Production of thin film of multicomponent inorganic semiconductors under quasi-equilibrium conditions

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Issues of improving the properties of semiconductor thin film and their reproducibility, as well as improving and reducing the cost of manufacturing technology stimulate research and development of new, advanced methods. Therefore, it is important to optimize the technology of getting reproducible, competitive, high-tech thin films of multicomponent semiconductor compounds with predetermined properties. In the given article it is shown that constructive and technological improvements of a method of thermal spraying in vacuum allow to minimize nonequilibrium conditions of film growth, keeping the advantages of thermovacuum spraying, such as high reproducibility, processability and productivity, a wide range of variations in the synthesis conditions, and, accordingly, the properties of condensates, maximum purity of growth processes, as well as ease of performing and management and cost-effectiveness of the process of getting perfect condensates. For this purpose, we have developed a special construction of a quasi-fusion evaporator and a device for getting semiconductor film in vacuum, as well as a version of a transparent “hot wall”. The resistivity, cross section and geometric dimensions of the cover and the heater of the developed structures were selected so that in the mode of resistive heating of the evaporator temperature gradient due to the difference in their electrical resistance, and, accordingly, the Joule heat of current, in the temperature range 673… 1473 K provided the temperature of the cover 1.1 ... 1.3 times higher than the temperature of the heater. Due to the elevated temperature of the cover, the solid fraction is either repelled on the sublimating (evaporating) surface and the walls of the crucible, or undergoes sublimation (evaporation) from the surface of the cover. Depending on the values of the sputtering rate, the grain size of semiconductor polycrystalline film varied from units of nanometers to several micrometers. Crystallinely ordered films were got at relatively low values of the sputtering rate (0.5...5 nm s⁻¹). It was set up the technological conditions for getting thin films of multicomponent semiconductors, which ensure the independence of the chemical composition of condensates from the evaporation rate in the wide range from 0.05 to 20 nm s⁻¹, uniform composition of the gas phase during sublimation, absence of inhomogeneous solids in films, wide range properties of condensates and their high reproducibility.

Key words: thin films, semiconductors, technological methods of obtaining, thermal spraying, quasi-equilibrium conditions.

Otrимання тонких плівок багатокомпонентних неорганічних напівпровідників у квазірівноважних умовах

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In previous reviews (Tsizh & Dziamski, 2019; 2020) we have given an analysis of existing methods for applying thin films of inorganic semiconductor materials. This analysis showed that the technological aspects of obtaining semiconductor films have been studied in detail for many years and today we have formed dozens of relevant methods and technological regulations. However, the issues of improving the properties of semiconductor films and their reproducibility, as well as improving and reducing the cost of production technology stimulate research and development of new, advanced techniques (Bunshah, 1994; Seshan, 2002; Hosokawa et al., 2008; Bahmut, 2014; Hartmut & Hamid, 2015; Antoniuk, 2016; Shalini, 2017). Therefore, a significant amount of our research was devoted to the optimization of the technology of reproducible, competitive, high-tech thin films of multicomponent semiconductor compounds with predeter-

The choice of method of manufacturing thin films is determined by the optimal expected set of their properties in combination with the maximum reproducibility, manufacturability and economy of the process. After analyzing the known methods of obtaining semiconductor condensates, we focused in more detail on thermal spraying in vacuum, which, despite the nonequilibrium conditions of films growth, has good manufacturability, a wide range of variations in synthesis conditions, and, accordingly, the properties of condensates, maximum purity of growth processes, reproducibility, productivity, as well as ease of execution and management, which makes it a method for many modern developments, in particular, for the creation of thin-film sensitive elements for gas sensors and other electronic devices, including for use in the food and processing industries. In addition, the results of constructive and technological improvements in the method of thermal spraying in vacuum give reason to hope to minimize the imbalance of the conditions of film growth and obtaining perfect condensates.

The application of multicomponent semiconductor thin films of materials such as compounds $A_3B_5$, $A_2B_6$, chalogenide glassy semiconductors, oxides and others was carried out in serial installations of vacuum spraying as previous generations, such as УРМ 3.279.011 with high-oil high-vacuum pump and УРМ 3.279.047 with high-vacuum ion-getter pump, and in the modern combined installation of vacuum spraying of thin films produced by “Tor International” (USA). Glass, quartz, sita-lead other plates were used for substrates. The substrates were heated by infrared radiation of quartz lamps, the temperature was controlled by chromel-aluminum ther-

To improve the quality and adhesion of condensates, chemical and, in some cases, ionization cleaning of substrates was performed before spraying. Technology was used and allows to quickly and efficiently remove contami-

In addition, before spraying, the substrates were heat-cleaned in vacuum by half-hour heating at 623 K.

The control of the sputtering speed and the thickness of the films during their growth was performed by the optical method, which is based on the interference of transmitted light beams, due to reflection from the boundaries of the films with the substrate and vacuum. In this case, the increase in the physical thickness of the films by a value equal to a quarter of the wavelength $\lambda$ of light, corresponds to an increase in the order of the interference extremum. Since in the field of film transparency the value of the refractive index weakly depends on $\lambda$, the interference pattern was isolated using an interference filter with a bandwidth of $\lambda = 774 \pm 15$ nm, which increases the accuracy of measurements. In addition, in the field of films transparency there are no undesirable pro-

Summarizing the results of the research, we can say that the developed methods and optimization of conditions of thermal spraying in vacuum ensure the formation of thin films with desired properties, which are necessary for the development of new electronic devices and other microelectronic products.
due to absorption. In the installations used by us blocks of optical control are provided, that allow modulation, isolation and amplification of the useful light signal, which provided the measurement of condensate thickness with an accuracy of at least 10 nm at the extremes and 20 nm between them.

In addition to controlling the thickness of the films in the spraying process, thickness measurements were performed on an МИИ-4 interference microscope and on two-beam spectrometers. Microinterferometer of Linnik МИИ-4 made it possible to measure the height of irregularities of thin films, such as etched edge, scratches and others from 0.1 to 5 μm with an accuracy of 6 % by using the phenomenon of interference reflected from the surface of the films and substrate, pre-separated light beams, coming from one point of the source. To increase the measurement accuracy, the films thickness with d <0.5 μm was determined in parallel from the values of the difference in optical densities D – D0. To do this, the wavelength at which 0.5 < D < 2.0 for films of this composition with 0.1 < d < 0.5 μm was chosen on the spectral dependence D, and the value of d was specified according to the calibrated dependence D (d). This allowed to increase the accuracy of measuring the thickness of the films up to 4 % in the thickness range of 0.1 ... 0.5 μm.

**Results and discussions**

Due to the disadvantages of the existing evaporators, we have developed a special design of the quasi-fusion evaporator and a device for obtaining semiconductor films in vacuum, schematically shown in Fig. 1 and 2, respectively, as well as a variant of a transparent “hot wall” (Fig. 3) (Aksimentyeva et al., 2018). The thermal quasi-fusion evaporator for vacuum spraying (Fig. 1) consists of a cylindrical quartz crucible (2) with a height of 25 ... 35 mm, a diameter of 15 ... 25 mm and a wall thickness of 1 ... 1.5 mm, which, together with the tablet (1) of the source semiconductor material, is placed in a tantalum or molybdenum heater (3), that provides uniform heating, and tightly, with a clamp (5), close the tantalum or molybdenum lid with 40 ... 60 holes with a diameter of 0.1 ... 0.3 mm, adapted to pass current through it.

A thin (~ 0.2 μm) layer of a mixture of oxides of indium and stannum (7) with optical transmission T = 97 % (λ = 633 nm) was applied to the outer walls of the chamber by high-frequency ion-plasma sputtering of the target (In2O3) 90 (SnO2) 10 in vacuum and the specific electrical surface resistance ρп = 300 Ohm·cm². At both ends of the chamber alternate thermal spraying in a vacuum of Cr-Cu-Ni films with a total thickness of about 2 μm and a width of 5 mm electrically conductive busbars (5) are applied for uniform current flow through the heater. In a cylindrical quartz evaporator (2) with a height of 30 mm and a diameter of 20 mm with a wall thickness of 1.5 mm load a tablet (1) of starting material. The evaporator is inserted into a tantalum, molybdenum or tungsten heater (3), which ensures uniform heating, and tightly closed with a tantalum lid (4) with fifty holes with a diameter of 0.2 ... 0.4 mm. The evaporation chamber is placed on the evaporator and the tires, the evaporator heater and the cover are connected to the heat source. A stainless steel disc holder (9) is placed on the chamber and a substrate (10) and a thermocouple (11) are attached to it. The substrate is heated by infrared radiation of quartz lamps. He-Ne laser ЛГ-278 and photodiode ΦД-7К are used for optical control of film thickness. Tablets of the starting material were compressed from a mechanical mixture of the required ratio of fine dispersed powders of the selected semiconductors. In both cases, the crucible heater and the lid were connected to a common source of electric heat.

Similar structural elements are present in the device, which is commonly called the “hot wall” (Fig. 3).

![Fig. 1. The design of a thermal quasi-fusion evaporator for spraying semiconductor thin films in vacuum: 1 – tablet of source material, 2 – quartz crucible, 3 – tape heater, 4 – perforated lid, 5 – sealing clamp](image1)

![Fig. 2. Device for obtaining semiconductor films in vacuum: 1 – tablet of starting material, 2 – quartz crucible, 3 – evaporator heater, 4 – perforated evaporator cover, 5 – conductive tires, 6 – quartz evaporation chamber, 7 – transparent resistive heater, 8 – slots on the cover, 9 – substrate holder, 10 – substrate, 11 – thermocouple](image2)
gradient along the vertical axis of the evaporator increases the variable interaction between the vapor and the source material, which improves the homogeneity composition of the gas phase. At the same temperatures of the lid and the heater there is a significant increase in the individual components on the inner side of the lid and their departure from the crucible is due to re-evaporation from the lid. This significantly slows down the spraying process, uncontrollably changes the composition of the vapor phase, and also causes the cover holes to stick. The speed of sublimation in this situation is reduced also because the electrical resistance of the cover decreases due to the condensation of semiconductors on it, while reducing the heat of the Joule, which heats it. In a situation where \( T_c > T_h \) at least 1.1 times the condensation of vapors on the inner surface of the cover is practically absent, semiconductor atoms fly out of its holes without the above-described double sublimation or re-evaporation, spraying can be carried out at temperatures lower than \( T_c = T_h \). It is convenient to enter some coefficient \( S = T_c/T_h \) as the effective capacity of the evaporator. Then the required temperature gradient of the cover and heater, determined by us empirically for semiconductors of group AIBIV, can be written as:

\[
1.1 < S < 1.3 \quad \text{at} \quad 600 \, \text{K} < T_h < 1400 \, \text{K}. \quad (1)
\]

The temperature limits of condition (1) are due to experimental data that at values of \( T_h \leq 600 \, \text{K} \) the sublimation process is very slow, with a significant (> 1 atomic %) deviation from the stoichiometry, and at \( T_h > 1400 \, \text{K} \) high temperatures of the heater material and, especially, the lids contribute to its rapid (after 2–3 loads of the crucible) burnout, which is accelerated by the corrosive action of semiconductor components at high temperatures.

From the dependences of the values of \( S \) on the degree of filling of the evaporator crucible with the starting material, we determined that when the crucible is filled by 30–70% there is a certain stabilization of the temperature gradient of the lid and heater. Therefore, the first and last phases of spraying, as less stable and non-congruent, were performed using a damper.

The evaporators developed by us allowed to create molecular fluxes of vapors of subliming compounds of regulated intensity homogeneous in composition in a wide range of application conditions, which made it possible to get homogeneous, reproducible films of stoichiometric composition at different spray rates. In the case of using evaporators with non-compliance with ratio (1), the quality of the films deteriorated sharply: welded protrusions appeared due to the sedimentation of the solid fraction of steam, for the same concentration of the source material, the chemical composition of the film significantly depended on the spray rate, there was often a strong deviation from the stoichiometric composition (up to 5 ... 7 atomic %), deteriorating the homogeneity of the films in area and reproducibility of their properties, vaporization was accompanied by undesirable processes of sticking holes in the evaporator cover, which prevented the gas phase.
The described thermal evaporators have the following advantages over the known closed-type evaporators used for spraying thin films of semiconductor compounds:

- independence of the chemical composition of condensates from the evaporation rate in a wide range from 0.05 to 20 nm s⁻¹;
- uniform composition of the gas phase during sublimation;
- absence of inhomogeneous solid inclusions in the films;
- no sticking processes of the lid outlets.

In addition, in the device with a heating chamber (Fig. 2) tight connection of the evaporation chamber with the evaporator brings this construction closer to a quasi-closed volume, in this case, in contrast to the latter, it is possible to optically control the thickness of the films and their growth rate.

One of the most important technological parameters in the thermal spraying of semiconductor thin films in vacuum is the lining temperature (T₁) and the spray rate (Vₕ). T₁ influences on the ratio of components that condense and re-evaporate. Continuous predominant vapor condensation of this substance is possible only for temperatures lower than critical.

With the growth of T₁, the migration of sublimated molecules is increasing on the condensation surface, while the association of molecules of individual components improves, and although the reflection of their vapors also increases, the process of formation of homogeneous, stoichiometric condensates stabilizes. Vₕ spray rate has an influence on the structure and properties of semiconductor films. Due to the processes of re-evaporation and desorption from the substrate, which in turn depends on the temperature of the evaporator. Depending on the Vₕ values, the grain size of semiconductor polycrystalline films can vary from nanometer units to several micrometers. Crystallinely more ordered films were got at relatively low Vₕ values (0.5 ... 5 nm s⁻¹). Vₕ has also an influence on the composition of the films. For small (0.05 ... 0.2 nm s⁻¹) and large (30 ... 50 nm s⁻¹) Vₕ values, deviations of the molar ratio of semiconductor components from stoichiometric to a few percent were observed. In most works, the optimal Vₕ of semiconductor layers is in the range from a few tenths to several units of nm s⁻¹.

In addition to the values of T₁ and Vₕ, the depth of vacuum and the composition of residual gases in the spraying process have a significant influence on the structural features and properties of semiconductor condensates. In order to effectively control the growth processes and good reproducibility of the properties of thin films, it is necessary to ensure the cleanest possible conditions of preparation. This is achieved by improving the vacuum, increasing the purity of the source components, minimizing the influence of the evaporator material on the properties of the films.

**Conclusions**

This article shows that the construction and technological improvements of the method of thermal spraying in vacuum can minimize the nonequilibrium conditions of film growth, while maintaining the following advantages of thermovacuum spraying, such as high reproducibility, processability and productivity, a wide range of variations in the conditions of synthesis, and, accordingly, the properties of condensates, maximum purity of growth processes, as well as ease of execution and management and cost-effectiveness of the process of getting perfect condensates. Technological conditions for getting thin films of multicomponent semiconductors, which ensure the independence of the chemical composition of condensates from the evaporation rate in a wide range from 0.05 to 20 nm s⁻¹, uniform composition of the gas phase during sublimation, the absence of inhomogeneous solid inclusions in the films, a wide range of physical properties of condensates and their high reproducibility.

**Perspectives for further research.** Further research should continue to optimize the methods of getting thin films of multicomponent inorganic semiconductors in order to achieve the highest degree of equilibrium conditions of condensate growth and, consequently, to improve their properties. To do this, it is necessary to develop new constructions of devices for the synthesis of thin films and improve the technological regulations for their receipt.

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**Conflict of interest**

The authors state that there is no conflict of interest.

**References**


