contamination by group IV elements. The powder is insoluble in hydrocarbons but appears to be slightly soluble in dioxane, tetrahydrofuran, and tetraglyme; with the first two solvents there is a color change from yellow to orange, whereas with the third the change is from yellow to green-brown. Interestingly, there is only slow decomposition when **3** is exposed to the ambient atmosphere in a fume hood. Heating neat **3** for 22 h at temperatures in the range 380-410 °C gives white $GaCl_3$, a small amount of unidentified orange material, and black microcrystalline GaAs of approximately 93% purity by complete elemental analysis.[5] Decomposition to the same products also can be easily achieved by heating **3** for a few minutes with a cool flame (~400-500 °C). At the lower temperature of ~300 °C for 16 h, the resultant GaAs was red-brown (based on elemental analysis, it contains Cl and extra Ga in the ratio 3:1). Further decomposition experiments, under various conditions, and evaluation of the size of the resultant GaAs particulates are in progress.

Finally, that Ga-Cl bonds are present in **3** suggests there are a number of interesting possibilities regarding derivatives including, but not limited to, formation of truncated clusters as well as tertiary or quaternary precursors and compound semiconductors. Also, we anticipate being able to extend this methodology to the preparation of Al, In, and perhaps other III-V analogues of **3**.

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Preparation of Pigment Films on an Al Substrate by a Novel Thermoinduced Deposition Method

Sakae Hiruta, Katsuyoshi Hoshino,
Seiichiro Yokoyama,† and Hiroshi Kokado*

Imaging Science and Engineering Laboratory
Tokyo Institute of Technology
Nagatsuta, Midori-ku, Yokohama 227, Japan

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Phthalocyanine thin films have been extensively investigated for applications in the fields of electrophotography,[1] solar energy conversion,[2] and electrochemistry.[3] Films have usually been prepared either by vacuum evaporation[4] or by coating with a dispersion containing a small amount of binding polymer. Recently, two additional methods have been proposed: The micellar disruption[5] method is based on the anodic reaction of oxidizable micelles, and the surfactant electrolysis method[6] utilizes cathodic deposition of the pigment on an aluminum electrode. In this communication, we report a novel thermoinduced deposition method (TID method) to prepare copper (CuPc) and metal-free (H_2Pc) phthalocyanine thin films. This simple method allows the preparation of pigment thin films on an Al substrate without using a vacuum evaporator or an electrochemical apparatus.

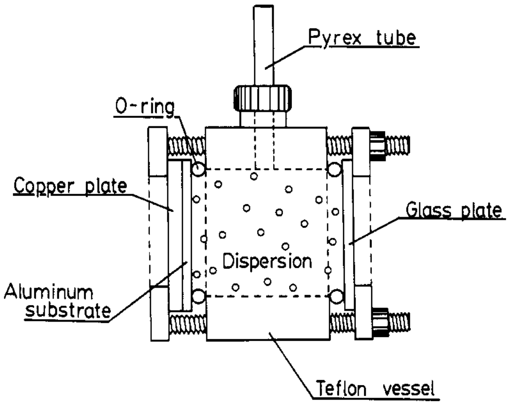

Figure 1. TID cell used for film formation.

The β form of copper phthalocyanine was donated to us by Dainippon Ink and Chemicals, Inc. (trade name Fastgen Blue TGR) and used as supplied. The purity is more than 99%. The α form of H_2Pc powder was purchased from Tokyo kasei Kogyo Co., Ltd., and purified by washing with hot water and acetone repeatedly.

Film-formation experiments were carried out as follows: 1 g of CuPc or 0.9 g of H_2Pc powder was dispersed in a 250-mL aqueous solution containing 2 mM poly(oxyethylene dodecyl ether) (trade name Brij 35) and 0.1 M LiBr. The dispersion was sonicated for 30 min and stirred for 24 h. The resultant dispersion was allowed to stand for 24 h, and then the supernatant was used in the following film-formation procedures.[7] The concentrations of CuPc and H_2Pc in the supernatants were determined to be 5.1 and 1.4 mM, respectively. These concentrations were determined by evaporating the dispersions, dissolving the resultant residues in concentrated sulfuric acid, and then obtaining UV-vis absorption spectra of the solutions in which phthalocyanine pigments dissolve in a monomeric form. The dispersion was injected into a cell containing an opening to which an Al substrate is attached through an O-ring (Figure 1). The area of the Al substrate exposed to the dispersion was 13 cm^2. The Al substrate (99.39%) was obtained from Tokai Kinzoku Co., Inc., and contains impurities such as Fe (0.43%), Si (0.14%), Cu (0.02%), and Ti (0.02%). The dispersion was allowed to stand in a constant-temperature chamber at 90 ± 1 °C, producing a homogeneous intense blue film on the Al substrate. The films obtained were washed with a mixture of ethanol (90 vol %) and water (10 vol%) for 50 h. FT-IR measurements of as-grown films revealed that they consisted of mixtures of CuPc (or H_2Pc) and Brij 35; however, the washing with the mixed solvent produced films of high-purity CuPc (H_2Pc, 98-99%). As a control experiment, the processing described above were carried out using pigment-dispersed solutions devoid of LiBr. No deposition was observed, indicating that the electrolyte is essential for the formation of the films.

Figure 2 shows scanning electron micrographs (SEM) of CuPc (A) and H_2Pc (B) film surfaces on the Al substrate. These films were formed by maintaining the phthalocyanine-dispersed solutions for 34 min at 90 °C. Figure 2C shows the SEM image of an Al surface exposed to an aqueous solution containing 2 mM Brij 35 and 0.1 M LiBr at 90 °C for 34 min. The surface morphology

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† Central Research Laboratories, Idemitsu Kosan Co., Ltd., 1280 Kami-izumi, Sodegaura, Kimitsu-Gun, Chiba 299, Japan.

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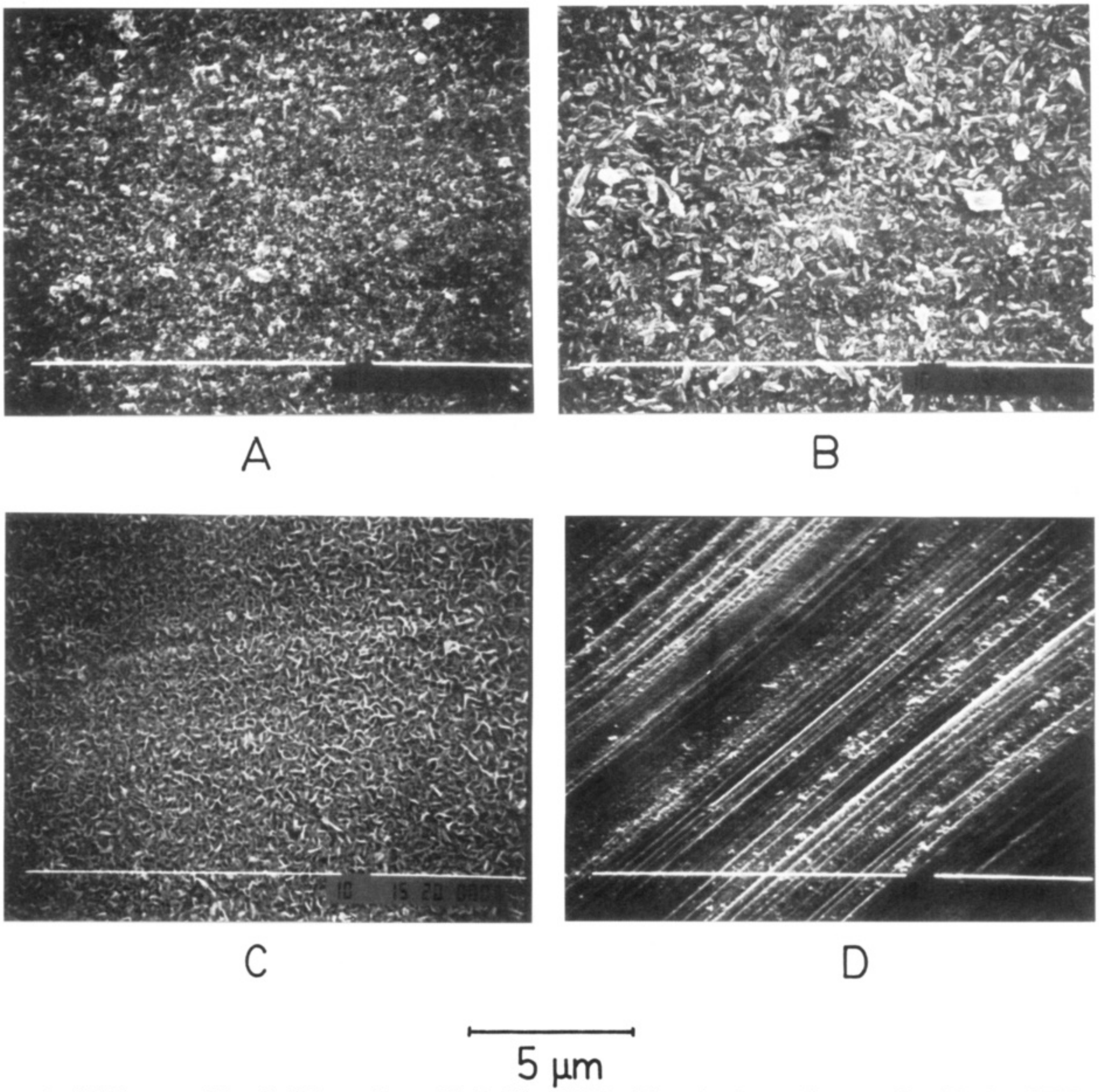

Figure 2. SEM images of deposited film surfaces of CuPc (A) and H_2Pc (B) on aluminum substrates. C and D show SEM images of aluminum surfaces after and before exposure to the electrolyte solution devoid of phthalocyanine pigments, respectively. Deposition temperature: 90 °C. Deposition time: 34 min.

differs from that of an Al substrate without exposure to the electrolyte solution at 90 °C (Figure 2D). X-ray photoelectron spectroscopic measurements of the Al 2p and Br 3d photoelectron peaks of the Al substrate before and after exposure to the electrolyte indicated that Br was incorporated in the Al oxide layer and that the Al surface was further oxidized, as indicated by the decrease in the metallic Al peak, by the exposure. This new oxide layer underlies the phthalocyanine films shown in Figure 2A,B. We have tried to measure the film thickness by the usual stylus (Talystep) and the interferrometric methods but failed because the mechanical strength and smoothness of the films are not sufficient to permit exact evaluation.[8] For this reason the thicknesses of the films were evaluated from the surface-coverage values, Γ (mol/cm^2), which is based on the assumption that the films are homogeneous over the whole surface: Calculated thicknesses of the CuPc and the H_2Pc films shown in Figure 1A,B were 1300 and 430 Å, respectively. This calculation is based on the assumption that phthalocyanine particles are loaded onto the Al substrate in hexagonal closest packing, taking the density values reported[9] and the particle diameter values measured for the phthalocyanines. Number-averaged particle diameters of CuPc and H_2Pc in the dispersions, measured by a centrifugal particle size analyzer (Shimazu SA-CP4L), were found to be 170 and 280 Å, respectively.

Reflection spectra of the CuPc and the H_2Pc films were identical in shape with the absorption spectra of the corresponding evaporated films.[10,11] The shape of these spectra revealed that the crystal forms of these films were

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[8] We have prepared a vacuum-evaporated film of CuPc on an Al substrate, and its strength was compared with films formed by the TID method. Scratch test of these films revealed that surface adhesion force between the Al substrate and the latter film was much greater than the former film. This implies that the latter is stronger than the former, but not so strong as to withstand stress applied by the stylus in measuring film thickness.

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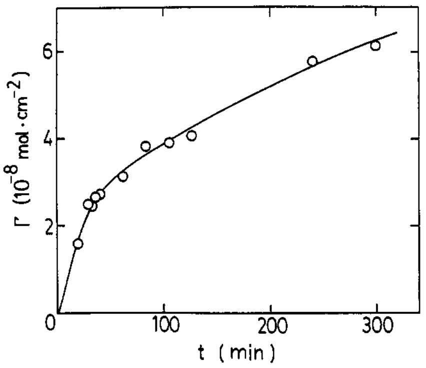

Figure 3. Plot of surface coverage (Γ) vs deposition time (*t*) for the films of CuPc. Deposition temperature: 90 °C.

the same as those of their powdered sources. Figure 3 shows a plot of Γ vs deposition time (*t*) for the CuPc film. One of the main features in this plot is that it shows a break at about 40 min, which separates higher and lower growth rate regions.

The investigation of high-temperature aqueous corrosion of Al has been reported by Draley et al.[12-14] They proposed that the corrosion proceeds at the most active cathode spots between Al metal and the air-formed oxide layer: Hydrogen ions in the bulk solution diffuse into the oxide and are reduced to gaseous hydrogen when the ions react at the metal–oxide interface; then the hydrogen gas generates enough pressure to rupture the oxide layer, leading to the breakup of the oxide and the formation of a new oxide layer. In the present research, the liberation of hydrogen gases was also observed in the film-forming experiments. This observation suggests the occurrence of the above-mentioned corrosion reaction at the local cathode of the Al substrate. In our systems, the corrosion of the oxide may be accelerated by the presence of aggressive anions (Br^-) in the dispersion.[15] On the basis of these considerations, the corrosion reaction may cause physical and chemical changes in the aluminum oxide layer, which induces the adsorption of the phthalocyanine particles in the bulk dispersion. At the present stage, adsorption sites on the new oxide layer have not yet been identified; however, the finding that no deposition took place using the dispersion devoid of LiBr suggests that the adsorption site may be a Br^--incorporated spot.

An important and attractive feature of the film-formation processes by the TID method is the fact that phthalocyanine films continue to grow even after the adsorption sites on the Al oxide are covered with a CuPc monolayer, $\Gamma = 2.9 \times 10^{-10}$ mol/cm^2 (Figure 3). One possible explanation for this is that phthalocyanine–Brij 35 aggregates forming an as-grown film may also act as adsorption sites for the next deposition. The elucidation of this film-formation mechanism is now under investigation by varying deposition conditions.

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Registry No. CuPc, 147-14-8; H_2Pc, 574-93-6; Brij 35, 9002-92-0; Al, 7429-90-5.

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Low-Pressure Chemical Vapor Deposition of Tungsten Carbide Thin Films

Ziling Xue, Kenneth G. Caulton,* and
Malcolm H. Chisholm*

Department of Chemistry, Indiana University
Bloomington, Indiana 47405

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Tungsten carbide (WC) is one of the most important constituents of modern cemented materials mostly due to its very high hardness and its exceptional inertness to chemical attack.[1] Previous reports of chemical vapor depositions of WC involved high temperatures (usually 700–1100 °C) and employed precursors ($W(CO)_6$ or WF_6) containing heteroatoms such as oxygen or halogens.[2] Chemical vapor deposition (CVD) from metastable volatile transition-metal compounds might be expected to provide low-temperature routes to thin films. Recently, Girolami et al. reported the CVD production of TiC thin films from the polyalkyl compound $Ti(CH_2CMe_3)_4$.[3] An all-hydrocarbon tungsten complex, e.g., $(Me_3CCH_2)_3W{\equiv}CCMe_3$, **1**, should reduce the heteroatom contamination during CVD production of WC thin films. Moreover, the carbyne carbon in **1** might be expected to be retained in the WC thin films due to the strong $W{\equiv}C$ bond in **1**, thereby providing a *single* facile pathway to tungsten carbide. Here we report CVD production of WC thin films from the volatile complex $(Me_3CCH_2)_3W{\equiv}CCMe_3$, **1** (mp 47–48 °C).[4]

Complex **1** was synthesized from $(Me_3CO)_3W{\equiv}CCMe_3$[5] and excess Me_3CCH_2MgCl in ethyl ether and then purified by sublimation at 50 °C and 3×10^{-2} Torr. CVD was performed under vacuum in a quartz hot-wall apparatus (base pressure 4×10^{-3} Torr and 360 °C). The substrates chosen for this study are p-type Si(100) wafers, Pyrex or quartz slides. They were washed with isopropyl alcohol and acetone and then rinsed with distilled water (in the case of the Si wafers, deionized water was used). The substrates were then placed at the center of the hot zone. The precursor was transported at 60–80 °C under vacuum to the deposition chamber. Highly reflective and smooth WC films formed on the substrates and on the wall of the hot chamber at the rate of about 3 μm/h. Gaseous components were collected in a liquid N_2 trap placed before the vacuum pump.[6] They were then vacuum transferred to an NMR tube (C_6D_6 solvent) and analyzed on a Bruker AM500 NMR instrument.

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