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Photochromism of Peroxopolytungstic Acid Thin Films, and Its Application to Area-Selective Chemical Plating

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Spin-coated thin films of peroxopolytungstic acid (PTA) showed pronounced photochromism under deep UV irradiation only when the films contained reducing reagents such as alcohols and glucose. Rapid decoloration took place in aqueous solutions of metal salts resulting deposition of each metal. A new area-selective chemical plating process was constructed using this photochromic reaction.

Peroxopolytungstic acid (PTA) is a strong solid acid consisting of protons and large polyanions, each polyanion containing typically twelve tungsten atoms.1) Recently, new interesting functions of thin amorphous films of PTA have been reported as listed below. 1) It is a spin-coatable inorganic deep UV resist.2) 2) Thin films of PTA coated onto conducting substrates show electrochromism.3) 3) The PTA films have the highest refractive indices among spin-coatable amorphous films reported so far; that is, 1.7 for as-spin-coated films and >2.0 when dried at 100 °C.4,5)

We show here, for the first time, that the PTA thin films show pronounced photochromic reaction only when they contain reducing reagents, and discuss coloration and decoloration processes. Moreover, we combined the photochromic reaction of PTA with its function as a deep UV resist to construct a new area-selective chemical plating process, with which we can make fine patterns of metal coating without etching the metal.

PTA was prepared from 3 g tungsten powder (for isopolytungstic acid (W-PTA)) or tungsten carbide powder (for heteropolytungstic acid (WC-HPA)) and H_2O_2 (15 ml of a 30% solution).1,4,5) Excess H_2O_2 was decomposed by heating at 60-120 °C until the solution turned yellow.4,5) Glassy PTA solid was obtained after drying the solution at room temperature. A spin-coating solution used were prepared from 0.45 g PTA and 1 ml H_2O; solutions in which glucose was added were used also. The former solution gave films with typical thickness of 140 nm (as measured by ellipsometry) on different substrates (glass, acrylic resin, and sintered alumina) by means of spin coating with rotation speed of 3000 revs/min.

The PTA films turned deep blue upon UV irradiation when they were continuously exposed to ethanol vapor (from liquid in a glass dish warmed at 40 °C on a hot plate); the light source used was a 10 W low pressure Hg lamp (60 cm-long tube) placed 12 cm above the film. Resultant absorption spectra are shown in Fig. 1. Changes in optical density (ΔOD) for a 140 nm-thick PTA film were more than 0.7 at 880 nm after 90 min irradiation; this value compares well with those for much thicker WO_3 films (a few μm) although the absorption spectra are similar in shape to those for colored WO_3 films.6) The glucose-containing films also exhibited photochromism as shown in Fig. 2, where ΔOD at 880 nm was

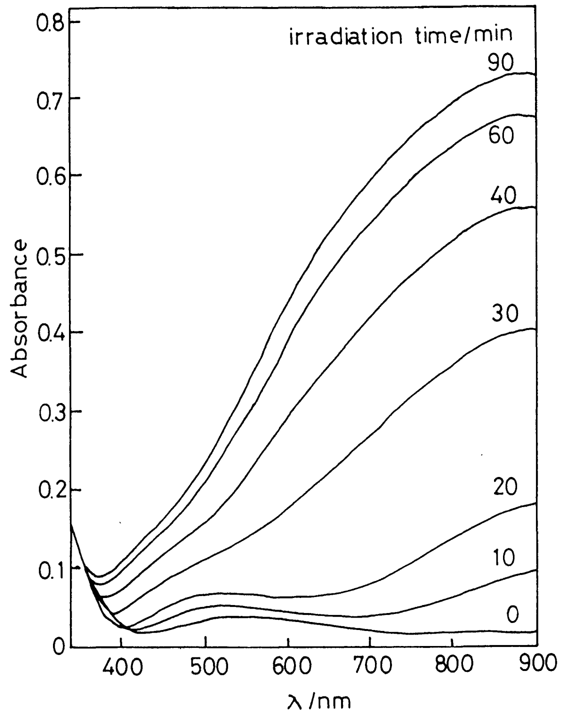

Fig. 1. Absorption spectra for a film of W-IPA (141.2 nm in thickness) irradiated with different periods of time under the existence of ethanol vapor; 10 W low pressure mercury lamp was used as a light source.

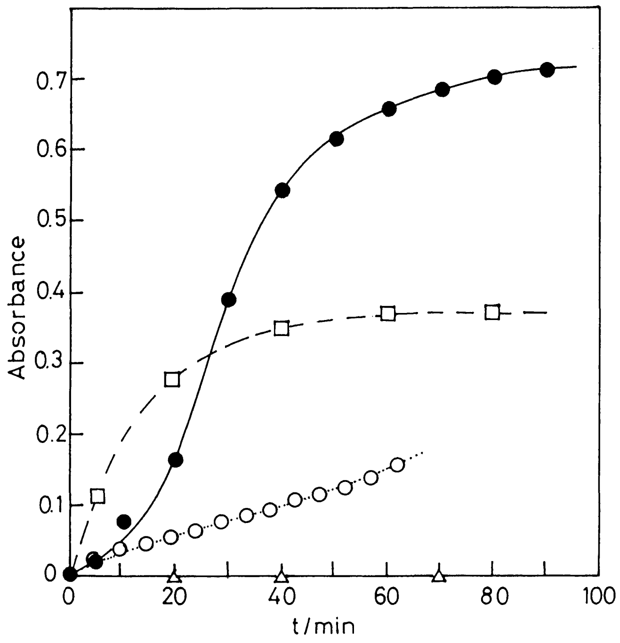

Fig. 2. Time course of changes in optical density of PTA films at 880 nm.
●: as-deposited film in contact with ethanol vapor. ○: dried film (120 °C, 10 min) in contact with ethanol vapor. Δ: as-deposited film in contact with water vapor. □: glucose-containing film (0.05g in 1 ml H_2O).

plotted against irradiation time. ΔOD initially increased rapidly with the irradiation time while ethanol gave an S-shaped curve as the figure shows. Thus, the glucose-containing films turned deep blue within 10 s when irradiated with a UV laser beam (10 mW He-Cd laser with wavelength = 325 nm and beam diameter = about 2 mm). W-PTA and WC-PTA gave almost the same results.

Other alcohols were tested also, and isopropanol and methanol gave ΔOD similar to the case of ethanol. Water is known to cause photocoloration of WO_3,[6,7)] but its vapor induced almost no coloration for the PTA films (cf. Fig. 2). Interestingly, PTA films prepared from a coating solution containing an alcohol did not show photochromism. This is likely because alcohol vapor escaped from the films very quickly.

Thus, we concluded that the PTA films showed photochromism only when they contained reducing reagents. Mechanism of the photochromism of the PTA films then appears to be different from that for WO_3. Electrons and holes are generated in the WO_3 film when the films were irradiated with UV light. The mobile holes in the WO_3 film react with reducing reagents in contact with the film surface to cause its photochromism.[6,7)] On the other hand, electrons and holes are localized probably in an excited state of the polyanions of PTA, and therefore, the photochromic reaction of PTA will take place in its film rather than at the film surface. Water molecules in the films are not easily oxidized in the film likely because the excited state of PTA is short-lived.

Decoloration was observed under dark conditions as shown in Fig. 3 ; ΔOD was decreased by about

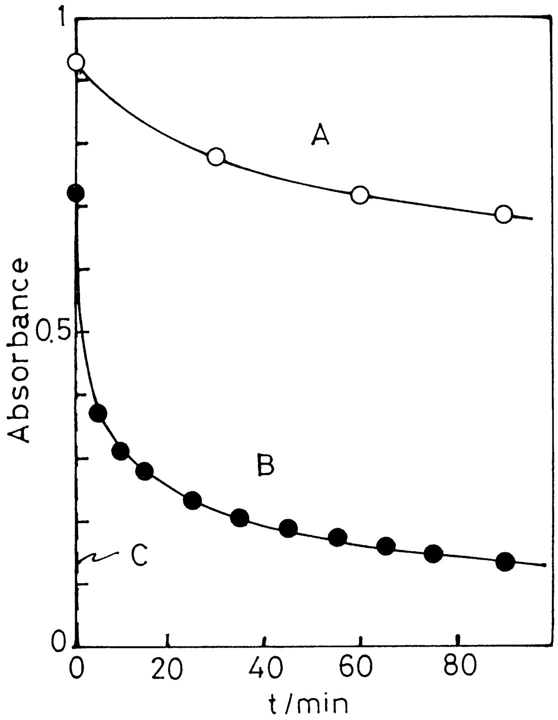

Fig. 3. Time course of changes in optical density of PTA films at the decoloration process (monitored at 880 nm). Curve A, at room temperature in air. Curve B, at 129 °C in air. Curve C (dashed line), in aqueous solutions of metal salts (e.g., $AgNO_3$).

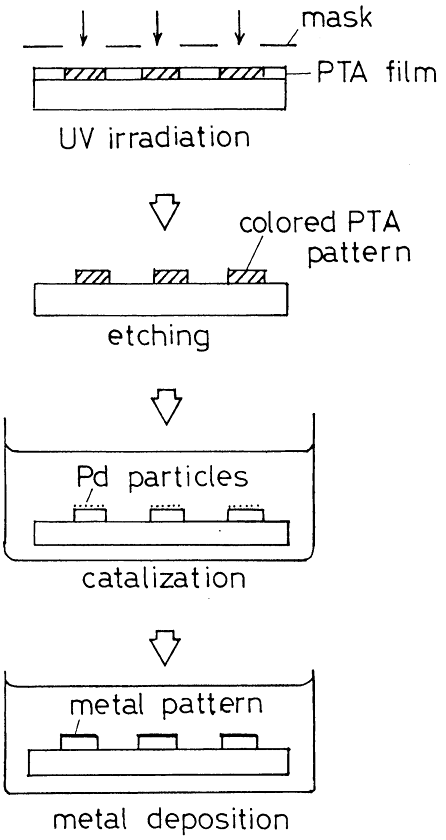

Fig. 4. Schematic illustration of the area-selective chemical plating process based on the photo-chromic reaction of the PTA films.

25% after 2 h in air (curve A). The figure shows also that the decoloration was enhanced by heating the film (curve B) or by immersing it into aqueous solutions containing metal ions (curve C). Among metal ions tested, Ag^+, Ni^{2+}, Pd^{2+}, Fe^{3+}, and Cu^{2+} were effective; moreover, high H^+ concentration caused rapid decoloration also. In these solutions, ΔOD was changed from its initial value (about 0.7) to near zero within 10 s, and the film turned brown showing metal deposition; bubbles (H_2 most probably) were observed for low pH solutions. Thus, corresponding metal particles were deposited onto the film surfaces. The decoloration was induced most likely by a reaction between electrons in the film and metal ions in solution; this type of decoloration with metal ions was also reported for WO_3.8) Decoloration in air is probably due to the reduction of oxygen absorbed from air into the films. A similar decoloration mechanism was proposed for photochromism of Mo-based polyacid crystals.9) Thus, it was verified that electrons were accumulated in the films during the photochromic reaction of the PTA films. We believe that alcohols and glucose liberated electrons and protons when oxidized just as the case of WO_3,6,7) and thereby heteropolyblue (reduced PTA10)) resulted. The S-shaped curve observed for alcohols (cf. Fig. 2) can be explained considering the following three factors: 1) softening by alcohols, 2) photohardening of the films, and 3) competition between coloration and decoloration. Since the alcohols used are good solvents of PTA, the films will be softened when they absorb alcolhol vapor. Thus, diffusion of oxygen may be much quicker than that in solid PTA while the irradiation time is short, and hence, the decoloration takes place efficiently; in fact, aerated PTA solutions containing alcohols did not show photochromism. When the film is hardened during the cource of irradiation, the diffusion of oxygen is slowed, and consequently the decoloration will be inefficient.

The irradiated part of the PTA films turns insoluble,2) and at the same time, has strong reducing power as shown above. We can thus construct a new chemical plating process by using these properties of the PTA films. That is, metal fine patterns can be deposited chemically onto different substrates. For chemical plating, we employed a 1 mmol/dm^3 $PdCl_3$ aqueous solution and an acidic Ni-plating bath (pH 6). An experiment for demonstration is illustrated schematically in Fig. 4. First, the PTA film was irradiated through a mask under the existence of alcohol vapor. The films containing glucose was used also. Second, the film was etched with distilled water so that only the colored part remained. Third, the patterned film was immersed into an aqueous solution of $PdCl_3$ to deposit Pd metal particles as a catalyst. Forth, the film was immersed into a Ni-plating solution after drying at 30–100 °C for 1 h. Shiny patterns of Ni were thus obtained on different substrates: glass slides, sintered alumina plates, and acrylic resin plates. The as-deposited films passed a peeling test using an adhesive tape, and heating at 200 °C increased the hardness of the films. Also maskless patterning was possible by using lasers.

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