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Electron–Beam Radiation Effects in the Multilayer Structures Grown by Periodical Deposition of Si and CaF_2 on Si (111) †

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Abstract: The formation of $CaSi_2$ films on Si (111) by molecular-beam epitaxy (MBE) of CaF_2 under fast electron beam irradiation was investigated. The method of a high planarity $CaSi_2$ film synthesis assisted by electron-beam-irradiation was developed. We combine two approaches to reduce the film roughness, a post-growth electron irradiation and co-deposition of additional Si during CaF_2 growth. Application of solid phase epitaxy technique at the initial stage of film growth allows us to reduce surface roughness down to 1–2 nm.

Keywords: crystal structure; nanostructures; electron-beam radiation; molecular-beam epitaxy; calcium compounds; silicon

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1. Introduction

The CaF_2 and $CaSi_2$ materials have a slight difference in the parameters of the crystal lattice with silicon [1], which allows the epitaxial growth of the multilayer heterostructures based on these materials on silicon substrates. The possibility of obtaining multilayer structures with conducting $CaSi_2$ layers separated by a CaF_2 dielectric can be used for development of future nanoelectronic devices. At this moment, there are quite a few works devoted to the study of this system. Calcium silicide films obtained on Si (111) and Si (001) surfaces can have different phase compositions. It was found that, with a simultaneous deposition of Ca and Si on a hot substrate with increasing temperature, there is a tendency to form a phase with the highest silicon content, i.e., Ca_2Si-CaSi-$CaSi_2$. It was established that Ca_2Si films are narrow-band semiconductor materials, and CaSi and $CaSi_2$ films are semimetals. On the base of these silicides, approaches to obtaining materials with various functional properties are being developed [1–13]. Recently we proposed a method for $CaSi_2$ synthesis using electron beam irradiation during the growth of CaF_2 layers with molecular beam epitaxy (MBE) [14–16]. The method is based on the electron-beam-stimulated decomposition of CaF_2 into Ca and F [17] in the surface layers. Fluorine is desorbed from the surface, and remaining calcium atoms bind chemically with silicon atoms, which come from the Si substrate at sufficiently high temperatures (>300 °C) under electron irradiation [15]. Calcium silicide produced in this way is a nonhomogeneous three-dimensional material representing a triangular network of elongated crystallites protruding from the surface of the CaF_2 film by tens of nanometers. These crystallites are oriented along directions {110} and have a characteristic length of ~1 μm. The situation is similar to $CaSi_2$ films grown by Braungart and Sigmund [18], who have exposed a heated Si substrate to Ca vapor. We recently found a way to produce more homogeneous $CaSi_2$ films [19]. The idea is to introduce additional intermediate silicon layers into the growing CaF_2 film. The preliminary results show that under certain conditions the $CaSi_2$ film growth under simultaneous e-beam irradiation can occur in a layer-by-layer mode. In addition, we have tested another opportunity to increase the $CaSi_2$ film homogeneity by post-growth electron irradiation after CaF_2 deposition [20]. So far, however, there has been no notable success in this direction. Both type of structures, obtained with electron irradiation during CaF_2 epitaxial growth and after CaF_2 film formation, revealed the problem of high surface roughness. The average surface roughness in the irradiated region is 6–8 nm for films irradiated during CaF_2 film growth and 25–30 nm for films formed with post-growth irradiation (the values are given for the same thickness of the deposited film, irradiation dose and substrate temperature). These data indicate that the considered methods do not provide the necessary planarity of $CaSi_2$ epitaxial films.

The purpose of this work is to develop the method of a high planarity $CaSi_2$ film synthesis assisted by electron-beam-irradiation. We combine two approaches to reduce the film roughness, a post-growth electron irradiation and co-deposition of additional Si during CaF_2 growth. Also, following to Morar and Wittmer [1,21] we apply the technique of solid phase epitaxy with subsequent annealing at the initial stage of film growth which allows us to reduce surface roughness down to 1–2 nm.

2. Materials and Methods

The experiments were carried out on the "Katun-100" molecular-beam epitaxy (MBE) unit under ultrahigh vacuum conditions equipped with a CaF_2 effusion source with a graphite crucible. Films were grown on Si(111) substrate. For all samples, a standard procedure of a double surface cleaning is carried out before the growth [19]. The crystal structure of the deposited layers was studied by Rapid High-Energy Electron Diffraction (RHEED) method. Electron beam irradiation was made with the accelerating voltage of 20 Kev and the current density of 50 $\mu A/cm^2$. The beam incidence angle was 4°. The same electron-beam was used for modification of properties of growing film. The epitaxial CaF_2 film growth was carried out at the deposition rate of 0.3 Å/s and consisted of two steps. At the first step, a 2 nm thick CaF_2 layer was deposited at the room temperature. Then this amorphous layer was crystallized by annealing at 700 °C. The crystallization process was controlled by RHEED. At the second step, a multilayer structure containing 10 Si layers with thickness of one nm separated by two nm thick CaF_2 layers was grown at 550 °C. At the top of this structure, a two nm thick CaF_2 layer was deposited. At the next step, structures were subjected to post-growth electron irradiation with different exposure times (10, 20 and 60 min). During post-growth irradiation, electron beam did not shift, that means, the same area was irradiated as during growth. The thickness of grown films was controlled by ellipsometry. The phase composition was determined on the base of the Raman light scattering method. Surface morphology was studied by atomic force microscopy (AFM) and scanning electron microscopy (SEM). To highlight the effect of silicon co-deposition on the resulting smoothing effect of the film, we carried out a test experiment, where we grew the film under the same growth conditions, but without silicon co-deposition. The conductivity and magnetoresistance were measured on the strips as a function of the post-growth electron irradiation time. Contacts for transport measurements were created by soldering of silver wires using indium solder. The temperature dependences of the conductivity was measured using an SR850 synchronous amplifier in a transport helium Dewar vessel. The magnetoresistance was measured in a magnetic field up to 4 T.

3. Results and Discussion

RHEED studies confirm that the annealing at 700 °C leads to recrystallization of CaF_2 film deposited at room temperature (Figure 1a,b). RHEED data demonstrate that further growth of multilayer structure at 550 °C under electron irradiation results in the formation of crystalline film (Figure 1c). Post-growth irradiation during 10 and 20 min does not induce any changes in RHEED images, while longer electron exposure leads to additional RHEED reflexes, indicating the change in surface reconstruction (Figure 1d).

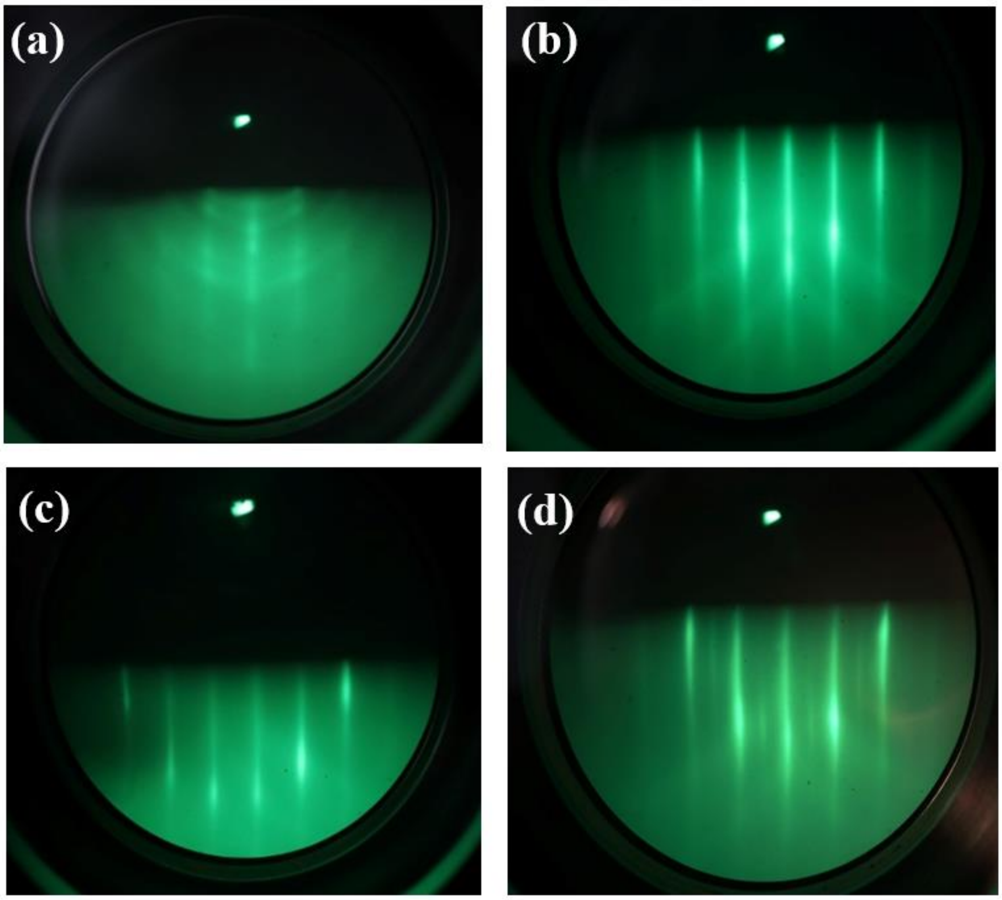

Figure 1. Top panels—RHEED images of surface of a 2 nm thick CaF_2 film deposited at room temperature, (**a**) as-grown 2 nm thick CaF_2 film, (**b**) after annealing at 700 °C. Bottom panels—RHEED images of multilayer structure with additional 2 nm thick Si cap layer (**c**) just after growth, (**d**) after 60 min post-growth electron irradiation.

AFM and SEM study of the first type structure show that in chosen growth conditions (co-deposition of additional Si during CaF_2 growth under electron irradiation) the flat islands of $CaSi_2$ in the form of hexagons are formed instead of elongated crystallites. The characteristic size of island is ~300–400 nm. The post growth irradiation leads to an increase in the number and size of islands. Figure 2 demonstrates SEM images of surface of as-grown film and after post-growth irradiation. It is clearly seen that the increasing of irradiation dose leads to overlapping of islands and a tendency to form a continuous film. However, if the exposure time is too long, the surface relief changes, the film becomes less planar due to the appearance of three-dimensional ripples. For example, after 60 min irradiation the average surface roughness consists of 6 nm. Results of AFM studies (Figure 3) show that the best planarity (lowest surface roughness ≈1 nm) is obtained for films with 20-min electron irradiation.

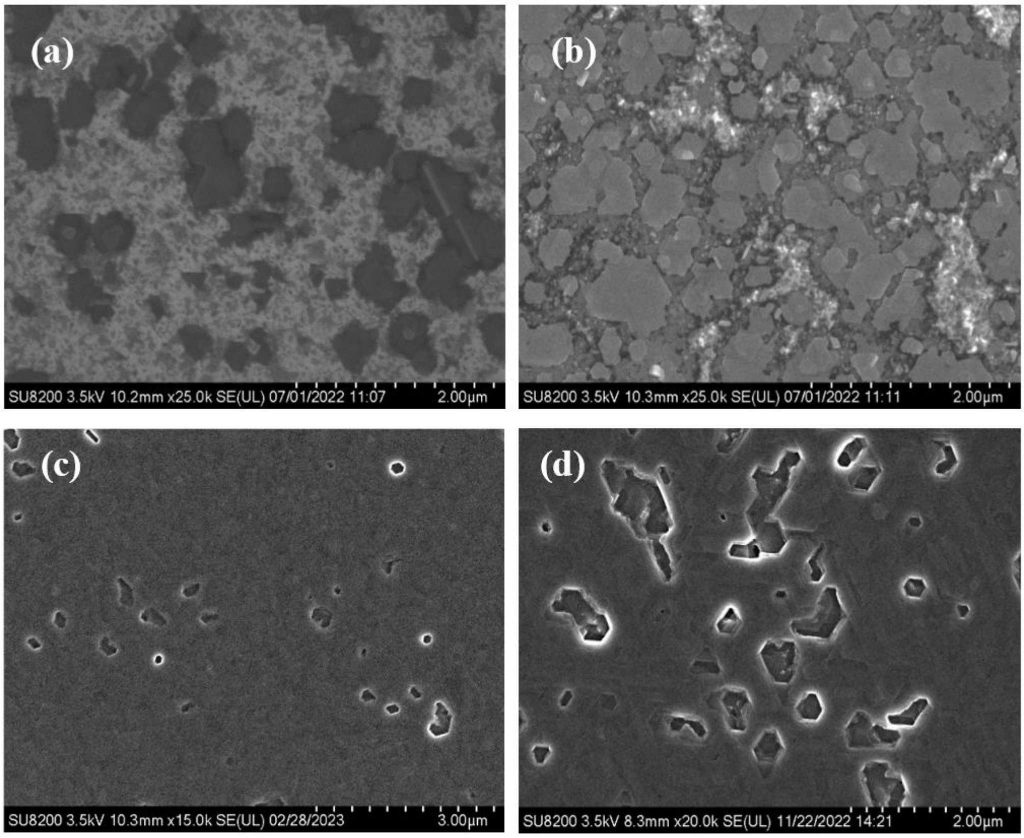

Figure 2. SEM images of surface of (**a**) as-grown CaF_2 film, (**b**) after 10 min post-growth electron irradiation, (**c**) after 20 min post-growth electron irradiation, (**d**) after 60 min post-growth electron irradiation.

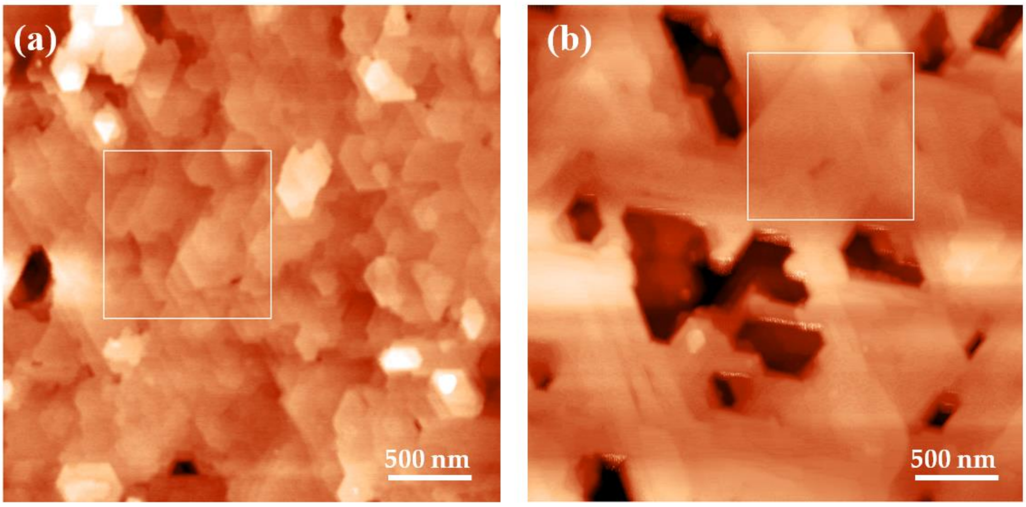

Figure 3. AFM images of the film synthesized with post-growth electron irradiation during 20 min (**a**) and with a 60 min post-growth electron irradiation (**b**). Height parameters in selected areas (white squares 1 μm × 1 μm): root mean square height Sq ≈ 1.07 nm for (**a**) and Sq ≈ 7.7 nm for (**b**); surface skewness Ssk ≈ −0.007 for (**a**) and Ssk ≈ 0.51 for (**b**); coefficient of kurtosis Sku ≈ −0.42 for (**a**) and Sku ≈ 0.17 for (**b**); arithmetic mean height Sa ≈ 0.87 nm for (**a**) and Sa ≈ 6.1 nm for (**b**). If one consider the whole area of the images, the parameters are as follows: Sq ≈ 2.1 nm for (**a**) and Sq ≈ 17.8 nm for (**b**); Ssk ≈ 0.27 for (**a**) and Ssk ≈ −1.67 for (**b**); Sku ≈ 5.21 for (**a**) and Sku ≈ 6.5 for (**b**); Sa ≈ 1.4 nm for (**a**) and Sa ≈ 11.7 nm for (**b**).

Test experiment, where we grew the film in the same growth conditions but without Si co-deposition, demonstrates that the exclusion of Si co-deposition results in worsening of the film planarity. For the film obtained after a 20 min post-growth electron irradiation the average surface roughness increases up to 5–6 nm. This result is in agreement with existing literature data on $CaSi_2$ growth by calcium deposition on Si substrates. Vogg et al. wrote in the work [22] that by increasing the calcium flux and lowering the substrate temperature one can achieve selective growth in the preferential direction, and essentially switch from two-dimensional to three-dimensional growth. In our case, calcium is supplied in the process of radiolysis of CaF_2 film, and silicon is supplied by diffusion from the substrate (under conditions without additional silicon deposition), so the situation is similar to the growth in Vogg conditions with large calcium flux, i.e., a three-dimensional growth mode is realized. If we deposit additional silicon, we change the ratio of calcium and silicon, in fact, reduce the effective calcium flux and change the growth mode to a two-dimensional one, which is observed in our experiments.

Raman measurements of samples in the irradiated regions give the spectra with three peaks typical of $CaSi_2$ layers obtained by electron irradiation during CaF_2 MBE ($CaSi_2$ polymorph 3R) [16]. In addition, the longer the exposure time, the higher the intensity of the peaks. Earlier we have observed such type spectra on $CaSi_2$ films synthesized under electron irradiation, but without additional peak at 430 cm^{-1}. Since the appearance of this peak correlates with a presence of boundaries between $CaSi_2$ regions and residual inclusions CaF_2, we attribute it to scattering at the boundaries of $CaSi_2$ formations.

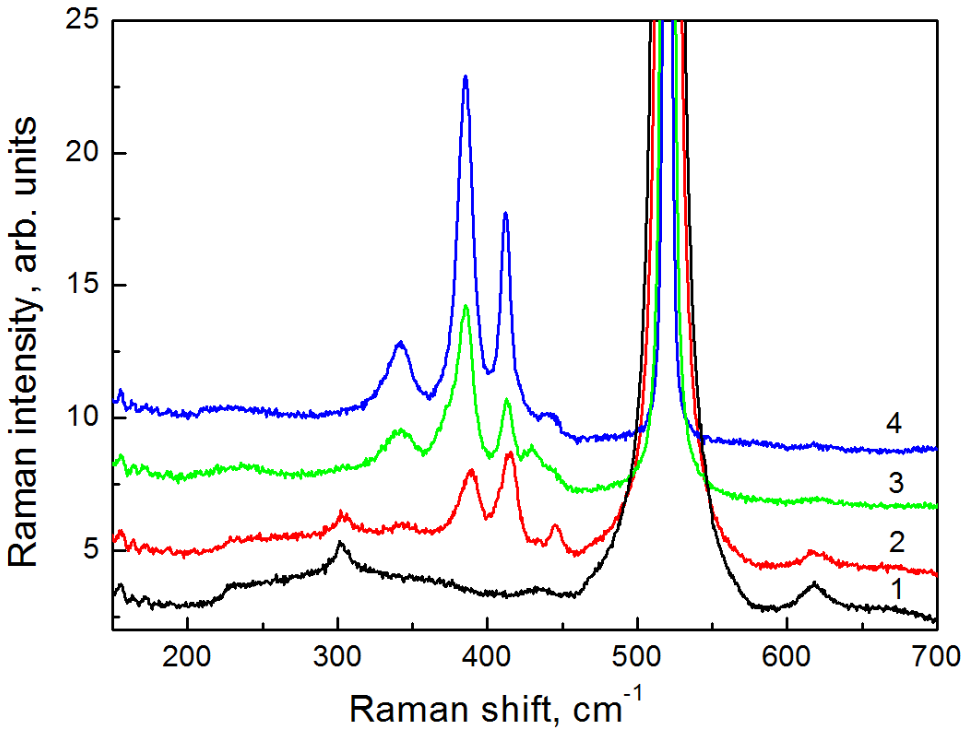

Figure 4. Raman spectra of the films synthesized with different type processing: (2) post-growth electron irradiation during 20 min, (3) post-growth electron irradiation during 10 min, (4) post-growth electron irradiation during 60 min. Spectrum (1) obtained on Si (111) substrate.

Figure 5 demonstrates a temperature dependence of conductance for three films grown under the same growth conditions but with different time of post-growth irradiation. The increase of the irradiation time from 10 to 60 min leads to an increase of the film conductivity. It corresponds to increase of the island lateral size and their overlapping observed in SEM study (Figure 1). Magnetoresistance (MR) data for these films are shown in the inset to Figure 5. Non-monotonic MR behavior with a transition from negative to positive MR was observed for all samples, with the larger contribution of positive MR for the larger irradiation time. The negative MR is usually associated with suppression of weak localization typical of the disordered electronic systems with low mobility. Positive MR is the result of the Lorentz deflection of the carriers [23] and also depends on the carrier mobility: $R(B) - R(B = 0) \sim 1 + (\mu B)^2$ (Kohler's rule [24]). This allows to estimate the mobility μ, which turned out to be 158 cm^2/Vs for sample 1230 cm^2/Vs for sample 2 and 330 cm^2/Vs for sample 3. These results support the structural data and indicate that the increase of irradiation time makes the samples more metallic.

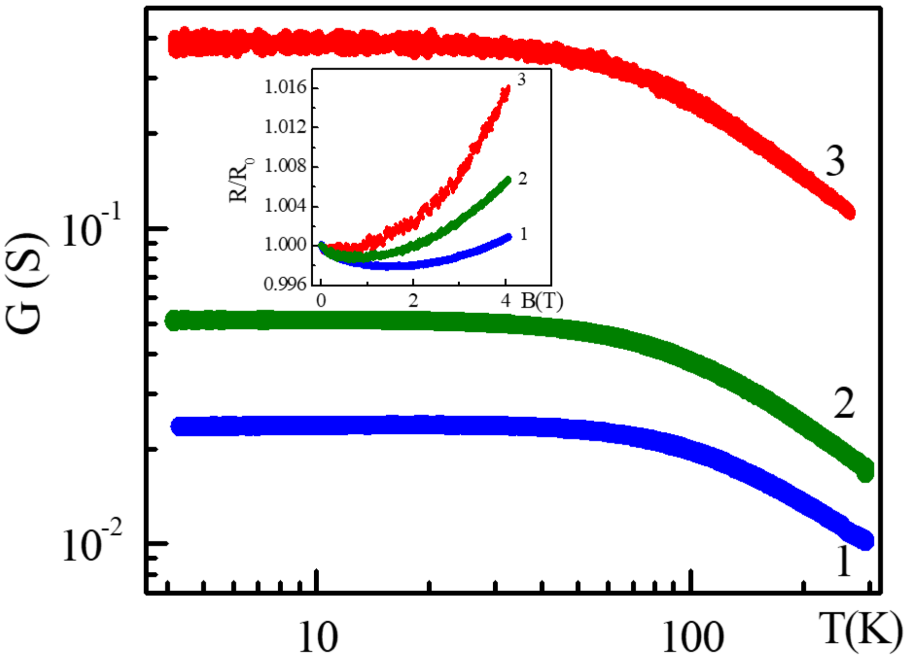

Figure 5. Temperature dependence of conductivity G for three films synthesized with different post-growth irradiation time (1—10 min, 2—20 min, and 3—60 min). Inset demonstrates the magnetoresistance of these films.

4. Conclusions

The study of structural properties of grown samples confirm that the developed approach can solve the problem of high surface roughness. The use of the solid-phase epitaxy method at the initial growth stage makes it possible to form a thin Ca-enriched layer under electron irradiation. Supplying additional Si to this surface one can form $CaSi_2$ two-dimensional islands parallel to (111)-surface of substrate. The post growth electron irradiation leads to an increase in the number and size of islands. The increasing of irradiation dose results in overlapping of islands and a tendency to form a continuous film. However, if the exposure time is too long, the surface relief changes, the film becomes less planar due to the appearance of three-dimensional ripples. The best planarity (lowest surface roughness) obtained after 20-min post growth irradiation. The conductivity for $CaSi_2$ synthesized films was found to increase with increasing time of post-growth electron irradiation.

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