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Chemical deposition and mechanical application of semiconductors thin films

B. Tsizh[1,2], Z. Dziamski[1]

[1]Kazimierz Wielki University in Bydgoszcz, Bydgoszcz, Poland
[2]Stepan Gzhytskyi National University of Veterinary Medicine and Biotechnologies Lviv, Ukraine

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Kazimierz Wielki University in Bydgoszcz, 30 Chodkiewicza, Bydgoszcz, 85-064, Poland.

Stepan Gzhytskyi National University of Veterinary Medicine and Biotechnologies Lviv, ekarska Str., 50, Lviv, 79010, Ukraine.
Tel.: +38-032-239-26-35
E-mail: tsizhb@ukr.net

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Features and main technological methods of forming thin layers of semiconductor materials by methods of chemical deposition and mechanical application are analyzed. The disadvantages of thermal sputtering and cathodic sputtering of thin films in vacuum for multicomponent semiconductor compounds are indicated. Features of chemical deposition of semiconductor films from the gas (steam) phase are presented. Such deposition involves the transfer of source material from the evaporator zone with higher temperature in the form of volatile compounds to the colder surface of the substrate, where the film growth occurs as a result of reaction of transported compounds or their decomposition. It is shown that the growth of the film during chemical vapor deposition is a process of layer-by-layer condensation of atoms or molecules, with the advantageous difference that during chemical deposition the latter are formed as a result of a heterogeneous chemical reaction when there is no need for average free path length of the gas molecules to be larger than the size of the deposition chamber, i.e. no need for critical degree of vacuum. Chemical deposition of thin films from solution is characterized as a process of precipitation of solute which occurs due to the fact that the ionic product exceeds the product of solubility, i.e. it is greater than the constant value characteristic of a saturated solution in the equilibrium state. We emphasize, that chemical deposition from an water solution allows to obtain homogeneous in thickness and structure fine-grained non-textured mechanically stable polycrystalline films with good adhesion to substrates and the required set of properties. The method of pulverization with subsequent pyrolysis is described. This is deposition from intracomplex organometallic compounds, which is based on thermally stimulated reactions between clusters of atoms, chemically active substances of liquid or vapor phase. The method of electrolytic deposition on electrically conductive substrates is characterized. The method is using appropriate salt solutions by co-deposition of individual components, or by deposition on the cathode of one of the components with its subsequent interaction with others present in the solution. We also describe the method of obtaining epitaxial thin films of semiconductor deposition materials. We note that the analyzed methods or their modifications are necessary tool today to create thin-film semiconductor structures with predetermined properties. In the same time, in each particular case the features of each method of obtaining thin semiconductor films should be comprehensively evaluated and, depending on the chemical composition, structure, topology and complex of expected properties, the most effective method should be applied.

***Key words:** thin films, semiconductors, technological methods of obtaining, chemical deposition, pulverization, electrodeposition.*

Хімічне осадження та механічне нанесення напівпровідникових тонких плівок

Б. Ціж[1,2], З. Дзямскі[1]

[1]Університет Казимира Великого в Бидгощі, Бидгощ, Польща
[2]Львівський національний університет ветеринарної медицини та біотехнологій імені С. З. Ґжицького, м. Львів, Україна

Проаналізовано особливості та основні технологічні способи формування тонких шарів напівпровідникових матеріалів методами хімічного осадження та механічного нанесення. Вказано недоліки термічного напилення та катодного розпилення тонких плівок у вакуумі для багатокомпонентних напівпровідникових сполук. Висвітлено особливості хімічного осадження напівпровідникових плівок з газової (парової) фази, яке передбачає перенесення вихідного матеріалу із зони випаровувача з вищою температурою у вигляді летючих сполук до холоднішої поверхні підкладки, де відбувається ріст плівки в результаті реакції транспортованих сполук одна з одною, або їх розкладання. Показано, що ріст плівки при хімічному осадженні з парової фази є процесом пошарової конденсації атомів чи молекул при тій вигідній відмінності, що при хімічному осадженні останні утворюються в результаті гетерогенної хімічної реакції, коли не потрібно, щоби середня довжина вільного пробігу молекул газу була більшою від розмірів камери для осадження, тобто не настільки критичний ступінь вакууму. Охарактеризовано хімічне осадження тонких плівок з розчину як процес випадання в осад розчиненої речовини внаслідок того, що іонний добуток перевищує добуток розчинності, тобто більший від постійної величини, характерної для насиченого розчину в рівноважному стані. Підкреслено, що хімічне осадження з водного розчину дозволяє отримувати однорідні за товщиною і структурою, полікристалічні, дрібнозернисті, нетекстуровані, механічно стійкі плівки з доброю адгезією до підкладок і необхідним набором властивостей. Описано метод пульверизації з подальшим піролізом – осадження із внутрікомплексних металоорганічних сполук, який ґрунтується на термостимульованих реакціях між кластерами атомів, попередньо розпилених хімічно активних речовин рідкої чи парової фази. Охарактеризовано метод електролітичного осадження на електропровідні підкладки з використанням відповідних розчинів солей сумісним осадженням окремих компонентів, або шляхом осадження на катоді одного із компонентів з подальшою його взаємодією з іншими, наявними в розчині, та спосіб отримання епітаксіальних тонких плівок напівпровідникових матеріалів осадженням з рідкої фази. Зазначено, що проаналізовані способи чи їхні модифікації є таким необхідним на сьогодні засобом створення тонкоплівкових напівпровідникових структур із наперед заданими властивостями, а в кожному конкретному випадку слід всесторонньо оцінити особливості кожного способу отримання тонких напівпровідникових плівок і залежно від хімічного складу, структури, топології та комплексу очікуваних властивостей застосувати найефективніший метод.

***Ключові слова**: тонкі плівки, напівпровідники, технологічні методи отримання, хімічне осадження, пульверизація, електроосадження.*

Introduction

In previous reviews (Tsizh & Dziamski, 2019; 2020) we described the features of different methods of obtaining the semiconductors thin films in vacuum, in particular, methods of thermal and cathodic spraying. These methods have a number of positive factors and advantages, such as a high degree of purity of the synthesis, wide possibilities of regulation by evaporation, sublimation or spraying of the source material and deposition conditions, as well as condensation on the substrate. Other advantages are: the needed selection of components for multicomponent compositions of films and a wide choice and the possibility of varying the technological parameters of deposition (the composition of the synthesis atmosphere, the temperature of the source material and the substrate, the sputtering rate). However, all these methods have disadvantages that limit their application. First of all, all methods of preparation in vacuum require special vacuum equipment, and it is cumbersome and expensive. In addition, in each of these methods, the starting material is subjected to either significant thermal heating, or bombardment by electrons or ions, or the action of other factors. This can lead to the rupture of chemical bonds in the molecules of the source material, energy excitation of atoms or molecules and other consequences that significantly affect the stoichiometry, structure and properties of condensates. These factors have led to the search for other ways to obtain semiconductor thin films, such as chemical deposition and mechanical application.

Various types of chemical deposition methods are widely used to obtain thin films of semiconductor materials, such as gas phase and solution deposition, spray by subsequent pyrolysis, electrodeposition and others, which are based on chemical reactions and are characterized by simple production technology and relatively high reproducibility. The following is a brief description of the types of chemical deposition of thin semiconductor films.

Chemical deposition from the gas phase

Chemical deposition from the gas (steam) phase involves the transfer of source material from the evaporator zone with a higher temperature in the form of volatile compounds to the colder surface of the substrate. There, the film growth occurs, as a result of reaction of the transported compounds, or, their decomposicion, as a rule with heterogeneous mechanism, the nature of which depends on the composition of the compound (Kalinkin et al., 1978; Kiriashkina et al., 1979; Chopra & Das, 1983; Mazurenko et al., 2001; Duniushkina, 2015). Thus, in this technology, the thin film is a substantially condensed solid phase of the isolated chemical reaction products. This reaction occurs near the substrate or on its surface as a result of the action of vapors of the corresponding compounds or reactive gases on it. There are options for activating the necessary chemical reactions using thermal or electromagnetic fields and radiation, electric arc discharge, electron bombardment or catalytically active substrate surfaces.

Variety of ways is beeing used to transfer the necessary compounds in the area of the substrate, namely: resublimation in a stream of inert gas, chemical transport reactions, which consist in the conversion of the source substance into a volatile compound transferring it to the substrate, decomposition of steam and condensation on the surface of the substrate of the source material. In the role of carrier gas and chemical reagent pure hydrogen is used, as well as its various mixtures such as H_2 + HCI, H_2 + HB_2, HCI + HB_2, or other gases. A variant of transfer by chemical transport reactions is the method of close transfer (sandwich method), in which the distance between the source and the substrate is 0.1...0.5 mm and the temperature difference is – 10...100 degrees (Mazurenko et al., 2001). Aslo a similar method of gas transport reactions in a quasi-closed volume can be used.

As in spraying methods, in vacuum, the growth of the film during chemical vapor deposition is a process of layer-by-layer condensation of atoms or molecules. It

advantage is, that in chemical deposition molecules are created as a result of heterogeneous chemical reaction, when there is no need for average free path length of the gas molecules to be larger than the size of the deposition chamber, i.e. no need in critical degree of vacuum (Duniushkina, 2015).

Chemical deposition from solution

From a chemical point of view, the deposition of thin films from solution is the precipitation of solute due to the fact that the ionic product exceeds the product of solubility, i.e. it is greater than the constant value characteristic of a saturated solution at equilibrium. In the first stage of the heterogeneous deposition process, the catalytic decomposition of semiconductors or their derivatives takes place with the formation of the corresponding ions (Hartmut & Hamid, 2015; Antoniuk et al., 2016). In the second stage, these ions interact to form the corresponding compounds in the volume of the solution and the growth of thin films on the substrate takes place. In order for the process of chemical deposition of films to be controlled and for spontaneous precipitation not to occur, appropriate complexing elements of the required concentration are sometimes added to the initial solution, which ensure the equilibrium conditions.

In this method, the ions that are part of the semiconductor compounds are successively deposited on those parts of the substrate that contain growth centers. The film growth process includes an initial stage with a low growth rate due to the induction period of critical nucleation in a homogeneous system on a clean surface, a stage of active deposition with a sharp increase in the deposition rate to values equal to the dissolution rate (solubility product), and a final stage, when the growth of the film stops.

Technological equipment for chemical deposition from solution is relatively simple. The substrates are placed in reaction baths, where the films grow at the required temperature and the solution is stirred. Due to the widespread use of this method in semiconductor technology a number of authors (Bunshah, 1994; Hartmut & Hamid, 2015) studied kinetics and thermodynamic features of the mechanism of chemical deposition of films of inorganic semiconductor materials from aqueous solutions, and theoretically and experimentally analyzed the influence of the composition and temperature of the bath on the process of formation and properties of films.

The method of chemical deposition from an aqueous solution allows to obtain homogeneous in thickness and structure polycrystalline, fine-grained, non-textured, mechanically stable films with good adhesion to substrates and the required set of properties.

Pulverization followed by pyrolysis

The method of pulverization followed by pyrolysis, or as it is also called, deposition from intracomplex organometallic compounds (IOC) is based on fast reactions between clusters of atoms previously developed by chemically active substances of the liquid or vapor phase. This technology involves spraying on a hot substrate an aqueous or other solution that includes salts of the components of a thin film (Chopra & Das, 1983; Seshan, 2002; Hosokawa et al., 2008). After reaching the surface of the heated substrate, the droplets of the solution decompose as a result of the endothermic pyrolytic process and the volatile reaction products are released in the form of vapor, while crystals settle on the substrate, which form a thin film.

Thus, the deposition process from the IOC includes spraying the initial solution and transferring its droplets to the substrate, thermal decomposition of salts and pyrolytic chemical reaction between the reagents – decomposition products, sedimentation of solid fractions on the substrate and evaporation of solvents. Heating the substrate to a temperature of about 500 ... 700 K is a prerequisite for this method, necessary for thermal decomposition of the solution, chemical interaction of individual components and the final processes of growth (union and recrystallization of individual groups of clusters, the formation of a continuous film).

One of the most important elements of technological equipment for chemical deposition from the IOC is a pulverizer, which sprays the chemical solution into small drops using purified carrier gas at certain pressures and flow rates. The technological parameters of the process, such as the shape of the jet, the size of the droplets, the spray rate etc., significantly depend on the configuration of the pulverizer into which the gas and solution enter. To date, a number of spray designs have been developed for spraying solutions of various semiconductor materials depending on the parameters of the expected films, which together with the substrate temperature and the composition of the initial solution determine the structure and properties of condensates.

Thin films obtained by pulverization followed by pyrolysis are usually polycrystalline and are characterized by high adhesion to the substrate, mechanical strength and stability. They have a rough surface in which the shape and size of the irregularities are determined by technological parameters, the grain size of the crystals is often 0.2 ... 0.5 μm, and their thickness can reach 5 μm.

Electrodeposition and other methods of chemical application

To obtain semiconductor thin films, the method of electrolytic deposition on electrically conductive substrates is applied. It is applied with appropriate salt solutions by co-deposition of individual components, or by deposition on the cathode of one of the components with its subsequent interaction with others present in the solution. To date, the influence of technological parameters of electrodeposition, such as the composition of the electrolytic bath, the shape of the active and counter electrodes, current density and others that determine the growth conditions, microstructure and properties of films is studied in details (Chopra & Das, 1983; Seshan, 2002; Hosokawa et al., 2008; Kalynushkin et al., 2009).

Preparation of semiconductor films by electrophoresis by depositing particles from a colloidal solution on the electrode is also well known.

To obtain thick films the method of screen printing is used, in which the substrate is applied using a stencil and squeegee, which, in addition to fine-grained powder of the main component, includes binders, organic suspension and solvent. Subsequent chemical reactions occurs in the

process of thermal annealing and formation of the appropriate composition. There are also various methods of pressing and sintering powders.

The method to obtain epitaxial thin films of semiconductor materials by precipitation from the liquid phase (liquid-phase epitaxy) is usual. This method is based on crystallization from a supersaturated solution, which is cooled in one of the solvents: In, Ga, Bi, Sn, Pb, Cd or other. The substrate is immersed in a solution saturated with the desired substance and heated to the desired temperature, followed by gradual cooling. The chemical composition of the solution, its cooling rate and deposition time determine the structure, properties and thickness of the films. Under optimal conditions, the condensate structure is a continuation of the monocrystalline substrate structure. Pre-evacuation of compounds is often required in liquid phase epitaxy technology up to $10^3...10^4$ Па, unsoldering the ampoules, heating in the oven to the desired temperature and tilting to an angle sufficient to cover the melt of the substrate.

Conclusions

From the above one can conclude, that as a rule, the equipment in chemical deposition methods is relatively simple and does not require a vacuum part, there is a possibility of effective control of chemical composition, film configuration, concentration of alloying impurities, deposition rate and other technological parameters. However, the disadvantages of chemical methods are the complexity of thermodynamics and kinetics of deposition processes, high toxicity, explosiveness, reactive and corrosive activity, limited choice of substrate materials, lack of masking capabilities, difficulty of controlling the homogeneity of films during growth, low purity of technological conditions compared to vacuum. Therefore, in each case, the features of each method of obtaining thin semiconductor films should be comprehensively evaluated and, depending on the chemical composition, structure, topology and complex of expected properties, the most effective method should be applied.

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