Phosphine Synthesis via Cathodic Reduction of Molten White Phosphorus

V. M. Vorotyntsev, G. M. Mochalov, and S. S. Balabanov

Nizhni Novgorod State Technical University, ul. Minina 24, Nizhni Novgorod, 603600 Russia e-mail: vlad@vorotyn.nnov.ru

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Abstract—Cathodic reduction of molten phosphorus in an acid electrolyte with the formation of phosphine is studied. The results demonstrate that the process can be accelerated by sonication, which increases the current density corresponding to phosphine synthesis by a factor of 5, up to 1 A/cm². It is shown that the electrochemical synthesis of phosphine is due to charge transport across the phosphorus film on the cathode. The optimized electrochemical synthesis conditions are described.

INTRODUCTION

High-purity phosphine is widely used as a starting material in microelectronics and semiconductor technology. It is used in vapor-phase epitaxy processes for the preparation of III–V semiconductors (gallium and indium phosphides) and for doping Group IV semiconductors.

On an industrial scale, phosphine is produced through acid hydrolysis of aluminum or calcium phosphide, followed by fine purification to remove water, sulfuric acid, hydrogen chloride, polyphosphines, hydrocarbons, and other impurities [1].

As shown earlier [2–12], electrochemical synthesis of phosphine is cheaper and easier to implement than chemical processes and is commercially viable.

Cathodic reduction of white and red phosphorus allotropes has been the subject of intense attention [1–28]. The current efficiency of this process in terms of phosphine is notably higher in the case of white phosphorus. Moreover, the molecular structure of white phosphorus facilitates the study of its hydrogenation. The mechanism of the cathodic reduction of molten white phosphorus is, however, not yet fully understood. It is, therefore, of interest to study this process experimentally and theoretically in order to elucidate its mechanism.

EXPERIMENTAL AND RESULTS

The kinetics of phosphine formation were followed using potentiodynamic, potentiostatic, and galvanostatic techniques.

Experiments were performed in the apparatus schematized in Fig. 1, which included a quartz electrolyzer (8) with an emulsion of molten white phosphorus in 40% aqueous orthophosphoric acid as electrolyte (5) [3]. To prepare the emulsion, the electrolyzer

was mounted in a thermostated ultrasonic bath (7). During experiments, the electrolyte temperature was maintained at 75–80°C. The cathode (4) was of nickel, and its surface area was 1 cm². When a potential was applied, a phosphorus film appeared on the cathode surface owing to the electrocapillary effect [3]. The anode (6) was a Pb rod with a surface area of 1 cm². The anode compartment was separated from the cathode compartment by a glass-fiber membrane. The cathode potential was measured by a P-5848 potentiostat using a Luggin–Haber capillary (3) and silver/silver chloride reference electrode (1) situated in a beaker (2) filled with a saturated aqueous potassium chloride solution.

The phosphine concentration in the cathode gas was determined on a Tswett-500 gas chromatograph equipped with a vacuum sample introduction system.

Chromatographic separation was performed at 90° C in a glass column 1.5 m in length and 3 mm in diameter, packed with PS-1 sorbent. The flow rate of the carrier gas (H₂) was 30 ml/min. The phosphine peak time was 1 min 57 s.

The components were detected at 130°C using a katharometer. The phosphine concentration was determined by an absolute calibration technique. As a reference, we used ultrapure (99.995 mol %) phosphine. Calibration mixtures were prepared by an exponential dilution technique, as described in the *Tswett-500 Series Chromatographs* user's guide. The relative error of each dilution was within 0.4%. The impurity detection limit was evaluated using the noise band width: an analytical signal was considered detected if its height was equal to or greater than the noise band width. The phosphine detection limit thus evaluated was 0.026 vol % at a sample pressure of 101.325 kPa.

Electrolysis was conducted under constant sonication or without it. In the latter instance, sonication was



Fig. 1. Schematic of the apparatus for electrochemical synthesis of phosphine: (*1*) silver/silver chloride electrode, (*2*) beaker containing a saturated aqueous KCl solution, (*3*) Luggin–Haber capillary, (*4*) cathode, (*5*) electrolyte, (*6*) anode, (*7*) ultrasonic bath, (*8*) electrolyzer.

only used in preparing the emulsion of molten phosphorus in the electrolyte.

The results obtained by the potentiodynamic technique (without sonication) are presented in Fig. 2. At potentials from -0.1 to -0.7 V, the current density increases, and no gas release occurs. Between -0.7 and -0.9 V, the current density drops to 0.02 A/cm². At potentials from -1 to -1.4 V, it rises again, and a gas containing 92 vol % PH₃ is released.

The absence of gaseous products at the cathode in the initial stages of electrolysis was also reported by Shandrinov and Tomilov [13]. In their experiments, gas evolution was detected after the quantity of electricity passed had attained $Q \simeq 3$ A h. A similar result was obtained from the area of the peak in Fig. 2, reduced to unit area of the cathode. Shandrinov and Tomilov [13] pointed out that, at a phosphine solubility in an aqueous electrolyte of 0.15 g/l, the solution would be saturated with PH_3 at Q as small as 0.2 A h. Therefore, no phosphine was formed in the initial stages of electrolysis. The observed Q = 3 A h was attributed to preliminary reduction of phosphorus and the formation of a hypothetical phosphorus hydride of composition P_4H_4 . Indeed, our results, as well as those reported in [13], attest to the formation of a phosphorus compound on the cathode. There is, however, no solid evidence that this compound has the above composition.

As shown earlier [3, 14–17], if the electrolyte contains Pb, Hg, Cd, Bi, Sb, Co, or Zn ions phosphine synthesis proceeds through the formation of intermediate phosphides of unknown composition. Moreover, the finding, also reported by Osadchenko and Tomilov [14], that the cathode gas contained an insignificant amount of diphosphine, a gas which always forms via consecutive attachment of hydrogens to P_4 molecules, suggests that one phosphorus atom is hydrogenated predominantly, presumably the atom near which a metal atom is oriented. Since we used a (soluble) Pb anode, and Shandrinov and Tomilov [13] used a Pb cathode, there are grounds to believe that, in the initial stages of electrolysis (before gas evolution), intermediate lead phosphides are formed, rather than P_4H_4 .

The formation of a metal phosphide is also evidenced by the polarogram of phosphorus reduction at a



Fig. 2. Current density as a function of the cathode potential without sonication (potentiodynamic technique).

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mercury dripping electrode in ethanolic solutions [29]. The polarogram also shows two phosphorus reduction peaks, but the first peak is shifted by 0.9 V compared to our results and occurs in the range -1 to -1.7 V, which may be related to the difference in formation potential between mercury and lead phosphides and also to the influence of the electrolyte composition.

The data reported in [13, 29] suggest that the assumed phosphide is partially hydrogenated: the decrease in the amount of free phosphorus near the first phosphorus reduction peak corresponds to a one-electron process; near the second peak, where gas release begins at the cathode, the current efficiency in terms of PH_3 exceeds 100% (based on a three-electron process).

In Fig. 2, one can see a narrow plateau around -1.4 eV, which corresponds to the maximum rate of phosphine release. The current density at this potential is 0.18 A/cm^2 . Further increase in potential leads to a steep rise in current density, but under these conditions the cathode gas contains only hydrogen, with no phosphine.

The data in Fig. 3 demonstrate that sonication shifts the onset of synthesis to -1.6 eV. In the range -2.2 to -2.6 V, there is a poorly defined saturation plateau, with a current density of 0.8–1.2 A/cm². Analysis of the cathode gas released under these conditions showed a phosphine content of 95–98 vol %. Further increase in potential leads to a gradual increase in hydrogen content, which is the only component of the cathode gas at -3.0 V.

The termination of phosphine formation at increased potentials is the result of the destabilization of the phosphorus film. With increasing current density, the consumption of phosphorus increases. As a consequence, the film becomes thinner and experiences electric breakdown (we observed blue glow of the cathode). When the cathode comes into contact with the electrolyte, vigorous hydrogen evolution begins, and the hydrogen bubbles destabilize the phosphorus film on the cathode.

The above observations lead us to assume that the reduction of phosphorus takes place on the phosphorus electrode, on the film surface, and that bringing the electrolyte into contact with the cathode stops phosphine formation. As is well known, white phosphorus is a dielectric: its electrical conductivity is 4×10^{-5} S/m [30]. It follows from Eq. (1) that, to ensure the observed current density at this conductivity of the film, its thickness must be on the order of 10^{-8} m. According to optical measurements, however, film thickness is about 10^{-5} m:

$$l = \frac{SgI}{E},\tag{1}$$

where *I* is the current, *g* is the conductivity of phosphorus, *S* is the cathode area, *E* is the cathode potential, and *l* is film thickness.

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Fig. 3. Current density as a function of the cathode potential under sonication (potentiodynamic technique).

The conductivity of the phosphorus melt was measured by an M4100/4 megohmmeter in a beaker, using platinum electrodes 1.3×10^{-5} m² in area, separated by 1.1 cm.

The measured conductivity of the phosphorus melt used in PH₃ synthesis was three orders of magnitude higher than the value reported in the literature: 2 × 10^{-2} S/m. Since the conductivity of liquid dielectrics is determined primarily by impurity ions [31], this discrepancy is attributable to the presence of impurities in the film. The likely impurity ions in the system under consideration are protons from the aqueous acid solution and Pb ions from the soluble anode.

The resistivity of the phosphorus thus determined was used to evaluate the thickness of the cathode film, which turned out to be close to that inferred from optical measurements. Thus, the conductivity of the phosphorus film is high enough to ensure the observed current density.

The fivefold increase in current density under sonication can be explained as follows: Since the electrical properties of liquid dielectrics are dominated by impurity ions, charge transport at the metal-dielectric interface is also mainly due to impurities. If a liquid dielectric is immobile, the ions forming in the contact layer are only removed via migration, whose velocity is limited by the low mobility of the ions. The excess charge appearing in the electrode zone is of the same sign as the electrode, which reduces the electrode overpotential and, hence, the electrode current [31]. Sonication sets the liquid dielectric in motion, sharply accelerating charge removal from the electrode zone owing to convection.

Using the galvanostatic technique, we measured the voltage as a function of time at a fixed current density from 0.95 to 1.25 A/cm² under sonication (Fig. 4). At



Fig. 4. Cathode potential as a function of time at j = (1) 1.25, (2) 1.20, (3) 1.15, (4) 1.10, (5) 1.05, (6) 1.00, and (7) 0.95 A/cm² (galvanostatic technique).

current densities from 1.05 to 1.25 A/cm², the voltage first increased with time and then saturated.

We believe that this behavior is due to the penetration of protons into the phosphorus film and subsequent reduction of the protons. As pointed out by Frumkin [32], the rate of this process depends on the energy spent for the transfer of a hydrated ion from the solution bulk to the adlayer (phosphorus film in our case). Therefore, increasing the voltage must increase the amount of reduced hydrogen, as confirmed by analyses of the cathode gas.

At a current density of 1.65 A/cm^2 , electric breakdown of the film occurred, bringing the electrolyte into contact with the cathode surface and giving rise to disintegration of the film.

In contrast, at current densities below 1.00 A/cm^2 the voltage first decreased with time and than stabilized at -2.2 V. Analysis showed that the cathode gas contained 98 vol % phosphine. Consequently, the electric-field energy was insufficient for the penetration of protons into the film, and the only reaction in the system was phosphine evolution.

Using the potentiostatic technique, we fixed the potential at a level of -1.6 to -2.2 V, where phosphine evolution had been observed earlier. We, however, revealed current oscillations with a gradual increase in amplitude, which eventually led to disintegration of the phosphorus film on the cathode. As a result, phosphine synthesis ceased, and only hydrogen was released. These findings confirm that the process takes place at the phosphorus electrode.

Current oscillations at a fixed voltage may be due to film thickness and resistivity fluctuations. The current in lower resistivity regions is then higher. As a result, the film thickness in such regions decreases, and their resistance drops further. The process develops to the point of complete phosphorus depletion in such regions. When the electrolyte comes into contact with the cathode metal, the vigorous hydrogen evolution destabilizes the film over the entire cathode surface, leading to well-observed disruption of the phosphorus film.

CONCLUSIONS

The present results in conjunction with earlier data indicate that phosphine synthesis takes place on the phosphorus cathode. The experimentally determined conductivity of phosphorus and thickness of the phosphorus film on the cathode are consistent with the observed current density.

The presence of Pb, Hg, Cd, Bi, Sb, Co, or Zn ions in the electrolyte increases the current efficiency in terms of PH_3 by an order of magnitude, which is due to the formation of intermediate, partially hydrogenated metal phosphides. It seems likely that those phosphorus atoms oriented on the metal experience predominant hydrogenation.

Sonication increases the current density corresponding to phosphine synthesis by a factor of 5, up to 1 A/cm^2 , which may be due to a change in charge transport mechanism in the phosphorus film—from migration to convection.

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