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Journal of Photochemistry and Photobiology A: Chemistry 92 (1995) 223–228

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

Polymer light-sensitive layers for photochemical etching of Al films

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Received 20 April 1995; accepted 14 June 1995

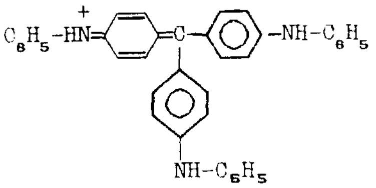
Abstract

The dry photochemical etching of aluminium films has been studied using the etchers (Opal Blue dye and acids), which are produced by illumination of the light-sensitive polymer layers cast on top of these films. These layers, consisting of different polymer binders, ferrocene [$(C_5H_5)_2Fe$], diphenylamine (DPA) and tetrabromomethane (CBr_4) have a high light-sensitivity owing to autocatalytic post-exposure accumulation of etchers. In this process the catalytic system Fe(III)/Fe(II) is formed directly from components dissolved in the polymer binder as a result of photochemical reaction. The Al film having a thickness of 0.65 μm is dissolved into the polymer layers completely after exposure $H_0 = 4$ mJ cm^{-2} to 365 nm.

Keywords: Dry photochemical etching; Aluminium film; Polymer layer; Light-sensitive charge transfer complex; Autocatalytic amplification

1. Introduction

The photochemical etching of metal films finds wide application in modern science and high technology, particularly in the manufacture of printed devices, integrated circuits, optical discs etc. For the fabrication of metallic images it is necessary to apply either photolithography [1] with multistaged wet processes or powerful pulses of ultraviolet excimer lasers for ablative etching [2,3]. The patterning of aluminium stripes has been also produced by pyrolytic laser chemical decomposition of trimethylaluminium in a vacuum chamber [4]. Our group developed an alternative dry resistless process for the photochemical etching of metal films sputtered onto a support by reactive halogen-containing fragments, acids and coloured products, which are produced by illumination of the light-sensitive polymer layer cast on top of these films [5,6]. Recent publication [17] has shown that the effective etcher for the Al films is the composition consisting of a polymer binder, DPA as a donor and hexabromodimethylsulfone ($CBr_3SO_2CBr_3$) or CBr_4 as acceptors (A) forming a light-sensitive charge-transfer complex DPA·A. The photoexcitation of the DPA·A complex involves electron transfer from the donor to the acceptor with formation of the radical-ions $DPA^{+\bullet}$ and $A^{-\bullet}$ and the products of their interactions including an acid and the blue dye 4,4′,4″-tri(anilino)triphenylmethane bromide [8] (Opal Blue)



which has an optical absorption maximum near 620–630 nm [8,9]. It was proposed [7] that the formation of the metallo-organic complex between Al and the triphenylmethane dye causes the dissolution of the Al film into the illuminated polymer layer.

This study attempts to increase the efficiency of the photoetching Al films using light-sensitive polymer layers with an autocatalytic amplification of the latent image as described earlier [10–12]. These layers consist of different polymer binders, $(C_5H_5)_2Fe$, DPA or diphenylbenzylamine (DPBA) and CBr_4. The light-sensitivity of these layers is caused mainly by the formation of charge–transfer complexes $(C_5H_5)_2Fe \cdot CBr_4$ and $DPA \cdot CBr_4$ which have the optical absorption maxima in range 370–400 nm [13].

2. Experimental section

The Al film was deposited onto a heated (70 °C) poly(ethylene terephthalate) substrate to a thickness of $h_0 = 0.65$ μm. A 3–5 μm thick polymer light-sensitive layer was cast from an acetone solution of a known composition

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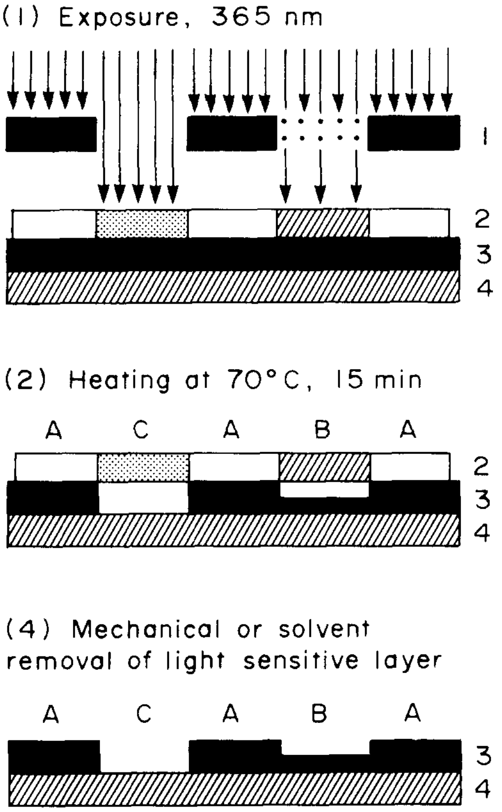


Fig. 1. Schematic diagram of photoetching metal and semiconductor films (1) mask (original), (2) polymer layer, (3) Al film, (4) substrate.

onto the Al film. The light-sensitive layer was covered with a thin poly(vinyl alcohol) film [10], in order to prevent diffusion of atmospheric O_2 into the layer during exposure and to realize autocatalytic amplification.

Polymer binders poly(methyl methacrylate) PMMA, poly(vinyl chloride) PVC, polystyrene PS, poly(2-methyl-1,3-dioxane-4,6-diyl) methylene PMDM, poly(vinyl acetate) PVAc and copolymer of vinyl acetate and crotonic acid CVACA were purified by precipitation from toluene solutions by adding hexane. Chemically pure grade amines (DPA and DPBA) and CBr_4 synthesized by electrochemical bromination of $CHBr_3$ were purified additionally by recrystallization from ethanol. Spectrograde solvents were used as supplied. The concentrations of ferrocene 1 mole dm^{-3} and CBr_4 2.1 mole dm^{-3} were used in all experiments discussed below.

Fig. 1 shows the scheme for photochemical etching of metallic films. The process consists of three steps. In step I, a triple layered structure consisting of (1) a poly(ethylene terephthalate) substrate, (2) the Al film and (3) the light-sensitive polymer layer is exposed to the 365 nm band of mercury lamp ($I_0^{365} = 8 \cdot 10^{-4}$ W cm^{-2}) until a latent image is formed in the polymer layer. In step II the structure is baked at 70 °C for 15 min. In this step the Al film is dissolved into the illuminated section of the polymer layer. The polymer layer is removed in step III, either peeled away or by immersion in acetone. After this, the etching efficiency was determined by the measurement of absorption of the Al film [OD(Al)] on a densitometer "Macbeth" TR 927. The Al film initial thickness 0.65 μm corresponds to OD(Al) = 4.

The absorption spectra of the light-sensitive polymer layers were recorded on a DU-7 Spectrophotometer (Beckman).

3. Results and discussion

3.1. Al etching

The exposure response curves for the Al film photoetching representing the dependencies of the Al film absorption, OD(Al), on the exposure, H (log scale), for the triple layered structure are shown in Fig. 2. The light-sensitive layers consist of PVC binder, $(C_5H_5)_2Fe$, CBr_4 with and without DPA or DPBA. The curve for the polymer layer containing DPA and CBr_4 without ferrocene is also given. As seen, with the lack of $(C_5H_5)_2Fe$ the layer containing CBr_4 and DPA in maximum concentration, 1.2 mole dm^{-3}, shows low light-sensitivity; the exposure, H_0, corresponding the complete removal of Al film, equals 120 mJ cm^{-2}. Illumination of the light-sensitive polymer layer containing $(C_5H_5)_2Fe$ and CBr_4 only has no result in the Al film etching. DPA added into this layer provides the photochemical etching of the metal film. The exposure H_0 decreases from 110 to 5.5 mJ cm^{-2} as the

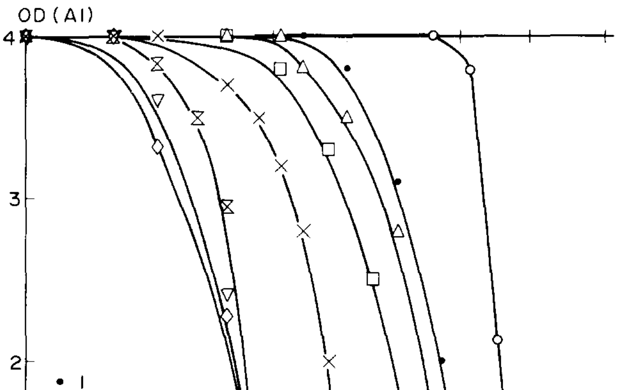


Fig. 2. Dependence of the Al film absorption, OD(Al), on the exposure dose, H, for triple layered structure. The PVC matrix contains CBr_4 2.1 mole dm^{-3} and (1) DPA 1.2 mole dm^{-3} or (2) $(C_5H_5)_2Fe$ 1 mole dm^{-3} and also (3–8) $(C_5H_5)_2Fe$ 1 mole dm^{-3} and DPA, mole dm^{-3}, (3) 0.06, (4) 0.17, (5) 0.3, (6) 0.4, (7) 0.6, (8) 1.2. (9) The PVC matrix contains CBr_4 2.1 mole dm^{-3} $(C_5H_5)_2Fe$ 1 mole dm^{-3} and DPBA 1 mole dm^{-3}.

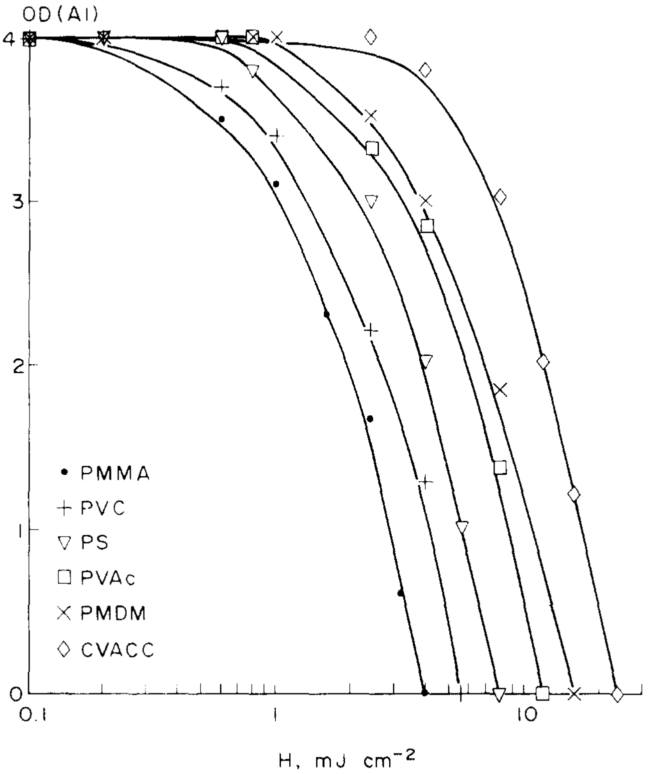


Fig. 3. Dependencies of OD(Al) on H for different polymer matrix containing $Fe(C_5H_5)_2$ 1 mole dm^{-3}, CBr_4 2.1 mole dm^{-3} and DPA 0.4 mole dm^{-3}.

DPA concentration increases from 0.06 to 0.4 mole dm^{-3}. The light-sensitivity ($1/H_0$) almost does not change at the following increase of the DPA concentration to 1.2 mole dm^{-3}. However, as seen in Fig. 2, at a high concentration of DPA a marked decrease is observed in the efficiency of the Al film etching when exposures are low, $H < 3$ mJ cm^{-2}. It lengthens the linear part of the exposure curve and increases its slope, $\gamma = -\Delta OD(\mathrm{Al})/\Delta \log H$. As noted in Fig. 2 for high concentrations of amines in the presence of $(C_5H_5)_2Fe$, the light-sensitivity decreases by about 60 fold when DPBA is added instead DPA.

Fig. 3 indicates the effect of exposure on OD(Al) when the different polymer binders containing $(C_5H_5)_2Fe$, CBr_4 and DPA 0.4 mole dm^{-3} are used. As seen, H_0 increases in the following order PMMA < PVC < PS < PVAc < PMDM < CVACC. The exposure doses $H_0 = 4$ and 23 mJ cm^{-2} for PMMA and CVACC respectively are required for the complete removal of the Al film.

Mechanisms of the photochemical and autocatalytic reactions ensuring the Al film etching are discussed below.

Mechanisms of the photochemical and autocatalytic reactions in polymer layers

Polymer layers containing ferrocene and CBr_4 are a typical example of compositions in which the catalyst is formed as a result of a photochemical reaction directly from photosensitive components [14]. Photoexcitation of the complex $(C_5H_5)_2Fe \cdot CBr_4$ leads to charge transfer [15].

$$(C_5H_5)_2Fe \cdot CBr_4 \xrightarrow{h\nu} (C_5H_5)_2Fe^+ + Br^- \cdots \dot{C}Br_3 (Br^{\bullet} \cdots CBr_3^-) \qquad (1a)$$

and subsequent thermal reactions of the ferrocenium cation $(C_5H_5)_2Fe^+$ with the free radical $\dot{C}Br_3$

$$(C_5H_5)_2Fe^+ + Br^- \cdots \dot{C}Br_3 \longrightarrow [Fe(III)Br_4]^- + \text{products} \qquad (1b)$$

with the formation of the tetrabromoferrate(III) anion $[Fe(III)Br_4]^-$ having the intensive absorption bands at $\lambda_{max} = 390$ nm and 475–480 nm and weak absorption at $\lambda_{max} = 690$ nm. It has been found [14] that the heating of the exposed layer at 70–100 °C ensures the amplification of the latent image. The key factor in this process is the formation of trivalent iron which as we know [16] induces the thermal reaction

$$Fe(III) + (C_5H_5)_2Fe \longrightarrow Fe(II) + (C_5H_5)_2Fe^+ \qquad (2a)$$

which followed by charge transfer to acceptor

$$Fe(II) + CBr_4 \longrightarrow Fe(III) + Br^- \cdots \dot{C}Br_3 \text{ (or } Br^{\bullet} \cdots CBr_3^-) \qquad (2b)$$

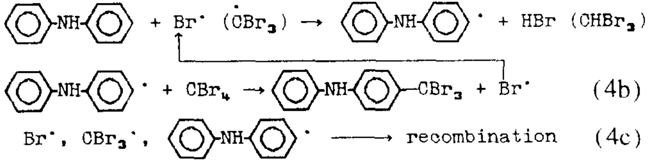
Thus the Fe(III)/Fe(II) pair, arising as a result of photoexcitation of the complex, catalyses the thermal electron transfer from ferrocene to CBr_4. The overall autocatalytic process can be formulated as follows [14]:

$$(C_5H_5)_2Fe + CBr_4 \xrightarrow{Fe(III)/Fe(II)} (C_5H_5)_2Fe^+ + Br^- \cdots \dot{C}Br_3 \text{ (or } Br^{\bullet} \cdots CBr_3^-) \qquad (3)$$

Then the thermal reactions (1b) are repeated.

Absorption spectra of the exposed polymer layers consisting of PMMA or CVACC matrix, $(C_5H_5)_2Fe$, CBr_4 and DPA are given in Fig. 4. The visible spectrum at $\lambda_{max} = 665$ nm recorded after exposure 480 mJ cm^{-2} without post-exposure thermal treatment belongs, as we know [9,17], to the primary coloured product (I) formed from DPA, which has the following structure C_6H_5–HN^+=C_6H_4=CBr–C_6H_4–NH–C_6H_5. This product arises also as a result of the photoexcitation of DPA·CBr_4 complex in the absence of the ferrocene [9,17]. It is known [18] that the free radical chain process

(4a)



(4b)

(4c)

takes place in the polymer layer containing DPA and CBr_4 after production of the free radicals in a result of the electron phototransfer from the donor to the acceptor molecule. The interaction of C_6H_5–NH–C_6H_4–CBr_3 with DPA leads to the formation of the above-mentioned primary coloured product

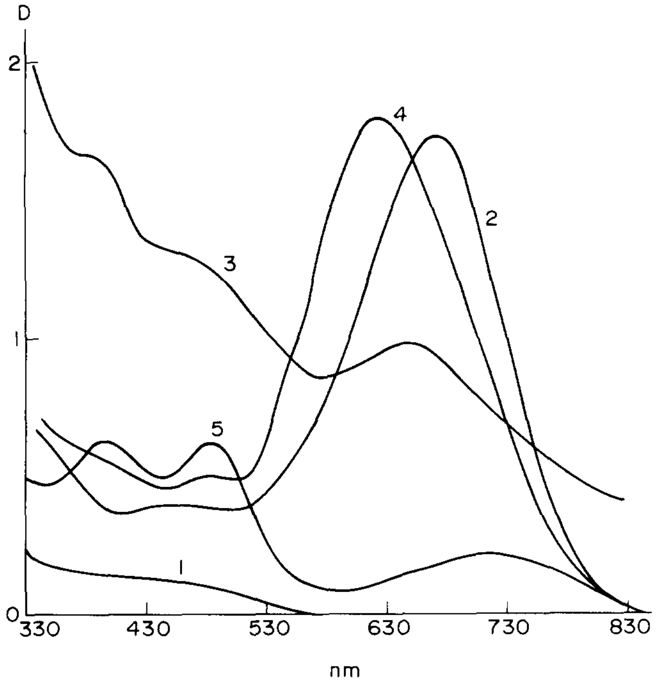


Fig. 4. Optical spectra of (1–4) PMMA or (5) CVACC matrix containing CBr_4 2.1 mole dm^{-3} and also (1) DPA 0.4 mole dm^{-3}, $Fe(C_5H_5)_2$ 1 mole dm^{-3} prior to exposure, (2) DPA 1.2 mole dm^{-3}, $Fe(C_5H_5)_2$ 1 mole dm^{-3} exposed to 480 mJ cm^{-2} without post-exposure heating, (3) DPA 0.4 mole dm^{-3}, $Fe(C_5H_5)_2$ 1 mole dm^{-3} after 5.6 mJ cm^{-2} exposure followed by a 15 min heating at 70 °C, (4) DPA 1.2 mole dm^{-3}, $Fe(C_5H_5)_2$ 1 mole dm^{-3} after 5.6 mJ cm^{-2} exposure followed by a 15 min heating at 70 °C, (5) DPA 0.4 mole dm^{-3}, $Fe(C_5H_5)_2$ 1 mole dm^{-3} after 5.6 mJ cm^{-2} exposure followed by a 15 min heating at 70 °C.

I. At the heating I reacts with DPA and forms the Opal Blue [9].

In the layers containing $(C_5H_5)_2Fe$, CBr_4 and DPA at low exposure, 5.6 mJ cm^{-2}, the latent image is formed and the post-exposure heating leads to autocatalytic accumulation of both $[Fe(III)Br_4]^-$ and Opal Blue dye. The optical spectra in Fig. 4 demonstrate that the formation of the anion $[Fe(III)Br_4]^-$ (maxima at 390, 475 and 690 nm) predominates over that of Opal Blue (maximum at 630 nm) in this process for the samples with the DPA concentration of 0.4 mole dm^{-3}. As is seen, the absorption of Opal Blue $OD(630)$ situated on longwave absorption of $[Fe(III)Br_4]^-$ is markedly higher for PMMA matrix in comparison with CVACC. From data in Fig. 4 it follows also that the accumulation of $[Fe(III)Br_4]^-$ is depressed while of Opal Blue increases with growth up the DPA concentration to 1.2 mole dm^{-3}.

The dependencies of the absorption at λ_{max} [$OD(\lambda_{max})$ at 630 nm for Opal Blue and at 605 nm for the photoproduct from DPBA] on exposure H for the PMMA layers containing the different additions were measured in the absence of Al film. These data are given in Fig. 5(a). As seen, one and the same exposure response curve (1) characterizes the colouration of the two ferroceneless layers containing DPA and DPBA. These dependencies change insignificantly after post-exposure heating. The exposure H_1 at which the absorption achieves the values $OD(\lambda_{max}) = 1$ equals 100 mJ cm^{-2}. The

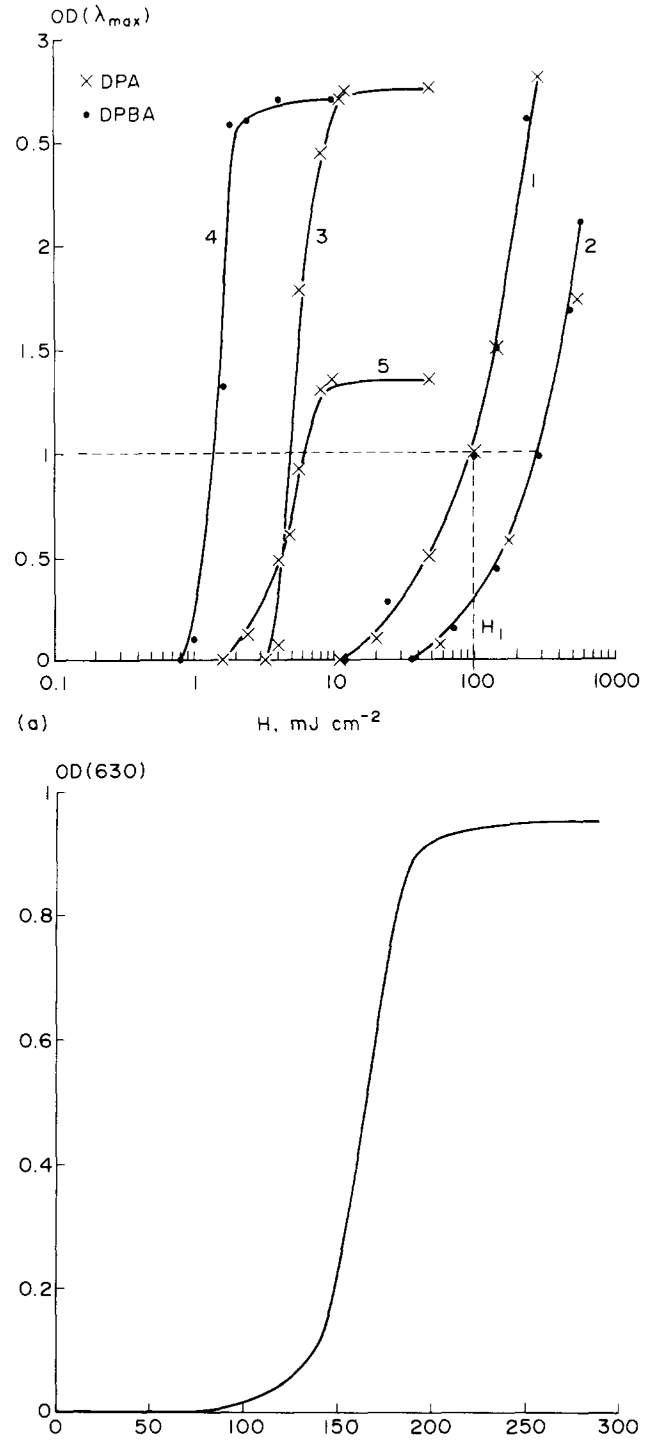
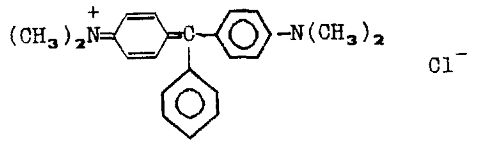


Fig. 5. (a) Dependencies of $OD(\lambda_{max})$ of coloured photoproducts on H for PMMA containing (1) DPA 1.2 mole dm^{-3} or DPBA 0.8 mole dm^{-3} and CBr_4 2.1 mole dm^{-3} after a post-exposure heating at 70 °C, 15 min: (2–5) $Fe(C_5H_5)_2$ 1 mole dm^{-3}, CBr_4 2.1 mole dm^{-3} and also (2) DPA 1.2 mole dm^{-3} or DPBA 0.8 mole dm^{-3} without post-exposure heating. (3) DPA 1.2 mole dm^{-3} after post-exposure heating at 70 °C, 15 min, (4) DPBA 0.8 mole dm^{-3} after post-exposure heating at 70 °C, 15 min, (5) DPA 0.4 mole dm^{-3} after post-exposure heating at 70 °C, 15 min. (b) Curve of the autocatalytic accumulation of Opal Blue at 70 °C after 5.6 mJ cm^{-2} exposure. PMMA contains $Fe(C_5H_5)_2$ 1 mole dm^{-3}, DPA 0.4 mole dm^{-3} and CBr_4 2.1 mole dm^{-3}.

added ferrocene increases the exposure H_1 to ~300 mJ cm^{-2} (curve 2). In Fig. 5(a) the light-sensitivity ($S_1 = 1/H_1$) for the DPA (curve 3) and DPBA (4) containing layers increases respectively 60 and 260 fold if the post-exposed heating (70 °C, 15 min) of the layer is used. The kinetic curve of the autocatalytic post-exposed accumulation of Opal Blue at 70 °C is given in Fig. 5(b). This curve characterizes a process of the autocatalytic amplification of the latent image.

The data obtained allow us to conclude that Opal Blue is accumulated in reaction (4) and subsequent thermal reactions owing to the formation of the free radicals $Br^{\bullet}$ and $\dot{C}Br_3$ in the autocatalytic process (3). When the DPA concentration increases a waste of these free radicals in reaction (4) causes the suppression of the $[Fe(III)Br_4]^-$ formation in the processes (1b) and (3), as shown in Fig. 4. Fig. 5(a) shows that the decrease of DPA concentration from 1.2 to 0.4 mole dm^{-3} (curves 3 and 5 correspondingly) in the layer consisting of PMMA, DPA, $(C_5H_5)_2Fe$ and CBr_4 brings about a lowering of the exposure at which the colouration begins from 3.1 to ~1.5 mJ cm^{-2}. This effect correlates with a marked decrease in the exposure at which the Al film etching begins when DPA concentration decreases from 1.2 to 0.4 mol dm^{-3} (Fig. 2, curves 8 and 6). It is possible that the high DPA concentrations entirely suppress autocatalytic reactions (2)–(3).

To confirm the mechanism of the etching the model PMMA layers containing only the citric acid or the dye and also both the components together were cast onto the Al film. We used the Malachite Green as a model dye having the structure



similar to that of Opal Blue. At the heating (70 °C, 15 min) the Al film does not etch by PMMA containing only Malachite Green. When the polymer layer contains only the citric acid the Al film warps a small amount but remains on support. Only the PMMA layer containing both the Malachite Green and citric acid dissolves completely the Al film at heating. Thus, the formation of the Opal Blue together with HBr via reactions (1), (3) and (4) causes the Al film etching.

It was established [10,11] that illumination and subsequent heating of the polymer layer containing, in addition to the ferrocene and CBr_4, the donor DPBA results in the autocatalytic accumulation of $[Fe(III)Br_4]^-$ and the colour product from DPBA, which is responsible for the optical absorption at $\lambda_{max} = 605$ nm. Unlike DPA, the interaction of the tertiary amines with free radicals involves the abstraction of a hydrogen atom from α-position relative to the nitrogen atom [19]. Therefore for DPBA the following reaction is possible:

$$(C_6H_5)_2N\text{–}CH_2\text{–}C_6H_5 + \dot{B}r(\dot{C}Br_3) \longrightarrow (C_6H_5)_2N\text{–}\dot{C}H\text{–}C_6H_5 + HBr(HCBr_3) \quad (5)$$

The α-radical exhibits powerful electron-donating properties and transfers an electron to acceptor in a dark reaction [20]. On this basis, one may postulate that the autocatalytic accumulation of the primary coloured product (II) from DPBA with the structure $(C_6H_5)_2\overset{+}{N}\text{=}CH\text{–}C_6H_5$ [17] and optical absorption band at $\lambda_{max} = 665$ nm involves the reactions (3), (5) and the following dark electron transfer

$$(C_6H_5)_2N\text{–}\dot{C}H\text{–}C_6H_5 + CBr_4 \longrightarrow (C_6H_5)_2N^+\text{=}CH\text{–}C_6H_5 + Br^- \cdots \dot{C}Br_3(Br^{\bullet} \cdots CBr_3^-) \quad (6)$$

On heating, product II reacts with DPBA and other components of the layer with the production of a stable dye ($\lambda_{max} = 605$ nm). From data in Fig. 5(a) it follows that the autocatalytic process including the reactions (5) and (6) with participation of DPBA proceeds with a greater efficiency as compared with the reaction (4) in the DPA containing layer. We do not know the structure of the stable dye from DPBA, nevertheless as seen in Fig. 2, it shows a very low efficiency of the Al film etching.

We believe that the mobility of the reactive component within polymer matrices determines (Fig. 3) considerable decrease of the light-sensitivity at replacing PMMA on PMDM, PVAc or CVACC. Indeed, it has been shown [12] that the acid or the divalent iron formed via reactions (1–4) catalyze the crosslinking PMDM or polymers containing vinyl acetate groups. This crosslinking decreases the components mobility and consequently the layer light-sensitivity. However, the polymer chains of PMMA have been established [21] to undergo the scission in interaction with radical products. The kinetic chain length of depolymerization increases strongly with increasing temperature.

4. Conclusion

Polymer layers utilizing the autocatalytic post-exposure formation of Opal Blue and HBr cause the dry photochemical etching of Al films and show high light-sensitivity to near UV and visible light. Thermally evaporated Al films on poly(ethylen terephthalate) substrate and light-sensitive polymer layers cast on top of these films were used. The layers consist of different polymer matrices, ferrocene, diphenylamine and tetrabromomethane. The light-sensitivity of the layers depends on a choice of a polymer matrix and decreases in the order PMMA > PVC > PS > PVAc > PMDM > CVACC. The 0.65 μm thick Al-film is dissolved into the PMMA or CVACC layers completely after exposure to 365 nm $H_0 = 4$ or 23 mJ cm^2 respectively.

Acknowledgements

The research described in this publication was made possible in parts by Grant No. 015 from the International Science and Technical Center and by Grant No. N2C000 from the International Science Foundation.

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