

# Growth and ellipsometric-spectroscopy of semiconducting Ca<sub>2</sub>Si thin films

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**Abstract.** New semiconducting materials technologically compatible with silicon are of practical importance for the design of novel electronic devices. Ecologically friendly semiconducting Ca<sub>2</sub>Si thin films are prepared by magnetron sputtering and sequent annealing in high vacuum. Their ellipsometric spectra are obtained by spectroscopic ellipsometry, and the optical properties of Ca<sub>2</sub>Si thin films at different annealing temperatures are analyzed. Results show that the refractive indexes of Ca<sub>2</sub>Si thin films reach their minimum at ~4.3eV, and the extinction coefficients reach their maximum at ~3.3eV.

**Keywords:** Ca<sub>2</sub>Si thin films; magnetron sputtering; annealing; spectroscopic ellipsometry

## 1. Introduction

New semiconducting materials technologically compatible with silicon and germanium are very practically important for the design of novel electronic devices. Due to its technical compatibility, silicides are attractive materials for use in microelectronic devices. Among them, the calcium silicide (Ca<sub>2</sub>Si), as a new semiconducting material with a direct band gap ( $E_g=1.9\text{eV}$ [1],[2],[3]), has been the interest of research in the recent Years for their potential applications in the silicon-based integrated Circuits and optoelectronic devices[4][5][6], as well as the abundance of their raw materials in natural resources and their non-toxicity. It is very necessary to study the semiconducting calcium silicide because Ca-Si system has many specific phases according to its phase diagram[7][8].

In present reports, most of Ca<sub>2</sub>Si bulk materials and thin films are prepared by melt growth[7][8][9][10] and the thermal evaporation of magnesium source on silicon substrates[6][9][11][12], respectively. There is few about the magnetron sputtering method for preparing Ca<sub>2</sub>Si thin films which can be used in industry. In our work, Ca<sub>2</sub>Si thin films are grown successfully on p-type Si(100) substrates by magnetron sputtering for the first time, and the ellipsometric-spectroscopic data of Ca<sub>2</sub>Si thin films annealed at different temperatures (750–850°C) are analyzed in the photon energy range of 1.5–4.5eV.

## 2. Experimental

Elemental calcium (purity 99.5 wt%) layer was deposited on Si(100) substrates (purity 99.999 wt%) using radio frequency magnetron sputtering at room temperature. The Si(100) wafer was degreased with solvent, etched in HF solution (HF:H<sub>2</sub>O = 1:9), and rinsed with deionized H<sub>2</sub>O, and then dried prior to loading into the vacuum chamber, which was then pumped down to a base pressure of ~10<sup>-6</sup> Pa. No special preheating process for Si(100) was done before the Ca<sub>2</sub>Si growth. The samples in a molybdenum box to be annealed, deposited by magnetron sputtering, were sealed in quartz tube in vacuum of 5\*10<sup>-4</sup> Pa, and annealed at different temperatures of 750–850°C for 1h. The growth conditions used in experiments were listed in Table 1.

The structural properties of the resultant silicides were characterized by an X-ray diffraction measurement (XRD) (D/max-2200, Rigaku Corporation, Japan; Cu<sup>kα</sup> Radiation:  $\lambda=0.15406\text{nm}$ ;  $\theta-2\theta$  Scan-

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Mode, Step: 0.04°) and the surface morphology was characterized by scanning electron microscopy (SEM)(HITACHI S-3400N) at an acceleration voltage of 30 kV. In addition, the optical analyses were made using ellipsometric-spectroscopy as a versatile and powerful optical technique[13] [14][15].

Table.1.Growth conditions of the samples

substrate type	Ar gas flux (sccm)	sputtering power (w)	sputtering time (min)	base pressure (Pa)	annealing time (h)	annealing temperature (°C)
p-type Si(100)	10	85	6	$4.6 \times 10^{-6}$	1	750,782,795, 800,850

### 3. Results and discussion

#### 3.1. SEM characterization

The surface morphology of the samples was characterized by SEM.The SEM images of the thin films annealed at 750°C for 1h are shown in Fig.1 and Fig.2.It is observed in Fig.1 that polycrystalline silicide films are obtained,which are very compact,and the grain sizes are also uniform.Fig.2 shows a cross-sectional SEM image for the Si-based silicide layer consisting of irregular shaped domains with a 100 μm size.

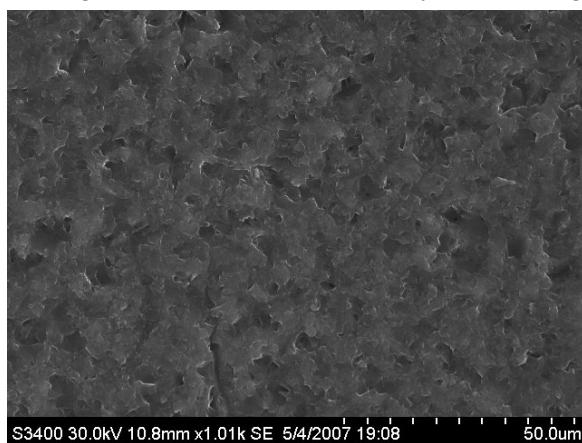


Fig.1. Plan-view SEM image annealed at 750°C

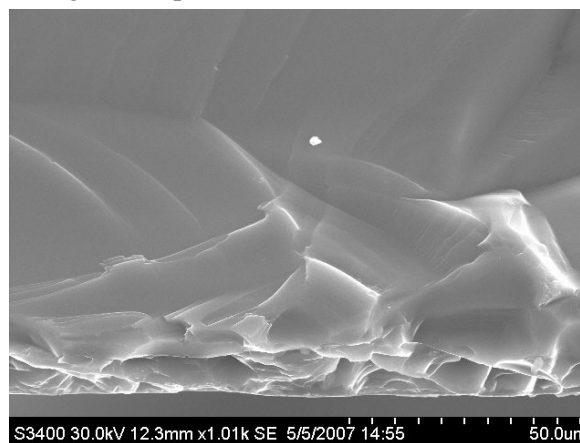


Fig.2. Cross-sectional SEM image annealed at 750°C

#### 3.2. XRD characterization

Crystal structure of the silicide thin films was characterized by XRD.The XRD pattern for the sample annealed at 750°C for 1h is shown in Fig.3.From the experimental result,It is confirmed that the main phase of the film is Ca<sub>2</sub>Si phase though few other silicide phases exist. The existence of multiple silicide phases in Ca-Si system leads to the simultaneous formation of few other silicide phases during the growth.

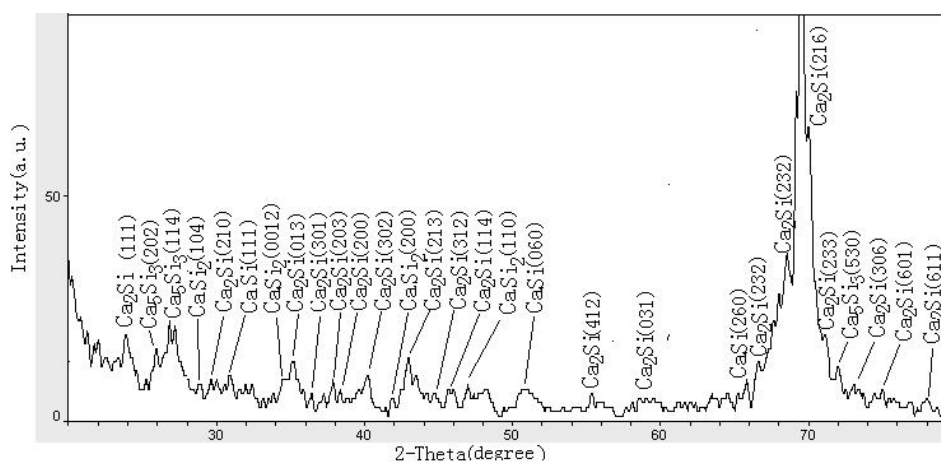


Fig.3. XRD pattern of sample annealed at 750°C for 1h

#### 3.3. The refractive indexes and the extinction coefficients

The refractive indexes and the extinction coefficients of Ca<sub>2</sub>Si thin films annealed at different temperatures are shown in Fig.4, Fig.5, respectively. The refractive indexes of the samples are 0.5-3.6 in the photon energy range of 1.5-4.5 eV in Fig.4. The refractive index of the film annealed at 750 °C is the largest, which reflects the film is the most compact, while the refractive index of the film annealed at 782 °C is the smallest, which reflects the film is looser. The refractive indexes of the samples annealed at different temperatures reach their minimum at 4.3 eV.

As shown in Fig.5, the extinction coefficients of Ca<sub>2</sub>Si thin films range from 0.7 to 3.4 in the photon energy range of 1.5-4.5 eV, and they reach their maximum at 3.3 eV.

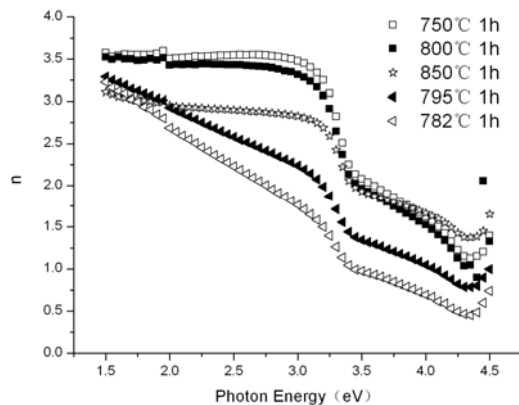


Fig.4. Refractive indexes of Ca<sub>2</sub>Si films

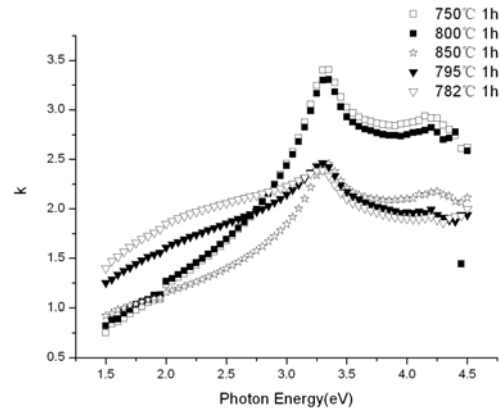


Fig.5. Extinction coefficients of Ca<sub>2</sub>Si films

The dependence of the dielectric function and complex refractive index on the photon energy  $E$  can be explained by Lorentz's dispersion theory [16].

## 4. Conclusion

Ecologically friendly semiconducting Ca<sub>2</sub>Si thin films have been prepared by annealing the Ca films deposited on Si substrates by magnetron sputtering system. SEM results indicate Ca<sub>2</sub>Si thin films prepared are compact and grains are uniform. The ellipsometric spectroscopic data of Ca<sub>2</sub>Si thin films annealed within the temperature range of 750–850 °C show the refractive indexes of Ca<sub>2</sub>Si thin films reach their minimum at ~4.3 eV, and the extinction coefficients reach their maximum at ~3.3 eV.

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