



# Initial CaF<sub>2</sub> reactions on Si(1 1 4)-2 × 1: Isolated silicides, faceting and partial CaF adsorption



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## ABSTRACT

When CaF<sub>2</sub> molecules are deposited on Si(1 1 4)-2 × 1 held at 500 °C, two kinds of isolated and symmetric Ca-silicide units are initially formed. With increasing CaF<sub>2</sub> deposition to 0.4 ML, instead of the terrace being filled with them, a trench composed of (1 1 3) and (1 1 7) facets appears on the surface as a result of substrate etching induced by dissociated F atoms. Selectively on this (1 1 3) facet, a 2 × 2 CaF overlayer is formed uniformly. In the present studies, using scanning tunneling microscopy and synchrotron photoemission spectroscopy, the origins of such isolation of Ca-silicide units on the (1 1 4) terrace as well as selective adsorption of CaF on the (1 1 3) facet have been disclosed.

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## 1. Introduction

Both CaF<sub>2</sub> and Si have the face-centered cubic system of lattice mismatch less than 0.6%. Since the band gap of CaF<sub>2</sub> is about ten times larger than that of Si, the epitaxy of CaF<sub>2</sub> on Si substrates has attracted considerable interest for its application to novel electronic devices such as Si-based resonant-tunneling diodes [1,2].

The stability of the crystalline CaF<sub>2</sub> surfaces depends on the dipole moment in the repeat unit perpendicular to the surface [3]. Among them, CaF<sub>2</sub>(1 1 1) is the most stable surface, since its effective dipole moment is cancelled due to the symmetrical F<sup>-</sup>-Ca<sup>2+</sup>-F<sup>-</sup> unit. On the other hand, CaF<sub>2</sub>(0 0 1) with a net dipole moment perpendicular to the surface has an enormous surface energy resulting in high instability. Therefore, the initial growth of CaF<sub>2</sub> on a Si substrate depends on the substrate orientation [4]. For example, on Si(1 1 1) held over 600 °C, the substrate is initially terminated by a CaF layer, on which the CaF<sub>2</sub> film is grown epitaxially [5]. Due to the strong Ca-Si bond, the CaF(1 1 1) layer has a surface energy lower than that of CaF<sub>2</sub>(1 1 1) [6]. On the other hand, on Si(0 0 1) held over 700 °C, only Ca silicide with a 2 × 3 structure appears at a low coverage [4,5,7]. On this Ca-silicide interface formed on Si(0 0 1), the nanowires bounded by {1 1 1} facets are grown not to the [0 0 1] direction but to the (1 1 0) directions [4,8]. Differently from the

growth on these low-index Si substrates, on a high-index Si(5 5 12) surface held at 500 °C, CaF-terminated nanofacets composed of (1 1 3) and (1 1 1) can be grown [9]. This result suggests that, a high-index (1 1 3) facet, generated by Ca-induced reconstruction, can also host a stable CaF overlayer. This gives a possibility to find a novel substrate to host a CaF overlayer. That is, if a high-index Si(1 1 x) surface between (0 0 1) and (1 1 1) is reconstructed to have a certain facet to host CaF, like (1 1 3), an insulating CaF overlayer with one-dimensional (1D) symmetry can be formed.

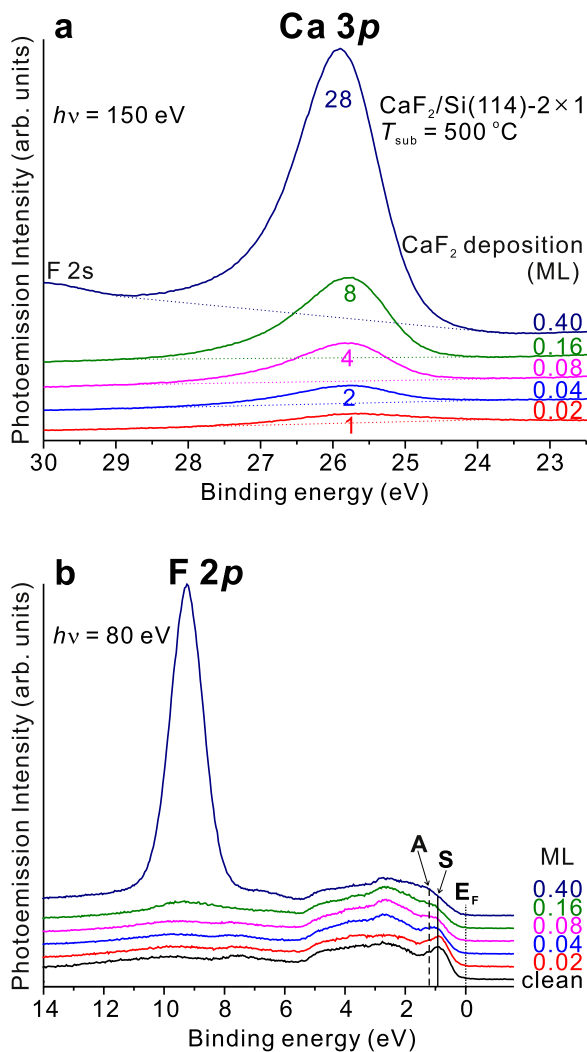
In the present study, a high-index Si(1 1 4) surface, inclined by 19.5° from (0 0 1) toward (1 1 1), has been chosen to find a possibility as a substrate to host a stable CaF overlayer. The reconstructed Si(1 1 4)-2 × 1 surface is originally composed of three kinds of 1D single rows such as dimer, rebonded atom and tetramer rows [10]. Therefore, 2 × 3 Ca silicides formed on Si(0 0 1) terraces cannot appear on Si(1 1 4). Instead, it is expected that a novel nanostructure is formed on Si(1 1 4). For getting information on the stoichiometry as well as the atomic structure of nanostructures, both high-resolution synchrotron photoemission spectroscopy (PES) and scanning tunneling microscopy (STM) have been employed.

## 2. Experiment

The photoemission experiments were conducted at the 8A2 undulator beam line of the Pohang Accelerator Laboratory (PAL) in Korea. An *n*-type (P-doped) Si(1 1 4) substrate with a size of 1.5 × 8.0 × 1.0 mm<sup>3</sup> was cut from a mirror-polished wafer

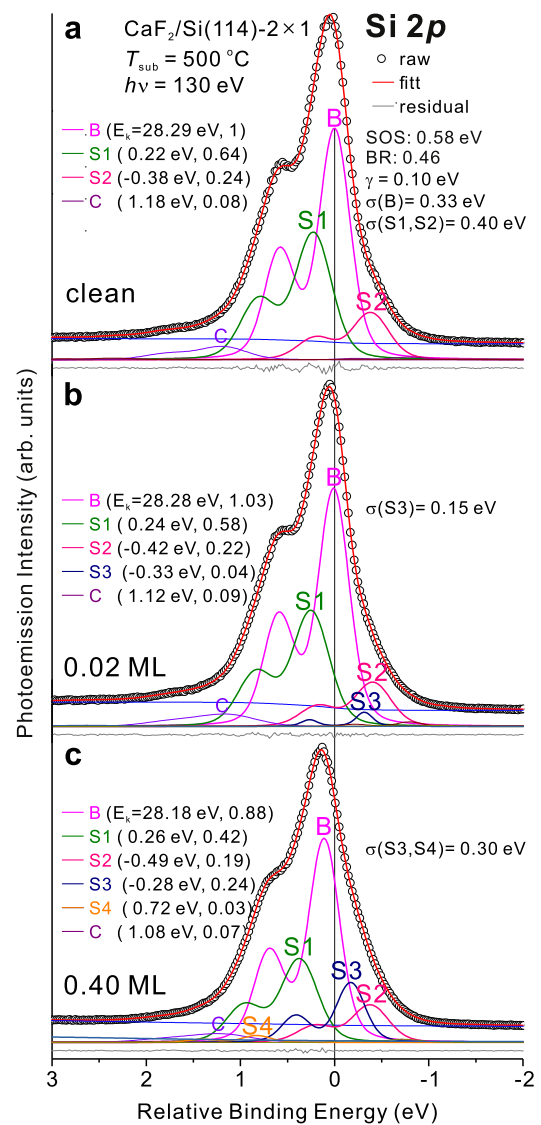
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**Fig. 1.** Photoemission spectra obtained at normal emission from  $\text{CaF}_2$ -deposited  $\text{Si}(114)$ . The substrate was held at  $500^\circ\text{C}$  during deposition. (a)  $\text{Ca } 3p$  core level. Numbers under the peak indicate the relative intensities above the background (dotted line). (b) Valence bands including  $\text{F } 2p$ .  $E_F$ : Fermi energy. States S and A are due to Si dangling bonds and  $\text{Ca } 4s$ -Si  $3p$  bonding, respectively.

(resistivity:  $1\text{--}10\ \Omega\text{cm}$ ) purchased from Umicore. Without any chemical cleaning, the substrate protected by a native oxide layer was mounted on a sample holder, transferred to an ultrahigh vacuum (UHV) chamber of  $1 \times 10^{-10}$  Torr and outgassed for 12 h at  $600^\circ\text{C}$ . The temperature was monitored by an optical pyrometer. A reconstructed  $\text{Si}(114)\text{-}2 \times 1$  surface was prepared through resistive heating at  $1150^\circ\text{C}$ , followed by slow cooling at a rate of  $10^\circ\text{C}/\text{min}$ . Molecules of  $\text{CaF}_2$  were sublimated from 99.95%  $\text{CaF}_2$  pieces (CERAC) in a Ta boat through resistive heating onto the surface held at  $500^\circ\text{C}$  at a rate of  $0.04\ \text{ML}/\text{min}$ . 1 ML is assigned to be eight atoms per unit cell, *i.e.*,  $6.34 \times 10^{14}$  atoms/ $\text{cm}^2$  [11]. The  $\text{CaF}_2$ -deposited surface was stabilized by extended annealing at  $500^\circ\text{C}$  for 10 min without  $\text{CaF}_2$  sublimation. Spectra of  $\text{Ca } 3p$ , valence bands including  $\text{F } 2p$  and  $\text{Si } 2p$  were obtained by a high-resolution electron analyzer, Scienta 3000, using 150-, 80- and 130-eV photons, respectively. For investigating atomic structures of these systems, the surfaces had been prepared under the identical conditions in the STM chamber. The STM images were obtained using an RHK UHV 300 controlled by an RHK SPM 100 in constant current mode at a tunneling current of 0.5 nA with electrochemically etched W tips and processed with the WSxM software [12].



**Fig. 2.**  $\text{Si } 2p$  core-level photoemission spectra obtained at normal emission using 130-eV photons at RT and their curve fittings. The substrate is held at  $500^\circ\text{C}$  during deposition. (a) Clean, (b) 0.02-ML and (c) 0.40-ML  $\text{CaF}_2$ -deposited  $\text{Si}(114)$  surfaces. Inside the parentheses of each component, the first number represents the SCLS relative to the binding energy of bulk component B in each spectrum, except for component B, where the kinetic energy ( $E_k$ ) is described instead; the second number represents the photoemission intensity relative to that of component B in (a).

All of photoemission spectra and topographic STM images were acquired at room temperature (RT).

### 3. Results and discussion

The photoemission spectra of the  $\text{Ca } 3p$  core level and the valence bands including  $\text{F } 2p$  states obtained from the  $\text{CaF}_2$ -deposited  $\text{Si}(114)\text{-}2 \times 1$  surface are shown in Fig. 1(a) and (b), respectively. In Fig. 1(a), the relative Ca intensities above the background are designated by numbers, 1, 2, 4, 8 and 28 under the peak. It increases proportionally to the deposition amount until 0.16 ML, but rapidly increases 40% more than that of the expected value, 20, at 0.40 ML. On the other hand, as shown in Fig. 1(b), the  $\text{F } 2p$  state does not appear distinctively until 0.16 ML, but it suddenly increases at 0.40 ML. In Fig. 1(a), at 0.40 ML, a bulge around 30 eV also originates from the  $\text{F } 2s$  core level. These spectra indicate that, after  $\text{CaF}_2$  molecules are dissociated to Ca and F atoms, Ca atoms remain on the surface and most of F atoms desorb from

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