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Technological Methods of Forming Thin Semiconductor Layers Part 1

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The review and analysis of the basic technological methods of formation of thin layers of semiconductor materials is presented. The timeframe for the occurrence of thin film technologies and the main centers of their localization are specified. It is shown that nowadays structure, properties and basic methods of obtaining thin films sufficiently well studied for not only simple but also complex, multi-component inorganic semiconductor materials, new areas of application and increase of requirements to the operational characteristics of devices on their basis require improvement of existing technologies and development of new methods for their synthesis, which involves a detailed analysis of the known, and the search for new, progressive methods of preparation. Due to the fact that the main methods for obtaining thin films of inorganic semiconductor materials are vacuum condensation and chemical precipitation, the first part of the review describes the methods of their vacuum application, in particular, thermal spraying in an open vacuum. It is shown that the most common way of obtaining thin films is the thermal spraying under resistive heating of the evaporator with the source material. We analyze the special structural and technological changes and improvement of traditional methods and systems of thermal spraying, which allow to equalize the ratio of the chemical composition of thin films and the source material, improve the stoichiometry of condensates, and ensure their homogeneity. The designs of thermal evaporators with resistive heating of crucibles in an open vacuum with sublimation or evaporation of one and two substances are presented. It is shown how these types of evaporators exclude the transfer of solid particles into evaporating or sublimation into the vapor phase and eliminate direct vapor deposition on the condensation surface, which more or less protects against heterogeneous condensate inclusions. It is shown that the methods analyzed or their modifications are nowadays the necessary means for the creation of thin-film semiconductor structures with predetermined properties, while vacuum deposition, in particular, traditional and modified thermal spraying in a vacuum due to its simplicity (but at the same time its ability to effectively control a large number of technological factors and create the necessary conditions for the growth of condensates) remains one of the most common ways of obtaining thin films, including inorganic semiconductors.

Key words: thin films, semiconductors, technological methods of obtaining, condensation in a vacuum, thermal spraying.

Технологічні способи формування тонких напівпровідникових шарів Частина 1

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Представлено огляд і аналіз основних технологічних способів формування тонких шарів напівпровідникових матеріалів. Вказано часові рамки виникнення тонкоплівкових технологій та основні центри їх локалізацій. Показано, що на сьогоднішній день достатньо добре вивчена будова, властивості та основні методи отримання тонких плівок не тільки простих, але і складних, бага-

токомпонентних неорганічних напівпровідникових матеріалів, але нові сфери застосування і підвищення вимог до експлуатаційних характеристик пристроїв на їхній основі потребують покращення існуючих технологій і створення нових методів їх отримання, що передбачає детальний аналіз відомих, та пошук нових, прогресивних способів препарування. У зв'язку із тим, що основними методами отримання тонких плівок неорганічних напівпровідникових матеріалів є конденсація у вакуумі та хімічне осадження, в першій частині огляду охарактеризовано методи їх вакуумного нанесення, зокрема, термічне напилення у відкритому вакуумі. Показано, що найпоширенішим способом отримання тонких плівок залишається термічне напилення при резистивному нагріванні випарника із вихідним матеріалом. Проаналізовано спеціальні конструкційні і технологічні зміни та вдосконалення традиційних методів і систем термічного напилення, які дозволяють вирівнювати співвідношення хімічного складу тонких плівок і вихідного матеріалу, покращувати стехіометрію конденсатів, забезпечувати їхню однорідність. Представлено конструкції термічних випаровувачів із резистивним нагріванням тиглів у відкритому вакуумі із сублимацією чи випаровуванням однієї і двох речовини. Показано, як дані типи випарників виключають перенесення в парову фазу твердотільних частинок матеріалів, які випаровуються чи сублимують, та усувають пряме потрапляння пари на поверхню конденсації, що в більшій чи меншій мірі застерігає від неоднорідних включень у конденсатах. Показано, що проаналізовані способи чи їхні модифікації є таким необхідним на сьогоднішній день засобом створення тонкоплівкових напівпровідникових структур із наперед заданими властивостями, а вакуумне осадження, зокрема, традиційне та модифіковане термічне напилення у вакуумі завдяки своїй простоті, але, одночасно, і можливості ефективно керувати великою кількістю технологічних факторів і створювати необхідні умови росту конденсатів, залишається одним із найпоширеніших способів отримання тонких плівок, у т. ч. неорганічних напівпровідників.

Ключові слова: тонкі плівки, напівпровідники, технологічні методи отримання, конденсація у вакуумі, термічне напилення.

Introduction

The technology of obtaining thin films of inorganic semiconductor materials began to be developed as early as the 1950s, but the longer proposals and prospects for the application of such layers in various fields of micro, opto-and acousto-electronics were ahead of real implementation and had no experimental confirmation due to the lack of effective methods for obtaining stable reproducible condensates with predetermined properties. Therefore, since the 1970s, a number of fundamental and survey papers appeared, including collections and monographs devoted to the issues of obtaining thin films of inorganic semiconductor materials, and in fact the scientific foundations of the methods of obtaining and doping condensates of the specified materials. It should be noted well-known in Ukraine and abroad scientific schools for research on the technology of obtaining and studying physical properties and the use of thin films of inorganic semiconductor materials at the V.Ye. Lashkarev-Institute of Semiconductor Physics of Academy of Science of Ukraine, Institute of Physics of Academy of Science of Ukraine, Institute of Monocrystals of Academy of Science of Ukraine, I.I. Mechnikov Odessa National University, Ivan Franko Lviv National University and others. The most famous among foreign are the schools of Stanford University (USA), the Delhi Institute of Technology (India), the University of Montpellier (France), the St. Petersburg Institute of Technology (Russia), as well as dozens of laboratories of almost all leading universities of the world and major e-industry firms. However, the complexity of dissociation-associative, sublimation, condensation, evaporation, adsorption-desorption, and others. physical processes in the formation of thin films of inorganic semiconductor materials, as well as significant and ambiguous dependence of the structure and properties of condensates on the conditions of obtaining and further stimulates the search for effective methods for their obtaining.

Methods of obtaining thin films of inorganic semiconductors

Inorganic semiconductor materials have a number of

characteristic properties that allow them to be grouped into separate classes of substances, depending on the crystalline structure, a set of physical and chemical properties and applications. Possibility of a wide choice of chemical composition and structure in inorganic semiconductor materials allows to adequately control electronic spectra and mechanisms of generation, transfer and recombination of charges in them, and therefore, to set up the necessary electrophysical, photovoltaic, optical and other properties in advance. Such valuable features as the ability to significantly change their properties under the influence of external factors, high photosensitivity in a wide spectral range, high probability of radiative recombination in direct optical transitions, relatively high mobility of carriers and others, like the presence of a large band gap (from 0.5 to 3.7 eV), high technological capacity, affordable cost and possibilities for wide changes of properties through the composition and technological factors of obtaining stimulated a wide the use of inorganic semiconductor materials and structures on their basis as elements of a variety of electronic devices.

To date, the structure, properties and basic methods of obtaining thin films of not only simple but also complex, multi-component inorganic semiconductor materials are well studied. However, new areas of application and increased requirements for the performance characteristics of devices on their basis require the improvement of existing technologies and the creation of new progressive methods of obtaining them. Therefore, in this review, the known methods for the preparation of thin films of inorganic semiconductor materials are analyzed and new are proposed.

The main tasks of the technologists in obtaining semiconductor thin films are the creation of layers with the necessary values of structural dimensions (thickness, area, configuration), given physical parameters, uniform distribution of the centers of electrical conductivity and photosensitivity, optical and other characteristics, as well as a number of special parameters, depending on the scope of application. Therefore, the choice of method of obtaining and technological regulations is determined by the requirements for the expected set of properties of condensates.

The main methods for obtaining thin films of inorganic semiconductor materials are vacuum condensation and chemical deposition. In the first part of our review, we will focus on the methods of open vacuum vapor deposition of thin films.

Methods of vacuum spraying

The vapor deposition, or vacuum spraying, is the traditional and most widespread method of obtaining thin films, including inorganic semiconductor materials. Depending on the method of obtaining the atomic or molecular flow of the expected condensate vapor, the conditions for the transfer of steam to the condensation surface and the condensation itself, the following types of deposition from the vapor phase are distinguished: evaporation in an open vacuum, epitaxial deposition or sputtering in a quasi-closed volume, and cathode sputtering.

Spraying in open vacuum

The physical foundations of processes occurring at the vacuum coating of thin films are known and described by many authors (Bunshah, 1994; Seshan et al., 2002; Bahmut, 2014; Hartmut & Khan, 2015; Shahinyan, 2017; Aksimentyeva et al., 2018). For inorganic semiconductors, the molecular stream of vapors of the source material is obtained with its evaporation or sublimation through resistive, electron beam or laser heating. Traditional and most commonly used is thermal spraying with resistive heating of the evaporator with the source material.

Despite the emergence of a number of new, progressive methods in recent decades, traditional and modified thermal spraying in a vacuum due to its simplicity, but at the same time, the ability to effectively manage a large number of technological factors and create the necessary conditions for the growth of condensates, remains one of the most common ways of obtaining thin films, including inorganic semiconductors.

When heated and further melting and evaporation or sublimation in a vacuum of semiconductor materials, as a rule, their dissociation occurs on separate components. When condensing on a substrate, there is an inverse reaction of formation of molecules of the initial compounds from the vapor of individual elements, or other types of reactions (Kalinkin et al., 1978; Bunshah, 1994; Hartmut & Khan, 2015). Due to the fact that the equilibrium pressure of the vapor of the individual components of the semiconductor compounds is different, the chemical composition of the vapor near the surface of the condensation under thermal vaporization in the open vacuum is different from the surface of the evaporation or sublimation, which leads to a significant deviation in the films as from the initial composition, and from stoichiometry. In addition, during thermal sputtering of semiconductors, the solid particles pollute the vapor,

which significantly degrade the morphology and properties of the resulting films. Therefore, in order to eliminate these disadvantages and obtain the specified chemical composition of homogeneous condensates without harmful inclusions, the special structural and technological changes are carried out, that improve traditional methods and systems that allow more or less equalize the ratio of the chemical composition of thin films and the source material, improve stoichiometry condensates to ensure their homogeneity.

Thus, for the thermal sputtering in an open vacuum, different types of evaporators are used to eliminate the transfer of solid particles to the vapor phase of the materials that evaporate or sublimate. These include a number of evaporators, which contain separate external elements of the reflection of the solid fractions of the vapor flow (Slutskaya, 1967; Golikov & Nahmanson, 1968; Bunshah, 1994), a point quartz evaporator (Kalinkin et al., 1978, Fig. 1, a), a quartz evaporator with a disk with holes (Kalinkin et al., 1978, Fig. 1, b), an evaporator with a compartment for the extraction of one of the components (Kalinkin, 1978, Fig. 1, c), a quartz bottle with a narrow neck and quartz wool (Chopra & Das, 1983, Fig. 1, d), a coaxial graphite evaporator with insulated chambers (Chopra & Das, 1983, Fig. 1, e), cylindrical shielded evaporator, evaporator with quartz tubing (Krasulin et al., 1973), conical quartz evaporation with insert (Eskofferi, 1964), tape evaporator, closed perforated plate (Holland, 1963), closed graphite evaporator (Nikol'skiy et al., 1968; Kalinkin et al., 1978), a multi-evaporator walls (Kalinkin et al., 1978; Chopra & Das, 1983; Bunshah, 1994) and others. As we see, the most characteristic feature for all evaporators is the lack of direct vapor entering the condensation surface, which more or less warns against heterogeneous inclusions in condensates.

In a number of cases (for example, in Chopra & Das, 1983; Bunshah, 1994), not only the experimental selection of the evaporator, but also the optimal form and size of the optimum model are theoretically motivated and calculated. The general disadvantages of the evaporators considered here are the nonequilibrium conditions of the growth of films, the dependence of the chemical composition of the films on the rate of spraying, and deviation from stoichiometry.

Often, modified variants of single-stage thermal spraying in an open vacuum, such as discrete (explosive) spraying, are used, in which small (50...300 mkm) particles of the source material by means of a special device such as a spiral vibrobunker or a belt conveyor are fed to the evaporator, whose temperature significantly exceeds the temperature of sublimation or evaporation of semiconductors, due to which these particles sublime (evaporate) before they touch the evaporator, and the films have chemical composition similar to the original one (Kalinkin et al., 1978; Kolesnikov, 1985; Bunshah, 1994; Sharma & Purohit, 1974).

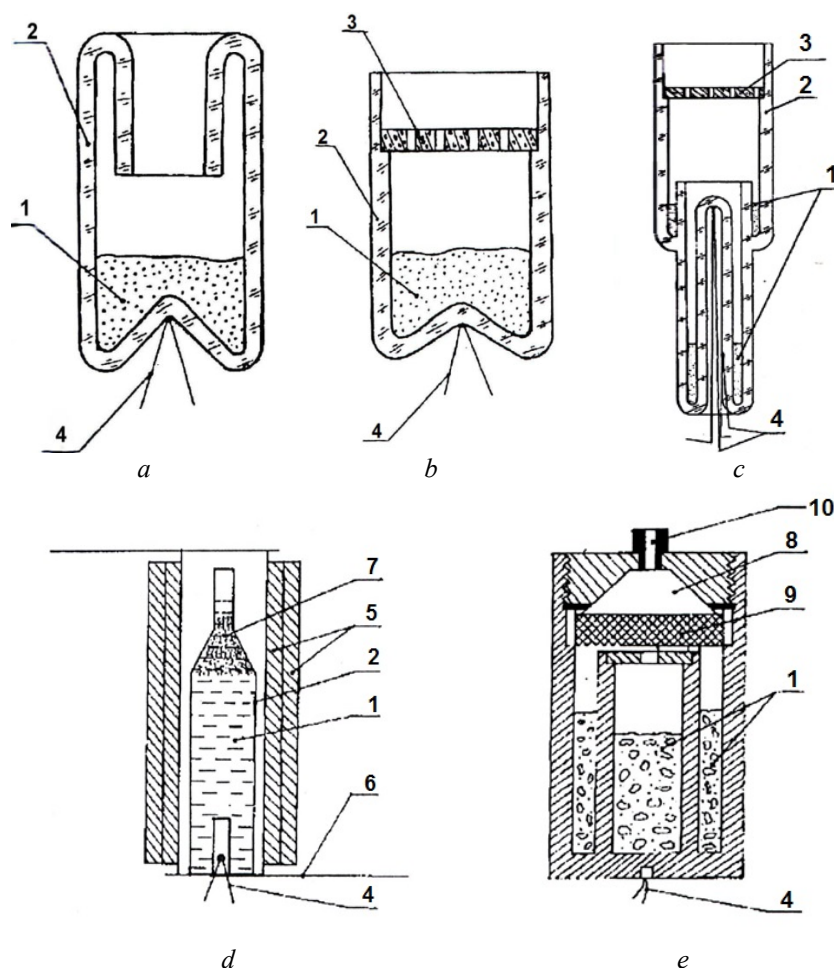


Fig. 1. Constructions of thermal evaporators with resistive heating of crucibles for spraying thin films of semiconductor materials in an open vacuum: 1 – source material, 2 – quartz crucible, 3 – disk with apertures, 4 – thermocouple, 5 – heater of evaporator, 6 – thermal screen, 7 – quartz cotton wool, 8 – mixing chamber, 9 – filter, 10 – outlet.

In order to obtain thin films of a certain chemical composition, the technology of compatible evaporation from several sources has been developed, in particular, the method of three temperatures: the substrate and two independent evaporators, each containing a separate component, as well as a number of its modifications (Sharma & Purohit, 1974; Kalinkin et al., 1978; Chopra & Das, 1983; Kolesnikov, 1985; Bunshah, 1994; Aksimentyeva et al., 2018).

To eliminate the contamination of the vapor flow and condensate with the material of the evaporator, the heating of the source material can be carried out by an electron or laser beam, which focuses on the source material and by its interaction heats its surface to evaporation (Galla, 1965; Kalinkin et al., 1978; Kolesnikov, 1985; Bunshah, 1994; Kalynushkin et al., 2009). Such methods, in addition to the high degree of substrate cleanliness and thin film, in some cases allow the obtaining of specific properties of condensates, for example, the density of defects of a crystalline structure is much lower than in other methods (Chopra & Das, 1983), and also in the broadest sense, to regulate their sensitivity to external factors, which is especially important, for example, when creating sensory environments.

Also, original, non-traditional methods, for example, thermal evaporation with further regulated ionization of

the vapor flow (Grytskevych et al., 1984), evaporation from the diffusion cell (Kalinkin et al., 1978; Chopra & Das, 1983), sputtering in electric and magnetic fields, etc., are also noteworthy.

Also special variants of obtaining thin films are known, with a given structure or orientation, such as molecular-beam epitaxy (Arthur, 1979), graphoepitaxia (Geis et al., 1979) and others, which, due to the expensive, unique equipment necessary for their realization, constitute only academic interest and are used most often for fundamental research. But in the future, these methods, or their simplified modifications, can serve as a necessary tool for the creation of thin-film semiconductor structures with predetermined properties.

Conclusions

Despite the emergence in recent decades of a number of new, progressive methods for the synthesis of thin film condensates, vacuum deposition, in particular, traditional and modified thermal spraying in a vacuum due to its simplicity and accessibility, but at the same time, the ability to effectively manage a large number of technological factors and create the necessary conditions the growth of condensates, remains one of the most common ways of obtaining thin films, including inorganic

semiconductors. It is shown how special structural and technological changes are carried out with the goal to eliminate the disadvantages of thermal spraying of thin films in an open vacuum and to obtain a given chemical composition of homogeneous condensates without uncontrolled inclusions. Those changes improve traditional methods and systems that allow to more or less equal the ratio of the chemical composition of the thin films and raw materials, to improve the stoichiometry of condensates, to ensure their uniformity and to apply this method in many fields.

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