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Dry Photochemical Etching of Metallic Films

Anatolii V. Vannikov,* Antonina D. Grishina and Marine G. Tedoradze

A. M. Frumkin Institution of Electrochemistry, Russian Academy of Sciences, 117333 Moscow, Russian Federation.

The illumination of a light sensitive polymer layer cast on top of a metallic film (Al or Bi) leads to etching of the metallic film; the light-sensitive layer consists of a polymer binder, including aromatic amines and hexabromodimethylsulfone; the additional use of an optical amplification process results in a new, dry, highly sensitive method of metallic film etching.

The fabrication of metallic images finds wide application in modern science and high technologies, particularly in the manufacture of printed devices, integrated circuits, optical disks and so on. The production of metallic images requires either multi-stage wet processes[1,2] or exposure to powerful excimer lasers (ablative optical recording).[3,4] Laser ablation of thin metallic films (Cu, Ni) is accelerated in a halogenated methane (CCl_4, MeBr or CF_2Br_2) atmosphere[4,5] owing to photochemical formation of CuCl, CuBr or $NiBr_2$, respectively.[5,6]

Polyester matrices containing *tert*-amines (Am) and hexabromodimethylsulfone (HBMS) may be used as photoresists, the high sensitivity of which ($\simeq 10^{-2}$ mJ cm^{-2}) arises from optical and chemical amplification processes.[7] The sensitivity of the layer to near-UV and visible light is caused by the formation of Am·HBMS complexes that show electronic absorption at λ_{max} 360–380 nm and the long wave thresholds at 500, 600 and 650 nm if Am is diphenylamine (DPA), diphenylbenzylamine (DPBA) or dibenzylaniline (DBA), respectively.

The principal objective of this communication is to describe in some detail newly developed dry resistless process for the photochemical etching of metallic films by reactive halogen fragments which are produced by illumination of polymer layers cast on top of these films from acetone solutions of known composition. Polymer layers containing Am·CBr_4 complexes also photoetch the metallic films.

The metallic film etching process consists of three steps. In step 1, a structure consisting of a cellulose triacetate substrate, an evaporated metallic film and a light-sensitive polymer layer, cast on top of this film, is exposed to irradiation in the absorption band of either the Am·HBMS complex or a spectral sensitizer until a visible or latent image is formed in the polymer layer. The latent image is optically amplified by flood irradiation of the exposed sample with red and near-IR light, $\lambda \geq 650$ nm. In step 2, heating of the structure at 80–110 °C produces metallic film dissolution within 2–6 min. The light-sensitive polymer layer is removed in step 3 by peeling away or by immersion in acetone. After this, the etching efficiency was determined by measuring the light transmittance (T) of the metallic film in the 540–600 nm range (measured relative to the substrate). The light sensitivity (S) of the structure is estimated from the exposure H_{50} ($S = 1/H_{50}$) required to produce an increase in the transmittance of the metallic film to $T = 50\%$.

The immediate result of photoexcitation of the complex or added spectral sensitizer is electron transfer from Am to HBMS and formation of the radical cation $Am^{+\bullet}$ and intermediate particles $Br^{-}\cdots R^{\bullet}$ or $R^{-}\cdots Br^{\bullet}$ {here $R^{\bullet} = CBr_2{=}S(O^{\bullet})(O){-}CBr_3$, $R^{-} = [CBr_2{=}S(O_2){-}CBr_3]^{-}$}. The ensuing dark reactions lead to the generation of acids HR, HBr and a coloured product forming the visible or latent image.[7]

Light-sensitive polymer layers consisting of poly(vinyl chloride) (PVC) binder, DPBA, HBMS, the chemical sensitizer 4-(*N*,*N*-dimethylamino)benzaldehyde (DMABA) and a spectral sensitizer to the 480–620 nm region were used for photoetching of the Al films. We used the pyrylium dye 4-(2,6-diphenyl-4*H*-pyran-4-ylidenemethyl)-2′,6′-diphenylpyryl perchlorate (PD), λ_{max} 571 nm, as a spectral sensitizer. Fig. 1 shows the electronic spectrum of the layer containing [PD] 5×10^{-3} mol dm^{-3} and the spectral sensitivity $S(\lambda) = 1/H_{50}(\lambda)$ of photoetching the Al film having an initial absorbance $A(Al) = 4.5$ ($T = 7 \times 10^{-3}\%$). $S(\lambda)$ for the layer containing PD in very low concentration, $\approx 7 \times 10^{-5}$ mol dm^{-3}, corresponding to $A(PD) \approx 0.01$ at 571 nm, is also given. As shown in Fig. 1, the light sensitivity in the visible region is 15–26 cm^2 J^{-1}. The removal of PD and DMABA from the composition leads to a 100-fold decrease of the light sensitivity for the incident light λ 436 nm acting in the region, in which the optical absorption of PD is very weak (see Fig. 1). When PD is absent from the polymer layer the removal of DMABA only leads to a 3-fold decrease of the light sensitivity. Hence, PD does not function just as a spectral sensitizer. The addition of DMABA to the light-sensitive layer has previously been shown[7] to lead to additional thermal formation of acids. We also observed[7] that HBr transforms PD into a new dye (PD′) with a central ═CBr— group in place of the ═CH— group in PD. PD′ is a strong acceptor, $E^{red}_{1/2} \approx 0$ V (*vs.* saturated calomel electrode).[8] The incorporation of PD′ instead of PD into the layer cases thermal etching of the Al film even without illumination. Reaction (1) proceeds owing to the low ionization potential of

$$PD' + Al \xrightarrow{heat} PD'^{\bar{\bullet}} + Al^{+} \xrightarrow[M]{HBMS} PD' + Al^{+} + Br^{-}\cdots R^{\bullet} \longrightarrow RR'AlBr \qquad (1)$$

Al (6.0 eV). M is one of the components of the light sensitive layer (matrix, HBMS etc.).

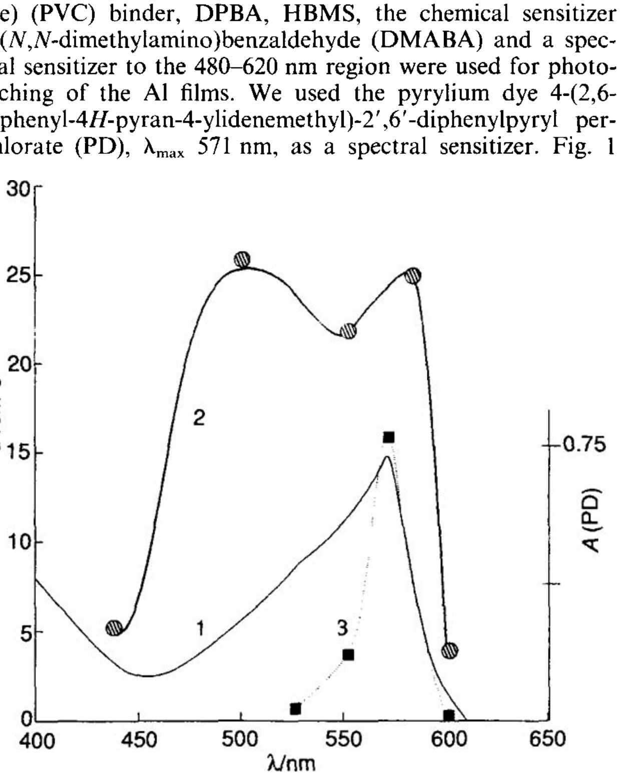

Fig. 1 Electronic spectrum of a PVC layer containing DPBA, HBMS, DMABA and PD (1). Spectral sensitivity $S(\lambda)$ for etching of an Al film by the layer (2, 3). [PD] 5×10^{-3} (1, 2) and 7×10^{-5} mol dm^{-3} (3); [DPBA] = [HBMS] = [DMABA] = 0.8 mol dm^{-3}. The layer was heated after exposure for 2 min at 110 °C

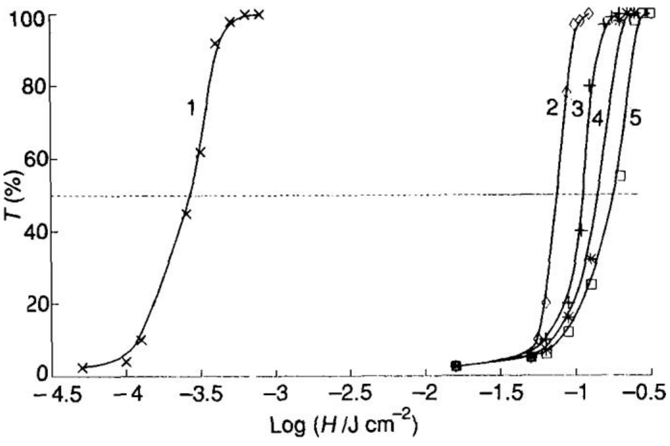

Fig. 2 Dependence of T on log H at λ 436 nm with (1) and without (2–5) optical amplification ($H = 0.06$ J cm^{-2}, $I_{oa} = 0.01$ W cm^{-2}). Layer contains [DPBA] = [HBMS] = 0.8 mol dm^{-3} (1–5) and additionally [indole] 0.04 mol dm^{-3} (1, 2). 1–3, PVC; 4, PS; 5, PMMA. The layer was heated after exposure for 6 min at 100 °C.

In Fig. 2 the dependence of the Bi film transmittance on the exposure dose H for the trilayer structure is given. The light-sensitive layer consists of a polymer matrix containing DPBA and HBMS. As shown in Fig. 2, the exposure at 436 nm is $H_{50} \approx 0.1$–0.28 J cm^{-2}. H_{50} increases in the order PVC < PS < PMMA; contrast coefficient γ ($= \Delta T/\Delta \log H$) ≈ 4.8–6. Similar values were obtained for the layers containing DBA and HBMS, whereas the system based on PVC, DPA and HBMS exhibits $H_{50} \approx 3.2 \times 10^{-2}$ J cm^{-2}, $\gamma \approx 3.2$ at 436 nm.

We believe that the initial stage of Bi-film etching is oxidation of Bi^0 by free radicals {$R = Br^{\bullet}$ or $[CBr_2{=}S(O)_2{-}CBr_3]^{\bullet}$},

$$Bi^0 + nR \rightarrow BiR_n \quad (\text{mainly } BiBr_3) \qquad (2)$$

formed under illumination, according to reaction (2) where $n = 1, 2, 3$. This process may also be responsible for the above-mentioned Al-film etching in the absence of PD in the light-sensitive layer. After reactions (1) or (2) during heating at 80–110 °C BiR_n dissolves into the polymer layer owing to interaction with the light-generated acids $H[CBr_2{=}S(O)_2{-}CBr_3]$ and HBr.

In order to increase the light sensitivity, the layers were

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exposed to latent image formation with subsequent optical amplification by flood irradiation of the exposed sample with red and near-IR light ($\lambda \geqslant 650$ nm). The light is absorbed only by the latent image centres that transfer the absorbed energy to the complexes, ensuring their dissociation into radical ions and the following thermal formation of the coloured products and acids.[7,8] Unfortunately the process is a two-quantum one and takes place only at high light flux. Moreover, optical amplification is absent in the DPA-based compositions. In order to provide optical amplification of the latent image in all the layers (including those containing DPA·HBMS complexes), indole was added to the polymer light-sensitive layer. The latter reacts with the intermediate products $Am^{+\bullet}\cdots Br^{-}\cdots R^{\bullet}$ (or $Br^{\bullet}\cdots R^{-}$) to form a new indole-containing coloured compound **I**. This compound has a wide optical absorption band in the visible range, λ_{max} 550 nm, with a long wavelength threshold at about 700 nm. **I** is a redox autosensitizer [eqn. (3)].[8]

$$ {}^1\mathbf{I}_0 \xrightarrow{h\nu,\,S-T} {}^3\mathbf{I}_1 \xrightarrow{Am} Am^{+\bullet}\cdots \mathbf{I}^{-\bullet} \xrightarrow{HBMS} {}^1\mathbf{I}_0 + Am^{+\bullet}\cdots Br^{-}\cdots R^{\bullet} \quad (\text{or } Br^{\bullet}\cdots R^{-}) \qquad (3)$$

The subsequent reactions of the radical species with the metallic film and indole lead to the additional formation of BiR_n and **I** in the exposed areas, respectively. Optical amplification occurs by a one-quantum mechanism during **I** photoexcitation at $\lambda \geqslant 650$ nm and proceeds under light from ordinary low intensity lamps. As shown in Fig. 2, using optical amplification the sensitivity to light with λ 436 nm reaches H_{50} 2.7×10^{-4} J cm^{-2} or $S \simeq 3.7 \times 10^3$ cm^2 J^{-1} ($\gamma \simeq 4$) for etching a layer based on PVC, DPBA, HBMS and indole. Similar values were obtained for DPA-based layers. For a PVC matrix containing DBA, HBMS and indole we obtained $S \simeq 3.3 \times 10^3$ cm^2 J^{-1} at λ 436 nm and 20 cm^2 J^{-1} at 633 nm – near to the long-wave threshold of the electronic absorption of the complex DBA·HBMS.

Contact printing was used when investigating the resolution capability of the structure. The resolution is better than 200 mm^{-1}.

In summary, we have developed a new dry process for the photochemical induced etching of metallic films (Al and Bi) using light-sensitive polymers containing Am·HBMS complexes. The light sensitivity of the process is $S \simeq 3$–30 cm^2 J^{-1}. It has been shown for the Bi film that the sensitivity increases to $S \simeq (3.3$–$3.7) \times 10^3$ cm^2 J^{-1} when optical amplification of the latent image is used.

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