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Journal of Photochemistry and Photobiology A: Chemistry 114 (1998) 159–162

Journal of Photochemistry and Photobiology A:Chemistry

Photochemical processes in photoresists containing electron donor molecules

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Received 4 July 1997; accepted 20 July 1997

Abstract

It is shown that the addition of donors (D) to a resist composition based on novolac resin and diazonaphthoquinone sulphonate (DQS) leads to linear increases in the quantum yield of DQS decomposition and light sensitivity of the resist as the ionization potential of the donor decreases. This is explained by exciplex D·(DQS)* formation and its subsequent dissociation into unstable $D^{\cdot +}$ and $(DQS)^{\cdot -}$ radical ions, resulting in indene carboxylic acid formation.

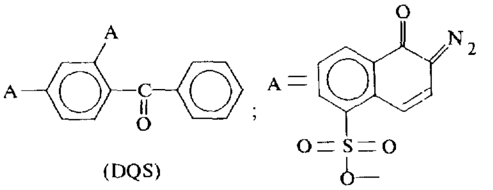
Keywords: Electron donor molecules; Photochemical processes; Photoresists

1. Introduction

Conventional positive-working photoresists based on novolac resin and diazonaphthoquinone sulphonate (DQS) have been the subject of many original papers, reviews and monographs (for example, see Ref. [1]). Real photoresists require an exposure dose H of 70–120 mJ cm^{-2}. The mass use of the photolithographic technique to obtain printed circuit boards, integrated circuits, etc. is economically advantageous if a high sensitivity of the resist can be provided. In order to carry out this task, resists allowing different processes of latent image amplification, such as chemical [2], autocatalytic and optical [3] amplification, have been prepared. Light sensitivities of 1×10^{3}–2×10^{2} cm^{2} J^{-1}, corresponding to H = 1–5 mJ cm^{-2}, have been achieved. However, the transition to the use of such photoresists requires the modification of technology and therefore considerable expense.

In this study, we investigate the effects of donor (D) incorporation on the photochemical properties and photolithographic sensitivity of conventional photoresists based on novolac resin and DQS. This investigation is also of scientific importance because it is based on fundamental phenomena, such as excited donor–acceptor complex formation and charge transfer.

Layers consisting of *m*-cresol-formaldehyde novolac base-soluble resin (NR) and the 1,2-naphthoquinone-(2)diazide-5-sulphonic acid diester of 2,4-dioxybenzophenone (DQS) (light-sensitive dissolution inhibitor) were investigated.



(DQS)

Ferrocene (Fc, $(C_5H_5)_2Fe$; ionization potential IP_D, 6.71 eV), triphenylamine ($N(C_6H_5)_3$; 6.8 eV), *p*- and *o*-phenylenediamine (H_2N-C_6H_4-NH_2; 7.5 and 8.0 eV respectively), diphenylbenzylamine ($(C_6H_5)_2N$-CH_2-C_6H_5; 7.55 eV), dibenzylaniline (C_6H_5-$N(CH_2$-$C_6H_5)_2$; 7.6 eV) and the bifunctional compounds *N,N*-dimethylamino-*p*-benzaldehyde ($(CH_3)_2N$-C_6H_4-CHO; 7.36 eV) and *N,N*-diethyl-*p*-nitrosoaniline ($(C_2H_5)_2N$-C_6H_4-NO; 8.4 eV) were used as electron donors.

2. Experimental section

The photoresist (thickness, 1–1.2 μm) consisting of *m*-cresol-formaldehyde resin, DQS (25 wt.% or 0.37 mol dm^{-3}) and the donor (no more than 6.5 wt.%) was cast from acetone solution onto a poly(ethylene terephthalate) substrate. Chemically pure grade amines and ferrocene were purified by recrystallization from ethanol. Spectrograde solvents were used as supplied.

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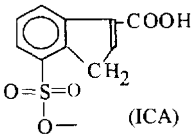
1010-6030/98/\$19.00
PII S1010-6030(97)00226-8

The films were exposed to varying amounts of 365 nm radiation ($I_0 = 8 \times 10^{-4}$ W cm^{-2}) at 10–30 °C. The exposed samples were kept at 20 or 56 °C for 5–30 min and were then developed in 0.6% aqueous solutions of KOH for $t_{exp} = 60$ s at 20 °C. After this, the film thickness (h) was measured with a microinterferometer (MII-4). It is well known [1] that the DQS photoexcitation produces indene carboxylic acid (ICA) dissolved in KOH.



(ICA)

The unexposed areas dissolve in the developing solution for $t_{unexp} = 20$–25 min. Thus the development selectivity is $t_{unexp}/t_{exp} = 20$–25. UV–visible and IR spectra were recorded with DU-7 (Beckman) and M-80 (Germany) spectrophotometers respectively.

3. Results and discussion

The electronic spectra of the resists with and without the donors show that only DQS exhibits a marked optical absorption at the wavelength used, $\lambda_{act} = 365$ nm, and therefore DQS photoexcitation causes the photochemical processes. As shown in Fig. 1, the exposure H_0 necessary for full removal of the layer, 1 µm thick, during development decreases as ferrocene is added to the resist composition: $H_0 = 72$ mJ cm^{-2} and is independent of the post-exposure bake temperature in the absence of the donor, but as ferrocene (0.2 mol dm^{-3} or 3.8 wt.%) is added, the exposure H_0 decreases to $H_0(D) = 22$ and 9 mJ cm^{-2} for samples kept at 22 °C and 56 °C for 5 min respectively.

It was determined by analysis of the optical density at 365 nm that the removal of the 1 µm resist layer requires 32% DQS photodecomposition independent of the presence of donor. The quantum yield η of DQS photodecomposition was evaluated from the formula

$$\eta = 1.196 \times 10^8 [\log(10^{OD_0} - 1) - \log(10^{OD} - 1)] / (H \lambda_{act} \epsilon)$$

where OD_0 and OD are the optical densities at 365 nm before and after the exposure H (mJ cm^{-2}), $\lambda_{act} = 365$ nm and $\epsilon = \epsilon(\lambda_{act}) = 1.54 \times 10^4$ dm^3 mol^{-1} cm^{-1} (measured using an acetone solution of DQS). It was found that the quantum yield equals $\eta = 0.12$ in the absence of donor.

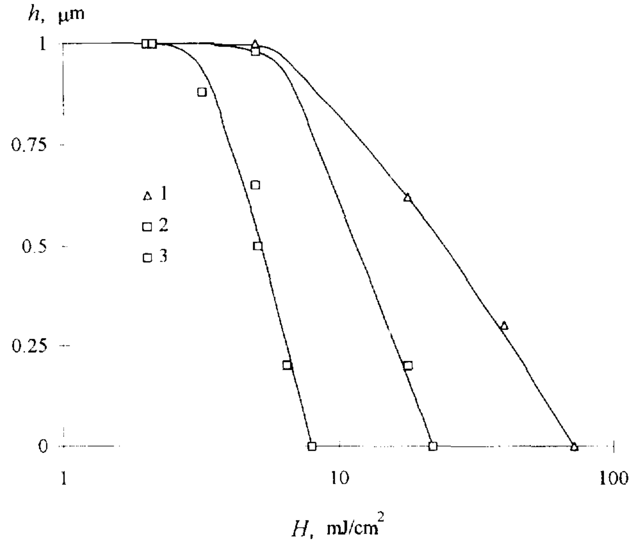


Fig. 1. Exposure–response curves. The resist contains $(C_5H_5)_2Fe$: 0 (1); 0.2 mol dm^{-3} (2,3). After exposure the samples were kept at 22 °C (1, 2) and heated at 56 °C for 5 min (3).

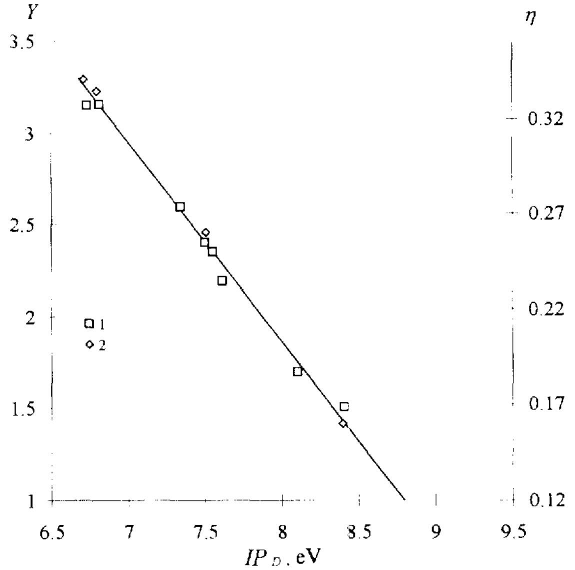


Fig. 2. Dependence of the amplification coefficient $Y = H_0/H_0(D)$ (1) and η (2) on the donor ionization potential IP_D. [D] = 0.2 mol dm^{-3}.

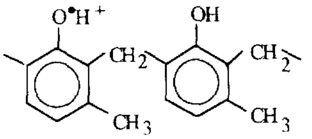
The dependences of the amplification coefficient $Y = H_0/H_0(D)$ and η on the donor ionization potential are shown in Fig. 2 ($H_0(D)$ and H_0 are the exposures necessary for full removal of the layer, 1 µm thick, with and without the donor). As shown in Fig. 2, η and Y linearly increase as IP_D decreases. These results demonstrate that the donor–acceptor interaction determines the photochemical and photolithographic characteristics of the system and that D·(DQS)* exciplex formation occurs; this exciplex dissociates into the unstable radical ions $D^{\cdot +}$ and $(DQS)^{\cdot -}$ leading to DQS decomposition

$$D \cdot (DQS)^* \rightarrow D^{\cdot +} + (DQS)^{\cdot -} \qquad (1)$$

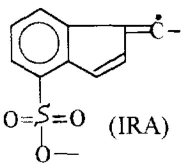
As shown in Fig. 2, the linear dependence $Y(\eta) \propto A - IP_D$ reaches $\eta = 0.12$ at an ionization potential of 8.8 eV. This value coincides with IP_D of $C_6H_2(OH)(CH_3)_3$ which may be considered as a low-molecular-weight analogue of NR. Therefore we can assume a charge transfer process

$$NR \cdot (DQS)^* \rightarrow NR^{\cdot +} + (DQS)^{\cdot -} \qquad (1a)$$

where $NR^{+\bullet}$ =

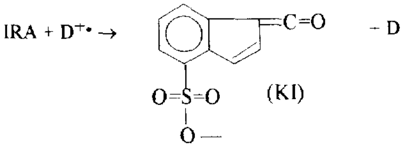


It was demonstrated [4] by gas phase mass spectroscopy using a chemical ionization technique that the molecular anion $(DQS)^{\bullet-}$ is not sufficiently stable and decomposes with the loss of N_2 and the formation of the intermediate radical anion (IRA) with the structure



(IRA)

The IR spectra of the samples with and without ferrocene show that illumination results in a decrease in absorption due to the diazoquinone group at 2100–2180, 1550–1650 and 1400 cm^{-1}, and the appearance of absorption of the unsaturated carboxylic acid at 1680–1760 cm^{-1}. Apart from the presence of ferrocene, the IR spectrum exhibits a broad band at 3450–2800 cm^{-1} due to the O–H stretching vibration in the presence of strong intermolecular hydrogen bonding [5]. This band reversibly appears as the temperature rises above 22 °C and is associated with the monomer–dimer equilibrium of ICA which gives mainly the monomer form above 22 °C. Thus ICA forms from IRA via a ketene intermediate (KI) probably as a result of reaction of IRA, $D^{\bullet+}$ and traces of H_2O



(2)

$$KI+H_2O \rightarrow ICA \tag{2a}$$

The photodecomposition of the dissolution inhibitor DQS additionally promotes the dissolution of the novolac resin as it is accompanied by a considerable increase in the intermolecular volume which facilitates the penetration of the developer into the layer [6].

Fig. 3 shows the dependences of the lithographic sensitivity ($S_0 = 1/H_0$) and quantum yield of DQS decomposition on the ferrocene concentration. As shown in Fig. 3, ferrocene concentrations above 0.22 mol dm^{-3} provide an increase in both S_0 and η by factors of 3.6 and 10 for samples kept for 5 min after exposure at 22 °C and 56 °C respectively. Unlike ferrocene, the amines (excluding *N,N*-dimethylamino-*p*-benzaldehyde) do not provide post-exposure amplification of the primary effect of illumination. The increase in η and S_0 (Fig. 3) due to the post-exposure heating of the ferrocene-containing layers may be accounted for by the known [7] radical cation formation ($D^{\bullet+} = (C_5H_5)_2^{\bullet}Fe^{+}$) in the reaction of ferrocene with quinones in acidic media

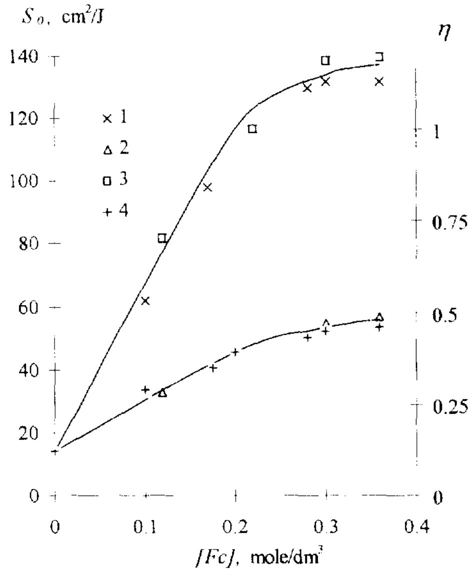


Fig. 3. Lithographic sensitivity S_0 (1, 2) and η (3, 4) as a function of the ferrocene concentration with (1, 3) and without (2, 4) post-exposure heating at 56 °C for 5 min.

$$(C_5H_5)_2Fe + ICA(H^+A^-) \rightarrow [(C_5H_5)_2Fe{-}H]^+ \ldots A^- \tag{3}$$

$$[(C_5H_5)_2Fe{-}H]^+ \ldots A^- + DQS \rightarrow (C_5H_5)_2^{\bullet}Fe^+ + DQS^{\bullet-} + ICA \tag{3a}$$

followed by the formation of IRA from $DQS^{\bullet-}$ and of ICA from IRA in reactions (2) and (2a). Reactions (3) and (3a) are then repeated.

Thus the addition of donors to compositions based on novolac resin and DQS provides linear increases in the quantum yield of DQS decomposition and lithographic sensitivity of the resist as the donor ionization potential decreases. This effect is caused by exciplex $D \cdot (DQS)^*$ formation and its subsequent ionic dissociation to give the unstable $(DQS)^{\bullet-}$ radical anion, which is transformed into ICA. The exposure H_0 necessary for full removal of the layer, 1 μm thick, during the development decreases from 72 to 8 mJ cm^{-2} as ferrocene (0.22–0.3 mol dm^{-3}) is added to the resist composition and the exposed samples are heated at 56 °C for 5 min.

Acknowledgements

This research was supported by Project No. 96-03-32375 from the Russian Foundation for Basic Research.

References

[1] W.M. Moreau, Semiconductor Lithography, Plenum, New York, 1988, Chapter 2.
[2] E. Reichmanis, L.F. Thompson, Chem. Rev. 89 (1989) 1273.
[3] A.V. Vannikov, A.D. Grishina, Russ. Chem. Rev. 62 (1993) 35.

[4] B.M. Du Sorbier, S. Kulkarni, P. Vouros, D.P. Kirby, J. Appl. Polym. Sci. 34 (1987) 447.
[5] G. Socrates, Infrared Characteristic Group Frequencies, Wiley, New York, 1980, p. 64.
[6] Y.I. Koltsov, J. Sci. Appl. Photogr. 38 (5) (1993) 45.
[7] E.G. Perevalova, M.D. Reshetova, K.I. Grandberg, Methods of Elemento-Organic Chemistry, Nauka, Moscow, 1983, p. 130 (in Russian).