Homogeneous Si films on $\text{CaF}_2/\text{Si}(111)$ due to boron enhanced solid phase epitaxy

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Abstract

The structure and morphology of $\text{Si}/\text{CaF}_2/\text{Si}(111)$ structures have been investigated by X-ray diffraction (XRD, GIXRD) and X-ray photoelectron spectroscopy (XPS). While CaF_2 films were grown via molecular beam epitaxy (MBE), Si films on $\text{CaF}_2/\text{Si}(111)$ are fabricated by surfactant enhanced solid phase epitaxy (SE-SPE). Here Boron was used as a surfactant to obtain semiconductor films of homogeneous thickness. The Si films are entirely relaxed while the CaF_2 films have both pseudomorphic and relaxed crystallites. After exposure to ambient conditions, the Si films have a very thin native oxide film. The homogeneous Si film partially prevents the incorporation of impurities at the interface between the Si substrate and CaF_2 via migration along residual defects of the CaF_2 film.

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1. Introduction

The performance of nanoelectronic devices is often based on quantum effects. For instance, the tunneling of electrons through ultrathin insulator films is the key to resonant tunneling devices (RTD) fabricated with insulator semiconductor structures. Here, the large conduction band offset (several eV) between semiconductor and insulator serves as a barrier for electrons.

It is advantageous to combine CaF_2 (band gap 12.1 eV) as an insulating material with Si (band gap 1.1 eV) since the lattice mismatch between both is extremely small (0.58% at room temperature) [1]. Thus, Si based resonant nanoelectronic devices can be developed. Here, CaF_2 films serve as tunneling barriers since the band offset of the conduction

band is approximately 2.5 eV. For resonant tunneling diodes (RTD) Si films of few nanometer thickness are confined by CaF_2 films. Therefore, it is necessary to deposit Si on CaF_2 films so that Si films of homogeneous thickness are grown, too. Although it is difficult to fabricate homogeneous Si/CaF_2 multilayers of nanometer thickness, the performance of RTDs based on these materials has been demonstrated in the mean time [2–5].

Ultrathin CaF_2 films grow very well on $\text{Si}(111)$ (layer-by-layer growth mode) since both the surface energy of CaF_2 and the CaF_2 –Si interface energy are small compared to the surface energy of Si [1,6]. It has been shown that Si films of several 100 nm thickness grow well on CaF_2 films at temperatures as high as 700 °C [7]. However, it is difficult to grow homogeneous Si films, which are only some nm thick, on CaF_2 at these high temperatures due to the disadvantageous relations between surface and interface energies. Si usually forms 3D Si islands on CaF_2 [8,9]. Therefore, strategies have to be investigated to circumvent

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this difficulty and to form homogeneous Si films on CaF_2 . Here, surfactants are advantageous since they presumably reduce both the free energy of films and the mobility of surface atoms as reported for surfactant-mediated epitaxy (SME) of semiconductors [10]. It has been reported that similar improvements are obtained for solid phase epitaxy of Si on CaF_2 films if surfactants (e.g., Sb or B) are deposited during the annealing process (surfactant enhanced solid phase epitaxy (SE-SPE)) [8,11]. The growth of smoother Si films on CaF_2 has also been reported when the CaF_2 films have been exposed to electrons prior to the deposition of Si [12]. This procedure can also be combined with surfactants as As [13].

In this paper, we report on SE-SPE of Si on CaF_2 films using B as surfactant. While a previous study [11] was focused on the morphology of Si films evolved during SE-SPE with B as surfactant, in the present case we investigated the structural properties of these Si films using synchrotron radiation as the major experimental technique (X-ray diffraction (XRD), and grazing incidence X-ray diffraction (GIXRD)). Additional information have been obtained from X-ray photoelectron spectroscopy (XPS) using a lab X-ray source.

2. Experimental

Both $\text{CaF}_2/\text{Si}(111)$ and $\text{Si}/\text{CaF}_2/\text{Si}(111)$ structures were fabricated via molecular beam epitaxy (MBE) under conditions of ultra high vacuum (UHV) in a VG80 Si MBE system. The base pressure in the UHV chamber is less than 10^{-8} Pa. Both CaF_2 and B were evaporated from standard graphite effusion cells while an e-beam evaporator is used to deposit Si. Four inch n-type $\text{Si}(111)$ wafers (n-type, Sb $10^{15}/\text{cm}^3$) are used as substrates which were cleaned ex situ by ozone treatment. In situ the passivating oxide was removed heating the substrates to 810°C for 60 min. The 7×7 reconstruction was controlled via reflection high energy electron diffraction (RHEED).

CaF_2 was deposited at 470°C on $\text{Si}(111)$ leading to CaF_2 films of excellent quality [6,14]. Additional Si was subsequently deposited on $\text{CaF}_2/\text{Si}(111)$ at room temperature. Afterwards the samples were annealed to 635°C while exposing them to B at temperatures $T > 500^\circ\text{C}$. The appearance of a corresponding RHEED pattern demonstrates that recrystallization of the Si film starts already at 500°C . The Si films, however, are polycrystalline if annealing is stopped at this temperature as demonstrated by atomic force microscopy (AFM) and XRD experiments. Therefore, higher annealing temperatures are necessary during SE-SPE to form single crystalline Si films. In addition, the surface of the Si film exhibits $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure due to adsorbed B. Therefore, B decreases the surface energy of the Si film by reducing the density of dangling bonds. Micrographs obtained from AFM after sample transfer to ambient conditions show the formation of crystalline Si islands. The surface roughness of $3.4\text{ \AA}$ rms roughness is extremely small [11].

Both $\text{Si}/\text{CaF}_2/\text{Si}(111)$ structures and $\text{CaF}_2/\text{Si}(111)$ reference structures were studied with synchrotron radiation (10 keV X-ray radiation with wavelength $1.24\text{ \AA}$) at HASYLAB (DESY, beamlines W1 and BW2) after transfer to ambient conditions. Additionally, X-ray photoelectron spectroscopy (XPS) was performed using the Mg K_{α} line of a conventional X-ray source (VG dual anode X-ray tube). The spectra were recorded with a hemispherical analyzer (Leybold EA10+) obtaining a resolution of 1.4 eV for Si2p if a pass energy of 25 eV is used. For the binding energy scale, the C 1s peak (284.5 eV) of carbon residues was used as reference.

3. Results and discussion

GIXRD has been performed to study different crystal truncation rods (CTR), namely the (01), the (10) and the (11) rod. Although the lattice constants of Si and CaF_2 are almost identical these materials have different Bragg conditions on these rods since CaF_2 is B-oriented (rotation of 180° with respect to the substrate, rotational axis = $[111]$ axis) if it is deposited for $T > 250^\circ\text{C}$ on $\text{Si}(111)$ [1,6].

Fig. 1 presents different sectional views of the reciprocal space where the Bragg conditions are noted with respect to both the surface coordination system and the more common bulk notation (Miller indices). Therefore, it is clear that the first Bragg condition on the (01) rod at $L = 1/3$ is due to B-oriented CaF_2 whereas the first Bragg condition on the (10) rod at $L = 1/3$ is due to the $\text{Si}(111)$ substrate. The Bragg conditions of both Si and B-oriented CaF_2 coincide on the (11) rod as well as on the specular (00) rod.

Curve (I) of Fig. 2(a) shows that the (01) rod at $L = 0.3$ splits into two peaks which are separated by $0.52\%\text{BZ}$ (percentage Brillouin zone) as obtained by fitting the peak profile with two Lorentzians. At this position in reciprocal space the experiment is exclusively sensitive to the B-oriented CaF_2 film since the Bragg condition of Si vanishes here due to its diamond lattice. The sensitivity to CaF_2 is also confirmed by periodical oscillations of the diffracted intensity on the (01) rod. Therefore, the film consists of two CaF_2 species with different lateral lattice constants. One species is (almost) pseudomorphic to the Si substrate. The other species ($K = 99.4\%\text{BZ}$) is due to relaxed CaF_2 . Both species, however, have the same film thickness.

A closer investigation of the (11) rod at $L = 0.1$ (curve (I) of Fig. 2(b)), however, reveals that the peak due to the so called pseudomorphic CaF_2 is at ($K = H = 99.9\%\text{BZ}$). Therefore, this species is slightly relaxed (lattice mismatch 0.48% with respect to bulk CaF_2). In the following, it will be called quasi-pseudomorphic. The sharp peak of the (11) rod at $L = 0.1$ is due to the Si substrate. It shows the excellent resolution of the instrument (transfer width 1500 nm). These results are obtained by fitting the peak with one Gaussian for the Si substrate peak and two Lorentzians for the two CaF_2 species. The average size of the CaF_2 crystallites is 120 nm and 70 nm for the quasi-pseudomorphic and the relaxed species, respectively, as

Fig. 1. Sectional views of reciprocal space for $\text{CaF}_2/\text{Si}(111)$. The small lattice mismatch between both materials has been neglected for the schematic drawing. Bragg conditions are shown with respect to both the surface Bragg indices used here and Miller indices more common in bulk diffraction. The reciprocal lattice of CaF_2 and Si are distinct on both the (10) and (01) rod (and equivalent rods) while they coincide on the (00) and (11) rods.

obtained from the full width half maximum (FWHM) of the CaF_2 peaks. The CaF_2 film consists of both species in equal amounts (taking into account both intensity and FWHM of the peaks).

In addition to that, the (10) rod at $L = 0.3$ was investigated (not presented here). This diffraction condition is sensitive to the Si substrate and A-oriented CaF_2 with an orientation identical to the Si substrate. The analysis indicates that a small amount ($<5\%$) of A-oriented CaF_2 forming stacking faults is also present. The formation of

Fig. 2. In plane scans (a) of the (01) rod at $L = 0.3$ and (b) of the (11) rod at $L = 0.1$. (I) $\text{CaF}_2/\text{Si}(111)$, (II) $\text{Si}/\text{CaF}_2/\text{Si}(111)$. The dashed lines show peaks due to quasi-pseudomorphic and relaxed CaF_2 . The dot-dashed profile presents the additional peak due to the Si film for (II). The sharp peak for (b) is due to the Si substrate.

stacking faults has previously also been reported in a transmission electron microscopy (TEM) study for CaF_2 films deposited at 600°C [15] and 720°C [16], respectively.

After deposition of Si on the CaF_2 film the shape of the diffraction peaks changes (cf. curves (II) of Fig. 2). No clear splitting of the (01) rod for $L = 0.3$ is observed at first glance. The profile, however, shows some asymmetric broadening to larger values of K . By fitting the profile with three Lorentzians, an additional peak is detected (dot-dashed line in Fig. 2). This peak is also observed for the (11) rod at $L = 1$. The position of this peak coincides with the peak due to the Si substrate. Therefore, we attribute this feature to a relaxed Si film on the CaF_2 film. The crystallites of the Si film have an average size of 90 nm as obtained from the halfwidth of the additional peak while the quasi-pseudomorphic and relaxed crystallites of the CaF_2 film have average sizes of 180 nm and 60 nm, respectively. The Si film has both A-oriented and B-oriented crystallites (with respect to the B-oriented CaF_2 film) as the investigation of the (10) rod demonstrates (not presented here). This result was confirmed by an analysis of the azimuthal profiles of different rods (not presented here). Twin formation has also been observed in TEM investigations of Si films deposited at 700°C on $\text{CaF}_2/\text{Si}(111)$ [15].

More information about the crystalline quality of the films is obtained from specular diffraction (XRD, $\Theta - 2\Theta$ scans) close to the first Bragg condition of the (00) rod (cf. Fig. 3). The intensity oscillations confirm the high crystalline quality of the film structure. The large periodicity of both sample (I) and sample (II) is due to the CaF_2 film. The short periodicity of curve (II) is due to the thicker Si film. The CTR has been analyzed within the kinematic approximation including layer distances as well as film thicknesses and roughnesses [17]. Since the CaF_2 film has both relaxed and quasi-pseudomorphic species both were separately considered in the CTR analysis. In addition, it has been taken care of the stoichiometry

Fig. 3. Crystal truncation rod (CTR) of the (00) rod (specular diffraction, Θ - 2Θ scan) close to the first Bragg condition $L = 1$ (bulk indices (111)). (I) $\text{CaF}_2/\text{Si}(111)$ and (II) $\text{Si}/\text{CaF}_2/\text{Si}(111)$. Long period oscillations are due to CaF_2 films (thickness (I) 36.1 Å and (II) 39.3 Å, respectively). Short period oscillations are due to the Si film (thickness 110 Å).

of the well known CaF interface layer [1]. Details of the XRD analysis are presented in Table 1.

Comparing the results for the CaF_2 film of both samples (cf. Table 1), it is clear that the additional Si film of sample (II) has no influence on the crystallographic structure of the relaxed part of the CaF_2 film while a slight compression is observed for the quasi-pseudomorphic part. The quasi-pseudomorphic CaF_2 has a larger vertical lattice constant than the bulk value ($d_{\text{CaF}_2-\text{CaF}_2}^{\text{bulk}} = 3.154$ Å) which is obtained for the relaxed CaF_2 (within the experimental error). Both values are comparable to previous XRD [16,18] and X-ray standing waves (XSW) [19] studies which were performed for films deposited at higher and lower temperatures, respectively. These previous studies did not distinguish relaxed and quasi-pseudomorphic CaF_2 . The Si

film, however, exhibits almost the bulk lattice constant ($d_{\text{Si-Si}}^{\text{bulk}} = 3.136$ Å). Therefore, it is entirely relaxed within the experimental error.

Since we measured both the vertical and the lateral lattice constants of the CaF_2 film we can calculate the Poisson ratios $\nu_{111} = -\frac{\delta a/a}{\delta d/d}$. In this way, Poisson ratios $\nu_{111}^{\text{CaF}_2/\text{Si}} = 0.44(\pm 0.11)$ and $\nu_{111}^{\text{Si}/\text{CaF}_2/\text{Si}} = 0.66(\pm 0.21)$ were obtained from our data for both, the bare CaF_2 film and the Si covered CaF_2 film, respectively. These values are much larger than the bulk value of $\nu_{111}^{\text{CaF}_2} = 0.256$ for the [111] direction calculated from bulk elastic constants [20,21]. However, combining the measured lateral lattice constant and the bulk Poisson ratio leads to a vertical lattice constant of 3.126 Å which is beyond the experimental result (including the experimental error). Therefore, it is clear that the Poisson ratio of the film is larger than the bulk Poisson ratio. In addition, the Poisson ratios calculated here are very close or exceed the theoretical limit $\nu = 0.5$ for isotropic crystals [22].

Remarkable is the difference of the interface distance between Si substrate and the CaF interface layer comparing sample (I) and sample (II). On the one hand, sample (I) shows the well known long distance interface previously reported for CaF_2 films without capping film which are exposed to air. The distance obtained here is closer to values previously reported for films deposited at 200 °C ($4.55(\pm 0.06)$ Å) [23] than for films deposited at 720 °C ($4.08(\pm 0.06)$ Å) [16]. The increased interface distance for samples exposed to air has been attribute to oxygen or other gas molecules which are incorporated at the interface after penetrating the CaF_2 film via migration due to defects [1]. On the other hand, the CaF_2 film covered with Si (sample II) has a smaller interface distance even after exposure to air. Although the interface distance for $\text{Si}/\text{CaF}_2/\text{Si}(111)$ is larger than the interface distance observed for $\text{CaF}_2/\text{Si}(111)$ under UHV conditions with XRD [18,24] and XSW [19,25], the smaller interface distance of (II) compared to (I) demonstrates that Si protects the entire structure from defect mediated incorporation of impurities.

Finally, we also investigated the samples with XPS. A Si 2p line typical for clean Si shows only sample (I) while an additional peak due to SiO_2 is observed for sample (II). This is due to the native oxide formed at the surface of the Si film. Native SiO_2 is not detected by XRD since it is amorphous. The detection of a Si 2p signal from sample (I) is in agreement with the extremely low attenuation of electrons in CaF_2 due to the large band gap [26]. In addition, the Si 2p peak shifts from 100.1 eV binding energy for sample (I) to 99.3 eV binding energy for sample (II). This may be to band bending of the Si substrate compared to the Si film or to final state effects of the Si film. This, however, is not in the focus of this study (see Fig. 4).

On the one hand, almost no F signal is observed for sample (II) since the CaF_2 film is covered by the thick Si film. On the other hand, the Ca signal is not negligible. This is presumably due to the surface segregation of Ca previously reported for SPE grown CoSi_2 films on $\text{CaF}_2/\text{Si}(111)$ [27]. The shift of the Ca 2p lines is 0.4 eV

Table 1

Data obtained from the (specular) X-ray diffraction close to (001) Bragg condition (surface indices; equivalent (111) bulk indices) for $\text{CaF}_2/\text{Si}(111)$ and $\text{Si}/\text{CaF}_2/\text{Si}(111)$, respectively

	$\text{CaF}_2/\text{Si}(111)$	$\text{Si}/\text{CaF}_2/\text{Si}(111)$
<i>Si substrate</i>		
Roughness	$0.7(\pm 0.3)$ Å	$1.8(\pm 0.06)$ Å
<i>CaF₂ film</i>		
Thickness	36.1 Å	39.3 Å
Roughness	$4.1(\pm 0.4)$ Å	$6.6(\pm 0.4)$ Å
$d_{\text{Si-CaF}}$	$4.020(\pm 0.005)$ Å	$2.942(\pm 0.005)$ Å
$d_{\text{CaF}_2-\text{CaF}_2}^{\text{ps}}$	$3.187(\pm 0.005)$ Å	$3.176(\pm 0.005)$ Å
$d_{\text{CaF}_2-\text{CaF}_2}^{\text{rel}}$	$3.151(\pm 0.005)$ Å	$3.155(\pm 0.005)$ Å
<i>Si film</i>		
Thickness	–	110 Å
Roughness	–	$9.0(\pm 0.3)$ Å
$d_{\text{Si-Si}}$	–	$3.129(\pm 0.005)$ Å

$d_{\text{Si-CaF}}$ denotes the distance between the topmost Si layer and the CaF interface layer. $d_{\text{CaF}_2-\text{CaF}_2}^{\text{ps}}$ and $d_{\text{CaF}_2-\text{CaF}_2}^{\text{rel}}$ denote the layer distances of the quasi-pseudomorphic and the relaxed CaF_2 species, respectively.

Fig. 4. XPS data of (I) $\text{CaF}_2/\text{Si}(111)$ and (II) $\text{Si}/\text{CaF}_2/\text{Si}(111)$. (a) Si 2p (denote the additional peak due to SiO_2 for (II) and the shift of the peak position), (b) Ca 2p (splitting due to spin orbit coupling) and (c) F 1s. All photoelectron peaks have been recorded with 25 eV pass energy, except the F 1s peak of (II) where 200 eV pass energy has been used due to small intensity.

probably due to the different binding of Ca at the CaF_2 –Si interface and the surface of the Si film, respectively [1]. In addition, B is detected which may mainly be at the surface while some fraction may also be diffused into the Si film.

In summary, we present a detailed analysis of SPE of Si on $\text{CaF}_2/\text{Si}(111)$ which is enhanced by additionally deposited B during annealing (SE-SPE). The well re-crystallized and entirely relaxed Si film has homogeneous thickness. Both A-oriented and B-oriented Si crystallites are formed. On the one hand, a thin film of native SiO_2 is formed on top of the Si film under ambient conditions. On the other hand, the Si film protects the CaF_2 –Si(111) interface from incorporation of impurities. The CaF_2 film exhibits both relaxed and quasi-pseudomorphic crystallites. A negligible minority of A-oriented (compared to the B-oriented majority) is formed. The CTR analysis provides detailed information about the crystallography of the films.

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