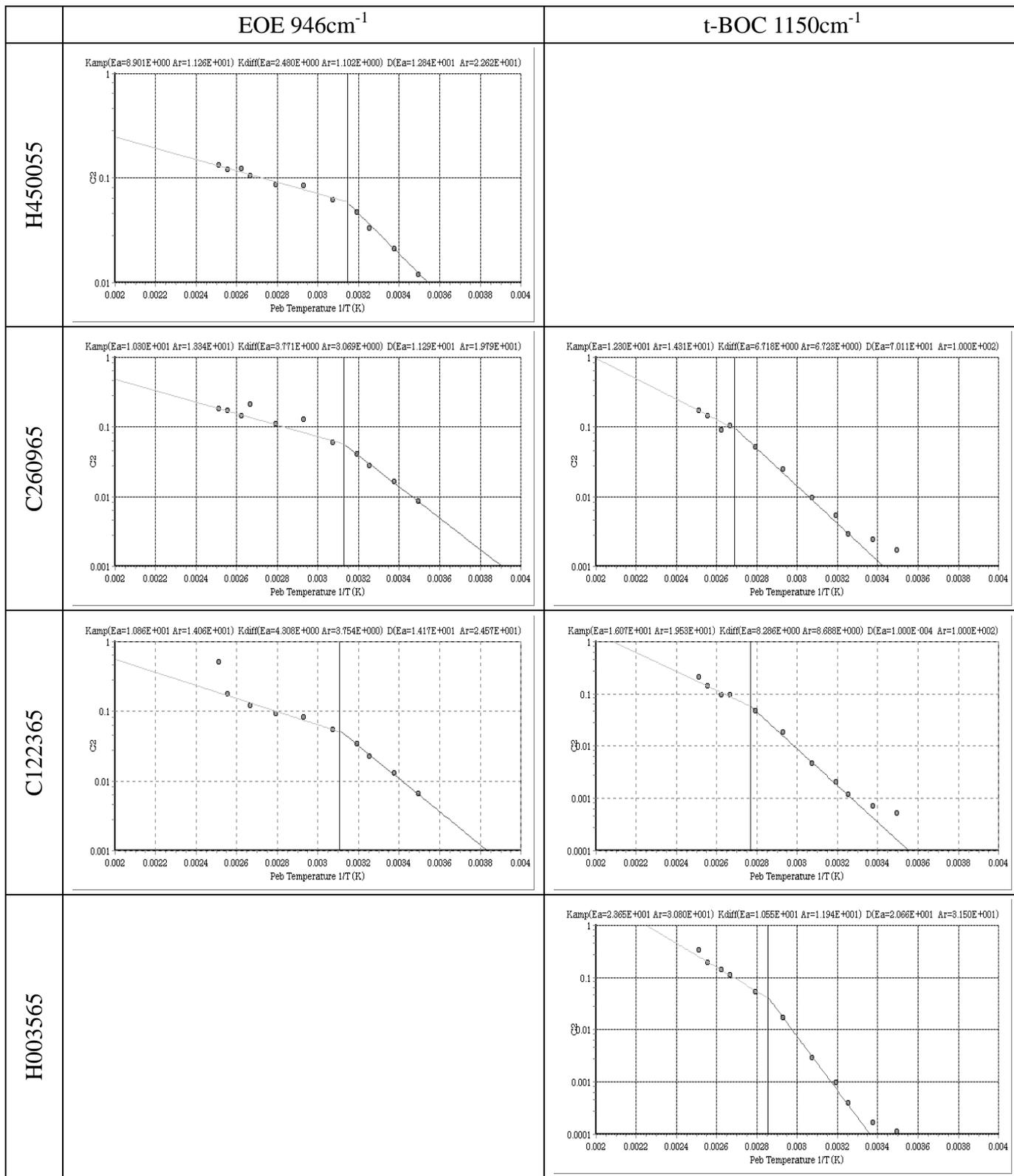


Fig. 7 Arrhenius plots of deprotection reaction constant C<sub>2</sub>

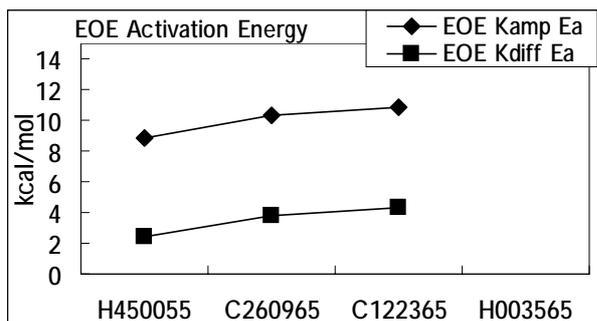


Fig. 8 EOE activation energy

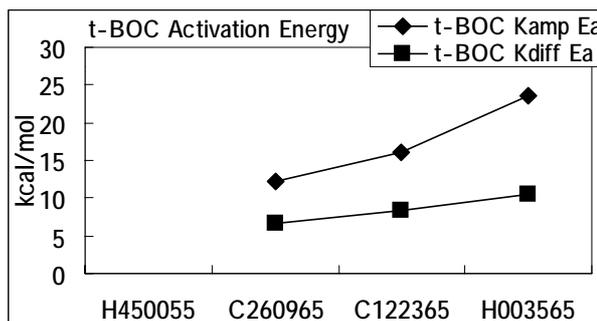


Fig. 9 t-BOC activation energy

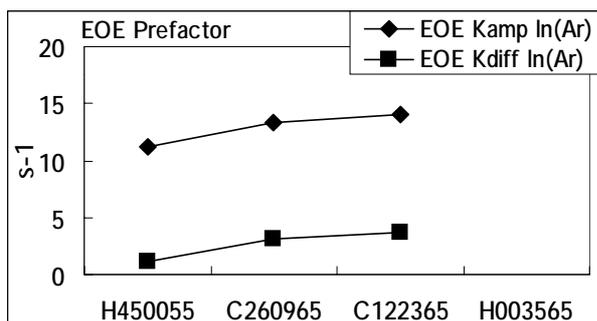


Fig. 10 EOE prefactor

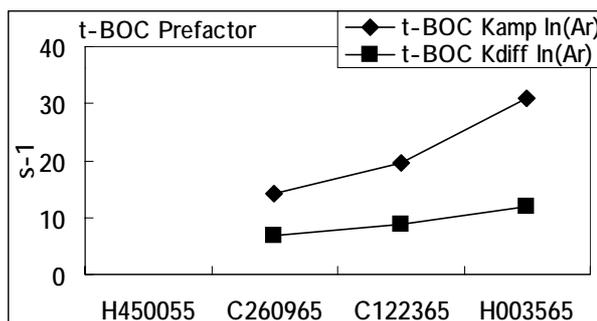


Fig. 11 t-BOC prefactor

Expo.Temp. [°C]	20	30	40	50	60	70	80
Protected by EOE H450055							
Dose [mJ/cm <sup>2</sup> ]	59.18	22.30	12.21	7.30	4.75	3.35	2.60
Protected by EOE C260965							
Dose [mJ/cm <sup>2</sup> ]	100	32.37	15.00	8.21	4.91	3.27	2.39
Protected by EOE C122365							
Dose [mJ/cm <sup>2</sup> ]	100	49.50	18.65	9.63	5.64	3.68	2.59

Fig. 12 Simulation results (250nm L/S) for PHS resist protected by EOE

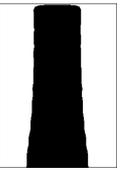
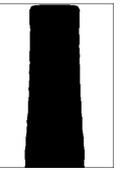
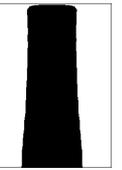
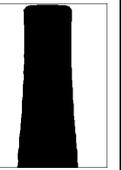
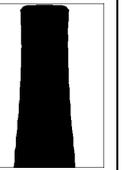
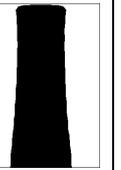
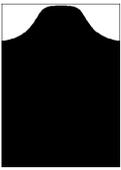
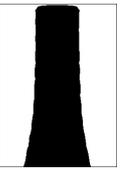
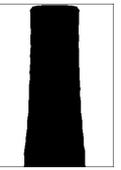
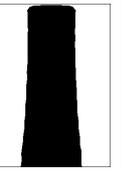
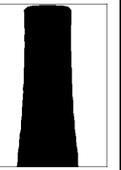
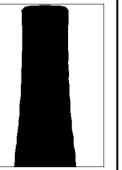
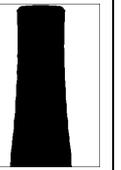
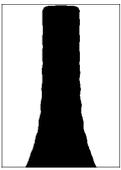
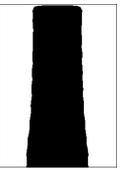
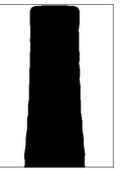
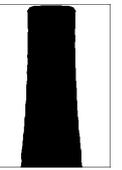
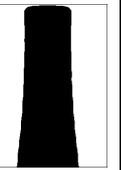
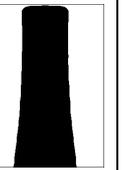
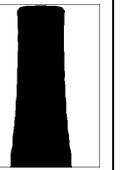
Expo.Temp. [°C]	60	70	80	90	100	110	120
Protected by t-BOC H003565							
Dose [mJ/cm <sup>2</sup> ]	500	51.57	13.42	5.78	3.09	1.92	1.34
Protected by t-BOC C122365							
Dose [mJ/cm <sup>2</sup> ]	500	76.78	25.31	14.07	9.70	7.76	6.91
Protected by t-BOC C260965							
Dose [mJ/cm <sup>2</sup> ]	141.70	36.94	20.22	13.94	11.38	10.59	10.94

Fig. 13 Simulation results (250nm L/S) for PHS resist protected by t-BOC