



**PECULIARITIES OF EPITAXIAL DIFFUSION CoSi_2 FILMS GROWN ON
THE SURFACE OF FLUORITE**

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ANNOTATION

The paper presents the results of analysis of epitaxial film $\text{CoSi}_2/\text{Si}/\text{CaF}_2(100)$, grown by the method of molecular-beam epitaxy. It has been proven that under certain thermal treatment conditions so-called epitaxial silicides are formed on the crystal structure, which can play the role of conductive layers or metal coatings.

The obtained data allow to draw conclusions about the film morphology and diffusion character in the CoSi_2 layer.

Key words

epitaxy, molecular-beam epitaxy, epitaxial film, solid-phase epitaxy, thermal cleaning, temperature, film, disilicide, thickness, intensity, Auger-signal.

Introduction

MRE technology is now widely used to create new semiconductor combinations and multi-layered compositions based on layers of elementary (Si, Ge) and multi-component (A_3B_5 and A_2B_6 , their triple and quadruple compounds) semiconductor materials. This ensures an improvement in the technical parameters of microelectronics devices, making it possible to manufacture both silicon IC and associated optoelectronic, detector and acousto-electronic devices on a single substrate that expands the functionality of electronic devices. Practical implementation of such structures will allow to manufacture on their basis a number of theoretically predicted earlier devices of integrated microelectronics, as well as a number of new devices. One of the promising developments in this field is the technology «silicon-on-dielectric» (SOD), which uses a layer on dielectric (sapphire, SiO_2 Si_3N_4) substrate or intermediate dielectric layer. The use of SOD -

structures in combination with the structural and technological features of IC provides effective opportunities to improve the most important electrophysical and techno-economic parameters of modern CMOP IC, including, improved indicators of energy consumption, speed and radiation resistance.

Relevance of the work is due to the fact that there are currently a number of unresolved issues, both in terms of epitaxial growth technology and in the understanding of the physics of growth and the detector of ionizing radiation based on epitaxial heterostructures $\text{CoSi}_2\text{-CaF}_2\text{-Si}$, the application of which opens up new possibilities for creating instrument structures with unique technical characteristics.

The development of molecular ray epitaxy (MRE) technology has led to the possibility of creating monolithic epitaxial heterostructures that combine semiconductors, metal and dielectric [1,2]. Such structures are a promising basis for the implementation of new devices for microelectronics, functional electronics and integral optics. Currently known experimental models of transistors and integrated circuits, formed on silicon heterostructures $\text{CoSi}_2\text{-CaF}_2\text{-Si}$ or $\text{NiS}_2\text{-CaF}_2\text{-Si}$, AlGaAs-Si , $\text{Si-GaF}_2\text{-Si}$ [2]. There are also attempts to create optoelectronic devices based on heterostructures of A_3B_5 and A_2B_6 compounds on Si or $\text{CaF}_2\text{-Si}$ [3].

The possibility of using single-crystalline alkaline-earth fluoride as substrates for the epitaxial growth of a number of compounds has recently attracted the attention of researchers. This is due, among other things, to the parameters of their crystalline structure, which allow epitaxy of the main semiconductor materials: silicon, germanium, arsenide - halium to be carried out on said compounds. In addition, as dielectrics, they can be insulating substrates when using semiconductor technology. Finally, due to the optical and luminescent properties combined with the listed advantages, these materials can be used in optoelectronics.

Successful attempts of epitaxial growth on substrates BaF_2 and SaF_2 . Barium fluoride substrates were carried out epitaxy of compounds of type A_4B_6 [1]. In [2] describes for the first time the epitaxial growth of cobalt silicon and disilicide on the surface of CaF_2 (100). It should be noted that CoSi_2 cobalt disilicide has a cubic fluorite lattice with a constant lattice close to silicon and calcium fluoride. It has metallic properties. Thus, silicon, CaF_2 and CoSi_2 represent a unique set of "semiconductor-dielectric-metal" with close structural parameters, allowing to realize their epitaxial growth on each other.

Methods of research

In this paper the results of analysis of epitaxial film $\text{CoSi}_2/\text{Si}/\text{CaF}_2$ (100), grown by the method of molecular ray epitaxy (MRE) fig.1 are given. The obtained data allow to draw conclusions about the film morphology and diffusion character in the CoSi_2 layer.

The CoSi_2 film on CaF_2 (100) was grown by molecular ray epitaxy in a supervacuum plant with a basic vacuum of 10^{-8} Pa. The molecular fluxes of cobalt and silicon were formed by electron beam evaporators. On the surface of the CaF_2 substrate after thermal cleaning by heating in vacuum for 30 min. 300°C was deposited a thin 50 \AA thick silicon buffer layer.

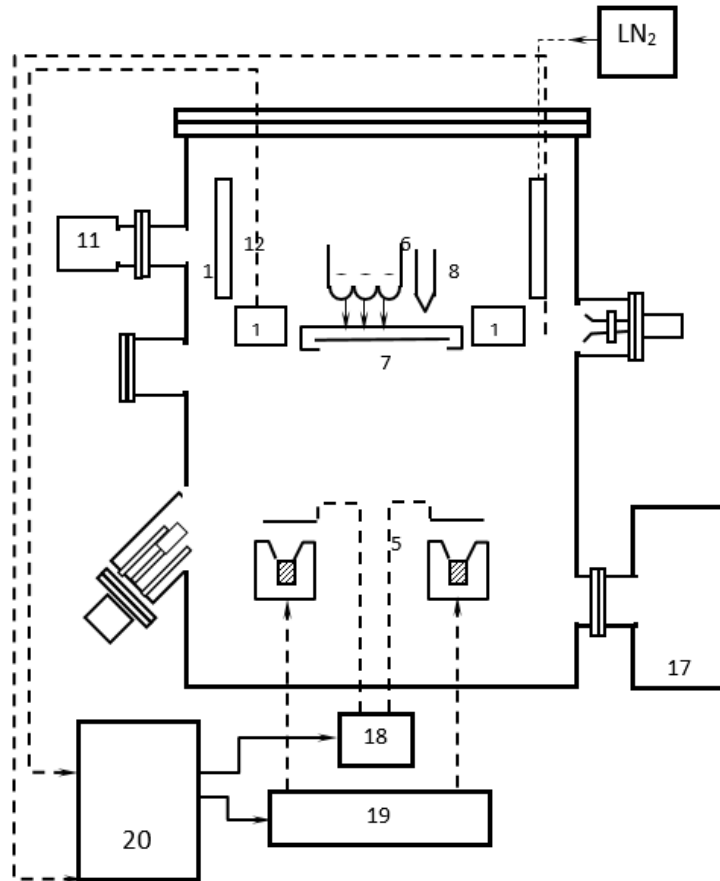


Fig. 1. MLT-growth chamber 1: 2.3 - ERE, 4 - effusion source, 5 - sample, 6 - manipulator, 7 - heater, 8 - thermocouple, 9 - electronic gun RED, 10 - fluorescent screen, 11 - quadruple gas analyzer, 12 - cryopanel, 13.14 - quartz rate of deposition sensors, 15.16 - flaps, 17 - ion pump, 18 - pneumatic valve control, 19 - ELI power supply, 20 - ECM Personal Computer.

Deposition was made on the substrate at room temperature, then the temperature rose 700°C . At the same time there was a solid phase epitaxy, which

resulted in the formation of a film of mono-crystalline silicon on the surface of the fluorite. This layer served as a buffer for the subsequent cobalt disilicide epitaxy.

CoSi epitaxy was carried out by simultaneous deposition of silicon and cobalt from two sources with a flow ratio of 2:1. The temperature of the substrate at the epitaxy was 650°C. With rapid electron diffraction, the reflection showed an epitaxial growth of the silicide layer and a buffer layer on the substrate. The thickness of CoSi epitaxial film was 300 Å.

Results and Discussion

The CoSi₂/Si/CaF₂ (100) epitaxial film has been investigated by Auger-electron spectroscopy. The auger profile of the specimen is shown in Figure 2.

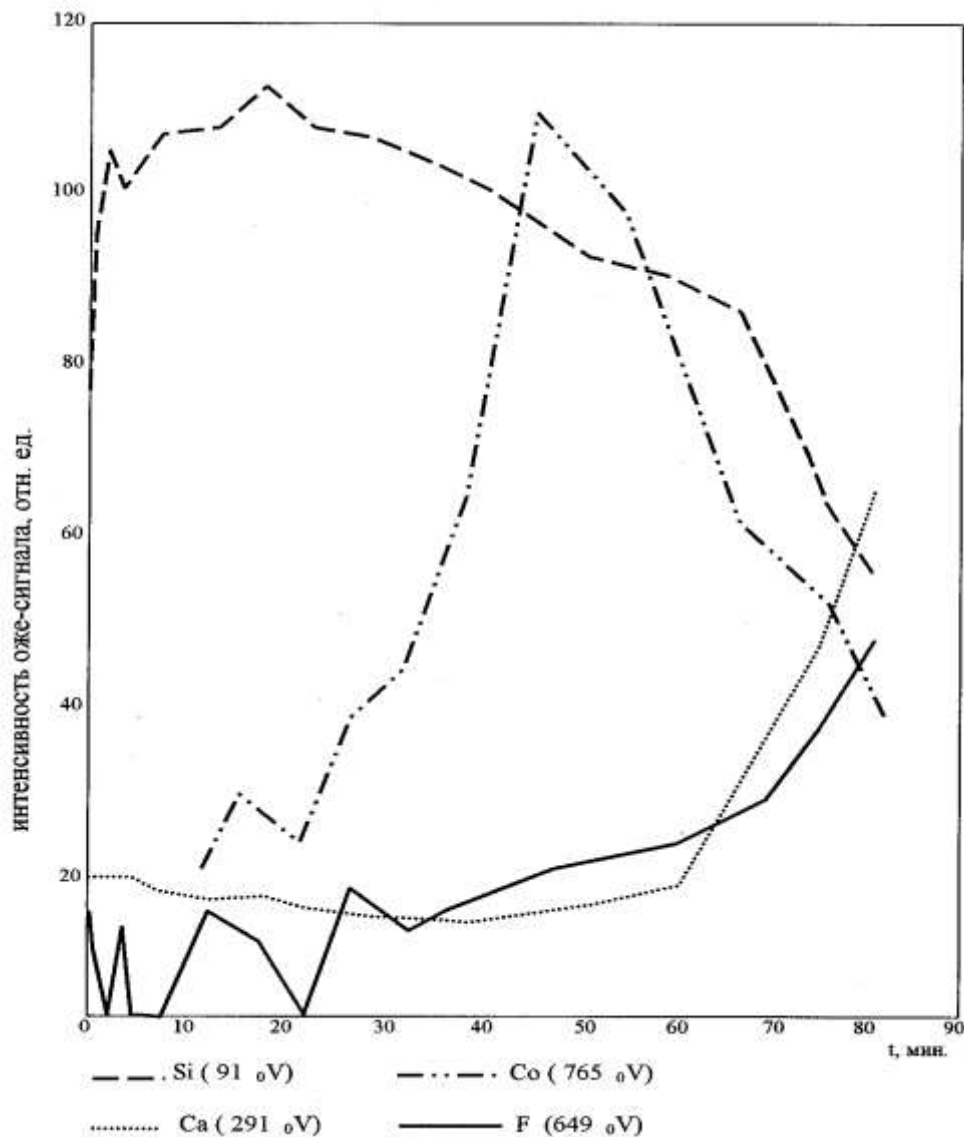


Fig.2. CoSi₂/CaF₂ (100).

There are no cobalt atoms in the near-surface region, while the silicon signal has a high intensity. At some depth, a signal from cobalt appears, the intensity of



which increases dramatically with depth. When approaching the substrate, the intensity of the silicon and cobalt signals decreases simultaneously while increasing the Auger signals of calcium and fluorine.

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Thus, there is a layer of silicon on the film surface, while cobalt silicide itself is present at some depth. It should be noted that this effect cannot be explained by film growth conditions, as the film was formed by simultaneous deposition of cobalt and silicon, with the molecular fluxes being kept constant during the growth process.

At the same time, the presence of pure silicon on CoSi_2 and CaF_2 films formed on silicon substrates was previously observed [3,4]. At present, the reasons for this effect are not fully understood. In terms of surface thermodynamics, the observed phenomenon can be explained by the fact that the free energy of the silicon surface is less than the energy of the nickel and cobalt disilicides. Thus, the process of forming a silicide layer on the surface of the film can be energetically beneficial, as it reduces the free energy of the system.

However, thermodynamic analysis does not provide information on the mechanism of formation of the surface layer of silicon. The authors [3] believe that for NiSi_2/Si there is diffusion of nickel atoms from the surface to the boundary of the partition, which should lead to the formation of a layer depleted with nickel on the surface. In [5] it is allowed to diffuse silicon atoms through a layer of silicide to the film surface.

This paper is the first to describe a similar effect observed in $\text{CoSi}_2/\text{Si}/\text{CaF}_2$ (100) film. It is assumed that the layer of pure silicon observed in our case on the surface of the sample cannot be caused by the diffusion of silicon atoms from the depth, since it is impossible to get silicon from the substrate. Thus, it is obvious that a layer of silicon on the surface of the cobalt and nickel disilicides is formed by diffusion of metal atoms from the surface to the boundary of the film-substrate section [6-7].

OEC film spectra of $\text{CoSi}_2/\text{Si}/\text{CaF}_2$ (100) also show Ca and F₂ signals on the sample surface. This effect appears to be explained by the fact that the CoSi_2 film on the CaF_2 substrate is growing along the island mechanism due to the greater free energy of the CoSi_2 (100) surface compared to CaF_2 (100)/ γ CoSi_2 (100)=4130 erg.cm², γ CaF_2 (100) = 530erg. Due to this the Auger-analysis revealed the presence of atoms Ca and F on the surface [8-10]. In relation to the amplitude of the



Auger signals of these atoms on the sample surface and near the boundary of the CoSi₂/CaF₂ partition, one can judge the morphology of the surface, in particular to determine the extent of the CoSi₂ film coating:

$$\theta = \left(1 - \frac{S_{\text{CaF}_2}}{S_n} \right) = \left(1 - \frac{I_s}{I_i} \right); \quad (1)$$

where: S_{CaF_2} is the cumulative area of the CaF₂ substrate captured by the electron beam; S_n is the area of the electron beam; I_s - the intensity of the Auger - the Ca signal on the surface of the sample, relative unit; I_i - Auger-Ca signal intensity near the CoSi₂/CaF₂ partition boundary.

The Auger-signal intensity should be used for calcium rather than fluorine because the fluorine signal intensity (see fig. 2) is very irregular in the near-surface region. It can be assumed that there is an electron-stimulated desorption under the influence of an electron Auger analyzer.

The measurement of the calcium signal intensity at the boundary of the substrate film partition was complicated by the charging of the sample. Therefore, the signal intensity value was not used at the boundary of the partition, but near it. The ratio I_s / I_i was 0.3. So in our case, the coverage rate is $\theta = 70\%$.

Conclusion

The CoSi₂/Si/CaF₂ (100) film has been examined by Auger-electron spectroscopy. Dependence of film composition on depth and morphology of cobalt silicide film has been studied. Insulated character of CoSi₂ film on fluorite has been determined. The degree of substrate coating with film is estimated at 70%.

The presence of epitaxial film in the near-surface area of the layer enriched with silicon was revealed. This is likely due to the diffusion of cobalt atoms from the surface to the boundary of the "silicide-fluorite" section, which reduces the free energy of the film surface.

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