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SELECTIVE ZINC DEPOSITION ONTO METAL-LAMINATED ORGANOPOLYMERIC FILM

Kazunori MARUYAMA† and Shin OHNO
Technical Research Laboratories of NHK(Japan Broadcasting Corp.)
Kinuta, Setagaya-ku, Tokyo 157

The photo- and electron-exposures affected zinc vapour deposition onto a surface of metal-laminated polymeric film. In the copper-laminated polymethyl methacrylate film containing tetrabromomethane, ultra-violet rays and electron exposures caused the liberation of hydrogen bromides which reacted with surface copper to give copper(I) compounds. The thickness of the deposited zinc is related to the amount of copper(I) compounds produced on the surface.

It is well known that zinc and cadmium vapour depositions onto nonmetallic substrata are difficult. They do deposit however onto the metallic and the contaminated nonmetallic substrata. It is necessary for the zinc deposition that the substratum surface has a nucleus for a condensation of zinc vapour.1)

The authors have previously reported on a metal imaging system using electron exposure and electroless nickel plating or zinc vacuum evaporation onto a copper-laminated polymeric film containing a precursor of chelating agent.2) In this case the change of surface chemical properties were made by a chelating reaction between the copper and the chelating agent through the successive treatments of electron exposure in vacuo and heating in air.

The authors now report on selective zinc deposition onto a thin metal layer laminated on photo- or electron-sensitive polymeric film without the post heating process. The specimen was a metal-laminated polymeric film coated on a transparent electro-conductive Nesa glass®. The surface metal was laminated onto the polymeric layer of 20 to 30 angstroms in thickness. The metal lamination was performed using the conventional vacuum evapolation under a pressure of 10^{-5}Torr. The metals laminated onto the polymeric layer as adsorbents were aluminum, iron, copper, silver and tin. The polymeric layers were polymethyl methacrylate(PMMA), poly(vinyl chloride)(PVC), a copolymer of vinylidene chloride and vinyl chloride(PVDc, VC/VDc [mol ratio]=4), a copolymer of acetophenone and formaldehyde(AF). In the case of PMMA, some films contained diphenylketone(DK), 1,2,3,4,5,6-hexachlorocyclohexane (HCC), tetrabromomethane(TBM), triiodomethane(TIM).

The photo(UV)-exposure was performed in air using a low pressure mercury lamp (253.7 nm, 2.3×10^{15}photons/cm^2/sec). The electron exposure was performed in vacuo

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†Present address; The Department of Materials Science and Technology, Technological University of Nagaoka, Kamitomiokacho, Nagaoka-shi, Niigata 949-54

using a scanning electron microscope(SEM) at 15 kv. After the exposure, the specimen was set in zinc vapour produced by usual vacuum evaporation under a pressure of 10^{-5}Torr. The zinc vapour pressure in the evaporation vessel was regulated by the heating temperature of the vapour source.

The zinc vapour was deposited uniformly onto the nonexposed copper-laminated film. Figure 1 shows the relation of the deposited zinc thickness and its absorbance at 600 nm (A_{600}). As a result of quantitative analysis carried out by colorimetric method using 1-(2-pyridylazo)-2-naphtol (PAN), the relation of zinc film thickness and its absorbance at 600 nm was linear with the thickness of under 400 angstroms. The thickness of 100 angstroms corresponds to A_{600}=1.0. In this study, the zinc thickness was estimated by value of A_{600}. The absorbance of deposited zinc on the specimen was measured using a Hitachi 323® spectrophotometer.

The zinc deposition onto the exposed specimen was affected by the laminated metals on it as adsorbent and exposing conditions. Figure 2 shows the relation between the irradiation time of UV rays and thickness of deposited zinc onto the various metals laminated onto the PMMA film containing TBM. In Figure 2, thicknesses of deposited zinc on laminated metals of iron, tin and copper grew similarly with an increase of irradiation time until they attained inflection points. On the other hand, thicknesses of deposited zinc on laminated metals of silver and aluminum decreased directly in relation to the length of irradiation.

On the copper-laminated film containing TBM, the surface products were analysed by colorimetric methods using PAN and 4,7-diphenyl-1,10-phenanthroline (Batho). The PAN reacts both with copper(I) and copper(II) ions. On the other hand, the Batho reacts only with copper(I) ion. As a result of analysis using PAN, the amount of copper(I) and copper(II) ions in a tetrahydrofran(THF) solution washed out the surface products on the exposed film grew with an increase of UV irradiation time. However the amount of copper(I) ion detected by the Batho grew only in initial stage of UV irradiation (vide post).

Figure 3 shows the relation between the amount of copper(I) ions detected in the THF solution dissolved the organic part of the laminated film and the irradiation time. In Figure 3, the change of detected copper(I) ions corresponded with the thickness of the deposited zinc. The copper(I) ions detected from the nonirradiated part of the specimen may be produced by aerial oxidation of copper. It has been reported that the irradiation of UV rays onto TBM causes the liberation of bromine radicals.3) In the present, the liberated bromine radicals may abstract hydrogens from the PMMA matrix molecules to produce hydrogen bromides. They then diffuse thermally onto the surface and react with copper to increase the amount of copper(I) bromide initially. Further irradiation causes continued liberation of hydrogen bromides, which react with copper(I) compounds to produce copper(II) compounds probably. These oxidation reactions may cause the changes of surface chemical properties affecting the growth and decay of a zinc deposition nucleus.4,5)

As mentioned above, the zinc deposition onto the copper-laminated specimen is thought to be affected by the oxidation state of copper. Like copper, such metals as tin and iron behave favorably in more than three oxidation states. This characteristic may be related to the inflection points shown in Figure 2. On the other hand, there are two oxidation states of aluminum and silver. For example, for silver

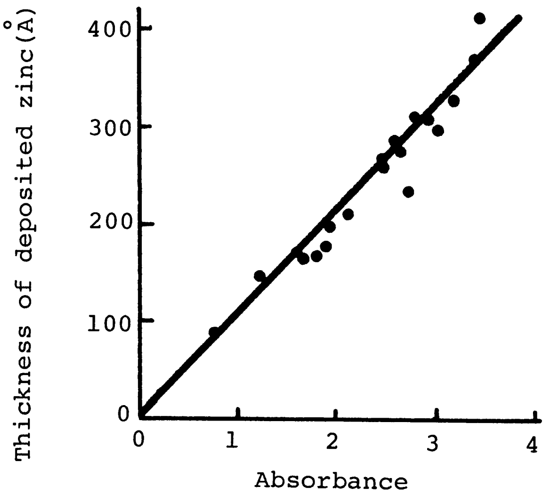

Figure 1. Relation of deposited zinc thickness and its absorbance at 600nm.

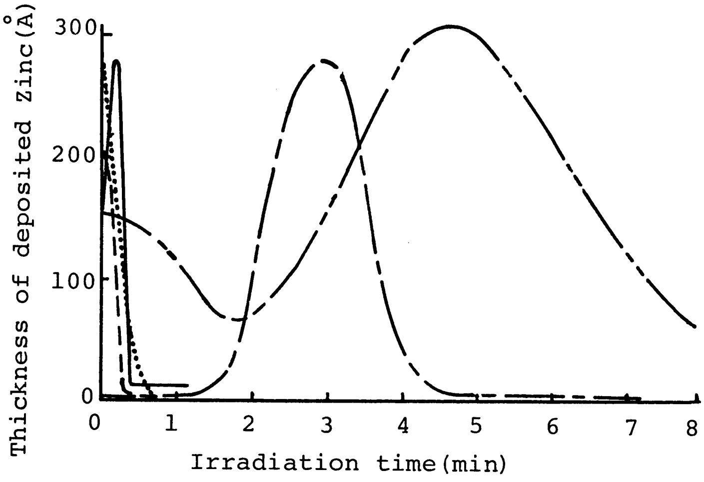

Figure 2. Relation of UV-irradiation time and deposited zinc thickness on various surface metals.

——— : Copper, ········ : Silver, — — —: Aluminum, ——-——: Iron, ——·——: Tin. Surface metals were laminated on PMMA films containing TBM(33 wt%).

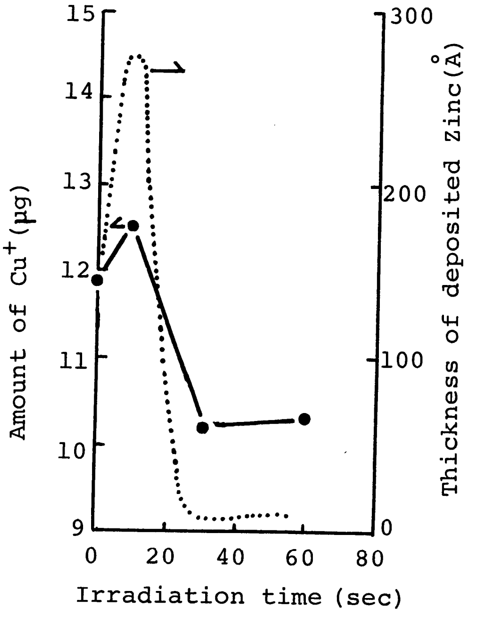

Figure 3. The effects of UV-irradiation:(a) on the amount of copper(I) ions on surface, (b) on the deposited zinc thickness.

——— : Amount of copper(I) ions, ········ : Deposited zinc thickness. Specimen: copper-laminated PMMA film containing TBM(33 wt%), laminated copper on the film was 25 μg.

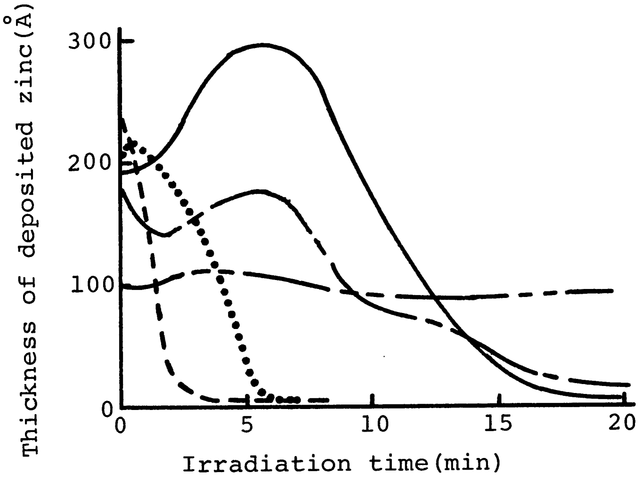

Figure 4. The effects of matrices on the photo-induced changes of zinc deposition.

——— : PMMA film containing HCC, — — — : DK/PMMA, ——-——: TIM/PMMA, •••••• : AF film, ——·——: PVDc film. Surface metal: copper, Additives content: 33 wt%.

there are silver(0) and silver(I). The oxidation of silver(0) produces only silver(I) compounds, which may be related to the single change of the thickness of zinc deposited on silver. Further investigation is required to clear these problems.

Figure 4 shows the effects of polymeric layers on the zinc deposition onto the copper-laminated specimen. In the polymeric layers of Figure 4, the layer consisting of PMMA and TBM produced the result of the most sensitive to the UV exposure. On the copper-laminated PVDc film containing TBM, the UV exposure did not induce the zinc deposition. Aithough the PVDc has a photo-sensitivity, it has the lowest gas permeability.6) It may be difficult for hydrogen chlorides produced in the film by the UV exposure to diffuse to the surface. The photo-induced alteration of zinc depositions appeared also in the copper-laminated films consisting of a nonhalogenated polymeric layer, such as an AF film and a PMMA film containing DK. The DK in PMMA may catalyze a degradation of PMMA molecules by UV irradiation.7) It is not clear at present that the relation between the degradation of PMMA molecules and the surface changes.

Electron-exposure to the metal-laminated polymeric film also affected the zinc deposition. In this case, the thickness of deposited zinc is related to the charge density of the exposure. The copper-laminated PVDc film showed high sensitivity to the electrons in contrast with its low sensitivity to the UV irradiation. The bombarding electrons induced the liberation of hydrogen chlorides and structural changes enabling easy diffusion of hydrogen chlorides onto the surface metal layer. In the copper-laminated PMMA film containing nonadditives, the electron exposure affected the zinc deposition. The PMMA film is a typical electron-sensitive resist polymer used for to fablicate microelectronic devices of integrated circuits. The PMMA molecules were degrated to small fragments by electron exposure, and these thought to have reacted with the laminated copper. The effects of nonhalogenated organopolymeric layers of PMMA and AF on the zinc deposition are thought to be complicated problems. The authors are continuing further investigations.

While this paper reports only on the selective zinc deposition onto a modified surface of metal-laminated polymeric film, it is also possible to obtain the same results using the cadmium evaporation onto the same type of film.

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