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THE APPLICATION OF PHOTO-REDUCTION OF THIN CUPROUS IODIDE FILM FOR METAL IMAGE FORMATION

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The surface chemical properties of cuprous-iodide (CuI) film evaporated on a polymer layer containing a precursor reducing agent, 2-isopropoxy-1,4-naphthoquinone (IPNQ), were markedly affected by UV irradiation. The CuI was reduced by photoproducts of the IPNQ and the surface reductants attracted the zinc vapor in a vacuum evaporation vessel. Thus the UV exposure resulted in the zinc vapor deposition.

Additive-type metal imaging is a method utilizing metal deposition onto a latent image composed of an invisible amount of metal nuclei. It requires no etching process and makes a metal pattern showing a high resolving power. The authors have previously reported a dry-type micro metal-imaging system using electron- and photo-exposure and zinc vapor deposition.[1—3] In those reports, the specimens consisted of copper-evaporated polymer film containing precursor chelating agent or a halogen generator. The zinc vapor was deposited onto the exposed film surface and a fine pattern having a resolving power of over 500 cycles/mm was obtained by entirely dry processes. In these system, however, the surface copper layers were chemically unstable. Thus the specimen could not be stored for any long period before processing.

In this report, the authors describe photo-chemical changes in CuI-evaporated polymer film containing quinone compounds. Metal imaging utilizing this phenomenon and selective zinc vapor deposition has a stability to dark reaction and an ability to make fine patterns showing a high resolving power.

The specimen was a CuI-laminated poly-vinylbutyral (PVB) film containing IPNQ. A mixed solution of methanol and benzene (vol.ratio=1/2)containing desolved PVB and IPNQ was coated onto a glass substrate to a thickness of 3μm. The surface CuI was prepared by reaction between a thin evaporated copper film on the polymer layer and iodine vapor. The copper evaporation was done using conventional vacuum evaporation under a pressure of 10^{-5} Torr to a thickness of 20 to 40 Å. The evaporated copper film was set in an iodine atmosphere.

Photo-exposure was performed in air using a mercury-xenon arc lamp (Conrad-Hanovia, 600W) coupled with a monochromator (335nm, 1.6×10^{15} photons/s·cm^2). After exposure, the specimen was set in a zinc deposition vessel. The zinc pressure in the evaporation vessel was regulated by the heating temperature of the vapor source.

It is well known that zinc and cadmium vapor deposition onto nonmetallic substrata are difficult because of their high reevaporation rates. They do deposit however onto metallic and contaminated substrata. Zinc deposition did not appear on the original CuI-evaporated specimen although it appeared on the exposed one. This phenomenon suggests that the surface condition of the specimen is affected by UV irradiation.

The authors discuss here the changes in surface chemical properties to clarify the mechanism of the selective zinc vapor deposition. The methods employed to detect surface changes were as follows:

i) to check an affinity for zinc vapor,
ii) to measure the electrical conductivity of the surface CuI layer,
iii) to analyze the chemical components of the specimen.

Zinc vapor deposition was a direct and the most sensitive way to check surface chemical changes. The thickness of the zinc film on the specimen was obtained by the results of chemical analysis and optical density. As a result of quantitative chemical analysis carried out using α-pyridylazo-β-naphthol (PAN), the zinc film thickness and its optical density (absorbance at 600 nm) was seen to be linear with a thickness of under 400 Å.[1)]

Figure 1 shows the relation between the exposure time to UV rays and the evaporated zinc film thickness on the specimen. The zinc film thickness on the specimen grew as irradiation time was increased. With an exposure time of 2.5 min under constant evaporation, zinc was deposited to a thickness of 100 Å, corresponding to an absorbance of 1 at wavelength of 600 nm. This shows that the affinity of zinc vapor for the surface is apparently changed. In this case, UV exposure of over 1 min produced a distinct surface change.

The specimen having, the surface copper layer of 40 Å showed low electrical conductivity, while the

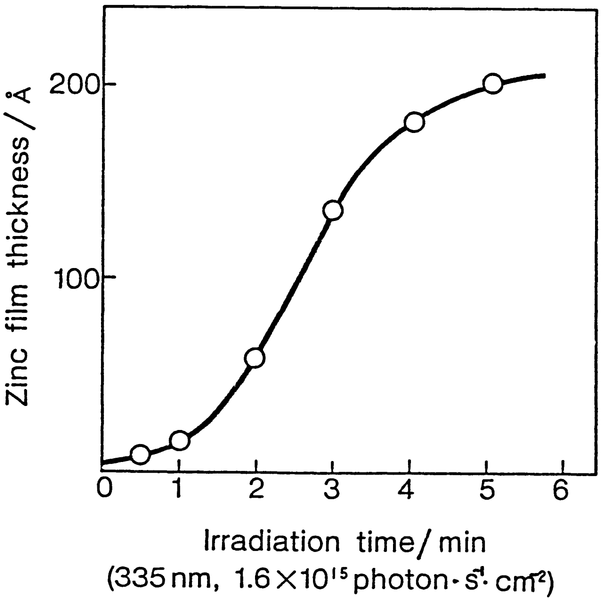


Fig. 1. Zinc deposition onto the exposed specimen.

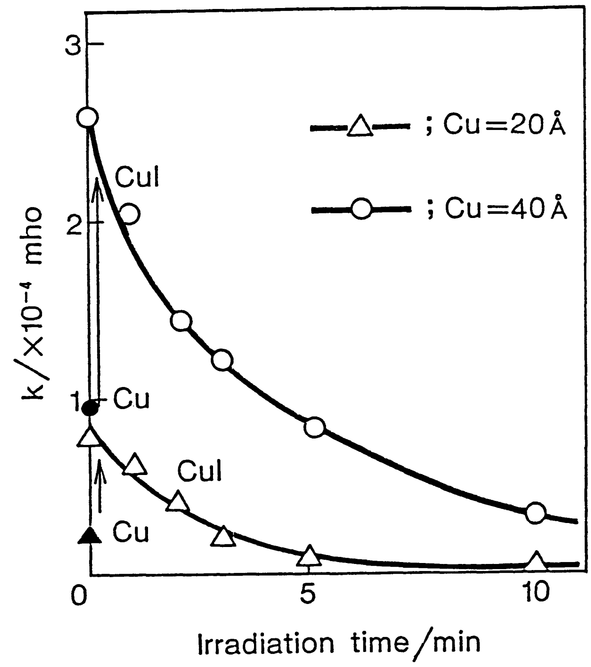


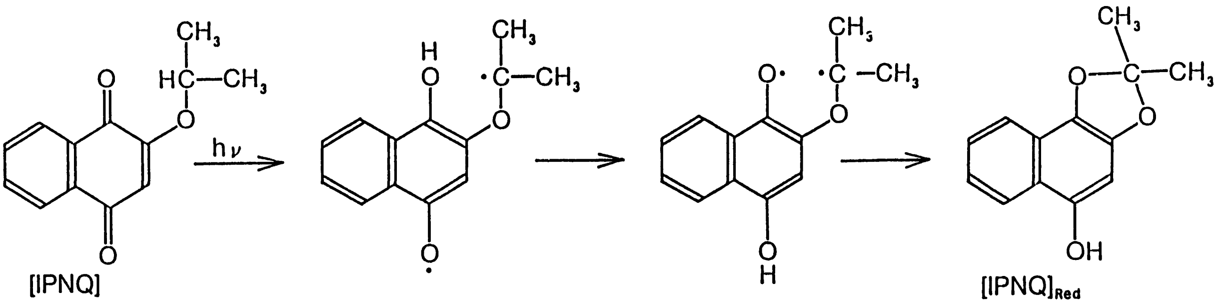
Fig. 2. The conductivity change in CuI layer caused by UV irradiation.

iodinated specimen showed higher conductivity.

Figure 2 shows the relation of electrical conductivity of the surface CuI layer to UV exposure time. The conductivity was measured by a method using an electrode of the comb type. The conductivities of the original copper layer with thickness of 20 and 40 Å were considerably lower than that of the iodinated layers. But they were increased by iodination. It is supposed that an island-type crystalline structure in the thin copper layer is converted to a homogeneous and continuous structure of crystalline CuI. On exposure, the conductivity of the surface layer gradually decreased. Moreover after exposure, the conductivity of the specimen increased again by iodination. These results suggested that the surface CuI layer was affected by the exposure.

The surface CuI layer was insensitive to UV rays of 335 nm. The polymer was also ineffective, although the IPNQ was sensitive to the UV rays. Thus the IPNQ was thought to be the key photosensitive component in the specimen and responsible for introducing the change in the surface CuI layer.

The IPNQ was changed to a reductant which was supposed to react with the copper products. The photochemical structural changes in the IPNQ are shown as follows:4)



Scheme 1. Photochemistry of 2-isopropoxy-1,4-naphthoquinon.

The relationship between IPNQ and CuI was checked briefly by noting the color change of CuI powder in a suspension. The CuI particles in a benzene solution containing IPNQ were colored to a pale brown by UV irradiation. It suggests that the surface of a CuI particle is influenced by the photochemical products of IPNQ. The redox properties of IPNQ in the specimen were estimated by the results of electrochemical measurement of the redox potential in an aqueous solution.

On the cyclic-voltammetry of the solution, the half wave potential of IPNQ in a mixed solution of ethanol and 0.5 M HCl aqueous solution (1/1) was evaluated at -0.05 V/SCE. It showed that the IPNQ was able to reduce the cuprous ion ($Cu^+ + e \longrightarrow Cu$, 0.276 V/SCE).

On the exposed specimen, the surface copper products were analyzed by colorimetric method using PAN and 4,7-diphenyl-1,10-phenanthroline (Batho). PAN reacts both with cuprous (Cu^+) ions and cupric (Cu^{++}) ions, although Batho reacts only with Cu^+ ions.

Figure 3 shows the changes in ionic species on the exposed specimen. On the irradiation time of 2 min, the detected amount of Cu^+ ions was the half of original amount. This is a similar trend to the change in electrical conductivity shown in Fig.2. Moreover, the detected amount of Cu^{++} ion was not influenced by the exposure.

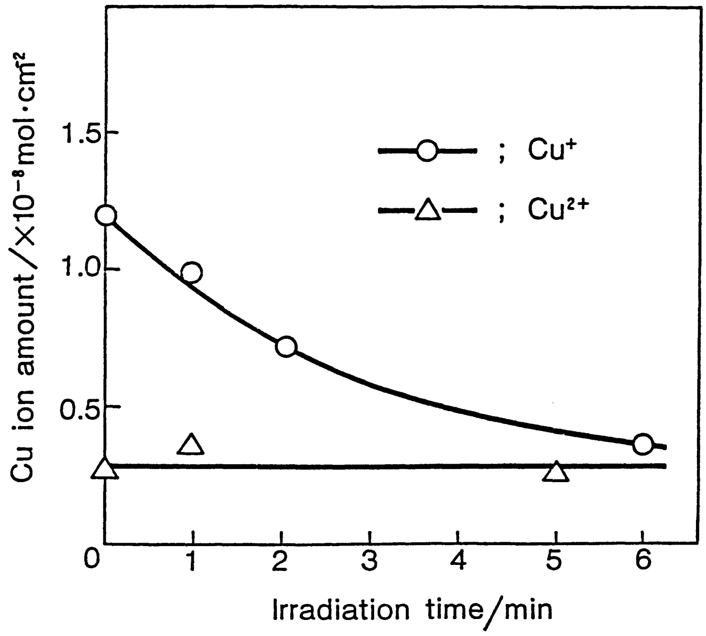


Fig. 3. Detected Cu ions amount in the exposed film surface.

The results obtained by the three analytical methods suggest that the surface chemical properties were apparently affected by UV rays. The major products on the exposed surface were supposed to be metallic copper. The reduction of CuI was carried out by the reductants of the IPNQ. Thus the main photochemical process was the redox of IPNQ.

The photochemical quantum yield of the IPNQ was estimated to be independent of the amount of it contained in the polymer layer. Regarding the photochemical structural change of IPNQ, it is suggested that the protons were abstracted from the polymer matrix or intermolecular proton donor groups of quinone. On the exposed specimen, the copper fragments were understood to act as the nuclei of zinc deposition. A fine zinc pattern having a resolving power of over 500 lines/mm was obtained by entirely dry processes.

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