Preparation of formylated Novolacs and their photoreaction

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Formylated Novolacs were prepared by the reaction of Novolacs with formic acid–acetic anhydride in the presence of pyridine in tetrahydrofuran at room temperature. When the resulting formylated Novolacs films were exposed to deep-ultra-violet light, photochemical decomposition of the formyl group was observed. This reaction generates Novolacs through decarbonylation of the formyl radical, which is formed in the first stage of the photo-Fries rearrangement. More than 50% of the formyl groups decomposed after an exposure of approximately $500\,mJ\,cm^{-2}$. Both negative and positive tone images can be manufactured by developing these films with a suitable solvent.

(Keywords: formylated Novolacs; photoreaction; microlithography)

INTRODUCTION

Resists for microlithography are indispensable for manufacturing integrated circuits (IC) and large-scale integrated (LSI) chips. Various kinds of resists, such as (1) a single-component resist having a reactive functionality in the polymer main chain or side chain[1,2], (2) a two-component resist consisting of a base polymer and a reactive modifying agent[3], and (3) a three-component resist composed of a base polymer, a latent catalyst and a dissolution retardant[4], have been employed for industrial applications. These resists can be further classified by the irradiation source, i.e. ultra-violet light, electron beam, X-rays and so on.

We have been investigating photoresists of type (1)[5–7]. It was reported that the photo-Fries reaction of aryl formate is applicable for deep-u.v. resist technology[8]. We are thus interested in this reaction in Novolacs, because Novolacs are one of the most useful base polymers for photoresists owing to their excellent resistance to swelling by developing agents and to plasma etching[9].

In this paper, we will describe the preparation and photoreaction of formylated Novolacs.

RESULTS AND DISCUSSION

Preparation of formylated Novolacs

The preparation of formylated Novolacs resin was carried out by the reaction of Novolacs with formic acid–acetic anhydride in the presence of pyridine. The i.r. spectrum of the resulting formylated Novolacs resin showed two carbonyl bands at 1755 and $1733\,cm^{-1}$, which are assignable to *cis* and *trans* conformers, respectively. The results are summarized in *Table 1*. The degree of formylation was estimated from the ^1H n.m.r. spectrum of the resulting Novolacs on the basis of the ratio of the formic proton (8.0–8.2 ppm) to the methylene proton (3.7 ppm). Although more than 80% of phenolic OH was formylated at 23°C, the acetylation reaction proceeded predominantly at 45°C and only 7% of phenolic OH was formylated. These results were coincident with those of the formylation of monomeric phenol derivatives[10]. The presence of *cis* and *trans* isomers was confirmed by ^1H n.m.r. spectroscopy. As shown in *Figure 1*, two signals ascribed to the formyl proton were observed at 8.2 ppm (*cis* conformer) and 8.0 ppm (*trans* conformer). The exposure of formylated Novolacs to deep-u.v. revealed that the carbonyl bands at 1755 and $1733\,cm^{-1}$ as well as the ether bands at 1194 and $1126\,cm^{-1}$ decrease rapidly, whereas a new absorption band at $3400\,cm^{-1}$ due to the hydroxyl group gradually increases with time. Typical i.r. spectra of formylated Novolacs before and after exposure are depicted in *Figure 2*. It was reported that the *cis* conformer of phenyl formate is less stable than the *trans* conformer, and hence the *cis* conformer decomposes rapidly[11]. The carbonyl band at $1755\,cm^{-1}$ completely disappeared and the absorption at $1733\,cm^{-1}$ remained somewhat after an exposure dose of $500\,mJ\,cm^{-2}$. This fact indicates that the *cis* conformer decomposes easier than the *trans* conformer.

As for the mechanism of photo-Fries rearrangement of aromatic ester, two basic mechanisms were proposed[12]: (1) homolytic cleavage of the excited molecule occurring at the ArO–COR bond, and (2) the formation of a bridged biradical intermediate occurring in a concerted manner. The latter mechanism may be unfavourable for photoreaction of formylated Novolacs because two positions, at least, *ortho* and *para* positions, are substituted by methylene bridges. Therefore, it can be assumed that photoreaction of formylated Novolacs produces phenoxy radical and formyl radical in the first step of the reaction, and then the recombination of the radical pair may be suppressed by the subsequent decomposition of the unstable formyl radical to carbon monoxide and hydrogen radical. Consequently, the photoreaction of formylated

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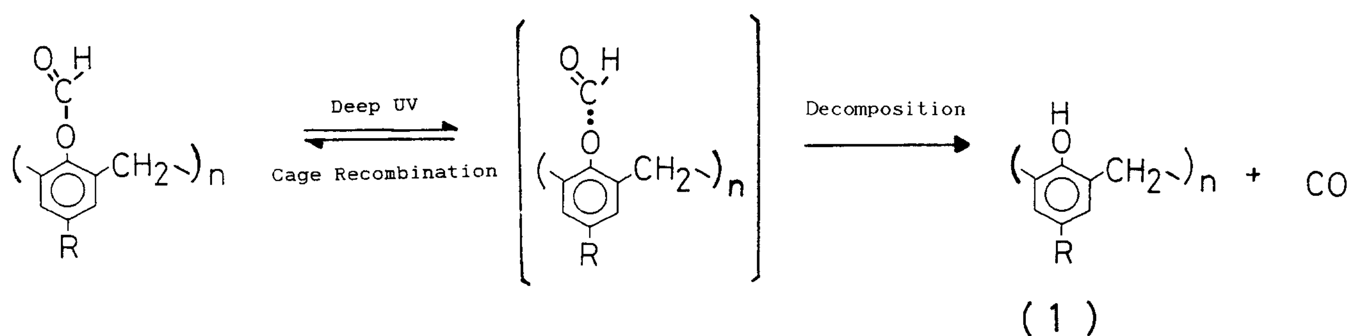
Table 1 The properties and reaction conditions of formylated Novalacs

No.	Novolacs	MW^a ($\times 10^{-3}$) M_n	M_w	Reaction conditions (°C)	(days)	Formylated Novolacs: Formyl group[b] (mol%)	Acetyl group[b] (mol%)	Sensitivity, $E_{1/2}$ (mJ cm^{-2}) Neg.	Pos.
1	PN[c]	0.89	1.6	23	4	91	9	600	400
2	PN[c]	0.89	1.6	45	1	7	90	>5000	–
3	*p*-CN[d]	0.51	0.66	23	4	85	15	500	200
4	*o*-CN[e]	0.71	1.02	23	4	84	5	100	100
5	*m*-CN[f]	1.56	3.96	23	4	81	17	200	200
6	*p*-t-BPN[g]	0.99	1.82	23	4	83	16		
7	PVP[h]		5.1	23	4	74	7	100	100

[a] Measured by g.p.c. (Shodex system-11: Showa Denko Corp.)
[b] Measured by n.m.r. (JEOL JNM-EX400: Nihon Densi Kogyo Corp.)
[c] PN: phenol Novolacs (TD-2093: Dainippon Ink and Chemicals Inc.)
[d] *p*-CN: *p*-cresol Novolacs (prepared)
[e] *m*-CN: *m*-cresol Novolacs (prepared)
[f] *o*-CN: *o*-cresol Novolacs (prepared)
[g] *p*-t-BN: *p*-t-butylphenol Novolacs (Hitanol 1154: Hitachi Kasei Kogyo Corp.)
[h] PVP: poly(4-vinylphenol) (Maruzen Petroleum Chemical Co.)



Scheme 1

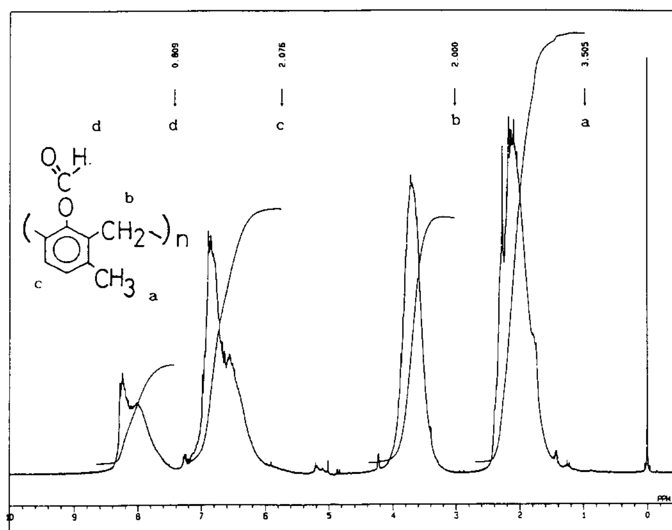


Figure 1 N.m.r. spectrum obtained from the formulated Novolacs

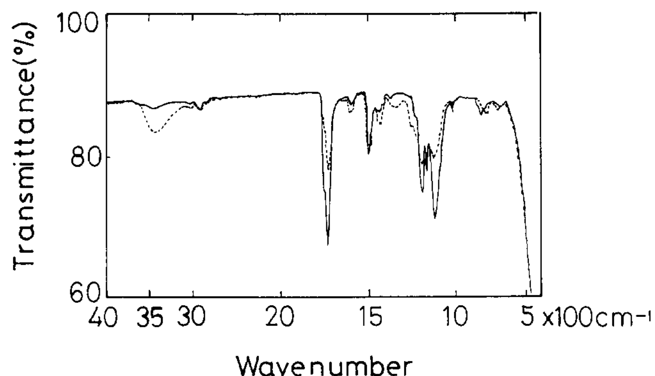


Figure 2 I.r. spectra of formylated Novolacs before (——) and after (- - - -) irradiation to 500 mJ cm^{-2}

Novolacs affords Novolacs (1) as shown in *Scheme 1*. In fact, mass spectrometric analysis of the gas produced in photoreaction of formylated Novolacs showed that the main product has mass number of 28 ($m/e = 28$). The subtraction spectrum of the formylated Novolacs before and after irradiation also indicates the yield of Novolacs as shown in *Figure 3*.

Microlithographic application

It is obvious that u.v. irradiation of the formylated Novolacs affords Novolacs. The large differences of the properties of the cast film on a silicon wafer before and after irradiation can be used for microlithographic applications. If we use a suitable alkaline developing reagent, a positive image might be obtained by dissolving the exposed area as shown in *Figure 4*. On the other hand, a negative image can be developed by dissolving the unexposed areas of the film in a suitable lipophilic solution as shown in *Figure 5*. Therefore, formylated

Novolacs may be useful materials with both positive and negative tone developing for microlithographic applications. In practical use, sensitivity is one of the most important factors. The sensitivity ($E_{1/2}$) was estimated from the relation between residual film thickness ratio of formylated Novolacs (d/d_0) *versus* the exposure energy (E) at $d/d_0 = 1/2$, as shown in *Figure 6*. The full curves and chain curves indicate the negative process and positive process, respectively. As listed in *Table 1*, formylated *o*-CN (No. 4) is the most sensitive towards deep-u.v. irradiation. Its sensitivity is comparable to that of formylated PVP, which has been reported to be a versatile photoresist material[8]. In contrast, acetylated PN (No. 2) is not suitable for such microlithographic applications, because its sensitivity is low. In fact, the i.r. spectra of acetylated PN before and after exposure to $500\,mJ\,cm^{-2}$ showed almost no differences with each other. This fact indicates that acetylated PN is insensitive towards deep-u.v. or the recombination reaction of a produced radical pair is predominant.

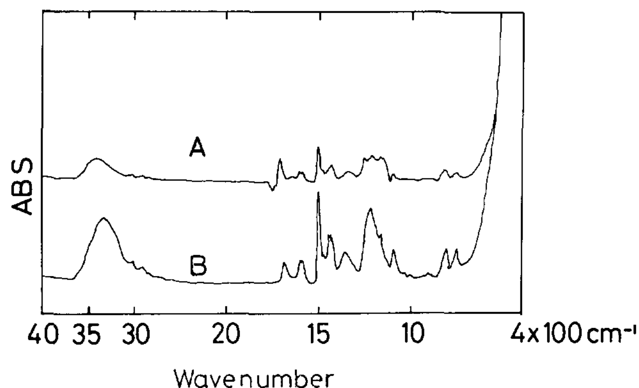


Figure 3 I.r. spectra of subtraction (A) of formylated Novolacs before and after irradiation, and Novolacs (B)

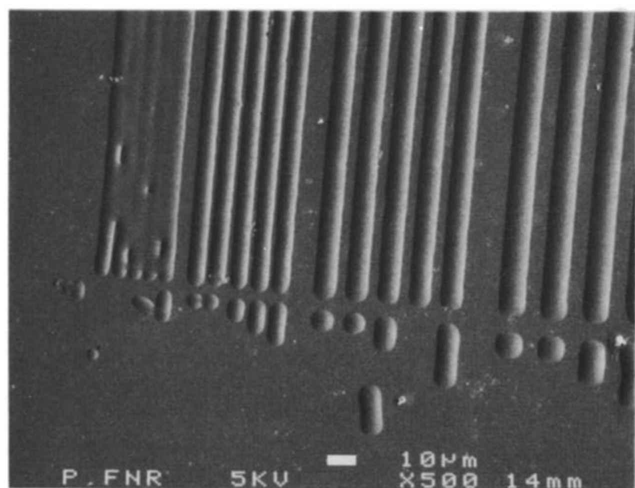


Figure 4 Micrograph of positive image of formylated Novolacs (scale bar is $10\,\mu m$)

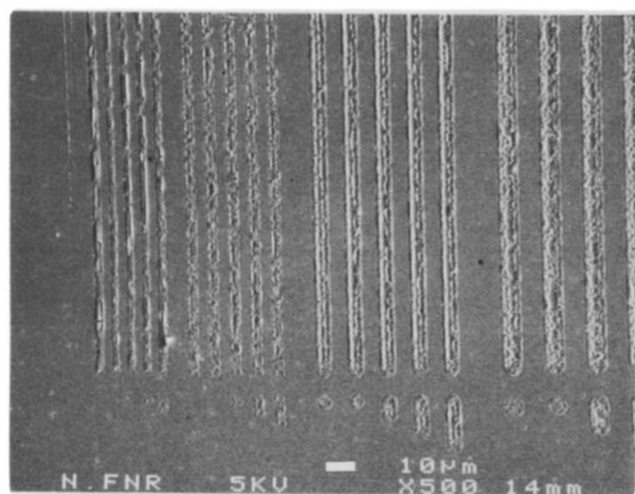


Figure 5 Micrograph of negative image of formylated Novolacs (scale bar is $10\,\mu m$)

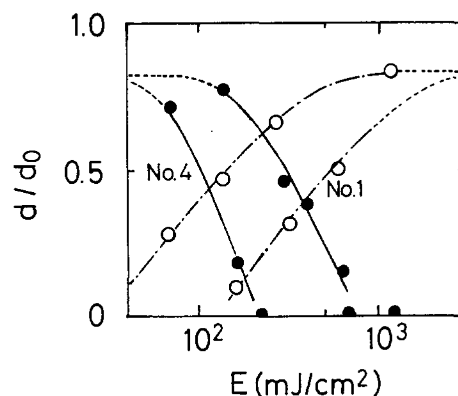


Figure 6 Relationship of exposure energy E ($mJ\,cm^{-2}$) *versus* ratio of residual film thickness of formylated Novolacs (d/d_0) in negative process (—·—) or positive process (——)

EXPERIMENTS

General methods

Unless stated otherwise, all reagents and chemicals were obtained from Tokyo Kasei. Phenol Novolacs, *p*-t-butylphenol Novolacs and poly(4-vinylphenol) were kindly offered by Dainippon Ink and Chemicals Inc., Hitachi Kasei Kogyo Corp. and Maruzen Petroleum Chemicals Co., respectively. Other Novolacs were prepared according to the usual procedure[13–15].

I.r., ^{1}H n.m.r. and u.v. spectra were recorded on Nippon Bunko IR-700, JEOL JNM-EX400 and Hitachi 330 spectrophotometer, respectively.

Preparation of formylated Novolacs

A typical procedure is as follows. To a solution of 2 g of phenol Novolacs and 1 ml of pyridine in 10 ml of tetrahydrofuran was added a formylating agent consisting of 4.0 g of acetic anhydride and 1.8 g of formic acid at 23°C. After the mixture was stirred at the same temperature for 4 days, the mixture was poured into a large volume of ice-cold water. The precipitated pale yellow solid was collected in a suction funnel, and washed sufficiently with water. Then purification was carried out by reprecipitation from acetone solution into water. The isolated solid was dried over phosphorous pentoxide under reduced pressure to give 2.1 g of formylated Novolacs. ^{1}H n.m.r. ($CDCl_3$): δ (ppm) = 8.2–8.0 (1H, formyl), 7.2–6.3 (3H, aromatic), 3.7 (2H, $-CH_2-$). I.r.: 1755 and $1733\,cm^{-1}$ (C=O), 1190, 1166, $1119\,cm^{-1}$ (C–O–C).

Lithographic test

A thin film ($0.7\,\mu m$) of formylated Novolacs was coated on a silicon wafer by means of a spin-coater (Mikasa 1H-D2). After the film was prebaked at 60°C for 30 min,

the wafer was exposed to deep-u.v. radiation by using a Xe–Hg lamp (Hamamatsu Photonics, SQ Xe–Hg Lamp 100 W L2422-03, 254 nm ellipse reflector E4168-02) through a test pattern. A 2.5% aqueous solution of tetramethylammonium hydroxide and a 2:1 mixture of trichloroethylene–chloroform were used as the positive and negative developer, respectively.

The sensitivity was measured as follows. A resist film covered with a pattern was exposed to u.v. radiation from the Xe–Hg lamp. After the wafer was immersed in the developer solution for 1 min, the resist film thickness was measured with a Talystep from Rank Taylor Hobson Ltd. The sensitivity ($E_{1/2}$) was estimated from the relationship in *Figure 6*; $E_{1/2}$ means the dose of irradiation that is required for $d/d_0 = 1/2$.

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