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Preparation of calcium silicide thin films on Si(100) and SiO_2 substrates by pulsed laser ablation of a Ca_2Si alloy target

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The Ca_2Si is a semiconductor with an optical band gap of 1.9 eV. In addition, it overcomes ecological and resources problems because of its non-toxicity and the rich deposits. So it is expected to be an ecologically friendly material for Si-ULSI compatible optoelectronics devices. Calcium silicide thin films were grown on Si (100) and SiO_2 substrates by pulsed laser deposition (PLD) using a Ca_2Si alloy target. At substrate temperatures higher than 20°C, Ca_2Si crystallites were grown. In addition, CaSi crystallites were co-generated. As the substrate temperature rises, the generation of CaSi phase became predominant. The results demonstrated that the CaSi phase preferentially grows and thus it is difficult to grow Ca_2Si single phase films. In order to grow the Ca_2Si phase, it is necessary to approach from the Ca-rich conditions. In addition the preparation should be made at substrate temperatures lower than 350°C to avoid the evaporation of calcium from the deposited film.

Key words: PLD, Ca_2Si, CaSi, semiconductor, ablation

1. INTRODUCTION

Nowadays, the ecological problem becomes acute and ecologically friendly materials, which overcome ecological and resources problems because of its nontoxicity and the rich deposits which are present on earth, are strongly desired. For example, in the information technology field, most compound semiconductors adapted for the optoelectronics are composed from non-ecological elements.

Oxygen, silicon, aluminum, iron and calcium are major abundant elements on the earth crust (-16 km in depth) and non-toxicity, hence these are typical ecologically friendly materials. In Ca-Si system, there are three compounds: $CaSi_2$ (trinomial-rhombehedral, a = 10.4Å, α = 21°30"), CaSi (base-centered orthorhombic, a = 4.590Å, b = 10.795Å, c = 3.910Å) and Ca_2Si (simple orthorhombic, a = 7.667Å, b = 4.799Å, c = 9.002Å) as shown in Fig.1 and Fig.2. The two former are metallic. On the other hand, the latter is expected to be a semiconductor[2] with a band gap of 1.9 eV, and an attractive semiconducting material for visible region as well as β-$FeSi_2$, which is an attractive one for infrared region[3]. Besides, this overcomes the ecological problem. However, there is little research for this material as yet.

The Pulsed laser deposition (PLD) has been

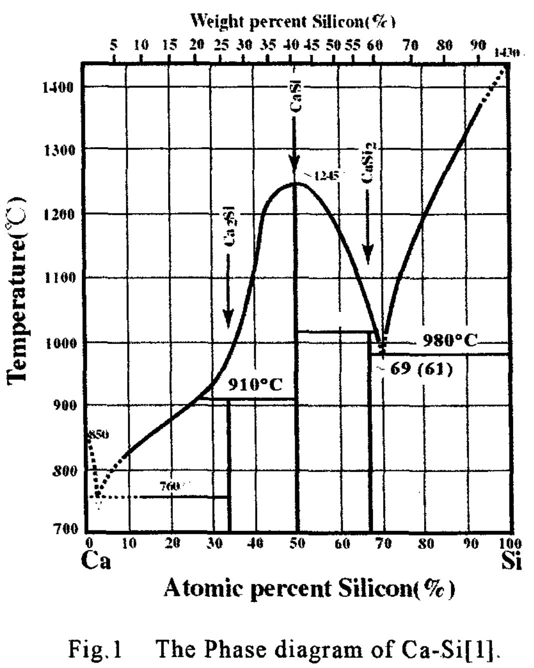


Fig.1 The Phase diagram of Ca-Si[1].

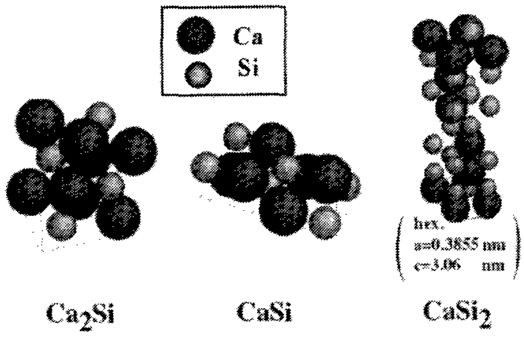


Fig.2 Crystal structures of Ca_2Si, CaSi and $CaSi_2$.

widely applied for growing the high quality thin films of a variety of materials[4,5,6]. This method has the following unique points: low temperature growth compared with other methods due to the deposition of high energetic species[7,8], high purity deposition because of only use of laser beam, and congruent transfer from the target to the film[9]. These points are expected to be extremely appropriate for the preparation of Ca_2Si thin films.

In this paper, we report the result of a study in which the thin films composed of Ca_2Si and CaSi crystallites were prepared by PLD using a Ca_2Si alloy target, and we found the following things. The fabrication of the Ca_2Si single phase films are extremely difficult because the CaSi is easily co-generated. The Ca_2Si film preparation should be made at the calcium-rich condition and at substrate temperatures lower than 350°C.

2. EXPERIMENT

The schematic of the equipment for film preparation is shown in Fig.3. Calcium silicide films with thickness of 200 ~ 300 nm were deposited on silicon (100) and SiO_2 substrates at temperatures in the range of 20 ~ 800°C by the PLD, using a Ca_2Si alloy target (99.99%) whose composition ratio between Ca and Si was 1:2. The substrates were set parallel with the target at a distance of 25 mm from the target. The laser sources used were an ArF excimer laser (Lambda Physik LPX350ST, λ = 193 nm, 24 ns). The irradiation area on the target was approximately 2 mm^2 and the laser fluence F was 4 J/cm^2. The typical deposition rate was 0.14nm/sec. The chamber for the film preparation was evacuated using a turbo molecular pump. The base pressure in the chamber was less than 10^{-6} Torr. The crystal structure and the surface morphology were studied by an X-ray diffraction equipment and a scanning electron microscope.

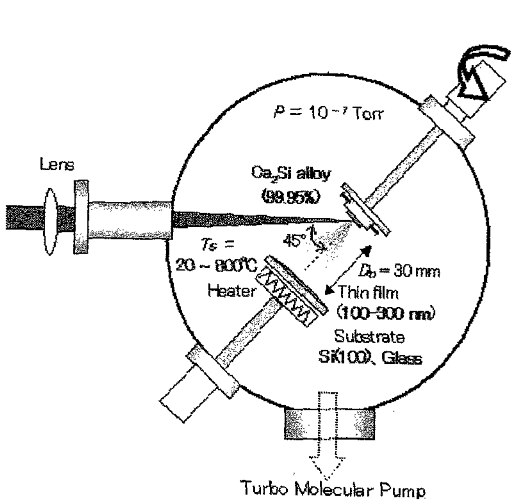
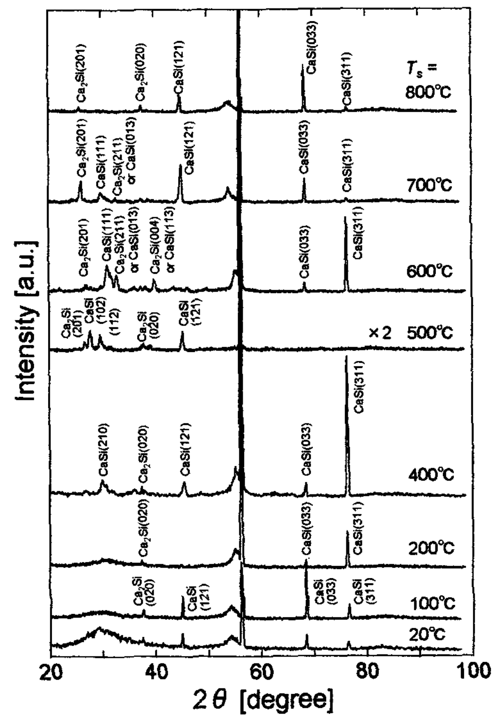
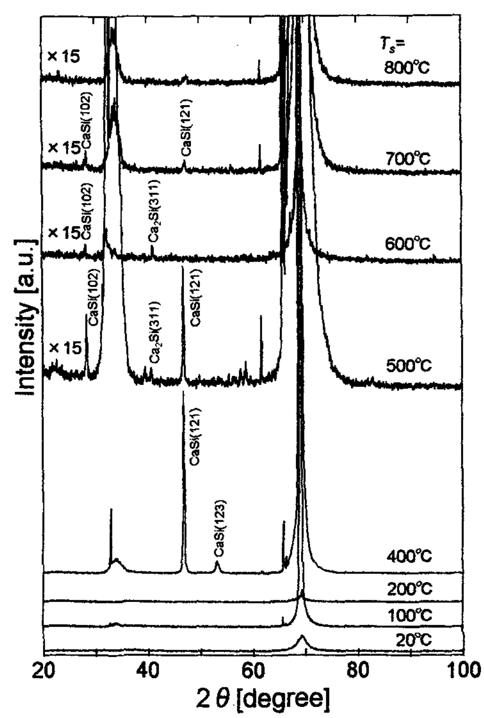


Fig.3 The experimental schematic for film preparation.



(a) 2θ (grazing incidence)



(b) 2θ-θ

Fig.4 X-ray diffraction patterns of the films deposited on Si (100) at various substrate temperatures. (a) 2θ scan (grazing incidence), (b) 2θ-θ scan.

3. RESULTS AND DISSCUSSION

Fig.4 (a) and (b) show the change in the X-ray diffraction pattern of calcium silicide films for various substrate temperatures by 2θ (grazing incidence) and 2θ-θ methods, respectively. As shown in Fig.4(a), even at substrate temperature of 20°C, the diffraction peaks of Ca_2Si(020), CaSi(121), (033) and (311) are observed. From temperature of 20°C, the Ca_2Si and CaSi are co-generated as a polycrystalline film. At higher substrate temperatures, a variety of peaks due to CaSi are observed predominantly. In also Fig.4(b), the peaks due to CaSi are observed mainly.

The evaporation curves of various metals are shown in Fig.5. The calcium has the extremely high vapor pressure compared with other metals, and thus the calcium is easy to evaporate at low temperatures. The film preparation in this study are made at less than 10^{-6} Torr. Hence, from Fig.5, it is predictable that the calcium evaporation from the deposited film begins from the substrate temperature of 350°C. As the substrate temperature rises, the CaSi generates more predominantly. This must be because the evaporation of calcium from the deposited film occurs and the calcium atoms are luck for the Ca_2Si generation on the substrate.

Fig.6 shows the X-ray diffraction patterns of the films deposited on SiO_2 substrate for various substrate temperatures. At substrate temperatures higher than 400°C, the peaks due to Ca_2Si and CaSi appear. Two phases are co-generated for SiO_2 substrates as well as Si ones. At temperatures less than 300°C, no peaks were observed. For the SiO_2 substrate, the mobility of the deposited species might be lower than that of Si substrate. As a consequence, the crystallites such as Ca_2Si and CaSi cannot grow.

The CaSi is generated easily in spite of providing the deposition species, whose composition ratio between Ca and Si are expected to be nearly 1:2 by using the Ca_2Si alloy target. In addition, for the film preparation on the SiO_2 substrate where the diffusion of Si atoms from the substrate into the film can be neglected, the Ca_2Si and CaSi are co-generated. Hence, the CaSi is easy to generate inherently, compared with the Ca_2Si. In order to grow the Ca_2Si thin film preferentially, the film preparation should be approached from the calcium-rich condition to prevent from the CaSi generation. In addition, the calcium has the high vapor pressure and it is easy to evaporate, and thus, the film preparation should be made at substrate temperatures less than

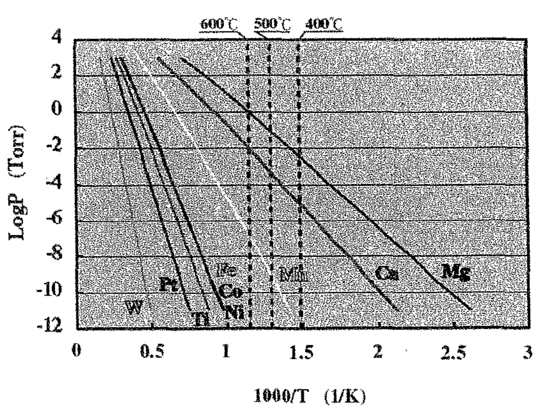


Fig.5 The vapor pressure curves of various metals.

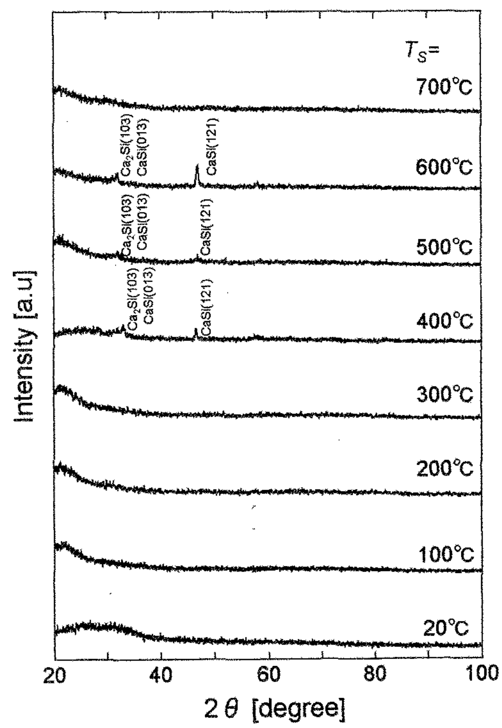


Fig.6 X-ray diffraction patterns of the films deposited on SiO_2 at various substrate temperatures. These were measured by 2θ scan (grazing incidence).

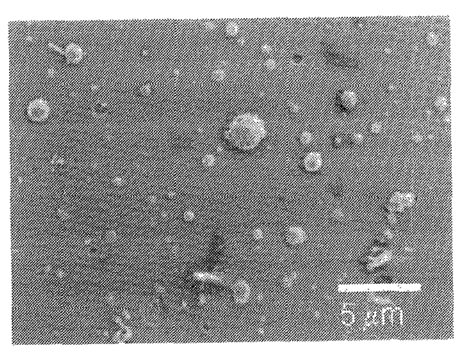


Fig.7 SEM photograph of a typical calcium silicide thin film.

350°C.

Spherical particles with diameters of 1~10 μm could be occasionally observed in spite of the laser irradiation conditions, as shown in Fig.7. These particles are called "droplet" and known well in pulsed laser deposition[10,11] for various materials. The droplet deposition for Ca_2Si target seems to be active compared with that of other materials such as graphite[10]. This is because calcium has the low melting point.

4. CONCLUSION

Calcium silicide thin films were grown on Si (100) and SiO_2 substrates by pulsed laser deposition (PLD) using an ArF excimer laser. Ca_2Si alloy targets were used. At substrate temperatures higher than 20°C, Ca_2Si crystallites were grown. In addition, CaSi crystallites were co-generated. As the substrate temperature rises, the generation of CaSi became predominant due to the evaporation of calcium from the deposited film. The results demonstrated that the CaSi preferentially grows and thus it is difficult to grow Ca_2Si single phase films. In order to grow the Ca_2Si, the film preparation should be approached from the Ca-rich conditions to prevent from the generation of CaSi. In addition, the preparation should be made at substrate temperatures less than 350°C to avoid the evaporation of calcium from the deposited film.

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REFERENCES

[1] T. B. Massalski, Bianry Alloy Phase Diagrams.
[2] O. Bisi, L. braicovich, C. Carbone, I. Lindau, A. Iandelli, G. L. Olcese, and A. Palenzona, *Phys. Rev.* **B 40**, 10194 (1989).
[3] K. Miyake, Y. Makita and T. Yoshitake, *The Review of Laser Engineering*, **28**, 77 (2000).
[4] Chrisey, D. B., Hubler, G. K.(ed.) *Pulsed laser deposition of thin films* (Wiley Interscience Publication, 1994).
[5] T. Yoshitake, T. Nishiyama and K. Nagayama, *Diamond Related. Mater.*, **9**, 689 (2000).
[6] T. Yoshitake, T. Nagamoto and K. Nagayama, *Mater. Sci. Eng. B*, **72**, 124, 15 (2000).
[7] J. P. Zheng, Z, Q. Huang, D. T. Shaw and H. S. Kwok, *Appl. Phys. Lett.*, **54**, 280 (1989).
[8] T. Yoshitake, *Jpn. J. Appl. Phys.* 36, L566 (1997).
[9] R. A. Neifeld, S. Gunapala, C. Liang, S. A. Shaheen, M. Croft, J. Prince, D. Simons and W. T. Hill, *Appl. Phys. Lett.*, **53**, 703 (1988).
[10] E. van de Riet, C. J. C. M. Nillesen and J. Dieleman, *J. Appl. Phys.*, **74**, 2008 (1993).
[11] T. Yoshitake, T. Nishiyama, H. Aoki, K. Suizu, K. Takahashi, and K. Nagayama, *Appl.Surf.Sci.*, **141**, 129 (1999).

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