Type B epitaxy of Ge on CaF$_2$(111) surface

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It was known experimentally that type B orientation, which is rotated 180° about the [111] axis, dominated the heteroepitaxial growth of Ge(111) on a CaF$_2$(111) substrate at an elevated temperature. We performed first principles calculations using density functional theory to determine the energetics of the Ge(111)/CaF$_2$(111) interface and found that the type B orientation of the Ge film is most likely a result of a direct bonding between Ge atoms and Ca$^{2+}$ at the CaF$_2$ surface with the top F$^-$ layer depleted. Our theoretical prediction is supported by our X-ray diffraction experiments on [111]$\times$121$\times$121 biaxially textured Ge/CaF$_2$ samples.

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1. Introduction

The structural transformations in the semiconductor-fluorite interface are of immense interest as a prototype for the study of the bonding between polar and non-polar materials, role of the stoichiometry in the band alignment and the kinetic effect on the growth of heteroepitaxial films. [1–5] It has been observed experimentally that the semiconductor films grown on [111] fluoride surface have either type A (where the film has the same orientation as that of the underlying substrate), type B (where the film has an orientation rotated by 180° about the substrate normal with respect to the underlying substrate) [6] or a mixed [7] epitaxial relation with the substrate. The epitaxial relation has been described to depend on the film growth temperature, the ionicity of the substrate, and the lattice matching conditions between the film and the substrate. [1,2,4,8–12] Recently, a dominant type B epitaxial growth of Ge on a [111]$\times$121$\times$121 textured CaF$_2$ surface was also found at an elevated substrate temperatures [13].

Since CaF$_2$ is a strongly ionic crystal, the charge makeup of the planes parallel to its surface depends on the crystal orientation [14]. For a CaF$_2$ (111) surface, the charged planes are arranged into neutral repeating unit (F–Ca–F) terminated with fluoride ion F$^-$ on the surface. The F$^-$ layer and the Ca$^{2+}$ layer in the neutral repeating unit have an orientation 180° rotated with respect to each other. If Ge is grown on a CaF$_2$(111) surface, the Ge film can have either type A or type B epitaxial relation with respect to the CaF$_2$. If the Ge follows the orientation of the naturally occurring F$^-$ termination layer of CaF$_2$(111), the Ge film will have a type A epitaxial relation. On the other hand, if the Ge follows the orientation of Ca$^{2+}$ layer (underneath the F$^-$ layer), the crystalline orientation of the Ge film will be 180° rotated about the substrate normal and the growth is type B. However, this requires a removal of the top F$^-$ layer from CaF$_2$(111) surface. In this paper, we report the result of first principles density functional theory (DFT) calculations and show that type B epitaxy is indeed energetically favorable among other orientations and Ge atoms are bound to Ca$^{2+}$ with the top F$^-$ layer depleted during the Ge deposition. Our result is consistent with our X-ray diffraction experiments where we observe type B epitaxy becomes more prominent with increasing Ge deposition temperature.

2. Theoretical model

Our DFT calculations were done using VASP [15,16] (Vienna ab initio simulation package) with PAW (projector augmented wave) [17] pseudopotentials. We used generalized gradient approximation [18,19] and the PBE (Perdew–Burke–Ernzerhof) [20] functional for the exchange-correlation energy functional. We chose a plane wave cutoff of 400 eV, and a k-point grid of 8$\times$8$\times$1 for the Brillouin zone integration. All the structures were minimized to a local energy minimum with forces on each atom less than 0.025 eV/Å.

The Ge/CaF$_2$ interface is modeled by a CaF$_2$(111)$-(1\times1)$ slab with 18 atomic layers. Both the top and the bottom of the CaF$_2$ slab are covered by a Ge film with 8 atomic layers forming two identical interfaces. The Ge film is assumed to have a (111) surface and compressed to fit the theoretical lattice constant (5.50 Å) of CaF$_2$. The Ge/CaF$_2$ structure is contained in a periodically repeating supercell that includes a vacuum space of 12 Å. To check whether the artificially compressed Ge film will affect our results, we also study Si films on CaF$_2$ as Si and CaF$_2$ have similar lattice constant. We find that the results for both Si and Ge are qualitatively the same. Therefore, a compressed film should not alter our results.

Three different types of CaF$_2$ surfaces are considered as illustrated in Fig. 1: (1) Interface F1, where CaF$_2$(111) surface has exposed F$^-$ ions with one dangling bond, (2) Interface CA, where the top F$^-$ layer is desorbed from the CaF$_2$(111) surface during Ge deposition, and (3) Interface F3, where the CaF$_2$(111) surface has exposed F$^-$ ions with 3

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dangling bonds, a plausible scenario if there are F atoms in the environment that can be adsorbed onto the CaF$_2$(111) surface during Ge deposition.

In addition, the deposited Ge film can be aligned differently to the underlying CaF$_2$ substrate. Consistent with experiments, we only consider the structures where the <110> axis of the Ge film and CaF$_2$ substrate are aligned. The Ge film can be uniformly translated with respect to the substrate, and the top layer atom in the CaF$_2$ will be at different registry of the Ge surface. We illustrate the different alignment for the CA interface in Fig. 2. The top Ca$^{2+}$ layer of CaF$_2$ can adopt the T1, T4, or H3 positions of the Ge(111) surface. T and H stand for top and hollow sites, respectively. The number following T or H indicates the number of bonds the Ca atom makes with Ge atoms. For the T1 site, Ca is directly below the Ge atom in the first layer of the Ge slab. At the T4 site, Ca can form a bond with a second-layer Ge atom, and also with three other Ge atoms in the first layer. If Ca is at the H3 position, it is directly below a Ge atom in the fourth layer, and can only form three bonds with the Ge atoms in the first layer. Moreover, the Ge film can either follow the fcc stacking sequence of the CaF$_2$ substrate (type A, see top panel in Fig. 2), or form a twin boundary at the interface (type B, see bottom panel in Fig. 2). This gives rise to six possible structures for CA interface. The case for the F1 and F3 interfaces are similar.

3. Energetics of Ge(111)/CaF$_2$(111) film

For the F1 interface, we find that the lowest energy structure corresponds to type B with the surface F atom at the H3 site of the Ge (111) film as depicted in Fig. 1(a). Although the F1 interface has the lowest surface energy for a clean CaF$_2$(111) surface, [14] the Ge film does not bind to the CaF$_2$ substrate, and the separation between the Ge and CaF$_2$ film is $\sim 3$ Å. The energy difference between different alignment and stacking are nearly degenerate (less than 10 meV per (1×1) unit cell). With CA interface, type B is the best with the surface Ca$^{2+}$ ions at the T4 positions of the Ge film as shown in Fig. 1(b). This structure is at least 0.05 eV per (1×1) unit cell lower than the other structures with CA interfaces, and the Ca atoms at the interface form ionic bonds with Ge. For the F3 interface, the lowest energy structure is type A with the surface F$^-$ ions at H3 positions of the Ge(111) as shown in Fig. 1(c). Our study reveals that the lowest energy structures preserve the bulk crystalline environment of the interface atoms for the CaF$_2$ substrate as in Fig. 1(b) and (c).

We also consider the possibility of missing-top-layer structure for the Ge film. In Figs. 1 and 2, the Ge films at the interface adopt a double-layer geometry such that the interface Ge atoms have one dangling bond. A missing-top-layer geometry is formed if the first Ge
layer is removed exposing the second Ge layer, which have three dangling bonds per Ge atom. We find that the formation energies of the Ge/CaF$_2$(111) structures are at least 0.5 eV per (1×1) unit cell higher than those with a double-layer Ge interface. This is because the surface energy of a missing-top-layer Ge film is substantially higher.

In order to compare the relative energetics between F1, CA and F3 structures for Ge/CaF$_2$(111) interface, we calculate the energy released when the lowest energy F1 structure is converted to the lowest energy CA and F3 structures as follows:

$$\Delta E_{CA} = \left( E_{CA} + 2\mu(F) - E_{F1} \right) / 2 \quad \text{and} \quad \Delta E_{F3} = \left( E_{F3} - 2\mu(F) - E_{F1} \right) / 2.$$  

$E_{F1}, E_{CA}$ and $E_{F3}$ correspond to the total energies of the structures in Fig. 1(a), (b) and (c) respectively, and $\mu(F)$ is the chemical potential of a F atom which depends on experimental condition (including temperature). The energy release as a function of $\mu(F)$ is plotted in Fig. 3. Negative $\Delta E$ implies that the conversion is favorable. The upper bound of $\mu(F)$ (−0.18 eV) corresponds to half of the total energy of a fluorine molecule. Since the CaF$_2$ substrate is thermodynamically stable with respect to segregation into bulk Ca metal and fluorine gas, $\mu(F)$ is bounded below by $(E(CaF_2) - E(Ca))/2 = -7.84$ eV, where $E(CaF_2)$ and $E(Ca)$ are the total energies of bulk CaF$_2$ and Ca metal, respectively.

We find that in a F-poor environment, the CA interface with type B geometry is the most favorable structure. For F-rich environment, however, the type-A F3 interface is the most stable. There is a ~1.5 eV window for $\mu(F)$ in which the CaF$_2$(111) with F1 interface can remain intact during Ge deposition. Since only Ge atoms are deposited during the experiment, there should be negligible amount of F atoms in the environment. Therefore, the top F− layer of the CaF$_2$(111) surface is likely removed during Ge deposition at an elevated temperature. This leads to the exposure of the Ca$^{2+}$ ions and generate a type B structure. As we shall see in the next section, our theoretical prediction is consistent with our observation in X-ray diffraction experiments.

4. Characterization of Ge(111)/CaF$_2$(111) film by X-ray diffraction

A biaxially textured CaF$_2$ film was first deposited on glass substrates without intentional heating using an oblique angle vapor deposition technique with a deposition angle of 65° with respect to the surface normal. This film consisted of ~900 nm tall vertically aligned nanorods and ~200 nm thick CaF$_2$ layer deposited under normal vapor incidence. [13] Germanium films were vacuum evaporated (base pressure of $5 \times 10^{-8}$ Torr, deposition pressure $8 \times 10^{-7}$ Torr) on the CaF$_2$ buffered glass substrates with substrate temperatures of 200, 250, 300, 350 and 400 °C. The Ge films grown at 200 and 250 °C substrate temperatures were amorphous and the films grown at 300, 350 and 400 °C had [111]<121> biaxial orientation similar to that of CaF$_2$ buffer layer described next. More details of experiments and morphology imaged by SEM can be found in ref. [13]. The crystallography and texture of the films were studied through X-ray diffraction (XRD) and X-ray pole figure analysis using Bruker D8 Discover diffractometer with Cu target (wavelength = 0.15405 nm). The X-ray pole figure is a graphical representation of the distribution of crystallographic orientation of the film. It is constructed by mapping the diffraction intensity variation of a particular (hkl) reflection satisfying the Bragg’s condition at a given 2θ for a large number of different tilt and azimuthal angular orientations of the sample.

Fig. 4(a) shows the pole figure constructed from the (220) diffraction peak of CaF$_2$ film. Likewise, Fig. 4(b) and (c) show the pole figures constructed from the (220) diffraction peaks of the Ge films grown at 300 and 400 °C, respectively. The white arrows at the bottom of Fig. 4(a)−(c) represent the projection of the incident vapor direction of CaF$_2$ on the substrate plane. These pole figures are consistent with the theoretical (220) poles projected along the [111] direction of a cubic crystal with the [111] direction tilted off the substrate normal by ~11°. The CaF$_2$(220) pole figure shown in Fig. 4(a) has one kind of poles labeled (022), (220), and (202) and does not have pole positions associated with growth twins. In contrast, the Ge(220) poles shown in Fig. 4(b) have two kinds of poles: one set of poles labeled (022), (220), and (202) have the same orientation as that of CaF$_2$(220) poles (type A) shown in Fig. 4(a), and the other set labeled by B(220) have an orientation rotated by 180° about the [111] direction of the underlying CaF$_2$ (type B). The intensities of the B(220) poles are generally higher than that of (220) poles.

A comparison of intensities of type A and type B poles of Ge film as a function of growth temperature is shown in Fig. 4(d). This was done by integrating a narrow slice (~5°) as illustrated in Fig. 4(c) of the pole figure in the direction of incident flux. The ratios of the intensities of type A to type B poles are approximately 1:1, 2:3 and 1:3 for Ge films grown at 300, 350 and 400 °C substrate temperatures, respectively. The higher intensities associated with the 180° rotated poles about the [111] direction of CaF$_2$ suggests that type B epitaxy

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Fig. 3. The energy release when the structure in Fig. 1(a) is converted to Fig. 1(b) (ΔE$_{CA}$) or Fig. 1(c) (ΔE$_{F3}$) as a function of the chemical potential of F atom, $\mu(F)$. The vertical dotted lines indicate our calculated bounds for $\mu(F)$ (see text for details). The range of $\mu(F)$ where the various interfaces are stable is also indicated above the horizontal-axis.

Fig. 4. The (220) pole figures of (a) CaF$_2$, (b) Ge/CaF$_2$/Glass at $T_{sub} = 300$ °C, and (c) Ge/CaF$_2$/Glass at $T_{sub} = 400$ °C. The symbols a, b, and c represent the twins of (220) poles about [111], [111] and [111] directions, respectively. (d) A fiber plot comparing the pole intensities of type A and type B poles in a narrow slice (~5°) between two dashed lines in Fig. 4(c)) of the pole figure in the direction of incident flux.
was preferred in the growth of Ge on CaF$_2$. In addition to the Ge [220] pole figures shown in Fig. 4(c), there are other weak poles labeled by $a$, $b$ and $c$. These poles labeled by $a$, $b$ and $c$ result from the twinning about B[111], B[111] and B[111] directions, respectively. The fact that there is a gradual dominance in the intensities of the type B poles as the growth temperature is increased and the weak poles that are the result of twinning about the type B orientation of the Ge film, suggests that a type B epitaxy was preferential in the growth of Ge on (111)-textured CaF$_2$ substrate. This is consistent with our theoretical prediction that type B epitaxy requires the removal of the top F$^-$ layer from the CaF$_2$ substrate. An elevated temperature can overcome the kinetic barrier owing to the top layer removal. The CaF$_2$ surface may contain other local facets in addition to the (111) surface, however, we believe that the dominant growth mechanism should be initiated by the (111) plane.

In summary, we have shown from first principles DFT calculations that during the heteroepitaxy of Ge on CaF$_2$(111) substrate, type B epitaxy is energetically favorable among other orientations with the Ge atoms bounded to Ca$^{2+}$. However, type B epitaxy requires the top F$^-$ layer of the CaF$_2$ substrate to be removed during Ge deposition. Our theoretical prediction is consistent with our X-ray pole figure measurement where an elevated temperature is required to observe type B epitaxy.

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