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Article / Book Information

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論 文 要 旨

THESIS SUMMARY

専攻： Department of	物質電子化学　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（　工学　）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Silicon, one of the most important element, is known due to its desirable properties for industrial applications in the 20th Century, and it will also be very important in this 21st century. In this century, amorphous silicon, nanocrystalline silicon, and silicon clathrate will become more important due to their unique properties. Sodium-containing silicon clathrates, the type-I (Na_8Si_{46}) and the type-II ($Na_{24}Si_{136}$) with the unique framework structure attract much attention due to the particular properties, such as thermoelectric properties and superconductivity. The other important compounds, amorphous silicon (a-Si) and nano-crystalline silicon (nc-Si), have also received much attention in biomedical applications, battery, solar cell and etc.. However, the knowledge for easy and cheap synthesis ways of those materials is not enough. Thus, this thesis studies the new synthesis methods of silicon clathrates, a-Si, and nc-Si through the precursor NaSi.

In chapter 1, the importance of *silicon* as the industrial material and the functionality of the silicon clathrate, amorphous silicon and nano silicon are described. Based on the past studies, what is the problem in the synthesis of those materials are pointed out.

In chapter 2, synthesis method and conditions for this study is explained. The preparation of the precursor, sodium silicide (NaSi), type-II silicon clathrate, a-Si and nc-Si are presented in detail. Furthermore, the experimental conditions of the x-ray diffraction measurements, electrochemical experiments, NMR and FT-IR measurements are described.

In chapter 3, the high purity of Na_xSi_{136} was synthesized by the decomposition of Zintl compound NaSi. The appropriate synthesis temperature was different from the other references. The heating temperature and time for the decomposition were researched with other conditions. The suitable condition is about 380 ^oC for a large evacuation tube (4.16 cm), and for 3 days. The high purity of the sodium silicon clathrate (Na_xSi_{136}) over 96 wt% was obtained with and x for Na_xSi_{136} was about 1. The pure type-II silicon clathrate through the etching by a NaOH solution at 60 ^oC in 2 minutes.

In chapter 4, the lithium contained silicon clathrate was tried to synthesize by the electrochemical, heat treatment, and ion exchange methods. The electrochemical study was carried out in the charge-discharge process with the voltage range from 0 V to 3.2 V. The plateau appeared at 0.3 V in the initial lithiation process, suggested the lithiation of the pristine clathrate. The experiment with the charge-discharge range from 0.25 V to 3.2 V showed the reversible insertion and removed of lithium for type-II. The result of X-ray diffraction also indicated the remaining of the type-II structure

after the lithiation and the delithiation process. In the reaction with metal lithium, the powder XRD results show the tendency to form lithium-silicon amorphous. The ion exchange experiments indicate that the $LiNO_3$ and $LiAlCl_4$ are not suitable for preparing lithium silicon clathrate.

In chapter 5, the reaction of NaSi and $AlCl_3$ was investigated. A mixture phase containing type-I, a-Si, and c-Si/nc-Si was obtained in the temperature range 90–180 °C. These serious of studies indicate the excess $AlCl_3$ and controlled heat treatment are necessary for the effective synthesis of a-Si. Both the type-I and type-II compounds were appeared with increasing the proportion of $AlCl_3$. The sodium-containing amorphous silicon (a-Si: Na) was synthesized by a reaction of NaSi and $AlCl_3$ with the 3 vs 9.9 molar ratio at 90 °C, and the nanocrystalline silicon with the particle size of 11 nm is obtained by annealing the a-Si at 600 °C under vacuum. The Raman spectrum showed both the character peaks of a-Si and nc-Si in a-Si sample. The EDX experiment indicated that 7.7 wt% of sodium contained in the a-Si. Moreover, the ^{23}Na MAS NMR spectrum indicated that 0.5 at% of sodium is doped in the a-Si. Almost all the sodium was removed by the crystallization. It is the first time to obtain the sodium-containing amorphous silicon. The electronic state of sodium in a-Si is the different from that in silicon clathrate.

In chapter 6, the results of the present study are summarized as below.

In summary, this research reveals a new synthesis method for sodium-containing a-Si. The silicon clathrate was synthesized through a systematic study for synthesis silicon clathrate. The pure type-II silicon clathrate was obtained firstly by the etching method. The electrochemical, heat treatment, ion exchange method was applied for synthesis lithium contained silicon clathrate, the negative results were obtained with the heat treatment and the ion exchange methods.