In this paper, we report on our attempt to make a thin film of Zn$_2$P$_2$ compound semiconductor by electrodeposition from aqueous solutions containing zinc and phosphorus species. First of all, we constructed the potential–pH diagram of the Zn-P-H$_2$O system at 363 K and found out the wide stable region of Zn$_2$P$_2$ at lower potentials. In the cyclic voltammetry on SnO$_2$ glass substrate, two cathodic current changes and an anodic peak were observed. This is similar results to Soliman et al., where the electrodeposition of Zn$_2$P$_2$ was succeeded. Consequently, the potentiostatic electrolysis thus was carried out to clarify the reduced substance and the reduction of SnO$_2$ was only observed. When Au electrode was used as an inert electrode, the formation of Zn$_2$P$_2$ was not also observed, while the Au-Zn compound was confirmed. It is considered that the precipitation of zinc predominantly occurs and the reduction of phosphate ions are kinetically difficult from the results of the cyclic voltammetry.

Potential–pH Diagram of the Zn–P–H$_2$O System

A potential–pH diagram is a powerful tool for understanding various electrochemical phenomena. In this study, we construct the potential–pH diagram of Zn-P-H$_2$O system to understand electrodeposition behavior of Zn$_2$P$_2$ previous to experiments. In order to construct a potential–pH diagram of Zn-P-H$_2$O system, two diagrams of the Zn-H$_2$O and P-H$_2$O are necessary. They were derived according to the method by Pourbaix.

The thermodynamic data for the construction of potential–pH diagram are listed in Table I. Here, we defined the activity $a_M$ of dissolved substance M with its molar concentration [M] in molarity (mol/dm$^3$), and the fugacity $f_g$ of gaseous species g with its partial pressure $p_g$ in atmosphere (atm). Since the electrolytic experiments were carried out at 363 K, the potential–pH diagram at the temperature was attempted. Unfortunately, some thermodynamic data at 363 K were not available, and we thus evaluated them by the following procedure.

For crystal species in Table I, we can obtain thermodynamic data at higher temperature from database. The data for aqueous species were evaluated by the following equation,

$$
\Delta G_i^\circ / \Delta T = \Delta G_i^\circ (298) - (T - 298) \Delta S_i^\circ (298),
$$

where $\Delta G_i^\circ / \Delta T$ is the standard Gibbs energy for the formation of species i at temperature T and $\Delta S_i^\circ (298)$ is the standard entropy for the formation of species i at 298 K. The values calculated according to the above equation are also listed in Table I. Here, the standard entropy of H$_2$PO$_2^-$, $S_{H_2PO_2^-}$, was estimated using the data of H$_3$PO$_3$ and H$_2$PO$_3^-$ since no data is available. The reaction for ionization of phosphoric acid, H$_3$PO$_4$, is expressed by

$$
H_3PO_4 = H_2PO_3^- + H^+.
$$

The standard entropy change of the above reaction, $\Delta S^\circ (2)$, is evaluated by the following equation.

$$
\Delta S^\circ (2) = S_{H_2PO_3^-} + S_{H^+} - S_{H_3PO_4}.
$$

and

$$
\Delta S^\circ (4) = S_{H_2PO_2^-} + S_{H^+} - S_{H_2PO_4^2-}.
$$

Both reactions of eqs. 2 and 4 are ionization reaction of hydrogen from OH belonging to tetrahedral PO(OH)$_3$H or PO(OH)$_2$H$_2$ to produce proton (hydrogen ion) and also tetrahedral ions, PO$_2$OH$^-$ or PO$_2$H$^2-$. Therefore, we expect the entropy change of eqs. 2 and 4 is similar. Actually, the standard entropy change of ionization of phosphoric acid, H$_3$PO$_4$, which is ionization of tetrahedral PO(OH)$_3$H to proton and PO$_2$OH$^-$, is $-87.86$ J/mol K that is similar to that of H$_2$PO$_2^-$. We thus assume that $\Delta S^\circ (4) = \Delta S^\circ (2)$, whereby we calculated the standard entropy of H$_2$PO$_2^-$ from eq. 5. Subsequently, we

$^4$ E-mail: yoshitaro-nose@mtl.kyoto-u.ac.jp

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obtained the standard Gibbs energy for the formation of $\text{H}_3\text{PO}_4^{-}$ at 363 K according to eq. 1. It is noted that because the extrapolated temperature range in eq. 1 is only 65 K, we do not expect any serious error associated from above assumption.

Figure 1 shows the potential-pH diagrams in acid region for Zn-H$_2$O and P-H$_2$O systems. The activity of dissolving substance was set to be 10 M. In this study, red phosphorus was regarded as a standard species of phosphorus, and phosphine, PH$_3$, was not considered. The diagrams were extended to the Zn-P-H$_2$O system. First, two diagrams of the Zn-H$_2$O and P-H$_2$O systems were superimposed. The various formation reactions of Zn$_3$P$_2$ or ZnP$_2$ from zinc and phosphorus species were considered by the similar procedure as Murase et al. For example, the boundary between $\text{H}_3\text{PO}_3$ and $\text{Zn}_2$ areas were determined by the reaction of the formation of $\text{H}_3\text{PO}_3$ and $\text{Zn}_3$P$_2$ shown by the following equation,

$$2\text{H}_3\text{PO}_3 + 3\text{Zn}^{2+} + 6\text{H}^+ + 8e = \text{Zn}_3\text{P}_2 + 6\text{H}_2\text{O}.$$  

Figure 2 shows the potential-pH diagram of the Zn-P-H$_2$O system in acid region at 363 K under the activity of 10$^{-2}$ M for dissolving substance and the partial pressure of 1 atm for H$_2$ and O$_2$ gases. From the figure, one can understand that there is the stable region of Zn$_3$P$_2$ shown by shadow that suggests the electrodeposition of Zn$_3$P$_2$ is possible by the reduction of aqueous species of zinc and phosphorus. However, in this case, the competition with the generation of H$_2$ gas due to its overpotential must be considered.

Experimental Procedure

Aqueous solution containing sodium metaphosphate, NaPO$_3$, and zinc dichloride, ZnCl$_2$, was used as an electrolyte for electrodeposition of Zn$_3$P$_2$ according to the experiments by Soliman et al. NaPO$_3$ and ZnCl$_2$ were dissolved in the deionized water with a specific resistance of larger than 5 x 10$^6$ Ωcm and their concentration is 10$^{-2}$ M. The resistivity of the solution was 5 x 10$^2$ Ωcm. The dissolution of NaPO$_3$ produces H$_3$PO$_4$ and/or H$_2$PO$_4^{-}$ in acid region. The pH of the solution was measured by pH meter and adjusted to 2.5 using H$_2$SO$_4$ at room temperature, 298 K, whereas electrolytic experiments were carried out at 363 K. The three-electrode cell was used for all experiments. Figure 1 shows the schematic picture for the experimental system in this study. A SnO$_2$ conductive glass substrate (ASAHI GLASS Co. Ltd., resistivity: 10 Ωcm) or Au film

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>$\Delta G_i^{[298]}$ / kJ mol$^{-1}$</th>
<th>$S_i^{[298]}$ / J mol$^{-1}$ K$^{-1}$</th>
<th>$\Delta G_i^{[363]}$ / kJ mol$^{-1}$</th>
<th>Reference</th>
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<td>Zn</td>
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<td>$-82.73$</td>
<td>60.25</td>
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<td>13</td>
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<tr>
<td>P (red)</td>
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<td>13</td>
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<tr>
<td>P (white)</td>
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<td>41.07</td>
<td>0</td>
<td>13</td>
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<tr>
<td>$\text{H}_3\text{PO}_4$</td>
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<td>$-1116.62$</td>
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<td>167.36</td>
<td>$-832.35$</td>
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<tr>
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<td>$-488.00$</td>
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<td>0</td>
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was monitored by thermometer. Cyclic voltammetry and potentiostatic electrolysis were carried out using the electrochemical analyzer (ALS, 660A). In both experiments, the solution was not stirred. The product substance after electrolysis was identified by a grazing incident X-ray diffraction (GI-XRD, PANalytical X’Pert Pro) with a copper X-ray tube and the composition was evaluated by an energy dispersive X-ray spectroscopy (EDX, EDAX VE-9800) using a scanning electron microscope (SEM, KEYENCE VE-7800). The angle of the incident beam against the surface of the sample was 1°.

Experimental Results and Discussion

Re-examination of electrodeposition on SnO2.— Figure 4 shows the cyclic voltammogram on SnO2 conductive glass for the solution containing NaPO3 and ZnCl2 together with the potential-pH diagram. The potential was swept from 0 V vs. SHE to a cathodic direction and subsequently switched at –0.59 V vs. SHE. We can observe two cathodic and an anodic current changes in the figure. The current change from –0.25 vs. SHE shown by ‘a’ in Fig. 4 is due to the reduction of proton to hydrogen gas considering from the potential-pH diagram. Another cathodic reaction was observed from –0.46 V vs. SHE that is shown by ‘b’. This cathodic current change is caused from the reaction from H2PO−4 to H2PO−3, which is the reaction from a pentavalent to a tetravalent species, considering from the potential-pH diagram. The anodic current peak shown by ‘c’ was observed around –0.23 V vs. SHE. This peak is considered to be a counter to the cathodic current change shown by ‘b’ because both current changes...
SHE came from the reduction of SnO2 as previously mentioned. The results of the cyclic voltammetry of this study are similar to that by Soliman et al., but the interpretation is different. Consequently, the potentiostatic electrolysis was carried out at –0.59 V vs. SHE for 1 hour in order to identify the reduced substance. The reduced substance was thus identified by GI-XRD and the results were shown in Fig. 6. It is considered that this comes from the adhesion of phosphoric acid to SnO2 after electrolysis. On the other hand, the peaks from Zn3P2 were not observed although Soliman et al. confirmed the electrodeposition of Zn3P2. Here, the equilibrium potential between Sn and SnO2 is –0.32 V vs. SHE at 363 K in the case of pH = 2.5, that was calculated using the data listed in Table I. Therefore, it is likely that the reduction of SnO2 to metallic tin occurs in the potentiostatic electrolysis and the cyclic voltammetry. Soliman et al. indentified the reduced substance as Zn3P2 by XRD. The peak positions of three strong lines for Zn3P2 and Sn are listed in Table II. These positions are relatively near and it is considered that Soliman et al. might confuse the reduction of SnO2 with the electrodeposition of Zn3P2. Figure 6 shows the EDX spectra before and after the electrolysis. Phosphorus was detected by EDX in the experiments where the reduction of SnO2 was observed as shown in Fig. 6. It is considered that this comes from the adhesion of the electrolytic solution since the redox potential to obtain red phosphorus is lower than –0.59 V vs. SHE. On the other hand, the peaks of ZnLα and ZnKα, which should appear around at 1 keV and 8.6 keV, respectively, were not detected. Consequently, it is concluded that the formation of Zn3P2 did not occur in this condition.

**Electrochemical behavior on Au electrode.**—When using SnO2 glass as WE, the formation of Zn3P2 was not observed due to the reduction of SnO2. Consequently, Au film electrodeposited on Cu plate was used as an inert electrode. Figure 7 shows the cyclic voltammogram on Au electrode containing NaPO3 and ZnCl2. The cathodic current change was observed around at –0.25 V vs. SHE shown by ‘a,’ which was considered to come from the generation of hydrogen gas. In actual, the bubble was observed on the electrode during the measurements. Considering from the potential-pH diagram, the reduction of phosphoric acid would occur at –0.45 V vs. SHE, however, the notable current change was not observed in this study. Therefore, it is concluded that the cathodic current change observed in SnO2 glass comes from the reduction of SnO2 as previously mentioned.

![Figure 6. EDX profiles of the SnO2 glass substrate before and after the potentiostatic electrolysis.](image-url)
In order to investigate the electrodeposition of Zn$_3$P$_2$, the cyclic-voltammetry was carried out to the lower potentials. In this experiment, three kinds of electrolytic solution were prepared: ZnCl$_2$, NaPO$_3$, and both ZnCl$_2$ and NaPO$_3$. The concentration of each species was 0.01 M. Figure 7 shows the cyclic voltammogram where the switching potential is −1.09 V vs SHE, together with a part of potential-pH diagram of the Zn-P-H$_2$O system. The current change from −0.25 vs. SHE, which is observed in all solutions, is due to the reduction of proton to hydrogen gas. In the solution containing only NaPO$_3$, another current change is not observed and the upset of the current might come from the generation and the desorption of hydrogen gas on Au electrode. On the other hand, the cathodic current change was also observed at −0.8 V vs. SHE in the solution containing only ZnCl$_2$. The dashed line shows the equilibrium potential between Zn$^{2+}$ and Zn in the potential-pH diagram.

The switching potential is −1.09 V vs SHE. The dashed line shows the equilibrium potential between Zn$^{2+}$ and Zn in the potential-pH diagram.

Figure 7. Cyclic voltammogram on Au electrode using each solution and a part of potential-pH diagram of the Zn-P-H$_2$O system shown in Fig. 2. The switching potential is −1.09 V vs SHE. The dashed line shows the equilibrium potential between Zn$^{2+}$ and Zn in the potential-pH diagram.

Figure 8. EDX profiles before and after the voltammetry when using Au electrode.

Figure 9. GI-XRD profiles of Au electrode (a) before the voltammetry, (b) NaPO$_3$ solution, (c) ZnCl$_2$ solution and (d) solution containing both ZnCl$_2$ and NaPO$_3$ after the voltammetry. Symbols show the reference data.
understood by considering the deviation from the stoichiometry. The results of XRD are consistent with those by EDX.

The formation of Zn₃P₂ was not observed on Au electrode although it was suggested in the potential-pH diagram of the Zn-P-H₂O system. The reduction of Zn²⁺ was found in the solutions containing ZnCl₂, while that of phosphate ions was not observed in the solution containing only NaPO₃. It is assumed that the reduction of phosphate ions is kinetically difficult and the current was consumed for the reduction of zinc ions although the reduction of both ions are needed for the formation of Zn₃P₂. Therefore, the suppression of zinc precipitation might be necessary to obtain Zn₃P₂. One of considerations is the use of ligand for Zn²⁺, which reduces the activity of Zn²⁺.

**Conclusions**

In this paper, we investigated the electrodeposition of Zn₃P₂ semiconductor from aqueous solution. First, we constructed the potential-pH diagram of the Zn-P-H₂O system at 363 K and clarified the wide stable region of Zn₃P₂ at lower potentials. Subsequently, the cyclic voltammetry was carried out in the same conditions as Soliman et al. and two cathodic current changes and an anodic peak were observed in the cyclic voltamogram, where the potential was switched at −0.59 V vs. SHE. It was considered that these current changes were not related to the electrodeposition of Zn₃P₂ from the viewpoint of potential-pH diagram although Soliman et al. claimed the electrodeposition of Zn₃P₂. In the electrolysis experiment at −0.59 V vs. SHE for 1 hour, the reduction of SnO₂, which was used as a substrate, was observed. When Au electrode was used as an inert electrode, the formation of Zn₃P₂ was not also observed although it was suggested by the potential-pH diagram. One of reasons is that the reduction of phosphate ions are kinetically difficult. In order to obtain Zn₃P₂ by electrodeposition from aqueous solutions, it is necessary that the reduction of Zn²⁺ is suppressed and that of phosphate ions is enhanced.

**Acknowledgments**

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**References**