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Electronic Structure of Single-Crystal CaF_2(111) with Nanoscale Phases of Ca and Si

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Abstract

The impact of Ca and Si nano-scale structures on parameters and density of states of single-crystalline CaF_2(111) was studied. It was shown that at low concentration of ions of Ar^+ ($D \leq 5 \times 10^{15}$ cm^{-2}) one witnesses formation of nanoscale phases on CaF_2 surface. It was revealed that these phases lead to narrowing of the forbidden band E_g between the phases by 4 - 4.5 eV. At higher concentrations ($D \approx 6 \times 10^{16}$ cm^{-2}) the surface completely is covered by Ca atoms. It was shown that deposition of $\theta = 10$ thick Si single layer on CaF_2 surface manifests island picture. The concentration of Ca and Si nano-scale phases on the surface of CaF_2 and the band gap of the phases were investigated as a function of ($h\nu$) of passing light. Nano-scale phases and nano-scale films of Ca were obtained by using the technique of bombardment with ions of Ar^+ of CaF_2 surface. Formation of nano-scale phases were accompanied by change in the composition and structure of CaF_2 zones located between the phases. These changes led to narrowing of the forbidden band of CaF_2 down to 7.5 - 8 eV. The concentration of Ca and Si nano-scale phases on the surface of CaF_2 and the band gap of the phases were investigated as a function of ($h\nu$) of passing light.

Keywords

Nano-Scale, Band Gap, Hetero-Structures, Surface, Bombardment

1. Introduction

The creation of electronic devices of new generation (microwave nanotransistors, ultra-large integrated circuits, optical resistors, solar cells, etc.) is mainly determined by the production of new materials (nanocrystals, nanofilms, nanomaterials) and nano-layered structures with desired physical properties. In this regard, one of the main problems of modern nanoelectronics is to obtain homogeneous silicon spatial quantum-dimensional structures on the surface of semiconductors and dielectric films.

Special significance is the phenomenon of self-organized formation of nanostructures (islands)—*i.e.* spontaneous formation of a large number of nanostructures due to the formation of the type "matrix-adsorbed atom" system itself. Such structures can be obtained by deposition of atoms of various elements on the surface of special substrates. However, the size of these islands and the distance between them are random.

By creating certain conditions, it is possible to obtain regularly spaced and equally sized nanostructures of high stability. In particular, such magic clusters were obtained in [1] on a reconstructed (7 × 7) surface of atomically pure Si(111) by sputtering ~0.3 aluminum monolayer at T = 550˚C under ultrahigh vacuum conditions.

In many cases, specially created defects or a reconstructed surface of a single crystal can be used as ordered nuclei. Our preliminary studies showed [2] that such defects can be created by the technique of low-energy ion bombardment in combination with annealing.

Over recently the composition, structure and electronic properties of $CoSi_2$/Si, Si/CaF_2, CaF_2/Si, SiO_2/Si nanoscale hetero-structures have been investigated by several researchers [3]-[8]. The above structures might be used in the fabrication of Metal-Oxide-Semiconductor (MOS) and Semiconductor-Insulator-Semiconductor (SIS) structures, barrier layers, and contacts for various devices [8] [9]. However, little or practically no significant research was done aimed at studying physical properties of surface of dielectric samples with embedded nano-scale crystals of metals and semiconductors.

This paper is devoted to the study of the composition, structure and electronic properties of regularly located nanocrystalline phases and homogeneous 20 - 30 Å (θ = 8 - 10 monolayers) thick Ca and Si films of single-crystal CaF_2(111) samples created on the surface with the consistent use of ion bombardment deposition.

The paper reports the study of the effect of formation of nanoscale phases and films of Ca and Si on the composition and electronic structure of the surface of single-crystalline samples of CaF_2(111). Over recently the composition, structure and electronic properties of $CoSi_2$/Si, Si/CaF_2, CaF_2/Si, SiO_2/Si nanoscale hetero-structures have been investigated by several researchers [1]-[6]. The above structures might be used in the fabrication of Metal-Oxide-Semiconductor (MOS) and Semiconductor-Insulator-Semiconductor (SIS) structures, barrier layers, and contacts for various devices [6] [7]. However, little or practically no significant research was done aimed at studying physical properties of surface of dielectric samples with embedded nano-scale crystals of metals and semiconductors.

The paper reports the study of the effect of formation of nanoscale phases and films of Ca and Si on the composition and electronic structure of the surface of single-crystalline samples of $CaF_2(111)$.

2. Experimental Procedure

Nano-scale phase of Ca was obtained in ultrahigh vacuum conditions by attracting the technique of bombardment of $CaF_2(111)$ surface by ions of Ar^+ in combination with thermal heating, whereas nano-scale phases of Si were obtained by Si deposition on the surface of CaF_2. Composition and electronic properties of the structures were investigated.

Composition and electronic properties of the structures were investigated by Auger Electron Spectroscopy (AES), Ultraviolet Photoelectron Spectroscopy (UVPS), Backscattering Spectrometry (BS) and by studying intensity I of passing light through samples as a function of energy. Photon energies $h\nu$ varied in the range 0.6 - 6.0 eV ($\lambda \approx 2000$ - 190 nm). Distribution of atoms across the depth was investigated by AES in combination with etching of the surface by Ar^+ ions.

3. Results and Discussion

Photoelectron energy distribution curve (EDC) for CaF_2 which was exposed to ions beam of Ar^+ with E0 = 1 keV with various doses is shown in **Figure 1**. Photoelectron spectroscopy results were obtained at $h\nu \approx 21, 2$ eV. It can be seen that on the spectrum line of "pure" CaF_2 the initial sharp increase in the concentration of photoelectron starts at 12.2 - 12.3 eV, which is mainly caused by release of electrons from the valence band EV onto vacuum.

The area under the curve of the energy distribution is proportional to the quantum yield of photoelectrons. Extrapolation of this section of the curve against the E_{phe} axis gives values ~12, 1 eV where E_{phe} is energy of photoelectrons. For CaF_2 the values of electron affinity (the width of the conduction band) is approximately χ ~0.1 eV, therefore it can be assumed that the width of its band gap E_g is ~12 eV. In the initial nearby section of the spectrum at energies of photoelectrons of 4 and 7.5 eV slightly intensive peaks are witnessed. The peak at $E_{phe} \approx 7.5$ eV might be due to the presence in lattice sites of a certain concentration of Ca that does form bonds with fluorine atoms, whereas the occurrence of the peak at $h\nu = 4$ eV might presumably be attributed to the presence of surface states.

The bombardment of CaF_2 by Ar^+ ions as a function of the dose of ions leads to the change in the composition and electronic structure of its surface layers. Precedent to dose levels $D = 10^{13}$ cm^{-2} there is no noticeable change in the structure of the curve I ($h\nu$).

Increasing dose to $D = 5 \times 10^{14}$ cm^{-2} leads to broadening of EDC, decrease of the intensity of the main peak ($E_{phe} \approx 14$ eV) and the quantum yield of photoelectrons, as well as causes the displacement of the beginning of spectrum (the edge of the valence band EV) towards lower energy levels. Meanwhile, amplitude of the peak at $E_{phe} \approx 7.5$ eV is slightly increased, and especially in the range of ~4 eV is smoothed.

Extrapolation of the starting part of the curve against the Ephe axis gives values ~10.8 eV; *i.e.*, the width of the forbidden band of CaF_2 decreases by 1.1 - 1.2 eV. At D = 5 × 10^{15} cm^{-2} the area under the curve in the main peak section reduces roughly threefold, the quantum yield of photoelectrons reduces more than twofold, and the value of E_g by 4.5 eV. Meanwhile, intensity of peaks in the range of 7.5 - 8 eV (usually characteristic of Ca) increases more than 6 - 7 times. At D = 5 × 10^{16} cm^{-2} the photoelectron spectrum structure characteristic of the dielectric CaF_2 completely transforms to the structure usually characteristic of the "metal-calcium" structure.

Figure 2 shows the dependence of the passing light intensity on photon energy in the range of 0.2 - 6 eV for single crystalline sample of $CaF_2(111)$ bombarded with Ar^+ ions with energy of E_0 = 1 keV with various doses. It can be seen that incase of both "pure" and ion-irradiated CaF_2, the energy $h\nu$ increases from 0.2 eV to 6 eV and the intensity I slowly decreases.

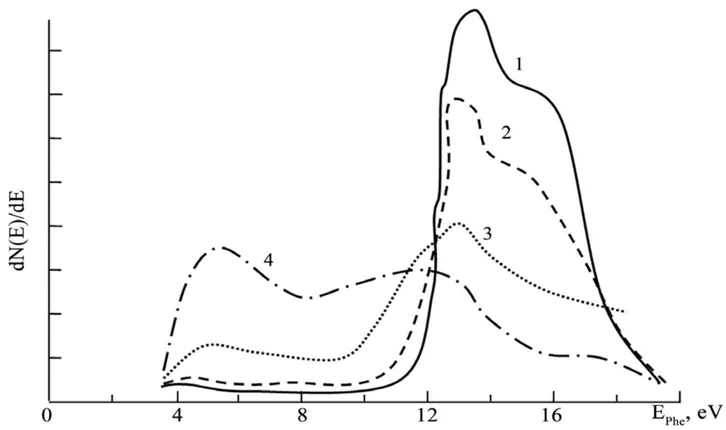

Figure 1. Photoelectron spectra of $CaF_2(111)$ exposed to the beam of Ar^+ ions with E_0 = 1 keV at D, cm^{-2} 1—0, 2—5 × 10^{14}, 3—5 × 10^{15}, 4—5 × 10^{16}.

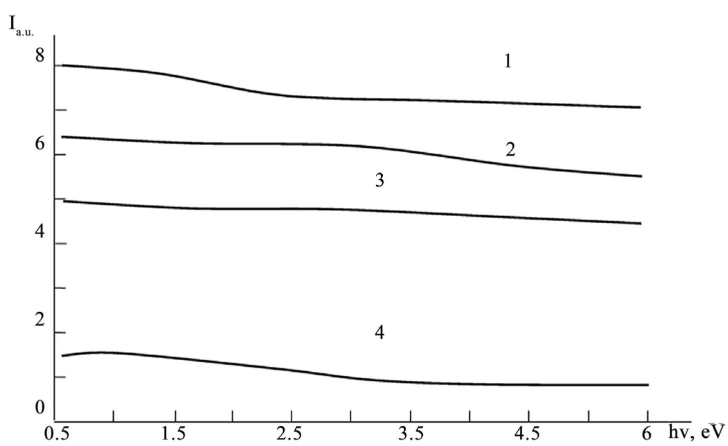

Figure 2. Intensity I of the passing light as a function of energy of photoelectrons for CaF_2 exposed to the beam of Ar^+ ions with E_0 = 1 keV at D, cm^{-2} 1—0, 2—5 × 10^{14}, 3—10^{15}, 4—5 × 10^{15}.

It should be noted that the value of intensity I of ion irradiated CaF_2 in the whole investigated diapason of h$\nu$is less than the intensity I of "pure" CaF_2. At D = 5×10^{14} cm^{-2}, the intensity I decreases on average 20% - 25%, while at D = 10^{15} cm^{-2} the average value of I reduces by 35% - 40%, and at D = 5×10^{15} cm^{-2} light intensity decreases 5 - 6 times. Following the bombardment with dose of D = 5×10^{16} cm^{-2} the light practically does not pass through CaF_2 films in the investigated area of hν = 0.6 - 6 eV.

The authors had previously shown [10] that at low doses of Ar^+, separate cluster phases enriched with Ca atoms shape on the surface of CaF_2. As the dose of ions increases, so the dimension of these phases does indeed and at D = 10^{15} cm^{-2} their size reach ~30 - 40 nm. At D > 10^{16} cm^{-2} overlapping of boundaries of individual phases takes place and the entire surface will be covered with atoms of Ca d ~10 - 15 Å thick.

Therefore, we assume that the change in UVPS curve's structure, reduction in the quantum yield of photoelectrons and in intensity of the passing light as the dose of ions boost, might be due to the increase in the size of cluster phases of Ca (**Figure 1**). Formation of these phases is allegedly accompanied bycertain increase in the concentration of Ca as well as in surface layers CaF_2not exposed to bombardment.

This in turn leads to the increase in the intensity of the peak of Caat hν = 7 - 7.5 eV displacement of starting part of the EDC of CaF_2 toward lower values of E_{phe}. These changes are associated with the formation of various defect states near the bottom of the conduction band and valence band. At D ≥ 5×10^{15} cm^{-2} the concentration of these states increases dramatically and narrow impurity bands occur which merge with the conduction bands and valence bands.

Consequently, the band gap decreases. In particular, at D = 5×10^{15} cm^{-2} the intensity of passing light was about 70% - 80%, and the value of E_g ~7.5 eV. It can be assumed that roughly 80% of the surface ofCaF_2 is covered with Ca atoms while the areas of CaF_2 previously not exposed to bombardment form impurity bands with width of ~4 - 4.5 eV. Starting from D = 4×10^{16} cm^{-2} light hardly passes through the CaF_2, *i.e.* the surface turns out to be completely covered with atoms of calcium.

Similar investigations (change in composition, change in the crystal and electronic structure) of Si nano-scale films grown on CaF_2(111) surface by molecular beam epitaxy were done. In order to depose Si epitaxial films, the system after each cycle of deposition was annealed at T ≈ 800 - 900 K. Down to the depth of θ ≈ 10 monolayers, the Si film had eneven character.

Solid homogeneous films formed down to $\theta \geq$ 10 - 15 monolayers. As a reference in **Figure 3** we placed micrograph of the surface of CaF_2(111) with Si film thickness of $\theta \approx$ 5 Si monolayers. It can be seen that the Si film is uneven. Dimensions of islands are within 500 - 1000 nm. **Figure 4** shows the I (hν) curve for CaF_2 film with film thickness of θ = 5 and 15 monolayers.

It is seen that in the case of film of θ = 5 monolayers thick the light intensity in the range of $h\nu$ = 0.9 - 1.2 eV decreases 3, 5 - 4 times (from 7.5 - 8 to 2 - 2.2). It is believed that 70% - 75% of the surface of CaF_2 is covered with Si film. In the case of films of θ = 15 monolayers thick, in the range of $h\nu$ = 0.8 - 1.1 eV the intensity I decreases from 7.5 - 8 to virtually zero, *i.e.* the surface appears to be completely covered by Si atoms.

4. Summary and Conclusions

One can believe that as a result of bombardment of CaF_2 with Ar^+ ions and depending on irradiation dose one can witness change in the electronic structure of the surface layers of ingot samples which is explained by the formation of nanocluster phases of Ca in the exposed areas of CaF_2, as well as by changes in the composition and structure of interphase (non-irradiated) areas.

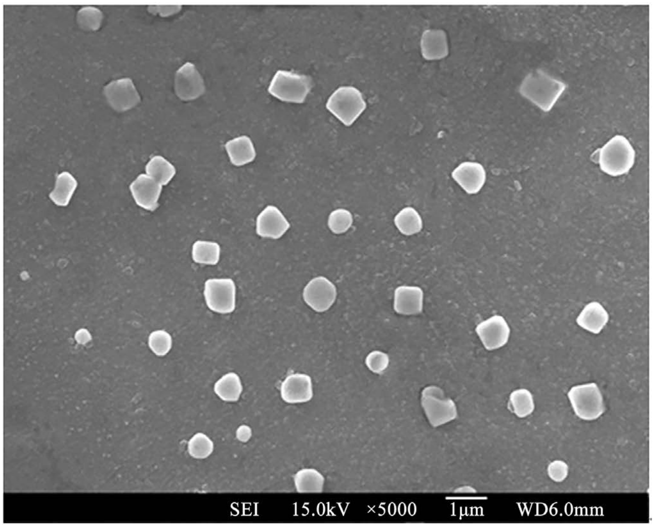

Figure 3. SEM images of $CaF_2(111)$ surface with a film thickness of Si $\theta \approx 5$ monolayers.

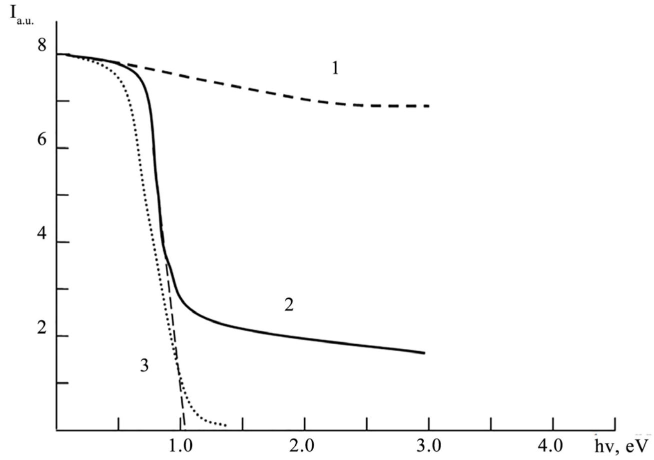

Figure 4. Intensity of passing light as a function of photon energy for "pure" $CaF_2(111)$ (curve 1) and CaF_2 with a film thickness of 5 Si monolayers (curve 2) and 15 monolayers (curve 3).

These defects at D ≥ 5 × 10^{15} cm^{-2} leads to the formation of impurity bands near the ceiling of the valence band and the bottom of conduction band of these areas of CaF_2; therefore E_g decreases by 4 - 4.5 eV. In the course of molecular beam epitaxy, and the growth of Si films on the surface of CaF_2 down to $\theta \approx 10$ monolayer thick, they had island-like character. Judging by the dependence curve and trend of intensity of the passing light (I) on the photon energy ($h\nu$), we have been able to determine density of coating on the surface of the CaF_2 consisting of Si films as well as defining the E_g of Si islands. In particular, at $\theta \approx 5$ monolayers the degree of coverage was 70% - 75%, and the silicon E_g ~1.1 eV.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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