Formation of Si-based Nanosheet Bundles and Morphological Modification of CaSi$_2$ Crystals by Thermal Treatment Using Chloride Compounds

Xiang Meng and Peiling Yuan
Graduate School of Science and Technology, Shizuoka University,
3-5-1 Johoku, Naka-ku, Hamamatsu 432-8011, Japan
Yasuhiro Hayakawa
Research Institute of Electronics, Shizuoka University,
3-5-1 Johoku, Naka-ku, Hamamatsu 432-8011, Japan
Kenta Sasaki, Keisuke Tsukamoto, Shinya Kusazaki, Yuya Saito, Yuki Kumazawa, and Hirokazu Tatsuoka
Graduate School of Integrated Science and Technology, Shizuoka University,
3-5-1 Johoku, Naka-ku, Hamamatsu 432-8561, Japan
(Received 23 December 2017; Accepted 24 April 2018; Published 31 May 2018)

Si-based nanosheet bundles were formed by Ca-atom extraction from CaSi$_2$ crystals by thermal treatment using FeCl$_3$, FeCl$_4$, NH$_4$Cl, and MgCl$_2$. The morphological property of the Si-based nanosheet bundles was examined. Though the Si-based nanosheets were formed under the stated thermal treatment conditions using FeCl$_3$, the formation of iron-oxide phases was accelerated at higher temperatures and longer duration times for the highest thermal treatment temperatures using FeCl$_2$. Thinner and thicker nanosheets were obtained using NH$_4$Cl and MgCl$_2$, respectively. The morphological properties of the Si-based nanosheet bundles were compared to each other and their formation mechanism was discussed in terms of the thermal instability of the chlorides, their vapor pressure and thermal treatment temperature profiles. [DOI: 10.1380/ejssnt.2018.218]

Keywords: Silicon; Electron microscopy; Silicides; Nano-films, stacks, and other nano materials; Nano structure chemistry, processing, and fabrication

I. INTRODUCTION

Low-dimensional materials have attracted much interest because of their enhanced or modified optical, electronic and mechanical properties compared to those of the bulk materials [1, 2]. A nanosheet bundle is also one of the important structures for technological applications [3]. The formation of Si nanosheet bundles by Ca extraction from CaSi$_2$ crystals by thermal treatment with metal chlorides has been previously reported [4-6]. However, details of the structural property of the treated nanosheets have not been clarified. Recently, the structural property of the Si-based nanosheet bundle formed using FeCl$_3$ was reported [7]. It was revealed that the structures of the nanosheets were basically the same as that of the Si-based nanosheets synthesized by inositol hexakisphosphate, C$_6$H$_{16}$O$_{24}$P$_6$, (IP6) [8]. However, the detailed structures of the nanosheets are only slightly modified compared to that of the IP6-treated nanosheets. It is important to clarify the difference in the detailed structures of the nanosheets, which depends on the nanosheet synthesis procedure.

In this paper, the morphological property of the nanoproducts formed using several chloride compounds, such as FeCl$_2$, FeCl$_4$, NH$_4$Cl, and MgCl$_2$, was characterized. It should be noted that water absorbing (deliquescent) metal chlorides, especially MgCl$_2$, were used as the source material. The morphological property of the Si-based nanosheet bundles was compared to each other and discussed in terms of their thermal instability and deliqueescency of the chloride compounds and thermal treatment temperature profiles.

II. EXPERIMENTAL

The CaSi$_2$ micro-walls were initially grown on Si(111) substrates [9]. Commercially-available CaSi$_2$ crystal powders were also used as the source material. The Si-based nanosheet bundles were then formed by Ca-atom extraction from the CaSi$_2$ crystals by thermal treatment with FeCl$_2$, FeCl$_3$, NH$_4$Cl, or MgCl$_2$. The chloride sources were stored in about 30-50% humidity. For the thermal treatment of the CaSi$_2$ crystals in the vapors, the Si substrates with the CaSi$_2$ micro-walls or CaSi$_2$ powders and the chloride powders were placed on opposite sides of each other inside a sealed stainless-steel cell in a N$_2$ atmosphere (Ar atmosphere for only MgCl$_2$ source) with detected oxygen of less than 0.1%. When using the chlorides and CaSi$_2$ crystals, except for the NH$_4$Cl-CaSi$_2$ powder, the cell was heated to the highest thermal treatment temperature of 550°C to 800°C and the temperature was maintained for 0 min to 300 min. The heaters were then turned off, and the cell was naturally cooled. The temperature profile of the thermal treatment is shown in Fig. 1(a). In the figure, only for the cases of, for example, the highest thermal treatment temperatures of 550°C, 600°C to 650°C and their duration times of 0 min, 0 min and 10 min, respectively, are shown. It is noted here that the “0 min” of the duration time of the highest thermal treatment temperature means the heaters were immediately turned off, when the cell temperature reaches the highest treatment.
FIG. 1. (a) Temperature profiles of the thermal treatment for the chlorides and CaSi$_2$ crystals, except for the NH$_4$Cl-CaSi$_2$ powder case. In the figure, only for the cases of, for example, the highest thermal treatment temperatures of 550°C, 600°C, and 650°C and its duration time of 0 min, 0 min and 10 min, respectively, are shown. (b) Temperature profile of the thermal treatment for the NH$_4$Cl-CaSi$_2$ powder. The dashed lines show the highest thermal treatment temperature of the process.

The nanosheet formation reactions have already begun during a rise in the cell temperature. After the thermal treatment process, the treated nanosheets were washed in ethanol a few times for a few minutes to remove the residual chloride compounds. When using MgCl$_2$, the resulting powders were further washed by an HCl solution (35–37 w/w%) for 1 h to remove MgO formed as a by-product. For the use of the NH$_4$Cl-CaSi$_2$ powder, the NH$_4$Cl and CaSi$_2$ powders were located in a loosely sealed quartz container, which was loaded into a vacuum chamber, then thermally treated. The thermal temperature profile for this case is also shown in Fig. 1(b). Further detailed information about the treatment conditions of the micro-walls and nanosheet bundles is described elsewhere [6, 7, 9]. Throughout this paper, for example, these nanosheets treated under the FeCl$_3$ vapor are denoted here as “FeCl$_3$-treated” nanosheets, etc.

The morphological and structural properties of the nanosheets were characterized by field-emission scanning electron microscopy (FE-SEM) with energy dispersion spectroscopy (EDS), conventional transmission electron microscopy (TEM), high-resolution TEM (HRTEM) with Fast Fourier Transform (FFT), and scanning transmission electron microscopy (STEM) with EDS. For the TEM sample preparation, the products were scratched off the substrates using a sharp-edged blade and dispersed in a small amount of ethanol, then transferred onto a lacey-carbon-coated copper grid and dried.

III. RESULTS AND DISCUSSION

Figure 2(a–d) shows a series of SEM images of the FeCl$_3$-treated nanosheets formed from CaSi$_2$ micro-walls and rooted on the Si substrates with the thermal treatment conditions at (a) the highest thermal treatment temperature of 550°C and its duration time for 5 min, (b) 600°C for 0 min, (c) 650°C for 0 min, (d) 650°C for 10 min, and (e) STEM image and corresponding EDS mappings of the FeCl$_3$-treated nanosheets on the Si substrates with the thermal treatment condition of 550°C for 5 min.

J-Stage: https://www.jstage.jst.go.jp/browse/ejssnt/
the CaSi₂ crystals are described elsewhere [9]. Figure 2(e) shows an STEM image and corresponding EDS mappings of the FeCl₃-treated nanosheets formed on the Si substrate with the thermal treatment condition of 550°C for 5 min. It is shown from the EDS mappings, for nanosheet (A), Ca atoms still remain, and O atoms are distributed the same as that of the Ca atoms. Cl atoms also remain as particles and correspond to the Ca-atom distribution. The Ca-atom extraction was not completed, and it is considered that the distributions of the O and Cl atoms cause oxidation of the Ca atoms and the formation of CaCl₂ particles, respectively. Fe atoms are slightly distributed in some regions. On the other hand, for nanosheet (B), almost only Si atoms are observed, and the Ca-atom extraction is almost complete.

Figure 3 shows (a) an SEM image and corresponding EDS mappings of the FeCl₃-treated nanosheet bundle formed from the CaSi₂ powders with the thermal treatment condition of 540°C for 60 min, and (b) cross-sectional view of Si-based nanosheet bundles formed from the CaSi₂ powder with the treatment condition of 540°C for 60 min. The EDS mappings show that the nanosheet bundle mainly consisted of Si, and Fe and O are partially distributed as particles around the bundles caused by the formation of an iron-oxide and/or an iron-hydroxide. It was found that the nanosheets with the thickness of a few tens of nanometers were obtained.

Figure 4(a–d) shows a series of SEM images of the FeCl₂-treated nanosheet bundles and other products formed and rooted on the Si substrates with the thermal treatment conditions of (a) the highest thermal treatment temperature of 555°C and its duration time for 10 min, (b) 570°C for 10 min, (c) 650°C for 0 min, and (d) 650°C for 10 min. The nanosheet formation reactions have already begun during a rise in the cell temperature, even though the duration time is “0 min” at the highest thermal treatment temperature. The nanosheets with a thick-
ness of several to tens of nanometers were also observed at the low treatment temperature. The nanosheets are stacked with a small void space to form a bundle. In addition to the formation of the nanosheet bundles, nanorods were formed around the nanosheet bundles, with the increasing highest thermal treatment temperature and the duration time. Figure 4(e) shows an STEM image of one piece of the nanosheet formed on the Si substrate with the thermal treatment condition of 555 °C for 0 min, and corresponding EDS mappings of Si, Ca, O, Fe, and Cl. The nanosheet mainly consists of Si. The other elements only slightly remain around the sheet, and the Ca-extraction reactions are almost completed in the sheet. On the other hand, Fig. 4(f) shows an STEM image of a part of the nanosheet formed on the Si substrate with the thermal treatment condition of 650 °C for 0 min, and the corresponding EDS mappings of Si, Ca, O, Fe, and Cl. The EDS mappings show that parts of the nanorods around the nanosheet mainly consisted of O and Fe. The EDS point analysis revealed that the observed chemical composition of the nanorods in Fig. 4(c, f) is Fe : O ≈ 1 : 2, and that in Fig. 4(d) is Fe : Si : O ≈ 2 : 1 : 4. It is considered that iron-oxide was formed around 570–650°C [10–12], and Fe₂SiO₄ was formed at 650°C for 10 min [13].

Figure 5(a) shows an SEM image and corresponding EDS mappings of the FeCl₂-treated nanosheet bundle formed from the CaSi₂ powders at the thermal treatment condition of 550 °C for 80 min, (b) cross-sectional view of Si-based nanosheet formed from the CaSi₂ powder at the thermal treatment condition of 555 °C for 3 min.

Figure 6 shows (a, b) SEM images of the nanosheets formed and rooted on Si substrates at the thermal treatment condition of 340 °C for 10 min, (c) an SEM image, (d) a TEM image of the cross-sectional view, and (e) an STEM image and corresponding EDS mappings of the NH₄Cl-treated nanosheet bundle formed from CaSi₂ powders at the thermal treatment condition of 550 °C for 10 min. Thinner sheets with the thickness of several to tens of nanometers were observed. The nanosheet consists of Si, while other elements only slightly remained in the nanosheet.

Figure 7 shows (a) an SEM image, (b) a TEM image of cross-sectional view, and (c) an STEM image and corresponding EDS mappings of the MgCl₂-treated nanosheet bundle formed from the CaSi₂ powders at the thermal treatment condition of 800 °C for 300 min. It was found that thicker nanosheets with the thickness of several tens up to one hundred nm were obtained. The EDS mappings showed that the nanosheet mainly consisted of Si, while the Mg and O atoms and the Ca and Cl atoms are distributed as particles to form MgO and CaCl₂, respec-
thermally treated CaSi$_2$ powders at the thermal treatment condition of 800°C for 300 min.

It was noted that the Si-based nanosheets were formed for all of the reactants, and no metal-silicide alloy was formed in this study. By-products, CaCl$_2$ and iron-hydroxide and/or oxide remained around the nanosheet bundles, not between the sheets nor in the sheets. It is not likely that the reactants of the metal chloride compounds directly react with the CaSi$_2$ crystals. The Ca extraction was successfully demonstrated. From Fig. 2(e), it is considered that the Ca extraction takes place layer by layer. The anisotropic reaction was reported for the case of the HCl reaction with CaSi$_2$ for the siloxene synthesis in the HCl aqueous solution [15]. The simple extrapolations of the reaction rates along the Si(111) and Si(110) planes around ~400°C are 1 mm/s and 0.1 mm/s, respectively. It is much higher than the reaction rate roughly up to ~50 nm/s. Thus, the actual reaction rate by the thermal treatment is diffusion controlled, namely, the supply of the tentatively-formed HCl or Cl$_2$ vapore is limited due to their deliquescency and in the N$_2$ (or Ar) atmosphere would not be negligible. HCl or Cl$_2$ directly reacts with CaSi$_2$, and the chloride compounds play a role as a source to supply HCl or Cl$_2$, the following discussions are provided.

Though Si-based nanosheets were formed under the thermal treatment conditions using FeCl$_3$, the formation of the iron-oxide phases was accelerated at the higher temperatures and the longer highest thermal treatment duration time using FeCl$_2$. The chemical reactions of FeCl$_2$ with residual H$_2$O and O$_2$ supplied by its deliquescency and/or in the atmosphere are as follows [10], during the initial stage:

$$4\text{FeCl}_2 + O_2 \rightarrow 2\text{FeClO} + 2\text{FeCl}_3 \quad \text{below 300°C},$$

$$12\text{FeCl}_2 + 3O_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{FeCl}_3 \quad \text{above 400°C},$$

during the middle stage,

$$4\text{FeCl}_2 + 2\text{H}_2\text{O} + O_2 \rightarrow 4\text{FeClO} + 4\text{HCl},$$

during the last stage,

$$4\text{FeCl}_2 + 3O_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{Cl}_2,$$

$$4\text{FeCl}_2 + 4\text{H}_2\text{O} + O_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{HCl},$$

and these reactions would take place at the position of the source materials, during the initial stage of the thermal treatment, because of its lower vapor pressure of FeCl$_2$, for example, \(~10^{-4}\) Pa around 300°C, and a partial pressure of FeSi$_2$ at the temperature of 550°C increases to \(~10^2\) Pa [17, 18]. The formation of iron oxides at the higher thermal treatment temperature is caused by the transport of FeCl$_2$ to the CaSi$_2$ crystals.

The chemical reactions of FeCl$_2$ with H$_2$O and O$_2$ are also reported as [11],

$$\text{FeCl}_2 + \text{H}_2\text{O} \rightarrow \text{FeO} + 2\text{HCl} \quad \text{below 500°C},$$

$$3\text{FeCl}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2,$$

$$\text{FeCl}_2 + 2\text{FeCl}_3 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{HCl},$$

$$6\text{FeCl}_2 + 6\text{H}_2\text{O} + O_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 12\text{HCl}.$$}

In addition, numerical calculations of the following reactions were as follows [12]:

$$4\text{FeCl}_2 + 4\text{H}_2\text{O} + O_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{HCl},$$

$$3\text{FeCl}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2,$$

$$2\text{FeCl}_2 + 9\text{O}_2 \rightarrow 6\text{FeO}_3 + 12\text{Cl}_2.$$}

The HCl and/or Cl$_2$ molecules are transported to the CaSi$_2$ crystals because of their higher vapor pressures, for example, \(~10^5\) Pa at \(~85.2°C\) for HCl, \(~10^5\) Pa at \(~34.2°C\) for Cl$_2$, [19] then extract the Ca atoms. The Ca atom extraction by HCl is described as follows:

$$3\text{CaSi}_2 + 7\text{HCl} \rightarrow 3\text{CaCl}_2 + \text{Si}_8\text{H}_6 \cdot \text{HCl}$$

(or $3\text{CaSi}_2 + 6\text{H}^+ \rightarrow \text{Si}_8\text{H}_6 + 3\text{Ca}^{3+}$) [20, 21],

$$3\text{CaSi}_2 + 6\text{HCl} + (3 + x)\text{H}_2\text{O} \rightarrow \text{Si}_8\text{O}_{3+x}\text{H}_6 + 3\text{CaCl}_2 + (3 + x)\text{H}_2$$ [22].

On the other hand, for the case of using FeCl$_3$, the partial pressure of \(~10^2\) Pa is obtained at the lower temperature around 300°C [18]. The possible dissociation reactions of FeCl$_3$ are

$$2\text{FeCl}_3(s) \leftrightarrow \text{Fe}_2\text{Cl}_6(g),$$

$$\text{Fe}_2\text{Cl}_6(g) \leftrightarrow 2\text{FeCl}_3(g),$$

$$2\text{FeCl}_3(g) \leftrightarrow 2\text{FeCl}_2(g) + \text{Cl}_2(g)$$

at 160–220°C [12]. The dissociation of FeCl$_3$ starts to take place around...
160°C [16], and at this temperature, the partial pressure of FeCl₂ is about 10⁻⁸ Pa, which is too low to evaporate, thus the FeCl₂ remains as a solid. On the other hand, the partial pressure of Cl₂ is higher, and the partial pressure of FeCl₂ is further reduced based on the law of mass action for the vapor pressure [23]. The Cl₂ molecules are preferentially transported to the CaSi₂ crystals, which causes the Ca extraction by [5],

\[
\begin{align*}
3 \text{CaSi}_2 + 3 \text{Cl}_2 &\rightarrow (\text{Si}_3) + 3 \text{CaCl}_2 \quad 20-40 \degree \text{C}, \\
3 \text{CaSi}_2 + 6 \text{FeCl}_3 &\rightarrow (\text{Si}_3) + 3 \text{CaCl}_2 + 6 \text{FeCl}_2 \quad 100-120 \degree \text{C}.
\end{align*}
\]

The deliquescency of FeCl₃ is much higher than that of FeCl₂. The FeCl₃ source includes much H₂O due to its high deliquescency. The chemical reactions of FeCl₃ with residual H₂O supplied by its deliquescency and/or in the atmosphere are given by

\[
\begin{align*}
\text{FeCl}_3 + 3 \text{H}_2\text{O} &\rightarrow \text{Fe(OH)}_3 + 3 \text{HCl}, \\
\text{Fe}_2\text{Cl}_6 + 3 \text{H}_2\text{O} &\rightarrow 2\text{Fe}_2\text{O}_3 + 6 \text{HCl} [24].
\end{align*}
\]

The reactions of FeCl₃ with H₂O and O₂ are also reported as [10],

\[
\begin{align*}
4\text{FeCl}_3 + 3 \text{O}_2 &\rightarrow 2\text{Fe}_2\text{O}_3 + 6 \text{Cl}_2, \\
\text{FeCl}_3 + \text{H}_2\text{O} &\rightarrow \text{FeClO}_3 + 2 \text{HCl}.
\end{align*}
\]

In addition, the following reactions are discussed [25]:

\[
\begin{align*}
x\text{OH}^+ + \text{Fe}_2\text{Cl}_6 &\rightarrow 2\text{Fe}_2\text{O}_3\text{Cl}_{6-x}^+ + x\text{HCl}, \\
2\text{Fe}_2\text{O}_3\text{Cl}_{6-x}^+ + 3 \text{H}_2\text{O} &\rightarrow 2\text{Fe}_2\text{O}_3(\text{OH})_x^+ + (6 - x)\text{HCl}.
\end{align*}
\]

Because these reactions take place at a lower temperature compared to the highest thermal treatment temperature, these hydroxides and oxides mainly remain with the source materials. The HCl molecules are transported to the CaSi₂ crystals to extract the Ca atoms.

Considering the thermal treatment temperature profile, these reactions take place from room temperature. Cl₂ and/or HCl with the higher vapor pressures preferentially react with CaSi₂, then the Ca atoms are bound to the Cl atoms, and are extracted from the silicide as CaCl₂. Based on the enthalpy of formation of CaSi₂ (−12.0 kcal/g-atom), HCl (−11.0 kcal/g-atom) and CaCl₂ (−63.4 kcal/g-atom) [26], the CaCl₂ is much more stable compared to CaSi₂ and HCl.

When using FeCl₂ as the source material, during the initial stage of the thermal treatment process, the HCl mainly plays the role to form the Si nanosheets. With the increasing temperature, FeCl₂ is also transported to the substrate, then iron oxide and its related materials are deposited. On the other hand, when using FeCl₃ as the source material, during the initial stage of the thermal treatment process, not only HCl, but also Cl₂ play the role to form the Si nanosheets. In addition, FeCl₃ is also actively evaporated due to its higher vapor pressure. However, the transport of Fe chlorides to the CaSi₂ crystals is lower, because of dissociations of the Fe chlorides.

When using NH₄Cl as the source material, the dissociation of NH₄Cl, such as,

\[
\text{NH}_4\text{Cl} \rightarrow \text{NH}_3 + \text{HCl},
\]

takes place at 338°C to 400°C [27, 28]. HCl molecules are significantly transported to the CaSi₂ crystals, thus the nanosheets are effectively formed by the direct dissociation of the source materials. Only about a 10-min duration time is necessary to obtain the Si-nanosheets, even though the CaSi₂ powder is used. Thus, the feature of the nanosheet formation caused by NH₄Cl shows a more similar to that of siloxene formation caused by HCl. Thinner nanosheets were formed compared to those of the other nanosheets formed using FeCl₂, FeCl₃, and MgCl₂.

For the case of using MgCl₂ as the source material, the dissociation of MgCl₂ with H₂O, such as,

\[
\begin{align*}
2\text{MgCl}_2 \cdot 2\text{H}_2\text{O} &\rightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O} + \text{MgOHCl} + 2\text{H}_2\text{O} + \text{HCl}, \\
2\text{MgCl}_2 \cdot \text{H}_2\text{O} &\rightarrow \text{MgCl}_2 + \text{MgOHCl} + \text{H}_2\text{O} + \text{HCl} \quad \text{at} 250 \degree \text{C}, \\
\text{MgOHCl} &\rightarrow \text{MgO} + \text{HCl} \quad \text{at} 300 \degree \text{C},
\end{align*}
\]

takes place [29]. HCl molecules are transported to the CaSi₂ crystals, thus the nanosheets are formed. Because of the higher treatment temperature of 800°C, thicker nanosheets were formed by reconstruction of the Si network in the crystals compared to those of the other nanosheets formed using NH₄Cl, FeCl₂, and FeCl₃.

It has been demonstrated that the Si-based nanosheet bundles were formed on the Si substrates or in the powder formed from CaSi₂ crystals using FeCl₂, FeCl₃, NH₄Cl, and MgCl₂. The morphology of the nanosheet bundles depends on the reactant and the thermal treatment conditions. This discussion is based on the assumption that HCl and Cl₂, generated by the thermal instability and deliquescency of the chloride compounds, play an important role in forming the Si-based nanosheet bundles. However, the discussion well explains the experimental results of the Si-based nanosheet formation. Thus, this nanosheet formation model is proposed to explain the thermal treatment condition dependence, including the reactant, on the structural and morphological properties of the Si-based nanosheets.

### IV. CONCLUSION

Si-based nanosheet bundles were formed by Ca atom extraction from the CaSi₂ crystals by thermal treatment using FeCl₂, FeCl₃, NH₄Cl, and MgCl₂. Though Si-based nanosheets were formed under the thermal treatment conditions using FeCl₂, the formation of iron-oxide phases was accelerated at the higher temperatures and longer duration time of the highest thermal treatment temperatures using FeCl₂. Thinner and thicker nanosheets were obtained using NH₄Cl and MgCl₂, respectively. The nanosheet formation model, based on the thermal instability and deliquescency of the chloride compounds, their vapor pressure, and the thermal treatment temperature profile is proposed to explain the reactant dependence of the structural property of the Si-based nanosheets. In the model, HCl and Cl₂ play an important role to form the Si-based nanosheets. The morphological modifications of the nanosheet bundles have been successfully demonstrated by the appropriate thermal treatments with the specific starting materials. Further characterizations of the bundle structures will be expected to evaluate the enhanced electric, thermal and thermoelectric properties of the Si-based materials.
ACKNOWLEDGMENTS

A part of this work was supported by JSPS KAKENHI Grant Number 17K06347 and the Cooperative Research Project Program of Research Institute of Electronics, Shizuoka University.

[1] X. Kong, Q. Liu, C. Zhang, Z. Peng, and Q. Chen, Chem. Soc. Rev. 46, 2127 (2017).
[2] K. J. Koski and Y. Cui, ACS Nano 7, 3739 (2013).
[3] H. Tatsuoka, W. Li, E. Meng, and D. Ishikawa, ECS Trans. 50, 3 (2012).
[4] H. Kautsky and L. Haase, Chem. Ber. 86, 1226 (1953).
[5] E. Bonitz, Chem. Ber. 94, 220 (1961).
[6] X. Meng, H. Imagawa, E. Meng, H. Suzuki, Y. Shirahashi, K. Nakane, H. Itahara, and H. Tatsuoka, J. Ceram. Soc. Jpn. 122, 618 (2014).
[7] H. Tatsuoka, K. Sasaki, M. Nakayama, K. Hikichi, Y. Kumazawa, X. Meng, and P. Yuan, Eng. Mater. 64, 51 (2016).
[8] X. Meng, K. Sasaki, K. Sano, P. Yuan, and H. Tatsuoka, Jpn. J. Appl. Phys. 56, 05DE02 (2017).
[9] X. Meng, A. Ueki, H. Tatsuoka, and H. Itahara, Chem. Eur. J. 23, 3098 (2017).
[10] K. Suganuma and T. Yagi, Nippon Kagaku Kaishi 1978, 319 (1978).
[11] Y. Nihira and T. Nomura, J. Jpn. Soc. Powder Powder Metall. 42, 598 (1995).
[12] M. Beck, S. Wirtz, V. Scherer, and F. Barhold, Chem. Eng. Technol. 30, 1347 (2007).
[13] C. Wang and L. L. Shaw, J. Sol-Gel Sci. Technol. 72, 602 (2014).
[14] S.-Y. Oh, H. Imagawa, and H. Itahara, Chem. Asian J. 9, 3130 (2014).
[15] G. Vogg, M. S. Brandt, and M. Stutzmann, Chem. Mater. 15, 910 (2003).
[16] L. E. Wilson and N. W. Gregory, J. Phys. Chem. 62, 433 (1958).
[17] I. Barin, F. Sauert, E. Schulz-Rhönhof, and W. S. Sheng, Thermochemical Data of Pure Substances (VCH, Weinheim, 1989).
[18] D. R. Stull, Ind. Eng. Chem. 39, 517 (1947).
[19] D. R. Lide and H. V. Kehiaian, CRC Handbook of Thermophysical and Thermochemical Data (CRC Press, Boca Raton, KL, 1994).
[20] J. R. Dahn, B. M. Way, E. Fuller, and J. S. Tse, Phys. Rev. B 48, 17872 (1993).
[21] S. Yamanaka, H. Matsu-ura, and M. Ishikawa, Mater. Res. Bull. 31, 307 (1996).
[22] A. Weiss, G. Beil, and H. Meyer, Z. Naturforsch. 34b, 25 (1979).
[23] H. P. Eichkoff and W. Metz, Carbon 25, 641 (1987).
[24] S. Itoh, I. Endo, K. Maki, and A. Kosaka, Tetsu-to-Hagane 62, 1035 (1976).
[25] J. A. Klug, N. G. Becker, S. C. Riha, A. B. F. Martinson, J. W. Elam, M. J. Pollin, and T. Proslier, J. Mater. Chem. A 1, 11607 (2013).
[26] O. Kubaschewski and C. B. Alcock, International Series on Materials Science and Technology: Metallurgical Thermo-Chemistry, Vol. 24, 5th Ed. (Pergamon Press, Oxford, 1979).
[27] E. Clementi and J. N. Gayles, J. Chem. Phys. 47, 3837 (1967).
[28] H. Zhang, Y. Chen, L. Fu, and J. Ma, J. Alloys Compd. 499, 269 (2010).
[29] S. Shimada, R. Furuichi, and T. Ishii, J. Soc. Chem. Ind. Jpn. 74, 2006 (1971).