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A PRODUCT ON THE SURFACE OF COPPER-EVAPORATED POLYMERIC FILM PREPARED BY SUCCESSIVE TREATMENTS OF ELECTRON BOMBARDMENT AND HEATING

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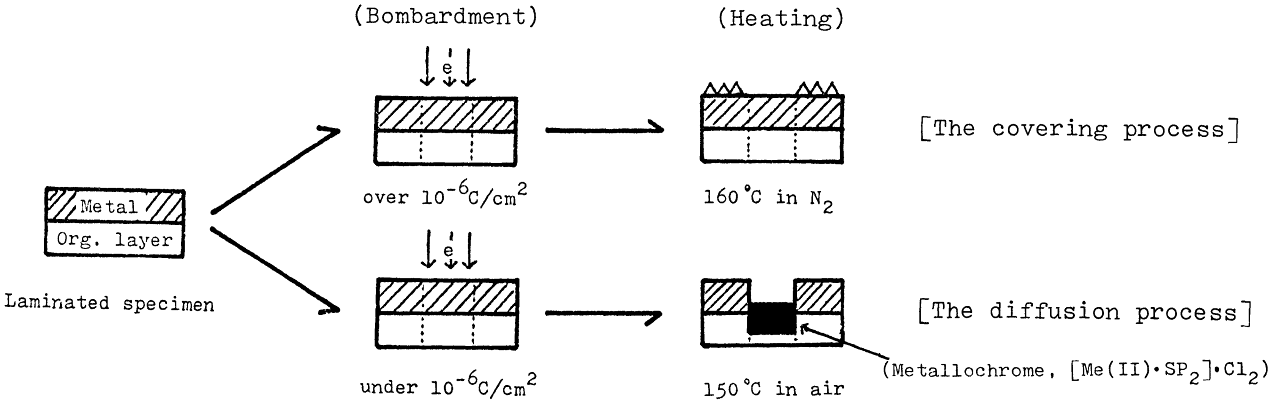
On a copper-evaporated polymeric film consisting of a poly(vinyl-chloride) type matrix and a photo- or thermo-chromic benzospiran compound, a hydrophobic covering product was selectively prepared under successive treatments of electron bombardment in vacuo and heating in nitrogen. In the part bombarded at a high intensity, the chemical properties of the surface copper were preserved during the heating. In the non-bombarded part, on the other hand the copper was covered by diffused components from the organic layer during the heating and the film surface was turned insoluble in acid.

Selective covering of surface copper occured under successive treatments of electron bombardment and heating. In a laminated specimen consisting of a thin copper film and a poly(vinyl-chloride)(PVC)-type matrix layer containing a photo- or thermo-chromic benzospiran derivative (1',3'-dihydro-1',3',3'-trimethylspiro[2H-1-benzospyran-2,2'-[2H]indole]; SP), the surface copper in the bombarded part (12 kV, 2×10^{-6}coulomb(C)/cm^2) did not show any sign of change but that in the non-bombarded part was covered by diffused components from the organic layer on post-heating in a nitrogen atomosphere at 160° C.

In the same type of laminated specimen, the surface copper appeared to diffused into the organic layer under successive treatments of electron bombardment in vacuo (12 kV, 7×10^{-7}C/cm^2) and heating in air at 150°C.1) This phenomenon was so affected by the atomoaphere during post-heating that the diffusion was not observed at heating in nitrogen,2) although the bombarded surface heated in nitrogen was covered by a hydrophobic substance insoluble in acid.
These two phenomena are shown as the following processes:



This paper discusses the covering process of surface copper in the laminated specimen. The study deals with the covering of surface copper in the treated specimen, the

ionic state of modified surface copper and the adsorption of SP on the surface of cuprous chloride particles in the liquid state. In the specimen, the organic layer consisting of a copolymer of PVC and poly(vinyl-acetate)(Sekisui Chem. Co. #Eslec C, T_g= 80°C) and SP-1 (6-nitro-8-methoxy substitute of SP; m.p. 164°C) or SP-2 (6-nitro substitute of SP; m.p. 176°C, both substitutes were synthesized by Niho Kanko Shikiso Kenkyujo, Ltd.). It was coated on a transparent Nesa glass (thickness about 3 μm). The copper layer was evaporated onto the organic layer at a pressure of 10^{-5} torr. and room temperature to a thickness of about 40 angstroms. The specimen was bombarded by medium-energy electrons at 12 kV in vacuo and heated on a hot-plate in nitrogen at 140 - 160°C.
The presence of a covering surface copper on the treated specimen was checked by its solubility in a hydrochloric aqueous solution of ferric chloride (bleaching solution). Being insoluble in acid the covering copper layer adhered to the organic layer. After bleaching the organic layer including inseparable copper was dissolved in a tetrahydrofran (THF) solution of hydrochloric acid (4.8×10^{-2}mol/l). The copper in the solution was detected by a quantitative colorimetry using pyridylazonaphtol dye (PAN). The ionic state of chlorinated surface copper on the treated specimen was determined by a qualitative colorimetry using bathocuproine dye (Batho). The adsorption of SP on the surface of cuprous chloride in a THF suspension was checked from photochromic characteristics and free copper content in its filtrate.

No distinct change occured in the color of the organic layer nor the surface of the specimen under the both treatments. By bombardment, the organic layer was tinged with pale yellow. By post-heating, the color faded away and the surface microstructure changed slightly. After the treatments, the surface copper layer in the bombarded part appeared to be covered by a hydrophobic substance insoluble in the bleaching solution. The copper on the non-bombarded surface was not soluble in THF solvent, but drifted in it as scale. The covered copper was insoluble in the bleaching solution, and adhered to the organic layer as an inseparable layer. Moreover, the residual copper did not dissolved instantly in a hydrochloric THF solution but required fairly long time for dissolution.
Table 1 shows the inseparable amount and thickness of surface copper on the bleached organic layer as functions of bombarding condition and heating temperature. The free copper in the hydrochloric THF solution of the organic layer was analyzed by the PAN•Cu chelating method. The solution was tinged with magenta by the addition of PAN.
The calibration curve between the absorbance of PAN•Cu at 570 nm and copper content in the solution was found to hold a linearity at copper contents below 1.5×10^{-6}g/ml.
In the non-bombarded organic layer containing SP-1, little copper was detected at heating temperature below 150°C. On heating at 160°C, however almost all the copper layer became an inseparable one on the organic layer. In the bombarded part, the detected amount of copper increased with rising bombardment intensity, but at intensities of over 2×10^{-6}C/cm^2, the amount decreased inversely with it. Particularly in the case of heating at 160°C, the detected amount from a part bombarded at intensity of 2×10^{-6}C/cm^2 was smaller than that in the non-bombarded part. In the treated organic layer containing SP-2, the amount of insepaprable copper was generally smaller than that of SP-1, but the inverse change in heating at 160°C did not appear.
In the same specimen, the opposite covering phenomena were seen on alteration of the treatment. In the bombarded organic layer, the electrons caused opening of the SP ring and the liberation of hydrogen chloride from the matrix. Moreover, the molecular chain network of the matrix polymer was loosened at temperature over 140°C. Thus the presence

Table 1. Transfer of copper from surface to organic layer under successive treatments.

SP derivative	Bombarding condition	Heating condition		Copper			
				Amount (g/cm^2)		Thickness (Å)	
	Charge density (C/cm^2)	Temp. (°C)	Time (min)	Initial 1)	Adhered to org. layer 2)	Initial 1)	Transfered to org. layer 3)
SP-1	0	140	5	3×10^{-6}	0	38	0
	0	150	5	3×10^{-6}	5×10^{-7}	38	6.3
	7×10^{-7}				2.3×10^{-6}		25
	1×10^{-6}				3×10^{-6}		38
	2×10^{-6}				2.3×10^{-6}		25
	0	160	5	3×10^{-6}	2.6×10^{-6}	38	33
	1×10^{-6}				3×10^{-6}		38
	2×10^{-6}				2.2×10^{-6}		27
SP-2	0	150	5	2.4×10^{-6}	6.5×10^{-7}	31	8.4
	1×10^{-6}				2.1×10^{-6}		26
	0	160	5	2.4×10^{-6}	1.2×10^{-6}	31	16

1) Evaporated copper in laminated specimen. 2) Amount detected from organic layer.
3) Thickness removed from surface.

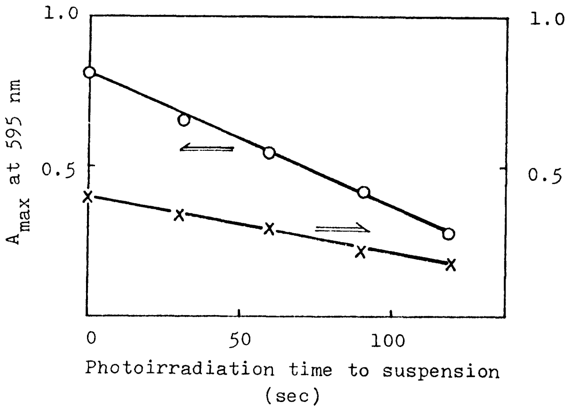
Bombardment: 12 kV; organic layer: thickness - 2.3 μm; SP content - 10 wt%.

of a covering of surface copper was related to the structural changes of the organic layer and the thermal diffusion of components formed by the bombardment. In the case of heating at 160°C, the thermal ring-opening of SP (thermo-chromism) and the decomposition of the matrix occured even in the non-bombarded part. In the part bombarded at intensities over $2 \times 10^{-6} C/cm^2$, however the matrix molecules were crosslinked with each other and the diffusion of components became so difficult that the covering did not appear on the surface. The basic mechanism of covering was the same in both cases, and the opposite results were mainly due to the structural change of the matrix in the organic layer. Moreover, the covering effect was influenced by the SP substitute in the organic layer: SP-1 was more effective than SP-2.

On post-heating, the liberated hydrogen chloride diffused to the boundary of the two layers. Even in nitrogen atmosphere, the surface copper was affected thereby and might be converted to a chlorinated salt. The ionic state of chlorinated copper on the surface was determined by the formation of cuprous bathocuproine chelate (Batho•Cu(I)), showing an absorption peak at 480 nm in a THF solution. Batho has particular effectiveness for detection of cuprous ions.[3] A mixture of the THF rinsing solution of a treated specimen (consisting of a copper and an organic layer containing only the matrix polymer) and the THF solution of Batho showed an absorption peak at 480 nm, which indicated that the chlorinated salt on the surface copper layer was cuprous chloride.

The adsorption of SP on the surface of cuprous chloride (CuCl) particles in a THF suspension was checked by photochromic effects and by the free copper content in its filtrate. The SP substitute, SP-1 or SP-2, shows a reversible photocoloration (photochromism) in THF solution. A photo-colored open-ring species showed an absorption peak at 600 nm (SP-1) or 595 nm (SP-1). It decayed thermally and a decoloring reaction (ring-closing) followed the first-order reaction kinetics. Thus the absorbance at the wavelength of the absorption peak expressed on a logarithm scale decreased linearly with time. In that curve, the extrapolated absorbance at decay time 0 gave the steady state value (A_{max}) of colored species in a difinite photoirradiating condition. The rate constants of the dark decay reaction in THF solution obtained from the slopes of the decay curves were nearly equal in both substitutes at 20°C. Thus the rough molecular absorption

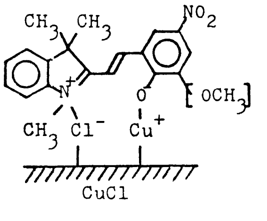
Fig. 1 Change of A_{max} of photochromic colored species in filtarte of suspension.



x : SP-1, o : SP-2
SP concentration in filtrate corresponds to 2.5×10^{-5}mol/l.
Photochromic coloration : UV irradiation (365 nm, 1×10^{16}photons/cm^2/sec, 30 sec), 20°C.

coefficints of photocolored species including thermal decay at 20°C were estimated to be 2.5×10^4 and 4.8×10^4 l/mol/cm for SP-1 and SP-2 respectively. The A_{max} value suggests generally the free SP content in solution. In the filtrate of a THF suspension containing SP and CuCl particles, A_{max} of the photochromic effect was affected by photoirradiation of the suspension.

Fig. 1 shows the change of A_{max} in the filtrate at various time lengths of UV irradiation of suspension. The A_{max} change showed the decreasing of free SP concentration in the filtrate with UV irradiation. This effect suggests that both SP substitutes are adsorbed on the CuCl particles in the state of colored open-ring species. The free copper in the filtrate of the suspension was analyzed by PAN·Cu method. In the filtrate of an UV irradiated suspension (365 nm, 1×10^{16}photons/sec/cm^2, 30 sec) consisting of THF (10 ml) and CuCl (10 mg), 0.4 mg of copper was detected. In that an irradiated suspension consisting of THF solution of SP (1×10^{-3}mol/l, 10 ml) and CuCl (10 mg), the detected copper amounts were 0.2 mg and 0.27 mg for the case of SP-1 and SP-2, respectively. Photoreduction of CuCl on a solid surface has been reported.4) A similar phenomenon is thought to occur in suspension. Thus the SP substitute adsorbed on the surface of CuCl is supposed to disturb its photodegradation. In this case SP-1 was a better adsorbent than SP-2 for inhibiting the photochemical change of CuCl. The adsorption of SP is considered to be caused by an ionic bonding between zwitter ions in its open-ring species and the CuCl surface, as shown below :



As a result, both in the formation of surface copper covering on treated specimens and in the adsorption onto CuCl particles in the liquid state, SP-1 showed better effects than SP-2. The thermocoloration of SP-1 in the organic layer was more distinct than that of SP-2. Moreover, the open-ring species of SP-1 had a chelating function which might assist the covering effect.

This covering process is useful for electron-lithography to form the metallic hardmask for producing integrated circuits. A negative-type pattern is prepared by a selective deposition of additional metal on the residual surface copper on the treated specimen (bombarding intensity; over 2×10^{-6}C/cm^2, heating; 160°C).

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