

# Preparation and Characterization of Epitaxial $\text{CaSi}_2$ and Siloxene Layers on Silicon

Günther Vogg<sup>1,\*</sup>, Nikta Zamanzadeh-Hanebuth<sup>1</sup>, Martin S. Brandt<sup>1</sup>,  
Martin Stutzmann<sup>1</sup>, and Martin Albrecht<sup>2</sup>

<sup>1</sup> Walter Schottky Institut, Technische Universität München, D-85748 Garching, Germany

<sup>2</sup> Institut für Werkstoffwissenschaften, Universität Erlangen-Nürnberg, D-91058 Erlangen, Germany

**Summary.** Epitaxial growth of thin  $\text{CaSi}_2$  films on various silicon surfaces is described. Transforming the silicide into siloxene leads to high quality epitaxial siloxene films with different orientations. The structural quality of  $\text{CaSi}_2$  and siloxene is investigated by transmission and scanning electron microscopy as well as X-ray diffraction analysis. Siloxene on (110)-Si enables direct observation of the anisotropic vibrational properties by IR transmission measurements. A diode structure was realized with siloxene by using contacts with different work functions as charge carrier injectors.

**Keywords.** Anisotropy of IR absorption;  $\text{CaSi}_2$  epitaxy; Diode structure; Structural analysis.

## Herstellung und Charakterisierung epitaktischer $\text{CaSi}_2$ - und Siloxenschichten auf Silizium

**Zusammenfassung.** Das epitaktische Wachstum dünner  $\text{CaSi}_2$ -Filme auf verschiedenen Siliziumoberflächen wird beschrieben. Die Umwandlung des Silizids in Siloxen ergibt unterschiedlich orientierte epitaktische Siloxenfilme von hoher Schichtqualität. Die strukturelle Qualität von  $\text{CaSi}_2$  und Siloxen wurde mit Hilfe von Transmissionselektronen- und Rastertunnelmikroskopie sowie Röntgendiffraktion untersucht. Siloxen auf (110)-Si ermöglicht einen direkten Nachweis der anisotropen Schwingungseigenschaften mittels IR-Transmissionsmessungen. Mit Siloxen und Kontakten mit unterschiedlicher Austrittsarbeit zur Ladungsträgerinjektion wurde eine Diodenstruktur hergestellt.

## Introduction

Siloxene, or more correctly 2D-poly[1,3,5-trihydroxocyclohexasilane], has first been prepared by *Wöhler* in 1863 [1]. Later, *Kautsky* and *Hengge* have systematically studied the properties of this material [2, 3]. Whereas siloxene prepared according to the recipe of *Kautsky* [4] is difficult to analyze structurally, the structure and chemical composition of *Wöhler's* siloxene has been identified by several groups [5, 6]. It consists of a backbone of two-dimensional Si layers nearly identical to the corrugated {111} double layers in crystalline Si. These layers are

\* Corresponding author

terminated on both sides by H- and OH-groups and stacked upon each other with a layer distance of approximately 6 Å. Siloxene is synthesized from  $\text{CaSi}_2$  which is the only known silicide already containing the described layered Si backbone structure. The calcium atoms are topochemically removed in concentrated HCl at low temperatures, leaving the Si layers intact. The two-dimensional polymer backbone is responsible for a variety of properties of this material which make it unique within Si based substances.

Studies concerning the chemical and physical properties of siloxene published so far have given rise to partly conflicting results. For example, the reported Si layer distances range from 5.5 Å [5] to 7 Å [6]. The only obvious conclusion is that small deviations in sample preparation and handling lead to structurally quite different compounds. To obtain a higher reproducibility it is necessary to carefully control the wet-chemical reaction of  $\text{CaSi}_2$  to siloxene. Similarly important is the reproducibility, homogeneity, and quality of the starting material. In this paper we report the growth of thin epitaxial  $\text{CaSi}_2$  layers on Si substrates. Chemical transformation of these epitaxial layers leads to highly ordered crystalline siloxene films with a good reproducibility. Such thin films are a prerequisite for more detailed studies of the notable anisotropy of the electrical, optical, and vibrational properties of siloxene which are otherwise difficult to perform. In addition, such films are necessary to evaluate the potential of siloxene for various device applications.

In this paper we briefly describe the preparation and characterization of thin  $\text{CaSi}_2$  and siloxene films on Si. We first review the epitaxial growth of  $\text{CaSi}_2$  on crystalline Si substrates with different orientations. Then, X-ray diffraction measurements on  $\text{CaSi}_2$  and siloxene films are presented. For further structural characterization, the vibrational properties of siloxene are examined by infrared transmission measurements using polarized light. Finally, transport results obtained for a novel calcium-siloxene-Si diode structure are presented.

## Results and Discussion

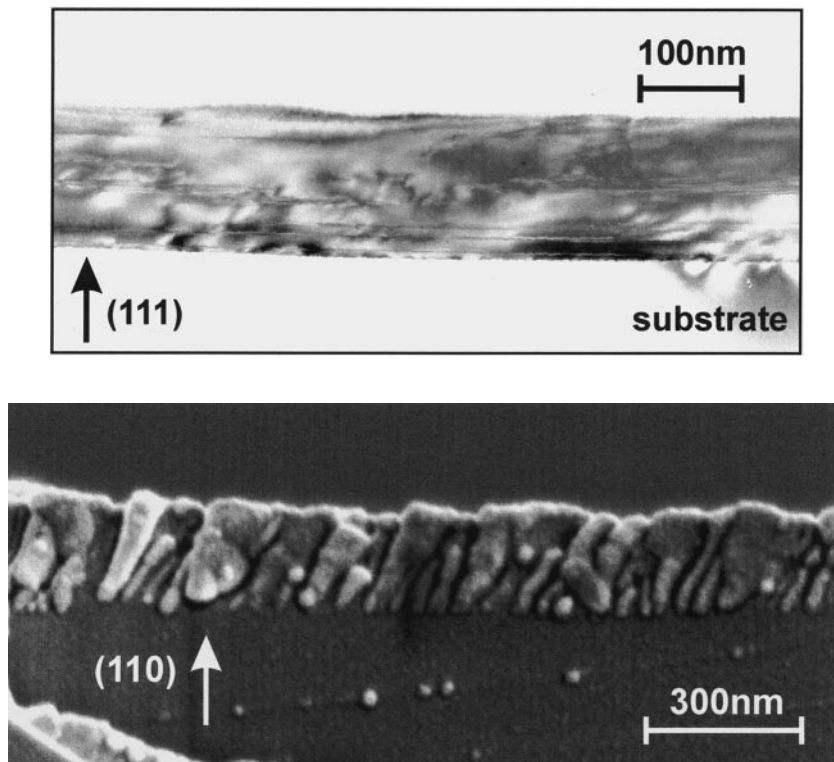
### *Epitaxial growth*

The starting material for thin epitaxial siloxene films on Si are  $\text{CaSi}_2/\text{Si}$  heterostructures grown by reactive deposition epitaxy (RDE) [7] of calcium onto a heated Si substrate. As well known for transition metal silicides, the crystal quality of the epitaxial  $\text{CaSi}_2$  layer depends strongly on the growth conditions, due to a sensitive equilibrium between nucleation and diffusion processes [8–10]. Our own studies, in agreement with previous work on other silicides, have identified Si to be the diffusing species in  $\text{CaSi}_2$ .

As expected, the Si layers in both  $\text{CaSi}_2$  and siloxene correspond to the {111} layers in crystalline Si and therefore play a dominant role in the growth of the silicide. Most notably, the Si layers cause a fixed relation between the substrate and the silicide lattice. In addition, the anisotropic crystal structure leads to different growth conditions and morphology for various substrate orientations. In particular, we observed that the Si layers in  $\text{CaSi}_2$  and siloxene grow parallel to the corresponding {111} layers of the Si substrate. Since there are four independent

(111) directions in crystalline Si, this can lead to inhomogeneous films with crystallites oriented in different directions. One can indeed observe this behaviour, again sensitively depending on the growth conditions. Using particular conditions, *e.g.* high Ca flow and low substrate temperature, one growth direction can be enhanced selectively, and therefore epitaxial films with a preferential orientation are obtained. Additionally, the use of different substrate orientations allows the growth of special and well defined layer orientations.

Epitaxial growth of  $\text{CaSi}_2$  on (111)-Si by solid phase epitaxy (SPE) has already been reported [11, 12]. With RDE we are now able to prepare high quality epitaxial films on (111)-Si with a thickness of several hundred nm. Structural quality and lateral homogeneity is clearly shown by SEM and TEM micrographs (Fig. 1a) and, as discussed later, by XRD measurements. An increased Ca flow during growth leads to a formation of vertical crystallites which typically originate at the edges of the planar crystals. This behaviour has been observed earlier by *Braungart* and *Sigmund* [13]. The crystallites representing the other possible (111) directions finally coalesce and form a  $\text{CaSi}_2$  film with a vertical layering. This is due to the anisotropic growth of  $\text{CaSi}_2$ : crystal growth parallel to the  $\text{CaSi}_2$  layers is obviously much easier and therefore faster than perpendicular to them.



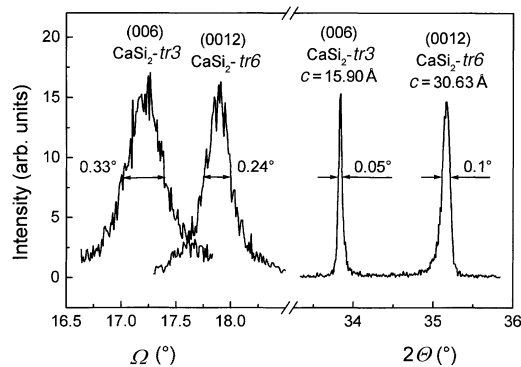
**Fig. 1.** a) Cross-sectional transmission electron micrograph of a 200 nm thick  $\text{CaSi}_2$  layer on (111)-Si substrate; b) cross-sectional scanning electron micrograph of a 300 nm thick  $\text{CaSi}_2$  layer on (110)-Si substrate

The same effect can be observed for (100) and (110) oriented substrate as well. In the case of (100)-Si the four (111) directions are equivalent, and the final layer orientation is therefore undefined. Macroscopically, a rectangular array of vertical crystallites is observed. (110) substrates, however, have a useful peculiarity. Two of the (111) directions are exactly perpendicular to the surface, causing a perpendicular orientation of the  $\text{CaSi}_2$  layer as well. Figure 1b shows the structure of such a layer in a side view. It consists of parallel oriented crystallites with a tilt of about  $10^\circ$  relative to the exact vertical position. Tilt and probably a high concentration of dislocations are the consequences of the theoretical lattice mismatch of 19% between the layer spacing of  $\text{CaSi}_2$  and the spacing of two next nearest Si-{111} layers in crystalline Si. Transforming the layer into siloxene should lead to structural destruction due to the increasing lattice constant. The presence of separated crystallites in the case of thin layers, however, enables various compensation processes so that a high crystalline quality is kept as well. We are therefore able to prepare samples with the  $c$ -axis of siloxene oriented parallel to the Si surface.

#### *X-ray diffraction measurements*

X-ray diffraction measurements were performed on both thin  $\text{CaSi}_2$  and siloxene layers grown on (111)-Si substrates. The diffraction pattern of a 300 nm thick  $\text{CaSi}_2$  layer (a similar layer is shown in Fig. 1a) is given in Fig. 2. On the right hand side, the (006) and (0012) Bragg reflexes of the  $\text{CaSi}_2$   $tr3$  and  $tr6$  modifications are seen in a Bragg-Brentano scan. These modifications differ in their stacking sequences (ABC and AABBBCC) which leads to slightly different lattice constants. The observed values  $c = 15.90 \text{ \AA}$  ( $tr3$ ) and  $c = 30.63 \text{ \AA}$  ( $tr6$ ) are nearly identical to those of bulk  $\text{CaSi}_2$  ( $15.98 \text{ \AA}$  and  $30.6 \text{ \AA}$ , respectively) [14, 15]. The line widths of less than  $0.1^\circ$  show the high quality of the silicide layers. From the integrated diffraction intensity one can estimate the ratio of the volume fraction of approximately 1:1 for  $tr3$  vs.  $tr6$  in an epitaxial layer.

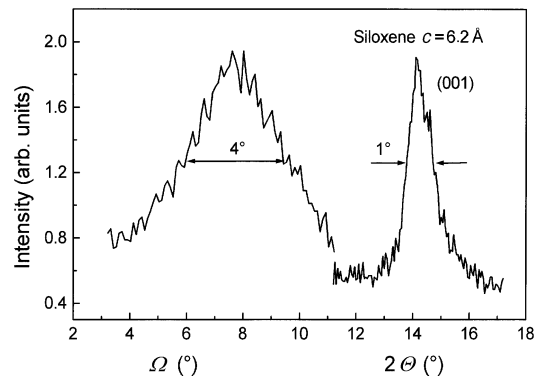
In the left part of Fig. 2 the corresponding rocking curves are shown. A comparison of the  $2\Theta$  and  $\Omega$  line widths of the  $tr3$  and  $tr6$  modifications of the



**Fig. 2.** X-ray diffraction pattern of a 300 nm thick epitaxial  $\text{CaSi}_2$  layer on (111)-Si substrate; rocking (left) and Bragg-Brentano (right) curves are plotted together

epitaxial silicide shows remarkably different line widths for  $tr3$  and  $tr6$  which is probably caused by a phase separation. *Morar* and *Wittmer* have observed pure  $tr6$ - $\text{CaSi}_2$  in very thin epitaxial layers on (111)-Si substrates [11, 12]. We therefore assume that at first the  $tr6$  modification grows on the Si surface, whereas the  $tr3$  modification is formed above this  $tr6$  layer. This assumption is supported by the fact that the lattice mismatch between the  $tr6$  modification and Si (0.4%) is somewhat smaller than that for the  $tr3$  structure (-0.6%). It is therefore energetically more favorable to form  $tr6$ - $\text{CaSi}_2$  directly on the Si surface. The lattice mismatch causes a strain and a variation in the  $c$ -constant, thus leading to a broadening of the  $2\Theta$  curve. For the  $tr6$ - $\text{CaSi}_2$  located directly on the Si surface, the broadening is remarkably asymmetric towards higher  $c$ -values due to the compressive strain in the  $a$ -direction. On the other hand, the adjacent Si single crystal reduces the overall distortion so that the  $\Omega$ -curve will be sharper. The  $tr3$  modification of  $\text{CaSi}_2$  is further away from the Si surface and therefore less strained (towards lower  $c$ -values) but more distorted, thus explaining the opposite ratio of the line widths. The asymmetric shape of both  $2\Theta$  curves could also be evidence for a continuous phase mixing at the interface between the  $tr3$  and  $tr6$  silicide layers.

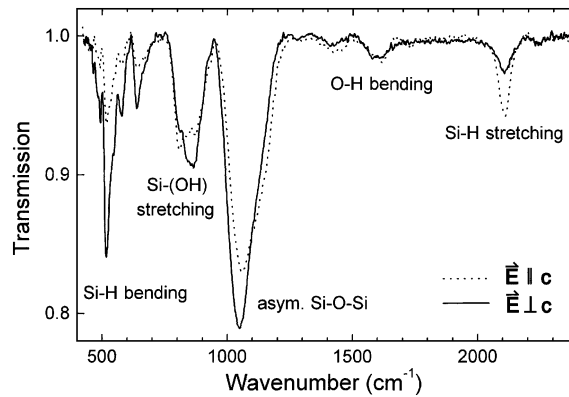
As expected, the crystalline quality decreases upon the topochemical reaction from silicide to siloxene. Figure 3 shows the (001) reflex of a 500 nm thick siloxene layer on a (111)-Si substrate. The  $2\Theta$  peak position at  $14.25^\circ$  corresponds to a layer spacing of 6.2 Å. The  $2\Theta$  line width of  $1^\circ$  must be taken as an upper limit because of the low resolution of  $1^\circ$  which was necessary due to the low signal intensity. Measurements with a better resolution showed a line width around  $0.5^\circ$ , which is nearly the same as observed for powder samples [16]. The asymmetric line shape indicates a distribution of layer spacings towards lower values of  $c$ . This may be caused by the beginning oxygen cross-linking of the siloxene layers during the measurement. On the other hand, the remarkable broadening of the rocking curve (line width  $4^\circ$ ) is not surprising if one considers the ease of distortion in a layered compound with weak *van der Waals* interlayer bonding as in siloxene.



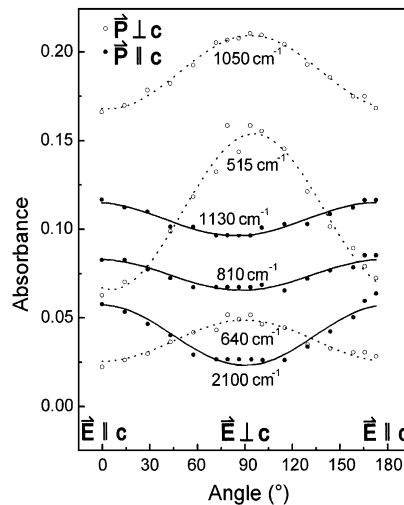
**Fig. 3.** X-ray diffraction pattern of a 500 nm thick siloxene layer on (111)-Si substrate; rocking (left) and *Bragg-Brentano* (right) curve are plotted together

### Vibrational properties

Nearly all properties of siloxene will be anisotropic due to the layered structure of the material. In the case of optical absorption and refractive index, this has already been noted by *Kautsky* [17]. A quantitative analysis of such anisotropies, however, requires thin siloxene samples in which the  $c$ -axis lies in the plane of the thin crystal. Due to the weak interlayer forces in siloxene, such samples are difficult to prepare from bulk material. Here, the epitaxial layers on (110)-Si substrates can be used as a convenient alternative. As a first example of the kinds of experiments possible with these layers, we show here the results of a detailed analysis of the local vibrational modes with respect to the orientation of their dynamic dipole moment  $\vec{P}$  in the crystal. Figure 4 shows the FTIR transmission spectra obtained for such a siloxene layer on a (110)-Si sample for the polarization of the infrared



**Fig. 4.** FTIR transmission spectra of a 300 nm siloxene layer on (110)-Si substrate for different orientations of the polarization of the electric field vector

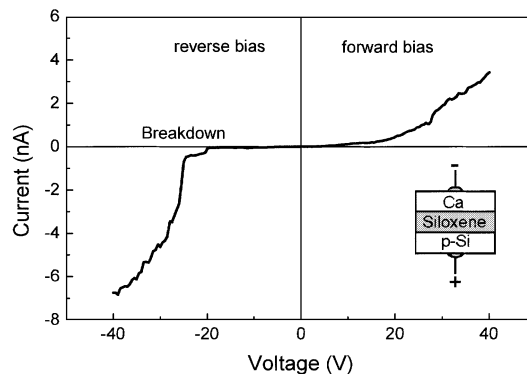


**Fig. 5.** Angular dependence of the IR absorbance for a 300 nm siloxene layer on (110)-Si substrate; the angle refers to the polarization of the electric field vector and the  $c$ -axis of the siloxene layers

electric field vector  $\vec{E}$  parallel and perpendicular to the  $c$ -axis. Nearly all vibrations observed show a relative change in the transmission of about 50% upon change of polarization. This can be seen more quantitatively in Fig. 5 where the angular dependence of the absorbance is plotted as a function of the angle between  $\vec{E}$  and  $c$ . Two sets of vibrations can be distinguished: 1130, 810, and 2100  $\text{cm}^{-1}$  for  $\vec{P} \parallel c$  (full circles in Fig. 5), and 1050, 515, and 640  $\text{cm}^{-1}$  for  $\vec{P} \perp c$  (open circles). Such a behaviour was certainly expected for the 2100 and 640  $\text{cm}^{-1}$  modes which represent Si-H stretching and bending, respectively. However, the data also indicate that the 515  $\text{cm}^{-1}$  mode linked to vibrations of the Si layers has an IR characteristic similar to the 640  $\text{cm}^{-1}$  mode. This is due to a coupling of the Si-H bending modes and the Si phonon observed more clearly in *Raman* spectroscopy under H-D substitution. Finally, the asymmetric Si-O-Si stretching modes around 1050 and 1130  $\text{cm}^{-1}$  indicate the presence of a significant concentration of impurity oxygen in the siloxene layer. Polarization dependent FTIR measurements show that oxygen is dominantly incorporated into the Si layer (1050  $\text{cm}^{-1}$ ); only a smaller fraction of the oxygen impurity atoms links adjacent layers (1130  $\text{cm}^{-1}$ ).

#### Electrical contacts

The strong photoluminescence and first indications of electroluminescence suggest that siloxene might be useful for active optical devices such as light emitting diodes. The particular structure of *Wöhler's* siloxene prohibits conventional doping with group III or V elements as in crystalline Si. Since a pn-diode can therefore not be realized at present, we applied a technique which has been used successfully to fabricate organic LEDs [18]. The luminescent layer is packed between contact materials with highly different work functions. These contacts then work as electron and hole injectors into the thin luminescent layer. Due to the low carrier mobilities in siloxene, the siloxene layer has to be extremely thin to give the charge carriers injected at the opposite ends the possibility to undergo radiative recombination. The activation energy for dark conductivity in these structures is between 1.1 and 1.2 eV, as expected for an undoped semiconductor with a band gap energy of 2.5 eV. Similar values have been observed previously in siloxene crystals [19]. Figure 6 shows an  $I$  vs.  $V$  curve obtained from a 500 nm thick siloxene layer



**Fig. 6.**  $I$  vs.  $V$  curve obtained from a 500 nm thick siloxene layer on Si; Ca and the p-type Si substrate were used as contact materials

on Si with Ca and the p-type Si substrate as contact materials. The  $I$ - $V$  characteristics show a rectification typical for a diode. However, the currents flowing through these devices are still very small, and therefore the electroluminescence is barely detectable. This is in part due to the siloxene layer thickness which had to be increased to avoid pinholes short circuiting the diode. Using siloxene on (110)-Si substrates would further increase the current through the device, since the mobility parallel to the Si layers is about a factor of 1000 higher than perpendicular to them [19]. Work to realize such improved siloxene diodes is currently in progress.

### Conclusions

The capability to fabricate epitaxial siloxene films with different orientations of the Si layers is an important step both with respect to further studies of the fundamental properties of this fascinating material as well as its applications. In particular, the anisotropic optical properties (polarization of photoluminescence, anisotropy of refractive index, optical activity) can now be determined quantitatively. However, both doping as well as stabilization of the material against photooxidation remain issues which have to be addressed prior to the successful realization of an efficient light emitting diode.

### Experimental

Thin  $\text{CaSi}_2$  films were prepared by thermal deposition of metallic Ca (Aldrich, purity >99.5%) onto heated Si substrates with different orientations ((111), (110), and (100)). The typical silicide layer thickness was several hundred nm. The layer morphology and especially the effect of different growth conditions were studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM).  $\text{CaSi}_2$  was then transformed into siloxene using *Wöhler's* method [1] (samples of  $0.5 \text{ cm}^2$  were immersed in 5 ml 37% HCl at  $0^\circ\text{C}$  for 30 min). Both  $\text{CaSi}_2$  and siloxene layers were examined by high resolution X-ray diffraction (XRD) for structural analysis (Philips Xpert triple axis diffractometer,  $\text{Cu-K}_\alpha$  line). The vibrational properties were studied by IR transmission measurements using a *Fourier* transform infrared (FTIR) spectrometer (Bruker IFS 113). For transport measurements, Ca was used as the front contact on epitaxial siloxene films, whereas a p-type Si substrate was used as back electrode. To avoid the influence of ambient gases on the transport measurements, these were performed in a high vacuum.

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