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#### Abstract

Mn-silicides have been synthesized by reaction between Si powder and MnCl<sub>2</sub> vapour. The growth temperature varied from 400 °C to 500 °C. The resultant silicides powders were characterized by X-ray diffraction (XRD). By powder reaction, the silicidation temperature can be decreased to 400°C. The dominant growth of HMS was obtained at the heating temperature of 500°C for 36h. The phase evolution was discussed and compared with bulk reaction. The electrical properties of Mn silicides tablets were measured.

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Keyword: MnSi<sub>-1.7</sub>; X-Ray diffraction (XRD); MnSi; Silicides; electrical properties

#### 1. Introduction

Semiconducting silicides have attracted much interest for their potential uses as environmentally friendly semiconductors [1]. Higher manganese silicides (HMS) with a composition near MnSi<sub>-1.7</sub> are some of the semiconducting silicides with a direct band gap of about 0.7 eV, which are stable at high temperature, and are considered to be appropriate semiconducting materials for use in infrared photovoltaic devices, such as thermophotovoltaic batteries [2]. MnSi<sub>-1.7</sub> has a tetragonal crystalline structure with a lattice constant of  $a = 0.553$  nm and an unusually long c-axis up to 10 nm. The unusual crystalline structure of MnSi<sub>-1.7</sub> makes it difficult to grow high quality films on highly symmetric Si substrates. At the same time, Mn-Si system indicates existence of several Si-Mn intermediate phases. Multi-phase reaction always degrades the quality of HMS films and bulk materials [3~7].

Several studies on the growth of HMS have been performed by solid phase epitaxy (SPE), reactive deposition epitaxy (RDE), ion beam epitaxy and molecular beam epitaxy (MBE) [4-7]. To improve the HMS continuity and

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completeness, surfactant growth techniques based on the methods mentioned above have been used. In the case of HMS films grown in the presence of a surfactant (Sb) flux, it is impossible to control thermoelectric properties due to the presence of the surfactant atoms in the films as impurity. Even literature data [8] showed that impurity of Sb doped into manganese silicide bulk material led to decreasing of thermoelectric performance. In our previous work [9], manganese silicide layers were grown on Si (111) substrates by exposure of the Si substrates to  $\text{MnCl}_2$  vapour. At temperature of  $400^\circ\text{C}$ , not any Mn or silicides were deposited on the substrate. The thermal treatment temperature of  $500^\circ\text{C}$  provided the appropriate growth conditions to form the  $\text{MnSi}_{-1.7}$  phase. The epitaxial  $\text{MnSi}_{-1.7}$  islands grew during the initial growth stage. As the heat treatment time increased, the epitaxial layer became continuous and covered the entire Si (111) substrate surface. However, the prepared films were too thin for practical applications. In present work,  $\text{MnSi}_{-1.7}$  was grown by using Si powder and  $\text{MnCl}_2$  as source materials.

## 2. Experiment

Mn-silicides powders were synthesized by exposure Si powder to  $\text{MnCl}_2$  vapour.  $\text{MnCl}_2$  was of analytical purity and was heated at  $200^\circ\text{C}$  for 4h in vacuum to dehydrate it. An appropriate amount of Si powder and excess  $\text{MnCl}_2$  were mixed before being put into a loosely sealed glass container. Then the container was loaded into a vacuum chamber which was pumped down to the base pressure of  $10^{-3}$  Pa. The container was heated and the growth temperature varied from  $400^\circ\text{C}$  to  $500^\circ\text{C}$ . During the heating process, Si powders were exposed to  $\text{MnCl}_2$  vapour. The phase composition of the resultant powders was characterized using X-ray diffraction (XRD). For the electrical measurement, the  $\text{MnSi}_{-1.7}$  powder were pressed at 10 MPa at room temperature to get tablets with a size of 1.5mm height and 5mm diameter.

## 3. Results and discussion

Fig.1 (a) shows the XRD spectra of Mn-silicides powder synthesized at the temperature of  $400^\circ\text{C}$  for 2 hours. The formation of  $\text{MnSi}_{-1.7}$  as dominant silicides phase was observed. At the growth temperature of  $500^\circ\text{C}$  for 2h (Fig.1b), the same resultant phase was obtained. However, at  $400^\circ\text{C}$ , the prolongation of growth time to 6h resulted in the enhanced growth of MnSi (Fig.2c). In Fig.2 (a) and (b), at  $500^\circ\text{C}$ , 4h and 6h's growth did not result in the evident growth of MnSi.

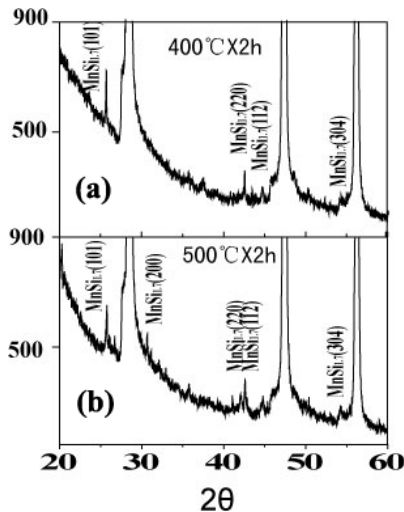


Fig.1 XRD spectra of Mn-silicides prepared at  $400^\circ\text{C}$  and  $500^\circ\text{C}$  for 2 hours, respectively.

In the reference [9], no deposition was observed on the Si substrates treated at 400 °C in MnCl<sub>2</sub> vapour. The dissociation of MnCl<sub>2</sub> and reaction of Si and Mn have been discussed in Ref.[9]. Considering the fact that the treatment temperature of 400 °C is too low for dissociation of MnCl<sub>2</sub> and reaction with bulk substrate, it can be concluded that surficial atoms on the Si powder are more active than atoms on bulk sample. The reaction of MnCl<sub>2</sub> and surficial Si atoms was responsible for the low temperature silicidation. At the same time, the solubility of Mn atoms in silicon is very low at this temperature ( $3 \times 10^{12} / \text{cm}^{-3}$ ) [10]. It can be assumed if the mixing occurred it must depend on the bonds breaking and new bond formation. As MnSi<sub>-1.7</sub> was formed, the Mn diffusion across the silicides layer was depressed since the metal was always thought inactive in the Si-rich silicides layer. Thus the MnSi phase was formed on the MnSi<sub>-1.7</sub> layer. Roughly speaking, the Mn-rich silicides have a lower enthalpy of formation [11], and the Si-rich phases are more stable. Theoretical prediction showed the first nucleation phase was Mn<sub>5</sub>Si<sub>3</sub> [12]. It has also been shown that the silicides growth strongly depends on the interface conditions and not simply on the free energy of formation. The further structural characterization of resultant silicides powder will be required to clarify the phase selection and formation mechanism of Mn-silicides by powder reaction.

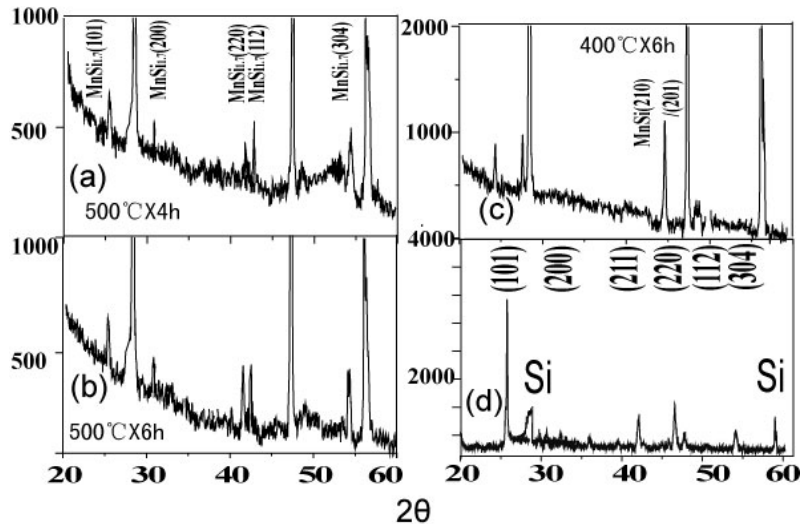


Fig.2 XRD spectra of Mn-silicides prepared at different conditions

In the Ca-Si and Sr-Si system, different phases formation was also found [13] by powder reaction. Heating the Si substrate in Ca or Sr vapour resulted in the formation of several silicide phases. However, by using Si powder, the single phase  $M_5Si_3$  ( $M=Ca, Sr$ ) was grown. These results will help us to clarify the interface condition dependence of silicides growth.

Based on the XRD characterization, the prolongation of growth time helped the formation of HMS at 500°C. Fig.2 (d) shows XRD spectrum of Mn-silicide powder after treatment for 36h at 500°C, in which the diffraction peaks was assigned as MnSi<sub>-1.7</sub> phase. Small amount of raw silicon powder can also be found. The tablets were made from the MnSi<sub>-1.7</sub> powders for electrical properties measurement. The electrical conductivity of tablet varied from 25 to 30 ( $1/k\Omega \cdot m$ ) at the temperature range of 300K -380K. Electrical conductivity and Seebeck coefficient of the tablet were shown in Fig.3. The power factor was calculated by  $\alpha^2\sigma$  [14]. The power factor was increased from  $1.12 \times 10^{-9} \text{ W/m}\cdot\text{K}^2$  (at room temperature) to  $1.21 \times 10^{-9} \text{ W/m}\cdot\text{K}^2$  (at 373K).

#### 4. Conclusions

Mn-silicides have been synthesized by reaction between Si powder and  $\text{MnCl}_2$  vapour. By powder reaction, the formation temperature can be decreased to  $400^\circ\text{C}$ . The dominant growth of HMS was obtained at the heating temperature of  $500^\circ\text{C}$  for 36h. The phase evolution was discussed and compared with bulk reaction [9]. The electrical conductivity and powder factor at the temperature range of 300 - 400K were measured.

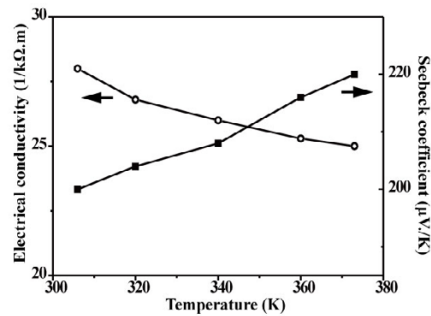


Fig.3 Electrical conductivity and Seebeck coefficient of the silicides tablet.

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