**OPTICAL AND ELECTRONIC PROPERTIES OF M_2Si (M=Mg, Ca AND Sr)
GROWN BY REACTIVE DEPOSITION TECHNIQUE**

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Single phase M_2Si (M=Mg, Ca and Sr) silicides were grown using Si substrates by thermal treatment of the substrates in the vapors of the metallic sources, M, and the electronic structures and optical property of the silicides were investigated. The electronic band structures of the silicides were calculated using the first-principles total-energy calculation program in pseudopotential schemes

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with plane-wave basis functions. The calculated optical reflectance spectra were also deduced from the theoretical band structures, and roughly agreed with the experimental results except for the low reflectance intensity around 2 eV. This suggests that the energy band gap of the silicides roughly agree with the calculated values of 0.15, 0.31 and 0.35 eV for Mg_2Si , Ca_2Si and Sr_2Si , respectively, within the underestimation of the band gap by the density functional calculation. The optical property of the silicides is also discussed in relation to the morphological structures of the silicides.

Key words: Silicides, Semiconductors, Structural properties, Optical properties and measurements

1. Introduction

Recently, semiconducting silicides, which consist of nontoxic and abundant materials, have attracted much attention for their potential to create new classes of environmentally conscious electronics¹. The II-group half silicides M_2Si ($\text{M}=\text{Mg}$, Ca and Sr) are categorized in this materials group. Magnesium silicide (Mg_2Si), which has a anti- CaF_2 -type structure with a lattice constant of 0.6351 nm, was reported as a narrow band gap semiconductor with the indirect band gap of 0.6~0.8eV.²⁻⁵ The Mg-based compounds were originally considered to be one of the thermoelectric materials operating above 200°C.^{6,7} The electronic properties of the silicides have been comprehensively investigated on a theoretical basis.⁸⁻¹³

On the other hand, Ca_2Si and Sr_2Si have orthorhombic structures with lattice constants of $a=0.7667$, $b=0.4799$, $c=0.9002$ nm for Ca_2Si , $a=0.8112$ nm, $b=0.5152$ nm and $c=0.9542$ nm for Sr_2Si .^{14,15} However, the theoretical results of Ca_2Si and Sr_2Si have not been experimentally examined because of the difficulty in growing the silicide layers and bulk crystals. Recently, semiconducting Ca_2Si and Sr_2Si were successfully grown on Mg_2Si bulk crystals and $\text{Mg}_2\text{Si}/\text{Si}$ substrates, respectively.¹⁶⁻¹⁸ However, no experimental optical properties have been reported.

In this study, it was demonstrated that the single phase M_2Si ($\text{M}=\text{Mg}$, Ca and Sr) silicides were grown by thermal treatment of the Si substrates in the vapors of the metallic sources, M, and the electronic structures and optical property of the silicides were investigated. The experimental optical reflectance spectra were obtained for the first time for Ca_2Si and Sr_2Si . In addition, the first-principles analyses of the electronic structures of the M_2Si ($\text{M}=\text{Mg}$, Ca and Sr) are also presented.

2. Experimental

Mg_2Si layers were grown on Si(111) substrates in Mg vapor at 500°C for 3 or 72h. The Mg source and Si substrates were placed in a loosely sealed container in a vacuum chamber. The Si(111) wafer was degreased with solvent, etched in HF solution and rinsed with deionized H_2O . Next, the wafers were immersed in a diluted hydrofluoric acid solution ($\text{HF}:\text{H}_2\text{O}=1:9$), and then dried prior to loading into the vacuum chamber, which was then pumped down to a base pressure of 10^{-3} Pa. No special preheating process for Si(111) was done before the Mg_2Si growth. Ca_2Si and Sr_2Si were grown at elevated temperatures using Mg_2Si bulk crystals and $\text{Mg}_2\text{Si}/\text{Si}$ substrates under a Ca or Sr vapor, respectively. The detailed growth conditions were described elsewhere.¹⁶⁻¹⁸ The

reflectance optical spectra were measured in the energy of 1.5 - 6.5 eV on the Hitach U-3010 spectrophotometer with integrated sphere at room temperature

3. Results and discussion

The electronic band structures of Mg_2Si , Ca_2Si and Sr_2Si were calculated using the first-principles total-energy calculation program¹⁹ in a pseudopotential scheme with plane-wave basis functions. It provides electronic structures within density functional theory (DFT)²⁰, and the dual-space Gaussian pseudopotentials (norm conserving) and an exchange-correlation functional (local-density approximation) with the parameters tabulated in reference²¹ are employed. The program allows a quick processing to find a solution. The crystalline structure of the silicides and their atomic coordination of the Mg, Ca, Sr and Si atoms are shown in Refs. 14 and 15. The calculated band structures and reflectance spectra of Mg_2Si , Ca_2Si and Sr_2Si are shown in Fig. 1. It was calculated that the energy band gaps of the silicides were 0.15, 0.31 and 0.35 eV for Mg_2Si , Ca_2Si and Sr_2Si , respectively.

The calculated band gap of 0.15 eV for Mg_2Si in this study agrees with that of 0.12 eV obtained by LDA as well⁸, but it is smaller than that the GW approximation (GWA) results of 0.45 eV⁸ and the empirical PP calculation of 0.53 eV². On the other hand, the optical property of Mg_2Si has been investigated, and the optical and dielectric constants were analyzed³, and the energy band gap of the Mg_2Si was experimentally obtained as 0.7 - 0.8 eV^{4,5}, which is still more larger than those of calculated values.

This discrepancy is probably due to the underestimation of the calculated energy band gap because the density functional calculation underestimates the energy band gaps of the semiconductors⁸. Namely although the all-electron GWA improves considerably the local-density approximation electronic structure of the semiconductors, it does not always provide the correct energy band gaps for small- and medium-band-gap semiconductors as originally inferred from pseudopotential GWA calculations. The discrepancy between the all-electron and pseudopotential quasiparticle band gaps is mainly traced back to differences between the exchange-correlation matrix elements obtained by the two methods⁸. In addition, most of the small- and medium-band-gap semiconductors GWA does not account for the whole correction of the band gap. The disagreement with the experiment is most probably due to the neglect of the core-polarization interaction and to effects beyond the GWA⁸.

On the other hand, for the Ca_2Si and Sr_2Si , Bisi et al. calculated the density of states (DOSs) of Ca_2Si using the linear-muffin-tin orbital (LMTO) method and concluded that Ca_2Si is a semimetal⁹. It has been reported that the band gap of Ca_2Si is 1.02 eV within the GWA, whereas its only 0.30 eV within the density functional theory (DFT)¹⁰. This DFT value is in good agreement with the value of 0.35 eV reported by Migas *et al.*¹¹. In addition, Ca_2Si is predicted to have a direct band gap of 0.362 eV at $\bar{\Gamma}$ and Sr_2Si has a slightly wider direct band gap of 0.402 eV at Γ ¹².

On the other hand, the experimental band gap of Ca_2Si was estimated as 1.9 eV by resistivity measurements²². However, it is also reported that Mg_2Si , $BaSi_2$ and Ca_2Si are

reported to be semiconducting with the band gap of 0.77, 1.3 and 1.9 eV, respectively⁵, but the author of the recent monograph of semiconducting silicides does not definitely treat the last as a semiconductors²³ by Y. Imai *et al.*¹². In addition, D. B. Migas *et al.* also reported that one has to be careful with the gap estimates in Ca_2Si (1.90 eV), Ca_2Sn (0.90 eV) and Ca_2Pb (0.46 eV) by resistivity measurements in Ref.22 because of the problems in the crystal structure determination. Although the GWA sometimes leads to a slightly underestimated interband transition for semiconductors¹⁰, it is considered that the band gap of 1.90 eV of Ca_2Si is unexpected.

Fig. 1. Calculated electronic band diagrams of (a) Mg_2Si , (b) Ca_2Si and (c) Sr_2Si . In addition, the calculated optical reflectance spectra of (d) Mg_2Si , (e) Ca_2Si and (f) Sr_2Si are also shown.

Fig.2 Experimental optical reflectance spectra of (a) Mg_2Si , (b) Ca_2Si and (c) Sr_2Si .

In Fig. 1, the calculated optical reflectance deduced from the calculated electronic band diagrams are also shown. The arrows show the characteristic features of the spectra. The features of the reflectance peaks of Mg_2Si have already been discussed well, and the interband transitions are considered to be due to $\Sigma_4 \rightarrow \Sigma_1$, $\Delta_5 \rightarrow \Delta_2$ for the 3.3 eV peak, and $L_3' \rightarrow L_3$, $\Lambda_3 \rightarrow \Lambda_3$, $\Delta_5 \rightarrow \Delta_1$ for the peak at 3.7 eV [2, 8]. However, few discussions about the interband transition have been made for Ca_2Si ¹³ and Sr_2Si . However, assuming that the interband transition energies of 3.45 and 3.18 eV calculated using the GWA give more accurate values; the reflectance peak near 3.5 eV for Ca_2Si is considered to be due to $S_v \rightarrow S_{2c}$ and $Z_{8v} \rightarrow Z_{2c}$ transitions.¹³

Figures 2(a), (b) and (c) show the experimental optical reflectance spectra for Mg_2Si , Ca_2Si and Sr_2Si , respectively. The experimental optical property well agrees with the calculated one for Mg_2Si . On the other hand, For Ca_2Si and Sr_2Si , the decrease in the amplitudes in the reflectance spectra of Ca_2Si and Sr_2Si are observed in the range around ~ 2 eV or less in Figs. 2(b) and (c). However, the characteristic features of the spectra in the higher energy range shown by the arrows well agree with the calculated spectra. The decreases in amplitudes in the reflectance spectra in the range of ~ 2 eV or less are related to the contribution of light scattering at the grain boundaries and inter-granular silicides characterized by different density of states.²⁴ Furthermore, the extinction coefficient of the silicide rises in the energy range of 0.1 to 2.0 eV, that can be related to energy losses of at the grain boundaries and inter-granular silicon layers.²⁴ This can be

also explained by the decrease in the joint density of states due to the increase in the number of dangling bonds in the inter-crystallite layers.²⁴

It is also observed that the small reflectance intensity is interpreted in terms of the defect density, disorder, crystalline/amorphous fraction and materials morphology, and it is mainly due to a longer optical path as the result of an efficient diffuse light scattering at the textured layer surface.²⁵ The reflectance decreases due to the surface roughness especially in the 2~3 eV range, which is demonstrated for Zn_3P_2 .²⁶

The difference in the structural property of the silicide surface between Mg_2Si and Ca_2Si (or Sr_2Si) is observed in Refs.16-18. For the Mg_2Si layer, the columnar domain structure along the growth direction is shown¹⁷. On the other hand, small granular domains with a size of $\sim 1\ \mu\text{m}$ are formed near the surface of the Ca_2Si ¹⁶ and Sr_2Si layers.¹⁸ In addition, the surface roughness of Ca_2Si and Sr_2Si would be more degraded than that of Mg_2Si , because the Ca_2Si and Sr_2Si layers are formed by out diffusion and re-evaporation of the Mg atoms from the layers.^{16,18}

The calculated values of band-gap for Mg_2Si , Ca_2Si and Sr_2Si are estimated as 0.15, 0.31 and 0.35 eV using the first-principles total-energy calculation program based on LDA, respectively. These values should be underestimated because of the differences between the exchange-correlation matrix elements obtained by the LDA and GWA methods, and the neglect of the core-polarization interaction and to effects beyond the GWA. However, the calculated optical reflectance spectra agree well with the experimental ones in the higher energy range, which suggests the accuracy of the calculated electronic band diagrams for Ca_2Si and Sr_2Si within the slight underestimation of the calculated band gap. This report shows the first experimental optical evidence that Ca_2Si and Sr_2Si are narrow band gap semiconductors. Further investigation will be required to clarify their electronic structure and optical property.

4. Conclusions

The optical properties of single phase M_2Si (M=Mg, Ca and Sr) silicides were characterized. The layers were grown by exposure of the Si and $\text{Mg}_2\text{Si}/\text{Si}$ substrates to Mg and Ca (or Sr) fluxes, respectively. The experimental reflectance spectra of Ca_2Si and Sr_2Si were characterized for the first time. The experimental spectra well support the calculated electronic band diagrams within the possible underestimation of the band gap by the density functional calculation for the silicides. The optical property of the silicides is significantly affected by the morphological structural properties near the silicide surface. Further investigations will be required to clarify the optical property of the silicides. However, it is expected that the silicides may be candidates as new narrow gap semiconductors.

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