therefore the vapor pressure of the PH_3 equivalent can be chosen to fit the particular experimental need.

While we have concentrated on phosphorus and phosphines in this work, we believe that the reaction technology is directly transferable to arsenic and arsines. For example, we expect that the reaction of $Ga(CH_3)_3$ with $As(TMS)_3$ will give GaAs under conditions that are similar to those we report for the preparation of InP. The relationship between structure, reactivity, and thermochemistry in the silylated arsines is expected to be the same as that in the phosphines, so we believe this prediction is warranted.

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Note added in proof: After this paper was submitted it was reported that $Ga(CH_3)_3$ and $As(Si(CH_3)_3)_3$ react to give GaAs (Berry, A. D.; et al. Symposium E. MRS Fall Meeting, Boston, MA, 1990, paper E2.8).

Supplementary Material Available: Tables listing positional and thermal parameters for **2**, summarizing crystallographic data; table of distances and angles, and the mass spectrum of **1** (6 pages); table of calculated and observed structure factors (4 pages). Ordering information is given on any current masthead page.

Preparation of a Novel Gallium Arsenide Single-Source Precursor Having the Empirical Formula $AsCl_3Ga_2$

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Properly sized clusters/crystallites of the semiconductor gallium arsenide (GaAs) are expected to exhibit a range of interesting and useful properties, among them being superior nonlinear optical qualities.[1] Notwithstanding this potential, schemes for the facile synthesis and isolation of such particulates had not been forthcoming until recently. In 1990, Alivisatos et al.[2] reported that GaAs nanocrystals are produced by a specific dehalosilylation reaction (eq 1)

$$\underset{\mathbf{1}}{GaCl_3} + \underset{\mathbf{2}}{(Me_3Si)_3As} \rightarrow GaAs + 3Me_3SiCl \qquad (1)$$

as initially carried out in our laboratories.[3] Furthermore, in some important experiments, they demonstrated that the same reaction carried out in quinoline afforded somewhat smaller crystallites that are soluble in pyridine as well as quinoline.[2]

Although the transformation described by eq 1 affords a relatively straightforward route to GaAs, both reactants must be manipulated in an inert atmosphere [*$(Me_3Si)_3As$ is pyrophoric*] by using appropriate equipment and laboratory technique. Thus, safer, less moisture- and air-sensitive precursors could well prove more useful and facilitate investigation of microcrystalline GaAs by those who may otherwise have to forego such studies due to the hazards and handling difficulties intrinsic to many gallium and arsenic compounds. Here we report that compounds **1** and **2** mixed in either a 2:1 or a 3:1 mole ratio react at room temperature to yield in each case the same relatively stable yellow solid product having the empirical formula $AsCl_3Ga_2$ (**3**, eq 2).[4]

$$\underset{\mathbf{1}}{2GaCl_3} + \underset{\mathbf{2}}{(Me_3Si)_3As} \rightarrow \underset{\mathbf{3}}{1/n(AsCl_3Ga_2)_n} + 3Me_3SiCl \qquad (2)$$

Upon heating, new single-source precursor **3** eliminates **1** via a novel reaction pathway to give microcrystalline GaAs (eq 3).[5]

$$\underset{\mathbf{3}}{1/n(AsCl_3Ga_2)_n} \rightarrow GaAs + \underset{\mathbf{1}}{GaCl_3} \qquad (3)$$

Substance **3** possesses a number of properties that make it a potentially useful material, and for those accustomed to handling moisture- and air-sensitive compounds, its synthesis is not difficult. Although there was a variation in the percentages of impurities in the yellow material obtained from seven separate preparations, three complete and four partial elemental analyses are consistent with an As:Cl:Ga ratio of 1:3:2 (within experimental error). The X-ray powder pattern for **3** contained only broad, diffuse lines approximately centered on the corresponding major lines in the pattern obtained from a bona fide sample of GaAs. It should be noted that we have made no effort to date to optimize the reaction conditions or make special intensive efforts to purify the yellow powder; however, the apparently exclusive As, Cl, Ga empirical composition of **3** may prove invaluable for obtaining GaAs free of any

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[1] For example, see the following and references therein: (a) Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 183–188. (b) Dagani, R. *Chem. Eng. News* **1990**, *June 11*, 21–25. (c) Sandroff, C. J.; Harbison, J. P.; Ramesh, R.; Andrejco, M. J.; Hegde, M. S.; Hwang, D. M.; Chang, C. C.; Vogel, E. M. *Science* **1989**, *245*, 391–393.

[2] Olshavsky, M. A.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 9438.

[3] (a) Wells, R. L.; Pitt, C. G.; McPhail, A. T.; Purdy, A. P.; Shafieezad, S.; Hallock, R. B. *Chem. Mater.* **1989**, *1*, 4–6. (b) Wells, R. L.; Pitt, C. G.; McPhail, A. T.; Purdy, A. P.; Shafieezad, S.; Hallock, R. B. *Mater. Res. Soc. Symp. Proc.* **1989**, *131*, 45–50.

[4] Typical procedure for the preparation of $AsCl_3Ga_2$ (**3**); reactants mixed in a 2:1 mole ratio: In an argon filled Vacuum Atmospheres HE-43 Dri-Lab, $GaCl_3$ (**1**, 2.237 g, 12.91 mmol) was transferred to a 500-mL bulb (equipped with a Teflon valve and a magnetic stir bar) by using a small amount of dry pentane to facilitate transfer. Following degassing on a vacuum line and addition of dry pentane (175 mL) by distillation under high vacuum, the flask was returned to the Dri-Lab. Upon addition, by pipet, of $(Me_3Si)_3As$[6] (**2**, 1.900 g, 6.452 mmol, slightly diluted with dry pentane) to the solution of **1**, the precipitate that formed quickly changed from white to yellow. After stirring for 16 days at room temperature, removal of the volatiles in vacuo afforded **3** as a yellow solid (2.09 g, 101% yield; 102% yield based on Me_3SiCl, see below). Mp measurement behavior: >100 °C, sample began to darken; 280 °C, orange; 290 °C, red–orange, and colorless crystals (presumably $GaCl_3$) formed in the cooler portions of the capillary. Anal. Calcd (found) for $AsCl_3Ga_2$: C, 0.00 (6.17); H, 0.00 (0.89); As, 23.36 (21.11); Cl, 33.16 (29.70); Ga, 43.48 (38.80); Si, 0.00 (0.22) (As:Cl:Ga mol ratio = 1.00:3.06:1.98). The volatiles were shown to contain 19.8 mmol of Me_3SiCl (102% of theoretical, based on **2**); determined as HCl after hydrolysis of volatiles and titration with standard NaOH.

[5] Typical procedure for the preparation of GaAs from $AsCl_3Ga_2$ (**3**): In an argon-filled Vacuum/Atmospheres HE-43 Dri-Lab, **3** (0.080 g, 0.25 mmol) was briefly washed once in boiling toluene, once in boiling benzene, and twice with hot pentane, and the resulting fine dry powder was carefully loaded into a sublimator equipped with a cold-finger condenser. Upon evacuation to 0.01 mTorr and slight warming with a heat gun to drive off any residual hydrocarbons, followed by the apparatus being sealed under static vacuum by a Teflon valve and heating from 40 to 260 °C over 1 h in an oil bath while cooling the condenser with tap water, small amounts of both yellow and white sublimates as well as an unsublimed orange powder were observed. Further heating for 22 h with a sand bath maintained between 380 and 410 °C gave additional yellow and white as well as orange sublimates and a black powder that on removal from the bottom of the sublimator and subsequent washing in the manner used for the precursor (vide supra), was shown to be microcrystalline GaAs (0.032 g, 90% yield). Anal. Calcd (found) for AsGa: C, 0.00 (5.17); H, 0.00 (0.35); As, 51.80 (47.94); Cl, 0.00 (2.41); Ga, 48.21 (44.95); Si, 0.00 (≤0.22) (As:Ga mol ratio = 1.00:1.01). X-ray powder diffraction pattern identical with that of a bona fide sample of GaAs. White sublimate, $GaCl_3$ (mp comparable to that of a bona fide sample, 74–76 °C).

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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

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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.

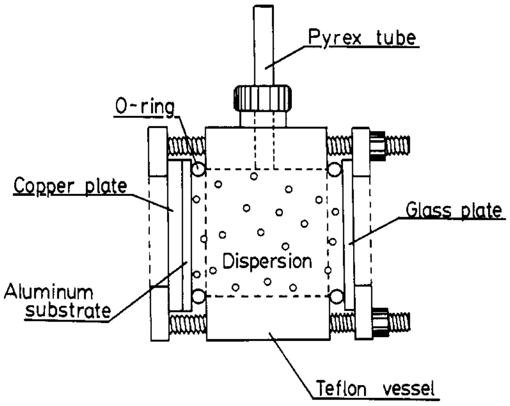

Figure 1. TID cell used for film formation.

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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