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DEVELOPMENT OF A TECHNOLOGY FOR THE PRODUCTION OF NANO-SIZED HETEROSTRUCTURED FILMS BY ION-PLASMA DEPOSITION

UDC 539

The study of films containing narrow-gap semiconductors is a very promising field related to the production of thermal sensors. In this work, we consider the possibility of obtaining the film coatings from silicides of Ba, Na, Ni, Co, Pd, Mn, and P and BaTiO₃ using ion-plasma methods. The production of film coatings from metal silicides and BaTiO₃ on the surface of crystalline silicon and mica and their electronic and X-ray structural characteristics are studied. The dependence of the properties of film coatings on the conditions of the film deposition is determined.

Keywords: metal silicides, X-ray phase analysis, Miller indices, interplanar distance, strict single-crystal structure, barium titanate, amorphous phase, crystalline phase.

1. Introduction

Obtaining the high-quality thin coatings of metals, alloys, and semiconductors is one of the most important tasks in the production technology of integrated circuit elements, various temperature and pressure sensors in general, and in micro- and nanoelectronics. Especially for the creation of thermal sensors, film elements produced from narrow-gap semiconductors

are needed. Metal silicides are ones of such semiconductors. Therefore, the production of thin-film and thin-sized elements from these semiconductors is an urgent task [1].

There are many different methods for obtaining the film coatings. The most popular methods of vacuum deposition of coatings on various kinds of surfaces are the thermal evaporation, electron beam evaporation, and various types of ion-plasma sputtering. In this case, just the methods of application of thin films are based on the sputtering of a material with ions of heavy gases. These include the ion-beam and magnetron methods of deposition of thin-film structures that have been intensively developed recently [2]. They have a number of advantages: the possibility to obtain new materials, oxides, good adhesion and physicochemical properties of films. The especially efficient production of microelectronics and solar en-

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ergy elements requires the application of multistructured coatings such as metal–semiconductor–dielectric–metal, *etc.*, which is related to the use of a variety of vacuum plasma equipments [3].

At present, it is impossible to imagine electronics without semiconductor heterostructures. Such structures are widely used to create light-emitting diodes, short-wavelength photodetectors, semiconductor lasers, solar cells, and other products of modern optoelectronics. The important conditions for the widespread use of such devices are a low cost and their resistance to high temperatures and other critical conditions.

A promising material for the creation of various optoelectronic devices on its basis is barium titanate. Barium titanate is a compound of oxides barium and titanium BaTiO_3 . The crystal modification of barium titanate with perovskite structure is a ferroelectric possessing the photorefractive and piezoelectric effects. Barium titanate is characterized by high values of the dielectric constant (up to 10^4 ; 1400 ± 250 at n.o.); on its basis, several types of ferroelectric ceramics have been developed and are used to create capacitors, piezoelectric sensors, and posistors [4].

In this work, apart from BaSi_2 , NaSi_2 , NiSi_2 , CoSi_2 , Rd_2Si , Mn_4Si_7 , we will study barium titanate, a compound of barium oxides and titanate. In experiments, BaTiO_3 was used in the form of a powder with a diameter of $1 \div 1.5$ mm. In addition, the target is made of the one-piece compound BaTiO_3 with a diameter of 76 mm. In the installation of magnetron sputtering systems in a high vacuum, we obtained thin films of BaTiO_3 on the surface of Si(111) single crystals. The deposition rate of barium titanate was 0.5 \AA/s , and the maximum thickness of a coverage was 100 \AA . If necessary, a specimen with a sputtered BaTiO_3 film subjected to the 30-min annealing at a temperature of $400 \text{ }^\circ\text{C}$ was used to study the electronic and optical properties of barium titanate.

Powder X-ray diffraction is a method for studying the structural characteristics of a material using X-ray diffraction (X-ray diffraction analysis) on a powder or polycrystalline specimen of the material under study. A result of our study is the dependence of the scattered radiation intensity on the scattering angle. The corresponding instrument is called a powder diffractometer. The advantage of the method

is that the debyeagram for each substance is unique and allows one to determine the substance, even if its structure is not known.

The X-ray phase analysis method was used to study the structure, composition, and properties of raw materials and annealing products. It was used to study the mineralogical and phase compositions [5]. A monochromatic X-ray beam was directed to a specimen of the test material ground into a powder. On a photographic film rolled into a cylinder around the specimen, the image (debyeagram) is obtained in the form of rings. The distance between the lines of the same ring on the debyeagram allowed us to find the Bragg reflection angles. Then, using the Bragg–Wulf formula, $2d \sin \theta = n \lambda$, we can get the ratio of the $\frac{d}{n}$ distance between the reflecting planes to the order of reflection.

Powder specimens of BaTiO_3 were studied by the X-ray diffraction and elemental analyses. Specimens were identified basing on diffraction patterns which were recorded on a computer-controlled XRD-6100 (Shimadzu, Japan) apparatus.

2. Production of Thin Films and Their Study

For the laboratory installation of magnetron sputtering PVD–DESK–PRO, using these devices, the technologies were developed to produce nanoscale films basing on conducting materials, namely, Ba, Na, Ni, Co, Pd, Mn, P, metal silicides, and BaTiO_3 compounds, as well as dielectric films of SiO_2 , Si_3N_4 , TiO_2 , Al_2O_3 , and other films with a more complex composition.

All films of silicides were obtained by the ion-plasma deposition of films in combination with the annealing under conditions of high ($P < 10^{-6}$ Pa) vacuum. Using the methods of Auger-electron spectroscopy (OES), ultraviolet photoelectron spectroscopy (UVES), elastically scattered electron spectroscopy (ESES), and high-speed electron diffraction (RHEED), the dynamics of changes in the composition and structure of the near-surface layer of the obtained silicides are studied. The Auger spectra are measured at the normal incidence of the primary beam with an energy of 3 keV. The photoelectron spectra are taken at $h\nu = 10.8 \text{ eV}$. The photon source is a standard gas-discharge hydrogen lamp of ultraviolet radiation with a wavelength of 115 nm. The

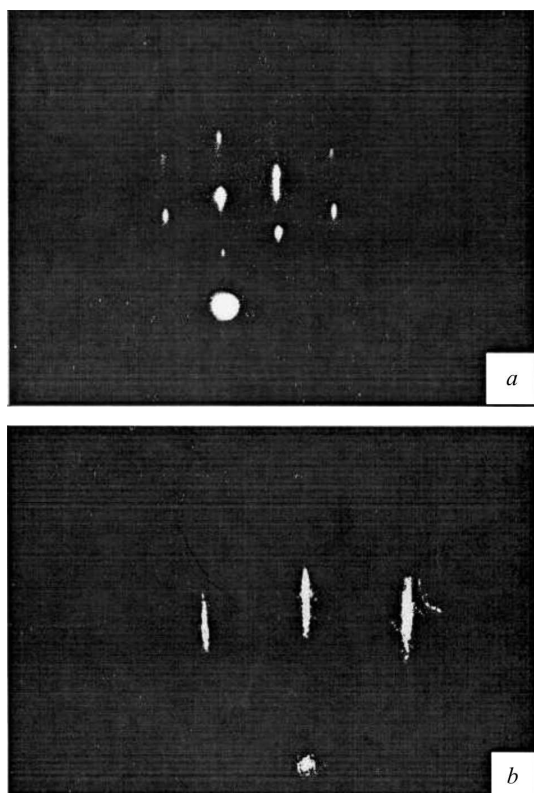


Fig. 1. RHEED patterns of the surface of epitaxial films BaSi₂/Si (100) (a) and NiSi₂/Si (100) (b)

Table 1. Type and lattice parameters of silicide films

| Silicide | In that work | |
|---------------------------------|--------------|-----------------------|
| | Lattice type | Lattice parameters, Å |
| Si | Cubic | $a = 5.45$ |
| BaSi ₂ | " | $a = 6.2$ |
| NiSi ₂ | " | $a = 5.42$ |
| CoSi ₂ | " | $a = 5.40$ |
| NaSi ₂ | " | $a = 6.54$ |
| Pd ₂ Si | Hexagonal | $a = 6.5; c = 3.45$ |
| Mn ₄ Si ₇ | Tetragonal | $a = 5.7; c = 15.3$ |
| SiP | Cubic | $a = 5.65$ |

RHEED patterns are taken at an electron energy of 75 keV using a standard EMR-102 setup. In this case, the electron beam hits the target surface at an angle of 85° relative to the normal. The heating was carried out from the rear side of the target by the radiation from a tungsten filament (up to $T = 900$ K) and by

the electron bombardment ($T > 900$ K). The laser annealing was carried out by the parallel fluxes of infrared radiation with a wavelength of 1.06 μm and a pulse duration of 10 ns.

Figure 1 shows the RHEED patterns of the surface of BaSi₂/Si(100) and NiSi₂/Si(100) epitaxial films. It is seen that the grown films have a smooth surface and a strict single-crystal structure without noticeable structural defects. Based on the analysis of RHEED patterns, the type and lattice parameters of the studied films were determined (Table 1).

It can be seen from the table that the lattice constants of the CoSi₂ and NiSi₂ films are very close to the lattice constant of Si. In addition, these silicides have very low resistivity (10^{-5} Ohm·cm). These factors make them very promising in the creation of multilayer nanoepitaxial MIS structures required for solid-state electronic devices [6].

In the case of BaSi₂ and NaSi₂, by varying the conditions, the ion-plasma technologies can controllably change the composition and thickness of the films and, hence, the lattice constant of the silicide [1]. This makes it possible to obtain transitional matching layers at the film-substrate interface, when their lattice parameters differ significantly from each other.

3. Results and Their Discussion

We have carried out the determination of the qualitative composition of the specimens, semiquantitative determination of the components of the specimens, determination of the crystal structure of the substance, as well as the precise determination of the unit cell parameters, determination of the arrangement of atoms in the unit cell (full profile analysis – the Rietveld method), and determination of the crystallite size (coherent scattering region) of a polycrystalline specimen. We have studied a texture in polycrystalline materials. In addition, the studies of the phase composition of the substance, the state diagrams, the assessment of the size of the crystals in the specimen, the accurate determination of the lattice constants, the thermal expansion coefficient, the analysis of minerals, Cu-Kα – radiation (β – filter, Ni, $\lambda = 1.54178$ Å tube current and voltage mode 30 mA, 40 kV) and a constant detector rotation speed of 4 deg/min with a step of 0.05 deg. ($\frac{\omega}{2\theta}$ -coupling), and the scanning angle varied from 10 to 80° have been executed. The X-ray power was 2 kW. The re-

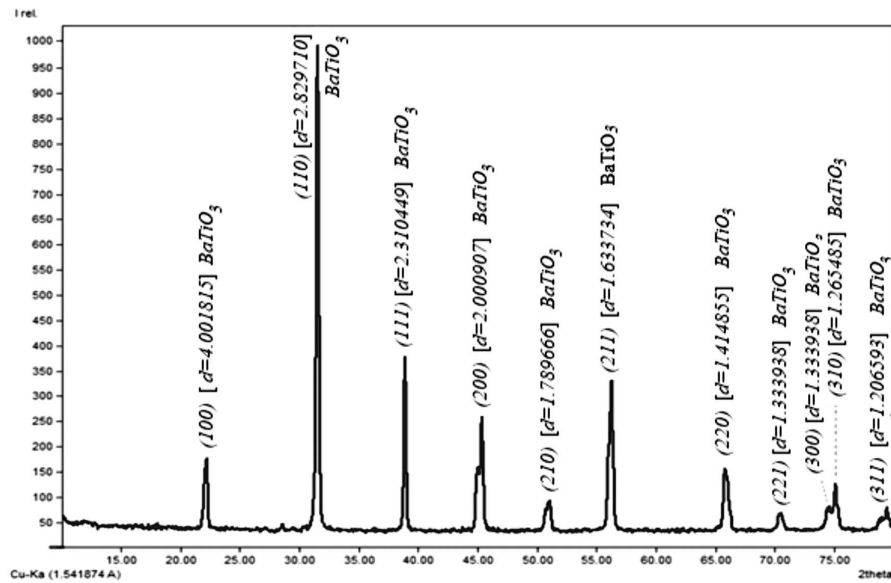


Fig. 2. Spectral dependence of BaTiO₃ obtained by a powder diffractometer. The Miller indices are given

sults were analyzed using the database [7]. The penetration depth of Cu-K α radiation is about 1 mm (980 μm) for light elements (carbon) and several μm for heavy elements (Ag, W). For most simple compounds of inorganic substances, the Cu-K α penetration depth is tens of microns (μm). Figure 2 shows the spectral dependence of BaTiO₃ obtained by the powder diffractometer method. In addition, the Miller indices are given, as well as the interplanar spacing d_{hkl} for those specimens. We used the Rietveld method [12] to refine the structure from powder data obtained with the use of X-rays. The principle of the method is to perform independent measurements of the intensity at each point of the diffraction pattern describing the line profile using analytical functions, instead of using the integral reflection intensity. The parameters of functions, structure, a device, and other characteristics are refined using the nonlinear least-squares method. Applying this refinement method, we determined the interplanar spacing d_{hkl} and Miller indices (hkl). In addition, using this method, we were able to accurately determine and designate the interplanar distance d_{hkl} and Miller indices (hkl), as can be seen in Fig. 2. As mentioned above, the powder X-ray diffraction allows the quantitative elemental analysis to be made. The elemental analysis performed by us using the “Search and Match” software [7] shows that the specimens

of BaTiO₃ have the following composition (in weight percent).

As is known from the literature data [8], Miller indices are applicable in all synagogues. As the Miller index increases, the interplanar spacing decreases [9].

Table 2 shows the data obtained by the powder X-ray diffraction on BaTiO₃.

For specimens of BaTiO₃ measured by the X-ray diffraction analysis using the “Search and Match” software [10], the degree of crystallinity and the amorphism were assessed. For barium titanate, this is as follows: the fraction of the amorphous phase is

Table 2. Below shows the data obtained by powder X-ray diffraction BaTiO₃

| No. | hkl | hw | 2θ | I_{calc} | I_{obs} | σ | d_{hkl} |
|-----|-------|----------|-----------|-------------------|------------------|----------|-----------|
| 1 | 100 | 0.070886 | 22.195 | 221.8 | 222.9 | 3.378 | 4.001815 |
| 2 | 1 1 0 | 0.076811 | 31.592 | 1324.3 | 1338.2 | 6.593 | 2.829710 |
| 3 | 1 1 1 | 0.083821 | 38.949 | 372.9 | 378.8 | 4.238 | 2.310449 |
| 4 | 200 | 0.091393 | 45.283 | 480.6 | 490.8 | 4.694 | 2.000907 |
| 5 | 2 1 0 | 0.099364 | 50.986 | 152.9 | 157.0 | 3.605 | 1.789666 |
| 6 | 2 1 1 | 0.107689 | 56.261 | 619.1 | 638.8 | 5.482 | 1.633734 |
| 7 | 2 2 0 | 0.125451 | 65.971 | 333.7 | 347.9 | 4.717 | 1.414855 |
| 8 | 2 2 1 | 0.134977 | 70.542 | 74.0 | 77.6 | 3.339 | 1.333938 |
| 9 | 300 | 0.134977 | 70.542 | 13.2 | 13.9 | 0.597 | 1.333938 |
| 10 | 3 1 0 | 0.145024 | 74.989 | 283.6 | 298.8 | 4.841 | 1.265485 |
| 11 | 3 1 1 | 0.155679 | 79.344 | 122.6 | 129.8 | 4.039 | 1.206593 |

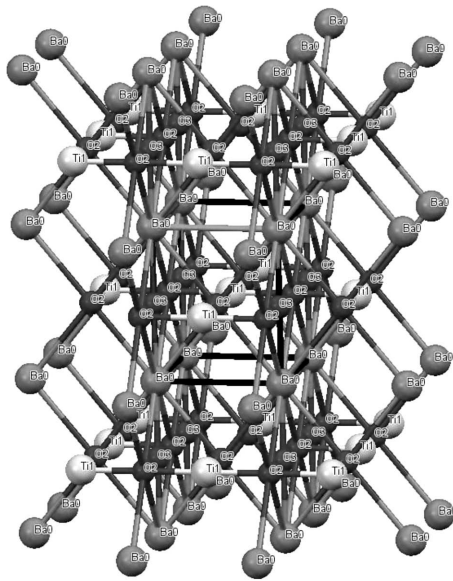


Fig. 3. Crystal structure (cubic structure sp. gr. Pm-3m)

Table 3. The results of measurement and the processing of X-ray diffraction data

| No. | Atoms | Atomic coordinates | | | Thermal factor B |
|-----|----------------|--------------------|---------|---------|--------------------|
| | | x/a | y/b | z/c | |
| 1 | Ba | 0.00000 | 0.00000 | 0.00000 | 0.15676 |
| 2 | Ti | 0.00000 | 0.00000 | 0.24696 | 0.16562 |
| 3 | O ₃ | 0.00000 | 0.00000 | 0.37505 | 0.16383 |

71.35%, and that of the crystalline phase, respectively, is 28.65%. The indexing, i.e., the determination of indices (hkl) for each line of the diffraction pattern and grating type, was carried out to identify impurities in the specimen by isolating reflections that do not belong to the main substance. In this work, we have determined the presence of hydrogen impurities in BaTiO₃.

Figure 2 demonstrates an X-ray pattern at room temperature and BaTiO₃ heated to 673 K. X-ray phase analysis at room temperature shows that, at several angles 22.19530, 31.59230, 38.49220, 45.28320, 50.98610, 56.26100, 65.97120, 70.54280, 74.54240, 75.08919, and 79.34417, the peaks of different degrees are visible. The main ideal peak is seen at an angle of 31.59230 degrees (101). When heated to 400 degrees, the angles of the peaks in the image do not

change, but the intensity does. The release of some light volatile elements during the heating and crystallization can be explained by the crystallization of the specimen [13]. In this X-ray phase analysis in the literature, a specimen heated to 850 degrees can manifest, in the X-ray phase analysis, peaks appearing at certain angles, although the peaks are very small in intensity and contrast. The analysis results measured at room temperature and 400 degrees Celsius show that the intensity of the peaks varied by a factor of 2.46.

The X-ray diffraction data were processed using the Fullprof program [14]. The results of measurements and processing of X-ray diffraction data are shown in Fig. 3 and Table. 3.

Processing the X-ray diffraction data by the full-profile method showed that the specimen has a cubic structure (sp. gr. Pm-3m) with the lattice parameters $a = 4.0018 \text{ \AA}$, $b = 4.0018 \text{ \AA}$, and $c = 4.0018 \text{ \AA}$, and the coordinates of atoms in the unit cell are given in Table 3. Figure 3 shows the crystal structure of BaTiO₃, which corresponds to the trigonal space group and consists of three chemical formulas: Ba, Ti, and O.

4. Conclusion

The composition, structure, and properties of silicide nanofilms have been studied. It is shown that NiSi₂, CoSi₂, BaSi₂, NaSi₂, and SiP crystallize into a cubic lattice, and the bonds between the atoms of a deposited element and Si have the ion-covalent character. In the case of Mn₄Si₇, we observe a tetragonal lattice, and Pd₂Si possesses a hexagonal one. It has been determined that metal silicide films are heterostructural with respect to silicon, and their bandgap is 0.5–0.7 eV.

The analysis of the X-ray diffraction spectra and electrophysical properties of barium titanate in the form of a powder and thin films with a thickness of 10–50 nm allowed us to determine the structure using the Rietveld method [12]. A decrease in the interplanar distance with increasing the Miller indices is found. Indexing was used to identify impurities in the specimens by isolated reflections that do not belong to the main substance. The elemental analysis was carried out in weight percent. For the first time, the degree of crystallinity and amorphism of the specimens are determined. The fractions of the amorphous

and crystalline phases for barium titanate are equal to 71.35% and 28.65%, respectively. It is shown that, after the heating, the intensities of the X-ray peaks for the specimen increase by a factor of 2.46 relative to those at room temperature.

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РОЗРОБКА ТЕХНОЛОГІЇ ВИГОТОВЛЕННЯ НАНОРОЗМІРНИХ ПЛІВОК З НЕОДНОРІДНОЮ СТРУКТУРОЮ МЕТОДОМ ІОННО-ПЛАЗМОВОГО ОСАДЖУВАННЯ

Дослідження плівок, що містять вузькощілинні напівпровідники, є дуже перспективним напрямком, пов'язаним із виробництвом теплових сенсорів. Ми розглядаємо можливість створення плівкових покриттів із ВаТіО₃ і сіліцидів елементів Ва, Na, Ni, Co, Pd, Mn та Р іонно-плазмовим методом. Такі покриття отримано нами на поверхнях кристалічного кремнію та слюди. Досліджено їхні електронні та рентгеноструктурні характеристики. Визначено залежність властивостей плівкових покриттів від умов їх створення.

Ключові слова: сіліциди металів, рентгенівський фазовий аналіз, індекси Міллера, міжплощинна відстань, структура монокристала, титанат барію, аморфна фаза, кристалічна фаза.