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Improved Resolution of Thick Film Resist (Effect of Development Technique)

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Abstract

In view of the fact that little analysis of the mechanism for the achievement of high resolution or a high aspect ratio in the thick-film resist process has been performed, we study development properties with respect to differences between the development methods employed for pattern formation using thick-film resist. This study identifies the most effective development method for thick-film resist and reports the mechanism of development. For this investigation, we use a development rate measurement system, a mask aligner, and lithography simulator to examine the dipping development method, the step puddle development method, the vibration development method, and the reverse development method. We employ a thick-film positive resist composed of diazo-naphthoquinone (DNQ) and Novolak resin, which is coated on a silicon substrate to a thickness of 24 σm. After pre-baking, the coated substrate is placed in a vacuum dessicator to remove water, followed by immersion in deionized water for a fixed period. A mask pattern is transfered to the resist coated substrate with a Mask Aligner Q4000 made by Quintel Corporation, and then the rate of development is measured. A laser microscope analysis of the result indicates that the step puddle development method gives the highest pattern resolution and sharpness, followed by the vibration development method, the dipping

development method, and lastly the reverse development method. The mechanisms of the development are studied by comparing the development contrast and the energy of activation involved in each development method, and by conducting resist pattern simulations. The results indicate that the factors responsible for retarding the progression of the development process and causing a degradation of pattern profile and resolution are development inhibition due to N_2 released from inside the resist during the development process, and due to products that are dissolved in the development solution.

Keywords: <Thick-film resist><Development Technique><Resolution>
<Nitride bubbles><Development rate measurement system>
<Mask Aligner><Lithography simulations>

1. Introduction

Thick-film resist is increasingly used in micro-electro-mechanical systems (MEMS), hard disks, tape bonding (TAB), bump formation on chips-on-glass (COG), chip-scale packages (CSP), and plating processes [1]. However, the thickness of such resist films precludes the direct use of thin-film resist processes for the manufacture of ICs. Reduced resolution is the major problem in processing thick-film resists, a fact that has been indicated by several researchers [2]. Therefore, thick-film resist requires photo-processes that have been specifically developed for thick films. In a previous report, we proposed a water-immersion process for thick-film resist [3]. In order to determine the optimal development method for thick-film resist, in the present work, we investigated the influence

of development methods on patterning performance. Using a Mask Aligner Q4000 [4] from Quintel Corporation, we performed resist patterning for each development method and investigated the resulting resolution and sharpness of patterns. In addition, we used a development-rate measurement system (resist development analyzer: RDA) [5] to evaluate development properties. Based on the measurement results, we studied the mechanism of the development methods employed. Specifically, for each development method, we measured the development contrast, and investigated the relationship between the development contrast and the pattern profile using the lithography simulator SOLID-C [6]. Based on the results of development-rate measurements at different development temperatures, we compared the reaction rate constants and the activation energies for each of the development methods. In addition, we investigated development inhibition using a model describing the formation of an N_2 deposition layer on the resist surface during the development process, and examined the effects of products soluble in the development solution. From the results thus obtained, we determined the best development method for thick-film resist, and inferred the mechanism.

2. Purpose of Research and Experimental Method

2.1 Purpose of Research

Figure 1 shows a scheme for a photochemical reaction involving diazo-naphthoquinone (DNQ) Novolak-based thick-film positive resist (hereafter Novolak resist). When exposed, the diazo-naphthoquinone in the thick-film Novolak resist decomposes into indene ketene, producing N_2. In a thick-film resist, the N_2 generated during

the exposure process is not released immediately from the resist film. Instead, it is released developer solution development progresses. These N_2 bubbles attach themselves to the resist surface, thus retarding the progress of development and causing problems such as reduced development activity and degraded resolution. In view of this situation, we evaluated the patterning and development properties of the resist using four development methods with varying degrees of N_2 release from the resist being developed. In this manner, we investigated the influence of N_2 produced during the development process on development properties, and elucidated the mechanism of development of thick-film resist. In addition, we determine and describe an optimal development method for thick-film resist.

2.2 Experiment Method

(1) Experiment Conditions

Figure 2 shows the configurations of the exposure, development, and analysis systems used in this research. In the present work, resist patterns were exposured using a Mask Aligner Q4000 made by Quintel Corporation (broadband exposure) [4]. For the observation of the resist pattern profile, a laser microscope VK-8550 (made by Keyence Corporation) was used. For the investigation of development properties, a resist development analyzer [5] was used. For resist profile simulations, a lithography simulator SOLID-C [6] was used. In addition, we used the Litho Spin Cup development system [7] designed for dipping, step puddle, vibration, and reverse development methods. Resist coated wafers were prepared at 23.7 °C and 31.7% humidity. Figure 3 shows the process flow employed for the preparation of the wafers. Thick-film resist (Tokyo Ohka Kogyo Co., Ltd.) was applied to a

silicon wafer to a thickness of 24 σm. The wafer were prebaked by the proximity baking method for 7 minutes at 110 °C. They were then placed in a vacuum dessicator for 1 hour to remove water, followed by immersion in deionized water at 15 °C for 30 minutes [3].

(2) Development method

Four development methods were employed: the dipping development method, the step puddle development method, the vibration development method, and the reverse development method. Figure 4 shows schematic diagrams of the development methods.

Dipping Development

Figure 4 (a) shows a schematic diagram of the dipping development (DD) method. The DD method involves the placement of a sample wafer, with the resist side facing up, in temperature-controlled developer without movement of the wafer or developer.

Step Puddle Development

Figure 4 (b) shows a schematic diagram of the step puddle (SP) development method. Temperature-controlled developer is supplied to the sample wafer via a nozzle under the following conditions: the sample wafer is spin at 100 rpm, the developer is supplied for 5 s, and development is allowed to proceed for 295 s in a stationary state. These steps are repeated three times.

Vibration Development

Figure 4 (c) shows a schematic diagram of the vibration development (VD) method. A sample wafer is resist side placing up, in temperature-controlled developer. In the development stage, both the developer and the wafer are vibrated continuously at a frequency of 50Hz (Amplitude: 50σm).

Reverse Development

Figure 4 (d) shows a schematic diagram of the reverse development (RD) method. A sample wafer is set upside down, in temperature-controlled developer, and development proceeds with both the developer and the wafer in a stationary state.

(3) Evaluation of patterning

Patterning was carried out using a Q4000 system, a mask aligner made by Quintel Corporation. Exposure was done by a vacuum contact exposure mode using broadband exposure light. Development was performed for 15 minutes using a special TMAH developer (Tokyo Ohka Kogyo Co., Ltd.) maintained at 23 °C for each of the exposure methods mentioned above. The resist used for evaluation was applied at line width 10 σm to 3.5 σm (Line:space = 1:1). The exposure dose was measured using the i line. The reference exposure dose (E_{op}) used in each development method was the optimum dose that gives equal lines and spaces of 10 σm.

(4) Evaluation of development contrast and simulation

For each development method, the development contrast of the resist was measured using an RDA [5] system with a monitoring wavelength of 950 nm. Exposure was performed using a Q4000, and sample wafers were created under various exposure times using a special TMAH developer. In addition, in order to check the relationship between development contrast and pattern profile, the measured development rate data was input into the resist simulator SOLID-C [6], and simulations were performed [8]. The simulation conditions were as follows: exposure lens NA: 0.1, coherence factor: 0.999, reduction ratio: 1:1, and focusing value: best focus. The resist line width was set at 10 σm to 4 σm (Line:space = 1:1). The

exposure dose was calculated using the reference exposure dose (E_{op}) used in each development method was the dose that converted a line width 10 σm (Line:space = 1:1).

(5) Evaluation of activation energy

For the evaluation of energy of activation, the development rate was measured over a range of developer temperatures from 13 °C to 35 °C, and the reaction rate constant was determined for the development process. For each development method employed, the energy of activation was determined by making an Arrhenius plot of the reaction rate constants obtained. Further, development inhibition was investigated in terms of collision theory [9] for collisions between N_2 molecules that adhered to the resist surface and N_2 molecules released from within the resist film.

(6) Evaluation of effect of developer replacement

For the evaluation of the effect of replacing the developer with fresh developer, a developer was prepared by dissolving a fixed amount of resist in developer maintained at 23 °C. The relationship between the concentration of soluble species and the rate of development was studied based on this procedure.

3. Experimental Results

3.1 Patterning Results

Figure 5 shows the results of a laser microscope observation of the resist patterns thus formed. The following resolutions were obtained the SP development method: 3.5 σm, the VD method: 4.0 σm, the DD method: 4.0 σm, and the RD method: 4.0 σm. Of the four development methods investigated, the Step Puddle development method achieved the

highest resolution. With regard to resist patterns, we compared the various development methods in terms of the thickness lose and the angle of the sidewall. The SP method achieved the largest sidewall angle and the least amount of thickness loss at the top, followed by the VD method, the DD method, and the RD method. The presence of residues in the resist spaces by the RD method was observed. Therefore, the most effective development method in terms of resolution and resist sharpness was found to be the SP method, followed by the VD method, the DD method, and finally the RD method.

3.2 Results of Measurements of Development Properties

Table-1 shows the results of measurements of development contrast, used as an index of resolution for the various development methods [10] (slope tanχ of the dissolution rate curve), ν measurements, and measurements of resist sensitivity (E_{th}). In decreasing order, the tanχ measurement results were: 3.4 for the SP method, 2.9 for the VD method, 2.3 for the DD method, and 1.3 for the RD method. In decreasing order, the results of measurement of ν#after development for 15 min were 14.6 for the SP method, 8.7 for the VD method, 8.0 for the DD method, and 3.0 for the RD method, in the same order as the tanχ measurement results. Similarly, in decreasing order, the results of measurement of resist sensitivity (E_{th}) after development for 15 min were 361.5 (mJ/cm^2) for the SP method, 377.4 (mJ/cm^2) for the VD method, 455.7(mJ/cm^2) for the DD method, and 510.4 (mJ/cm^2) for the RD method. Thus, the Step Puddle development method yielded the highest development contrast and ν value, as well as a high degree of sensitivity.

4. Discussion

4.1 Relationship between Development Contrast and Pattern Profile

The results of patterning indicate that the SP method achieves the steepest sidewall and the least decrease in the amount of film near the resist surface, followed by the VD method, the DD method, and the RD method. In this section, we discuss the reasons for this observation in terms of development contrast. Figure 6 shows a comparison of discrimination curves for the various development methods. The SP method yields the highest value, followed by the DV method, the DD method, and the RD method. This result suggests that the reason that the SP method is able to produce both high resolution and high rectangularity is an increase in development contrast. We performed simulations by inputting the discrimination data R(E) (where R denotes the average development rate through depth, and E denotes the exposure dose) obtained from the various development methods into a simulator. The results are shown in Fig. 7. The simulation results also indicate that the SP method produces the highest rectangularity, followed by the VD method, the DD method, and the RD method. Thus, development contrast data supports the relationship between the various development methods employed at present and determined the resulting resolution and rectangularity.

4.2 A Development Inhibition by Nitrogen

The question then arises as to what accounts for the fact that the SP, VD, DD, and RD methods, in the indicated order, yield resolution and rectangularity data in decreasing order. In the following, we discuss the reason for this phenomenon by comparing the

activation energies involved in the respective development methods. Table-2 shows reaction rate constants for the various development methods at exposure doses of 350 mJ/cm^2 and 700 mJ/cm^2. Figure 8 shows activation energies obtained by using the Arrhenius plot of the development rate constants. The activation energy and frequency factor were estimated from the slope of the Arrhenius plot of the reaction rate constant k_d and the development temperature [11] as follows.

$$\frac{d \ln k_d}{dT} \propto \frac{E}{RT^2} \tag{1}$$

where E denotes the activation energy (kcal/mol); T, the developer temperature (K); and k_d, the reaction rate constant (kcal) for development. At the 350 mJ/cm^2 exposure dose, the SP method yielded 29.97 (kcal/mol), followed by the VD method 11.25 (kcal/mol), the DD method 4.41 (kcal/mol), and the RD method 1.14 (kcal/mol). Thus, the SP and VD methods produced high values, whereas the DD and RD methods yielded low values. In the development of thick-film resist, N_2 is released from within the resist film during the development process. In the RD or DD method, no external force (i.e., vibrations or replacement of the developer) was applied to the wafer during the development process. Therefore, any N_2 that is generated adheres to the resist surface and forms an N_2 deposition layer. In particular, in the RD method, the N_2 generated from within the resist film bubbles and appears to form a thick deposit on the development interface of the resist, which may account for the formation of resist residues in the resist space. In contrast, in the SP and VD methods, the physical forces associated with the replacement of the developer and the continuous application of vibration during development effectively remove any N_2 layer that may attach to the resist surface during the development process. At the 350 mJ/cm^2 exposure

dose, which is low compared to the resist sensitivity (E_{th}), the development rate is slow, and the production of N_2 is moderate. Compared with the DD or RD methods, the SP and VD methods produce high activation energies. It appears that in these development methods involving the application of external physical forces (open-system development methods), the development reaction proceeds without being subjected to an N_2 layer-induced inhibition effect, and thus facilitates contact between the resist and the developer. The rate of reaction is limited only by the diffusion of the developer into the resist. On the other hand, in the DD and RD methods, the activation energy is lower than in the SP or RD method. In such development methods (closed-system development methods), where no external physical force is applied, it appears that the development reaction is inhibited by the formation of the N_2 layer, which minimizes contact between the resist and the developer. Also, it appears that the rate of reaction is limited by the release of N_2 from the resist surface into the developer. A similar trend was also observed at the high 700 mJ/cm2 exposure dose, although the difference between the DD and VD methods was small. Because the development reaction proceeds rapidly in a large exposure dose region, N_2 is produced extensively during the development process, and it appears that the development proceeds without adequate formation of an N_2 layer, probably due to the fact that any nitrogen produced is entrained into the N_2 bubbles. Figure 9 shows model diagrams of the formation of N_2 deposition layers in the closed- and open-system development methods.

We now consider this discussion in terms of a theory of collision regarding the N_2 molecules that adhered to the resist surface and the N_2 molecules released from within the resist film. The ratio between the number of effective collisions Z and the total number of collisions Z_0

between molecules is given by $e^{(-E/RT)}$.

In developer at 23 °C, the number of N_2 molecules generated from 1 ml of resist is

$$n = \frac{N}{RT} = \frac{6.2023 \times 10^{23}}{0.08204 \times 296 \times 1000} = 2.554 \times 10^{19} \quad (2)$$

where N denote Avogadro's number; R, the gas constant (l atm/deg mol); and T, the temperature (K) of the developer.

The total number of collisions Z_0 occurring among N_2 molecules for 1 s is given by

$$Z_0 = 2n^2\omega^2\left(\frac{RT}{M}\right)^{0.5} \quad (3)$$

where n denotes the number of N_2 molecules contained in 1 ml of resist; ů, the diameter (cm) of an N_2 molecule; and M, the molecular weight of N_2.

The number Z of effective collisions during a reaction is given by:

$$Z = Z_0 e^{\frac{4E}{RT}} \quad (4)$$

where E denotes the activation energy (kcal/mol).

Table-3 shows the number of collisions of N_2 molecules occurring on the resist surface during development for the various development methods. At the 350 mJ/cm^2 exposure dose, the SP method yields a value of 4.60×10^6(molecule/sec), the VD method, 3.06×10^{20}; the DD method, 3.44×10^{25} ; and the RD method, 8.94×10^{27}. These results indicate that the open-system development methods produce fewer collisions between N_2 molecules than the closed-system development methods, which suggests that the physical forces present in the open-system development methods minimize the attachment of N_2 molecules to the resist surface during the development process. When the 350 mJ/cm^2 and 700 mJ/cm^2 exposure doses are compared, the 350 mJ/cm^2 exposure dose produces more molecular collisions,

apparently due to the fact that at lower exposure levels, the N_2 deposition layer forms only slowly.

4.3 Effect of Replacement of the Developer with Fresh Developer

In view of the fact that both the SP and VD methods are open-system development methods, we then discuss why the SP method produced higher pattern rectangularity. The only difference between the two methods is the replacement of the developer. Therefore, we prepared a developer by dissolving a fixed amount of resist in the developer, and investigated the relationship between the concentration of dissolved species and the rate of development. The results are shown in Fig. 10. When the resist is dissolved into a resist developer, the rate of development increases between dissolved material concentrations of 0 and 2.6(mg/ml); however, the rate of development decreases when the concentration of dissolved material rises above a 2.6(mg/ml) threshold, apparently due to the fact that the dissolution of resist into the developer reduces the alkalinity of the developer, which in turn lowers development activity. Therefore, it can be inferred that in the Step Puddle method, two mechanisms, the active contact between the developer and the resist surface due to the effective removal of the N_2 deposition layer and the prevention of a decrease in development activity due to the replacement of the developer with fresh developer act synergistically to produce both high pattern resolution and high rectangularity.

5. Conclusions

We experimentally verified the resolution and rectangularity of difference development methods. The results indicate that the step puddle development method produces the highest

resolution and rectangularity, followed by the vibration development, dipping development and reverse development methods. The underlying mechanisms were considered by comparing the development contrasts and activation energies for the development methods, and by conducting resist pattern simulations. Further, we proposed a development inhibition model in which the N_2 molecules released from within the resist film during the development process attach themselves to the resist surface, form an N_2 deposition layer, and retard the development process. The model was constructed based on a theory of molecular collisions involving collisions between the N_2 deposition layer and the N_2 molecules that are released from the interior of the resist film. From the development inhibition model, it was determined that in comparison with the closed-system development methods (the DD and RD methods), the open-system development methods (the SP and VD methods) yield greater efficiency for the removal of the N_2 deposition layer, which is a development inhibition factor, and promote contact between the developer and the resist surface. In addition, we experimentally verified that the dissolution of soluble species into the developer reduces the development activity, and confirmed the ability of the replacement of the developer with fresh developer to prevent a decrease in development activity. Thus, the present work, as an approach to increasing the degree of resolution that can be achieved with thick-film resist, confirms the importance of a development technique that promotes contact between the developer and the resist surface through effective removal of the N_2 deposition layer during the development process, and prevents a decrease in development activity through the replacement of the developer with fresh developer.

As for the N2 gas foaming phenomenon from a thick film resist, the study of the pre-bake condition is a future subject.

6. Acknowledgements

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7. References

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Table 1. Development contrast (tanα), ɔ values, and E_{th} for the different development methods.

Development Method	tanα	ɔ value	E_{th}(mJ/cm^2)	E_{op}(mJ/cm^2)
SP Method	3.4	14.6	361.5	540.0
VR Method	2.9	8.7	377.4	550.0
DD Method	2.3	8.0	455.7	580.0
RD Method	1.3	3.0	510.4	590.0

Table 2. Development reaction rate constants at exposure doses of 350 mJ/cm^2 and 700 mJ/cm^2 for the different development methods.

(kcal / mol)

Development Method	Exposure dose: 350 mJ/cm^2	700 mJ/cm^2
SP Method	29.97	35.94
VR Method	11.25	14.87
DD Method	4.41	13.28
RD Method	1.14	9.46

Table 3. Number of molecular collisions between the N_2 deposition layer on the resist surface and the N_2 molecules released from the interior of the resist film.

(molecule / sec)

Development Method	Exposure dose: 350 mJ/cm^2	700 mJ/cm^2
SP Method	4.60×10^{6}	1.97×10^{2}
VR Method	3.06×10^{20}	6.50×10^{17}
DD Method	3.44×10^{25}	9.71×10^{18}
RD Method	8.94×10^{27}	6.42×10^{21}

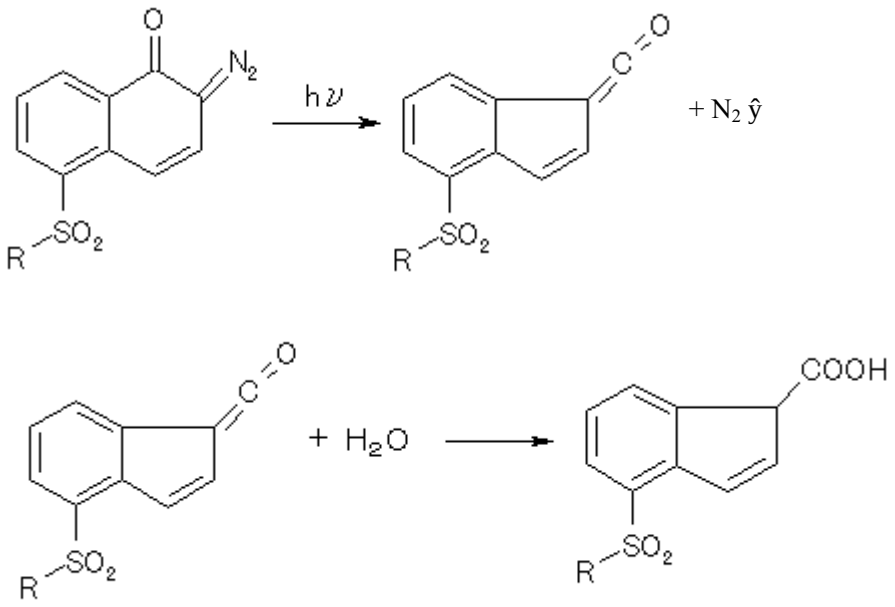
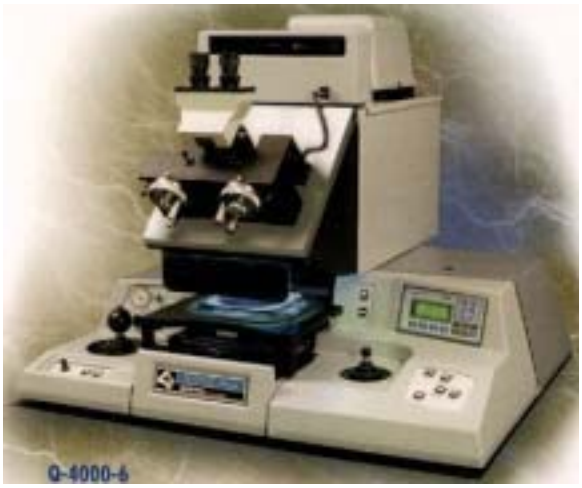


Fig. 1. Photochemical reaction scheme involving diazonaphthoquinone (DNQ) novolak-based positive resist.



Exposure system: Mask Aligner Q4000 (Quintel Corporation)

Development system: Litho Spin Cup

Resist development rate measurement system: RDA

Fig. 2. Configurations of exposure, development, and analysis systems.

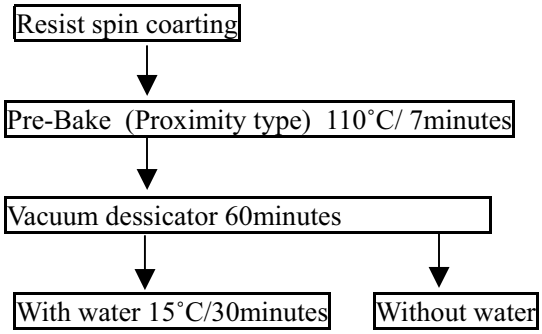
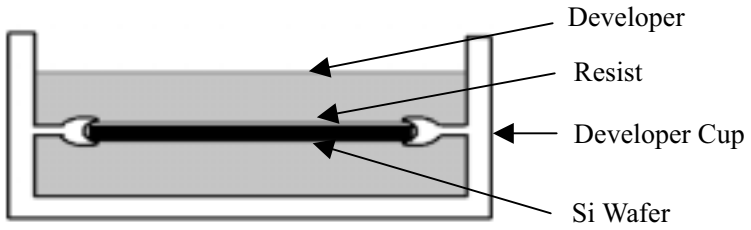
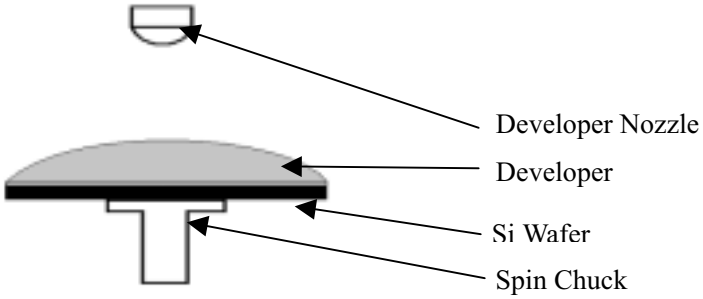


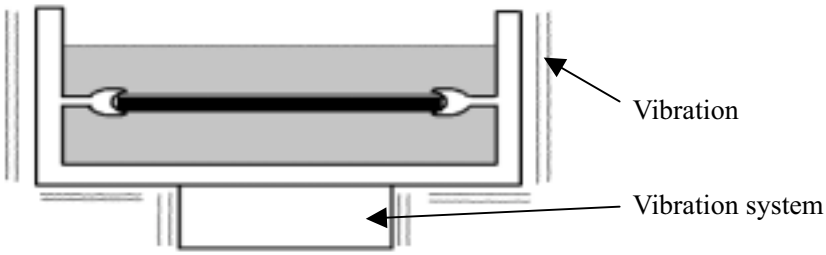
Fig. 3. Sample preparation process flow.



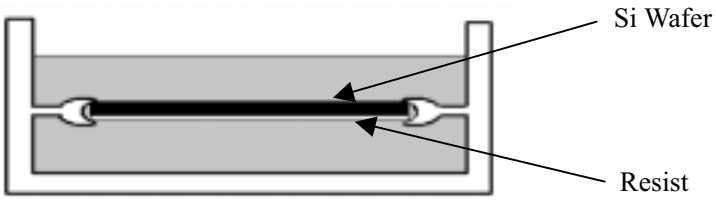
(a) Dipping Development Method (DD Method)



(b) Step Puddle Development Method (SP Method)

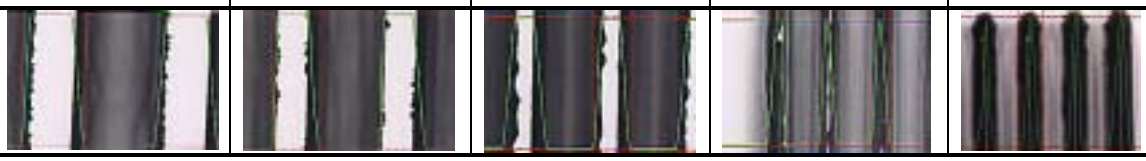
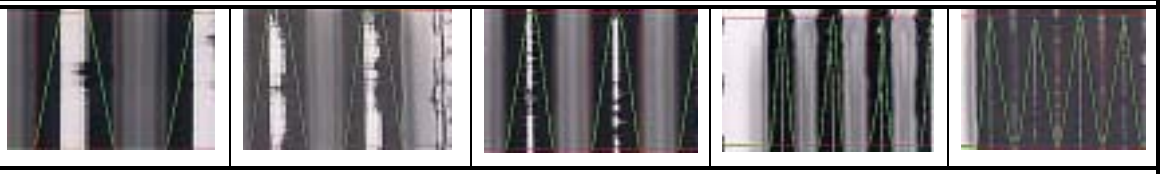
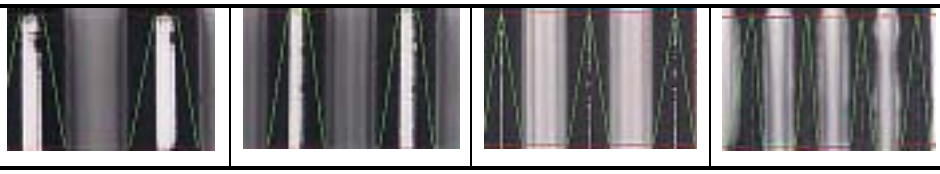
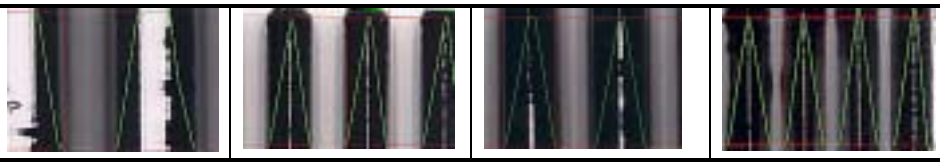


(c) Vibration Development Method (VD Method)



(d) Reverse Development Method (RD Method)

Fig. 4. Schematic diagrams of the development methods.

	Line Width (μm) Line : Space = 1 : 1				
	10	8	6	4	3.5
SP Method					
VD Method					
DD Method					No resolution
RD Method					No resolution

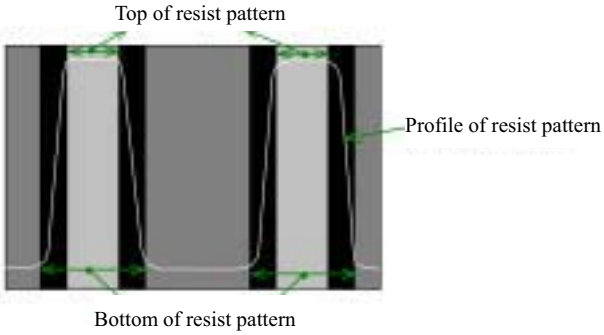
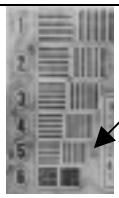


Illustration of resist pattern data

SP Method	VD Method	DD Method	RD Method
			 Resist residues

The resist residues in the space area

Fig. 5. Resist pattern observation results for the defferent development methods.

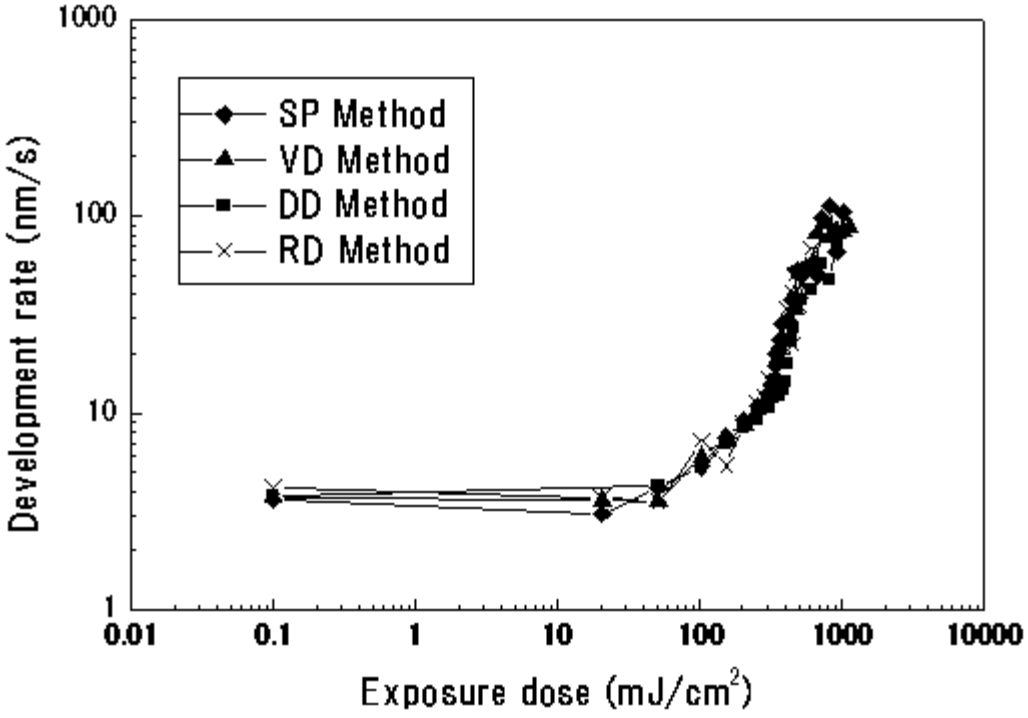
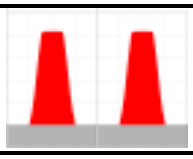
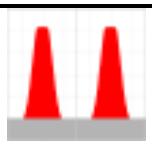
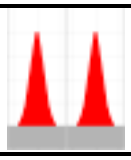
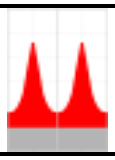
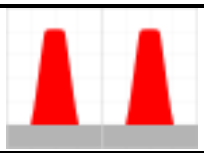
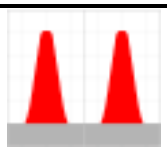
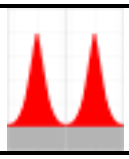
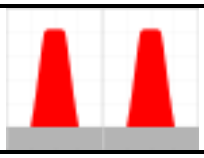
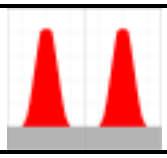
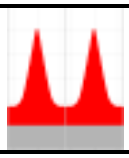


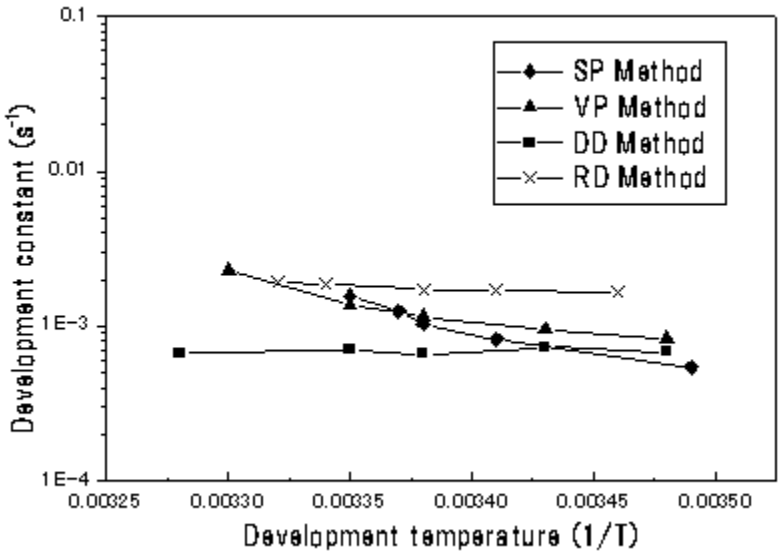
Fig. 6. Comparison of discrimination curves for the different development methods.

Line : Space = 1 : 1

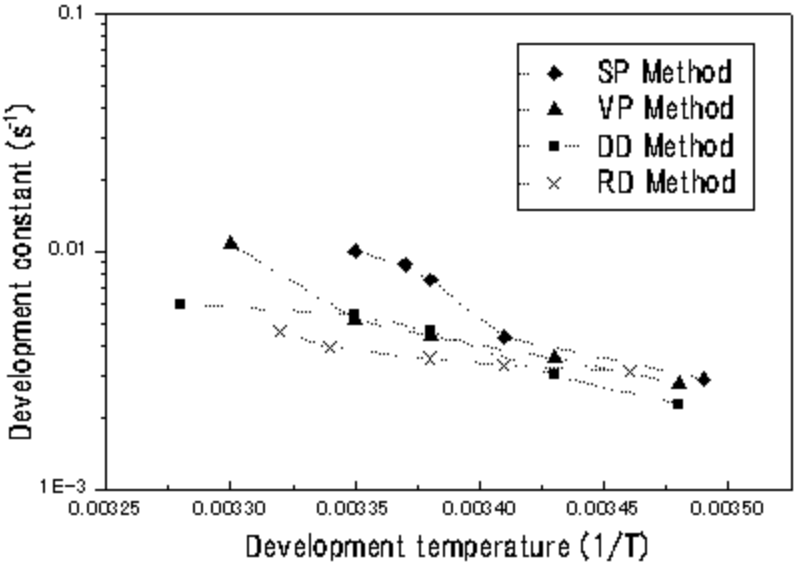
Line Width (μm)	10	8	6	5	4
SP Method					
VD Method					No resolution
DD Method				No resolution	No resolution
RD Method				No resolution	No resolution

	E_{op} (mJ/cm^2)	Line Width(μm)	10	8	6	5	4
SP Method	439.7	Sidewall Angle (˚)	83.3	82.9	82.7	82.1	--------
		Thickness Loss (%)	12.8	12.7	13.4	25.0	--------
VD Method	466.0	Sidewall Angle (˚)	82.9	82.6	81.4	--------	--------
		Thickness Loss (%)	13.8	13.8	15.8	--------	--------
DD Method	503.2	Sidewall Angle (˚)	82.2	81.4	------	--------	--------
		Thickness Loss (%)	14.6	14.9	------	--------	--------
RD Method	504.8	Sidewall Angle (˚)	82.3	81.4	------	--------	--------
		Thickness Loss (%)	13.6	13.8	------	--------	--------

Fig. 7. Results of resist pattern simulations for the different development methods.

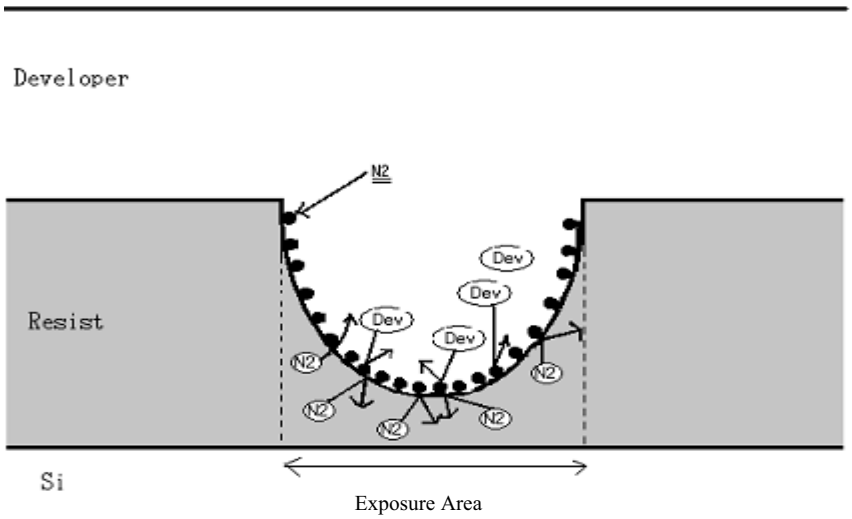


(a)

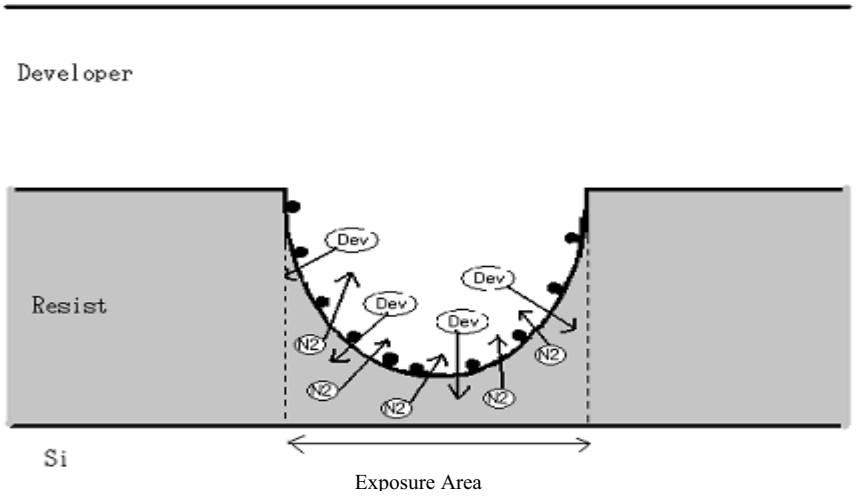


(b)

Fig. 8. Arrhenius plots for (a) 350mJ/cm^2 and (b) 700mJ/cm^2 exposure doses.



(a) Model of closed-system development methods



(b) Model of open-system development methods

Fig. 9. A model diagram describing the formation of an N_2 deposition layer on the resist surface during the development.

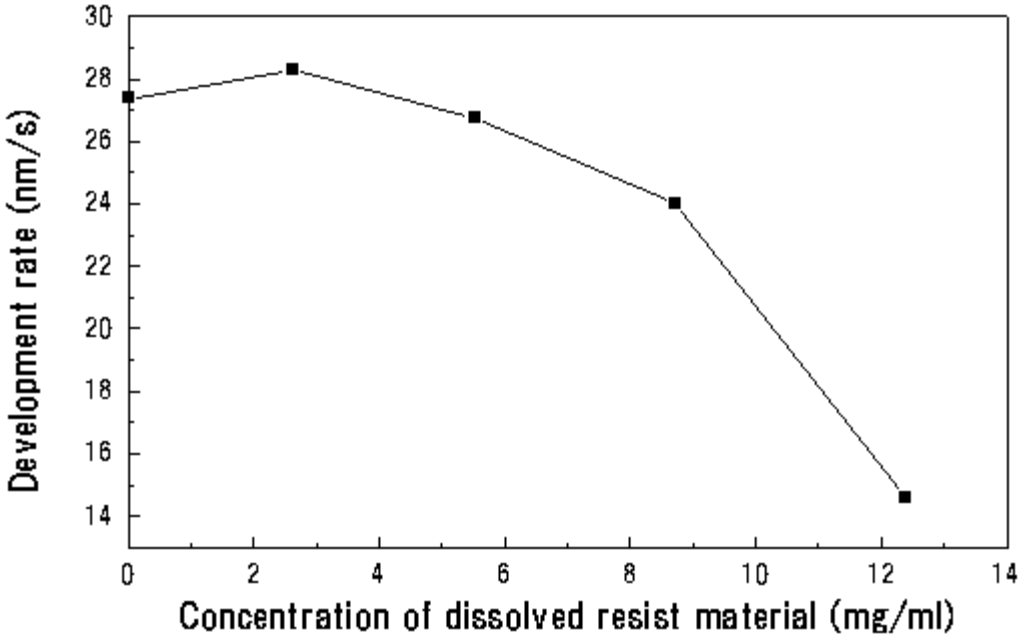


Fig.10. Relationship between the concentration of dissolved resist material and the development rate.