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Radiation-Induced epitaxial $CaSi_2$ film growth at the molecular-beam epitaxy of CaF_2 on Si

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ABSTRACT

We report on the studies of the 20 keV electron-beam irradiation (current density 50 μA/m^2) effects on the epitaxial CaF_2 film growth on a Si surface. It was found that, during the CaF_2 growth on Si, the area exposed to the electron beam suffers strong modifications, such as in the surface morphology and film chemical composition. With reflection high-energy electron diffraction, atomic force microscopy and Raman spectroscopy, it is shown that the electron beam action leads to the $CaSi_2$ layer synthesis at the interface of the silicon substrate and epitaxially growing CaF_2 film.

1. Introduction

Though the earth-alkali metal disilicide $CaSi_2$ has been known for more than 150, the interest in this material is growing due to the possibility of high-quality epitaxial $CaSi_2$ film growth on silicon substrates by the deposition of atomic Ca [1,2]. Two methods are usually used to obtain epitaxial $CaSi_2$ films on Si: the solid phase epitaxy (SPE) technique in growing thin $CaSi_2$ layers on Si [1,3], where Ca is deposited onto a Si(1 1 1) substrate and, then, the sample is annealed in ultrahigh vacuum; the other method is based on the Ca vapor reaction with a heated Si substrate [4]. The authors of [5] found that, in bulk CaF_2 crystals under electron-beam radiation, the fluorine desorption occurs with a simultaneous accumulation of Ca.

The aim of the present work was the study of the formation of $CaSi_2$ films under the electron-beam irradiation of the interface region between the silicon substrate and the epitaxial CaF_2 film growing on Si.

2. Experimental procedure

The experiments were made by means of the high-vacuum molecular-beam epitaxy (MBE) facility provided with a CaF_2 graphite-crucible effusion cell. Silicon substrates with (1 0 0) and (1 1 1) orientations were used. Before the growth, the standard procedure for the pre-MBE chemical preparation of Si substrates includes a preliminary cleaning of the substrates by annealing them in the working chamber during 6 h at the temperature of 400 °C. Then, at temperature 720 °C, the protective oxide was removed by a weak Si flow, and a 100 nm thick Si buffer layer was grown at 550 °C. Throughout the entire epitaxial growth period, the electron-beam irradiation was carried out along the crystallographic direction [1 1 0] at the accelerating voltage of 20 kV end the current density of 50 μA/cm^2. The CaF_2 deposition rate was 0.3 Å/s. The varied parameters were the substrate temperature (from 500 to 600 °C), substrate orientation and growth time.

The samples structure and content were studied by atomic force microscopy (AFM), reflection high-energy electron diffraction (RHEED) and Raman spectroscopy (RS). The AFM images were taken on a Solver P47-PRO atomic force microscope in the semi-contact mode. The Raman spectra were recorded at room temperature in the backscattering geometry. An Ar+ laser line with wavelength 514.5 nm was used for the excitation. Raman measurements were performed using a T64000 spectrometer manufactured by Horiba Jobin Yvon. In the present paper, we consider the results obtained just on the Si (1 1 1) substrate. CaF_2 was deposited onto the Si substrate heated up to 550 °C.

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3. Results and discussion

An image of the obtained sample after the CaF_2 layer growth is shown in Fig. 1. The area exposed to the electron beam action according to the RHEED data is inherent to epitaxial alkaline-earth metal films.

The AFM study of the samples shows that the irradiated surface morphology is strongly modified. The AFM surface image of the CaF_2 film grown on the Si (1 1 1) substrate at 550 °C and the AFM image of the surface region, after the electron beam action, irradiated with the RHEED beam, respectively, are shown in Fig. 2(a, b). The characteristic surface relief in the scanned regions is shown in Fig. 2(c, d)

It was found that isolated triangle islands oriented in the [1 1 0] direction are formed on the unirradiated CaF_2 surface (Fig. 2a). The standard deviation of this surface relief is several nanometers. The irradiated surface of the sample strongly differs from the unirradiated surface: no oriented islands are observed, and the surface roughness of the sample is strongly increased (Fig. 2(b, d)).

The results of the RS study are illustrated in Fig. 3. The comparison of the RS spectrum of Si (1 1 1) substrate and the thin CaF_2 film spectrum on Si (spectra *1* and *2*, respectively) shows that these spectra are almost identical due to the fact that the CaF_2 film was as thin as several nanometers. As a result, the RS spectrum of the CaF_2 film overlapped the big signal from the Si substrate. In the Raman spectra of thicker epitaxial CaF_2 films, we also observed weakly resolved peaks at 330 cm^{-1} and 680 cm^{-1}, which are the characteristic lines of bulk crystalline CaF_2 [6]. Spectrum *3*, registered in the electron irradiated area, exhibited substantial differences. This spectrum shows that the 520 cm^{-1} peak intensity, due to the Si substrate, was lower than that in spectra *1* and *2* (see the inset in Fig. 3). This result shows that an absorbing film was formed in the irradiated area of the sample. Also, the peaks at ~346 cm^{-1}, ~388 cm^{-1} and ~418 cm^{-1}, absent in both the initial Si substrate spectrum and the CaF_2 film spectrum, were observed in spectrum *3*.

The phonon-mode frequencies in our sample inside the irradiation spot, theoretical phonon-mode frequencies in $CaSi_2$ (space group $R\overline{3}m$) and the experimental data for bulk $CaSi_2$ crystals [7] are summarized in Table 1.

As it is evident from Table 1, the positions of the Raman peaks registered on the surface area inside the irradiated spot are in a good agreement with the theoretical and experimental data obtained in [7] for bulk $CaSi_2$ crystals. In paper [2], the temperature dependences for the synthesis of calcium silicide from thin Ca films deposited onto Si(1 1 1) substrates were studied. It was shown that the minimum temperature required for the formation of $CaSi_2$ films was about 350 °C. In our experiment, the substrate temperature was 550 °C. As it was not atomic Ca, but molecular CaF_2 that was deposited onto the substrate, additional factors causing the dissociation of CaF_2 molecules with the release of Ca and the fluorine desorption from the surface are necessary. Since the observed effect was manifested only inside the irradiation spot, it is the high-energy electrons that were such a factor. Under the conditions of our experiments characterized by the irradiated area and emission current, the maximum energy transferred to the Ca atom did not exceed 1.1 eV for the used energy of rapid electrons, whereas, for the F atom, the maximum energy transferred during the elastic interaction was 2.3 eV. The binding energy in CaF_2 is 8.3 eV. Therefore, the dissociation of CaF_2 molecules and the formation of $CaSi_2$ at the interface with the silicon substrate are determined by other mechanisms. Such other mechanism can be a high ionization level of CaF_2 under electron-beam irradiation. For the used electron-beam parameters, the energy per unit path length transferred from the rapid electrons to the electrons in target atoms was 6.5 keV/μm [8]. It is low-energy electronic excitations that are known to be contributing to the formation of stable point defects and their clusters in alkali-halide crystal lattices. [5].

It is known that the electron-beam irradiation of epitaxial CaF_2 films with the beam parameters close to the present data leads to the surface morphology modification with the appearance of pore-shaped macrodefects. The sizes of defects and their shape, and distribution in the surface layer depend on the irradiation dose [9,10]. What we did in the present studies was revealing the rapid electron beam action effects on Si during the molecular-beam epitaxy of CaF_2. It is shown that the electron beam action leads to the $CaSi_2$ layer synthesis at the interface of the silicon substrate and the epitaxially growing CaF_2 film.

Among the silicides that can be epitaxially grown on silicon, much attention has recently been paid to $CaSi_2$ because it has a unique layered crystalline structure consisting of hexagonal Si bilayers and trigonal Ca monolayers. Recently, it has been found that the silicon layers intercalated in $CaSi_2$ exhibit the electronic properties similar to those inherent to graphene [11]. An advantage of the method in the present research for the synthesis of epitaxial $CaSi_2$ films is a possibility of the local production of thin $CaSi_2$ films by monitoring the $CaSi_2$ film thickness at the accuracy to a monolayer by changing the irradiation dose and the initial Si layer thickness. Also, the present method allows encapsulating 2D $CaSi_2$ structures with CaF_2 dielectric films in one technological cycle. Since the lattice constants of Si, CaF_2 and $CaSi_2$ are practically similar, the radiation-stimulated growth of $CaSi_2$ allows one to

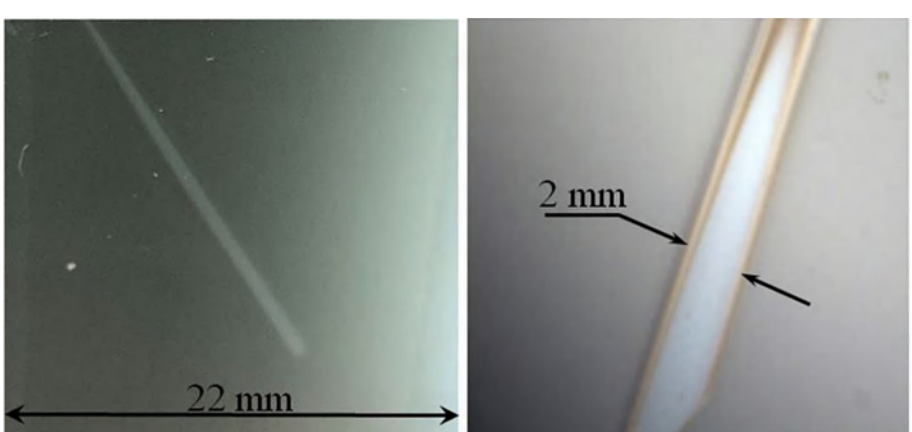

Fig. 1. Image of the electron beam action track on the CaF_2 surface (images were taken at different magnifications).

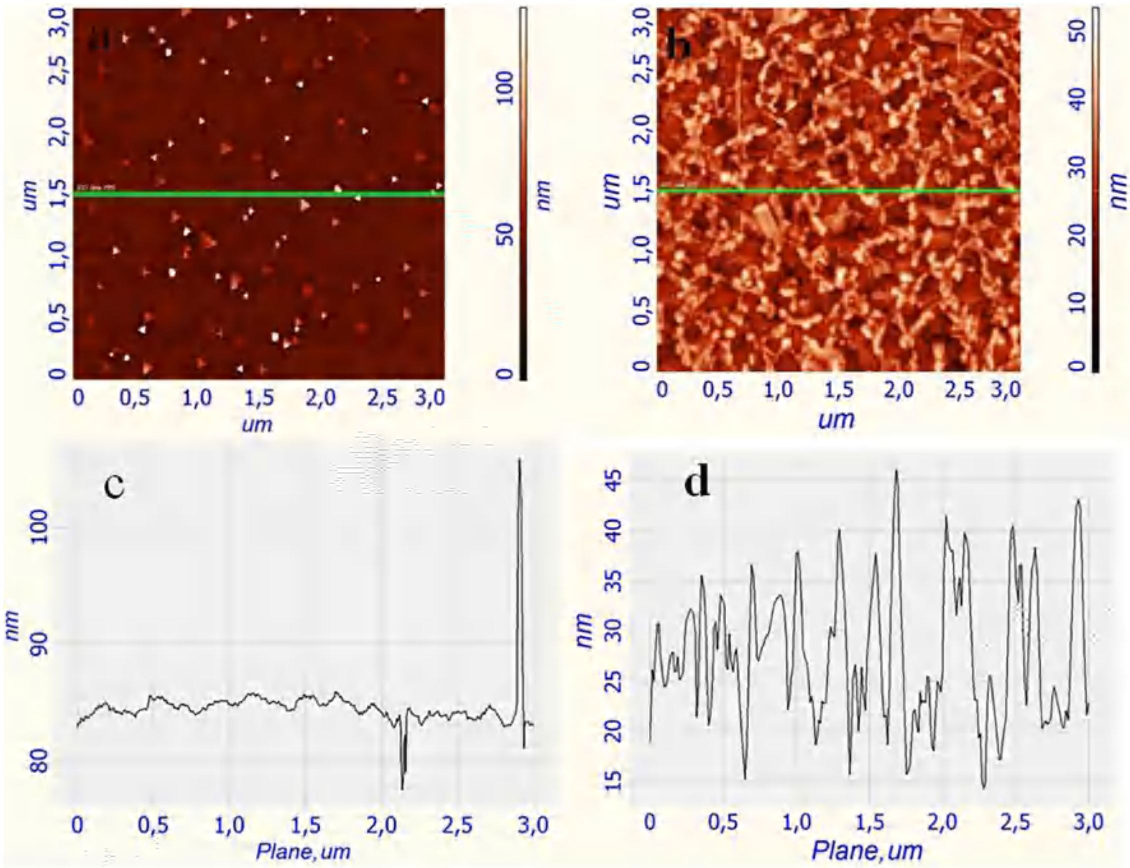

Fig. 2. (a) AFM image of the unirradiated CaF_2 film surface and (c) the relief of this surface along the line shown in Fig. (a); (b) AFM image of the irradiated part of film surface and (d) the relief along the line shown in Fig. (b).

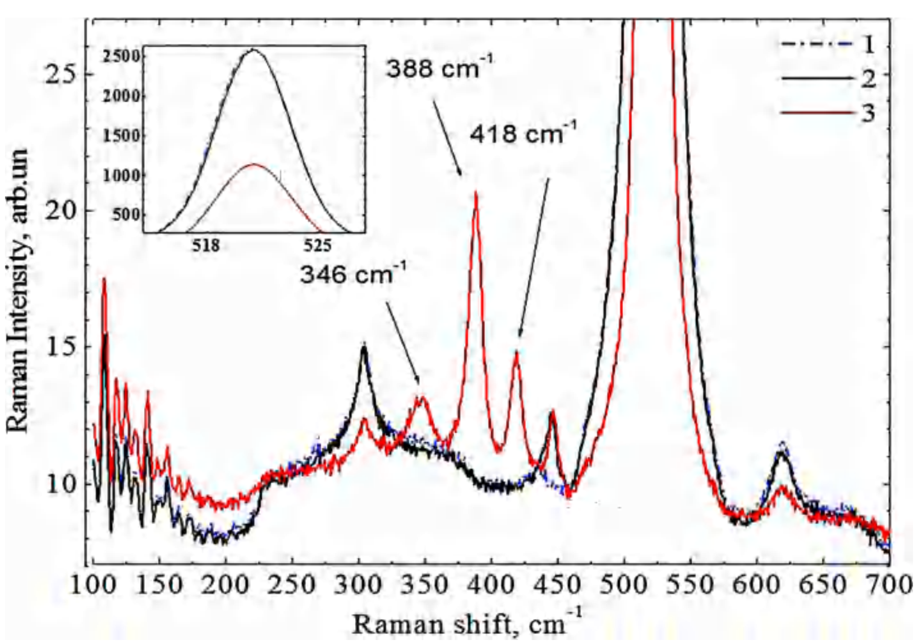

Fig. 3. Raman spectra: 1 – Si substrate, 2 – CaF_2 film grown on the Si substrate without electron irradiation, 3 – spectrum taken from the area exposed to the electron-beam irradiation during the CaF_2 film growth.

Table 1
Phonon-mode frequencies in $R\bar{3}m$ polymorphs of $CaSi_2$

Mode symmetry and participating atoms	Phonon-mode frequencies, cm^{-1} (our experiment)	Phonon-mode frequencies for $CaSi_2$, cm^{-1} (experiment) [7]	Phonon-mode frequencies for $CaSi_2$, cm^{-1} (theory) [7]
A_{1g}(Si2)	346	349	343
A_{1g}(Si)	388	393	371
E_g(Si)	418	427	429

obtain high-quality epitaxial multilayer structures prepared from these compounds.

The determination of dominating $CaSi_2$ formation mechanisms under the influence of high-energy electrons requires additional experiments and analyses, which are currently underway.

CRediT authorship contribution statement

Aleksey V. Kacyuba: Conceptualization, Methodology, Investigation, Writing - original draft, Visualization. **Anatoly V. Dvurechenskii:** Conceptualization, Methodology, Writing - review & editing, Supervision, Funding acquisition. **Gennady N. Kamaev:** Conceptualization, Methodology, Data curation, Visualization, Writing - original draft. **Vladimir A. Volodin:** Investigation, Validation. **Aleksey Y. Krupin:** Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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