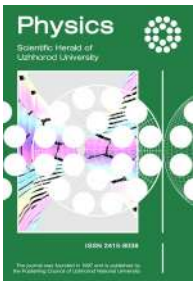
Scientific Herald of Uzhhorod University
Series "Physics"
Journal homepage: https://physics.uz.ua/en
Issue 49, 48-53
Received: 14.12.2020. Revised: 26.02.2021. Accepted: 27.05.2021



УДК 669.094.54:661
PACS 62.20.-x
DOI: 10.24144/2415-8038.2021.49.48-53

Sublimation Process for Obtaining Silicon Films from Molybdenum and Tungsten Disilicide

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Abstract

Relevance. In existing methods of sublimational evaporation of silicon by resistive heating, careful control and adjustment of heating parameters is required. The sublimation temperature is limited in the range of ~1620÷1670 K. During resistive heating of silicon, it is necessary to carry out its additional heating with an electron beam gun to a temperature of the order 1100 K, at which silicon becomes conductive. In addition, the deposition rate of the films is limited and less than 1 μm/h. Accordingly, electron beam heating of silicon is widely used, but the disadvantage of such a source is the presence in the stream of silicon atoms of the droplet fraction, due to rapid local overheating. This paper proposes to conduct a study of the sublimational evaporation of silicon from refractory metals.

Purpose. The purpose of the study is to extend the operating temperature range of silicon evaporation for more convenient control of regulation and increase the rate of silicon deposition by increasing the pressure of silicon vapour.

Methods. For sublimational deposition of silicon-based structures, a gas-phase method was used, which developed and obtained a source of $MoSi_2$ and WSi_2 atoms.

Results. This paper proposes to conduct a study of the sublimational evaporation of silicon from refractory metals. Sublimation sources, which are compounds of $MoSi_2$, WSi_2, are obtained by the gas-phase method from the hydrogen reduction reaction $SiCl_4+2H_2 \rightarrow Si+4HCl$. It is determined that the evaporation rate of silicon from refractory metals increases due to an increase in the vapour pressure of silicon, and the evaporation temperature range expands for more convenient control of the film deposition process. It is shown that the evaporation rate Si from a sublimation source $MoSi_2$ and WSi_2 is greater than the evaporation rate of silicon (resistive evaporation, electron beam method, evaporation from an effusion cell) at its sublimation temperature. The temperature range of sublimation deposition has been extended from 1780 to 2100⇄K, which greatly improves the control of sublimation temperature regulation.

Conclusions. Sublimation sources 1780 and WSi_2 extend the temperature range of silicon evaporation from 1780 to 2100⇄K for more convenient control regulation and increase the rate of silicon deposition by increasing the pressure of silicon vapour

Keywords: source of silicon atoms, refractory silicides, thin-film solar cells, silicon structures

Introduction

Intensive development of thin-film solar energy in recent decades has been observed all over the world. One of the main materials used in thin-film solar cells is silicon. The patterning of silicon-based structures for semiconductor devices is one of the main technological processes of modern electronics. Therefore, it is necessary to continuously

Suggested Citation:
Zhuravlov OYu, Shyian OV, Shirokov BM, Kolodiy IV, Sholohov SM. Sublimation process for obtaining silicon films from molybdenum and tungsten disilicide. *Scientific Herald of Uzhhorod University. Series "Physics"*. 2021;(49):48-53.

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develop and improve methods for obtaining such materials. Among the most common and safest methods for patterning silicon films for solar cells is physical deposition, since it does not require any toxic gaseous precursors. One of the critical parameters for controlling the properties of sprayed silicon films is their deposition pressure [1].

A variation of the molecular beam epitaxy method is the silicon sublimation method, which is characterised by obtaining a flux of Si atoms by heating a single-crystal Si bar to a temperature close to melting by direct transmission of an electric current. This method is simpler in hardware design, is characterised by clean vacuum conditions, but has limited capabilities for technological use and is used mainly in scientific research [2]. This method of heating leads to the fact that the process must be carried out in a narrow temperature range near the melting point of the working substance. This requires careful monitoring and adjustment of heating parameters. At the top, the temperature is limited by the melting point, and at the bottom, by the temperature at which the deposition rate is too low for mass production. In addition, the maximum vapour pressure in this source cannot exceed 5.3 Pa [3; 4], which is achieved at the melting point and limits the rate of film deposition. Furthermore, due to rapid local overheating, silicon "spills out" of the melt, and the steam Si contains up to 20% of clusters, condensation of which leads to the appearance of defects in the accreted layers [5].

In [6], it is also noted that the method of molecular beam epitaxy has a lower yield compared to other methods, such as gas-phase epitaxy. However, in gas-phase methods, it is difficult to obtain multilayer structures with a sharp separation boundary between layers due to the inertia of gas injection and pumping process. The molecular flow from the effusion cell (Knudsen cell) is created by thermal evaporation of an element or compound loaded into the cell. The cell is made of graphite, ceramic, or boron nitride [7]. For silicon, which has a high melting point and chemical activity in the molten state, the generated molecular fluxes from the effusion cells are not sufficiently pure due to interaction with the crucible material [8].

According to a review of the literature on methods for obtaining silicon structures (resistive evaporation, electron beam method, effusion cell evaporation), it can be concluded that one of the main materials used in thin-film elements is silicon, and the available deposition methods need to be improved. Research efforts towards expanding the operating temperature range of silicon evaporation for more convenient control regulation and increasing the rate of silicon deposition due to increased silicon vapour pressures is relevant.

Therefore, *the purpose of this study* is to improve the method for vacuum deposition of silicon-based semiconductor structures. For the furtherance this goal, it is necessary to perform the following *tasks*: 1) conduct an experiment to obtain sublimation sources using the gas-phase method; 2) develop silicon structures based on the obtained sublimation sources $MoSi_2$ and WSi_2; 3) study samples $MoSi_2$ and WSi_2 on a diffractometer; 4) determine the interdependence of the evaporation rate with time in vacuum, respectively, under conditions of different temperatures.

Materials and Methods

Sublimation sources, which are compounds of type $MoSi_2$ and WSi_2 were obtained by the gas-phase method from the hydrogen reduction reaction $SiCl_4+2H_2 \rightarrow Si+4HCl$ on a flow-type installation (Fig. 1). The reaction chamber was pumped out to pressure 10^{-1} Pa. Hydrogen was fed into the chamber at a given pressure, a molybdenum or tungsten substrate of size $8\times60\times0.5$ was heated to a temperature ~2100 K and thermal annealing was performed, the substrate temperature was lowered to 1400-1600 K, and then silicon tetrachloride $SiCl_4$ was fed into the chamber at a given divergence. The silicon deposition modes were selected so that only the highest silicide $MoSi_2$ or WSi_2 was formed during the solid-phase reaction of silicon with Mo and W Range of parameters of the gas-phase process for obtaining sublimation sources:

– substrate temperature – 1400-1600 K;
– reaction chamber pressure – 10-10^4 Pa;
– hydrogen consumption – 60-120 l/h;
– relation – H_2:$SiCl_4$ from ⇄ 10:1 to 50:1

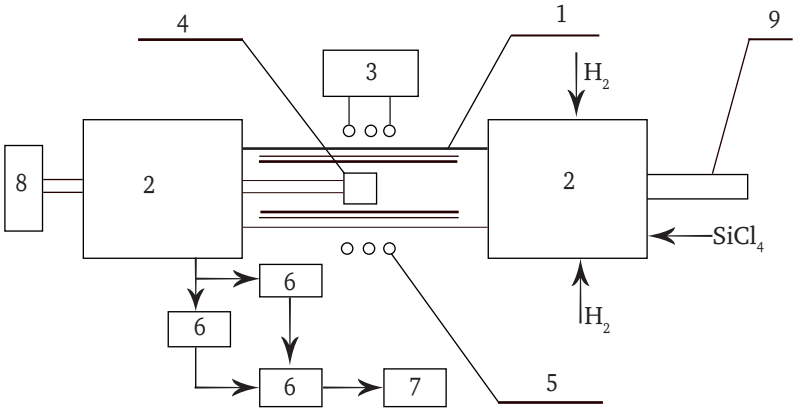

Figure 1. Installation diagram of a flow-through gas-phase deposition type
1 – reaction chamber; 2 – pre-chambers; 3 – RF generator; 4 – substrate; 5 – inductor; 6 – nitrogen traps; 7 – pre-pump; 8 – heater power source; 9 – viewing window

The production of silicon structures using the developed sublimation sources $MoSi_2$ and WSi_2 was carried out on an upgraded high-vacuum installation. The diagram of a high-vacuum installation for drawing structures Si is shown in Figure 2.

The high vacuum in the working chamber is maintained by a diffusion pump with a nitrogen trap designed to capture oil vapours. In the middle of the chamber there is a furnace with a tantalum heater for heating the substrate and a planar sublimation source $MoSi_2$ or WSi, heated by direct current transmission, located parallel to the furnace from below. The gap between the furnace and the source is covered by a flap. To prevent possible overheating of the chamber walls, there is a system of protective screens with windows for measuring the temperature of the substrate and a sublimation source with a pyrometer. The method of cleaning the substrate surface combined chemical treatment by oxidising agents.

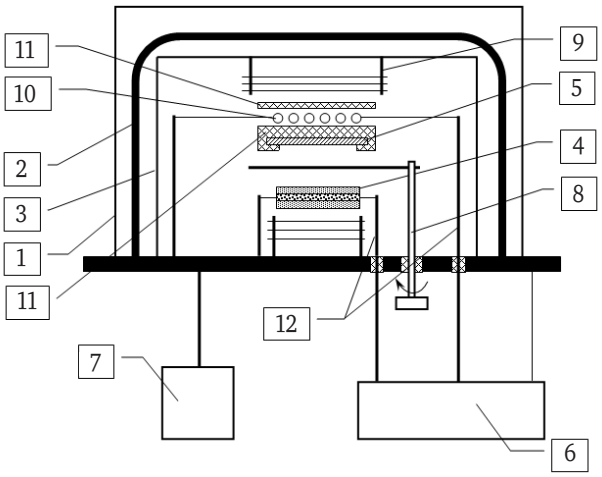

Figure 2. Diagram for installation for drawing Si structures
1 – external protective cap; 2 – working chamber; 3 – heat shield system; 4 – source of silicon atoms $MoSi_2$ or WSi_2; 5 – monocrystalline substrate Si; 6 – power supply unit for substrate heaters and sources; 7 – pumping system; 8 – flap; 9 – additional screens; 10 – heater; 11 – insulator; 12 – current leads

After loading the substrate and the sublimation source into the reaction chamber, the chamber was pumped to pressure 10^{-6} Pa. Then the sublimation source was closed with a flap and the single-crystal substrate was heated at a temperature of 1200 K for 20 minutes. A minute before the end of heat treatment, the source was heated to operating temperature. The substrate temperature was reduced to a deposition temperature of the order of magnitude 570-870 K. After that, the flap was opened and the sublimation deposition process was carried out.

Results and Discussion

Diffractometric studies of samples $MoSi_2$ and WSi_2 were performed on a Dron-4-07 X-ray diffractometer in copper Cu-Kα radiation using a Ni-selective absorbing filter. Diffracted radiation was detected by a scintillation detector. In the sample $MoSi_2$ (Fig. 3a), identified tetragonal molybdenum disilicide with lattice parameters: a=3,211 Å; c=7,868 Å. In the sample WSi_2 (Fig. 3b), a tetragonal tungsten disilicide with lattice parameters: a=3,222 Å; c=7,859 Å was identified (the reported values of the lattice parameters of molybdenum disilicide are a=3,202 Å; c=7,868 Å, tungsten disilicide a=3,211 Å; c=7,868 Å [9]).

Metallographic sections of molybdenum and tungsten silicide were performed. It is shown that the coating consists of clearly distinguishable columnar grains (Fig. 4). A similar microstructure is characteristic of the higher phases of molybdenum silicide $MoSi_2$ and WSi_2.

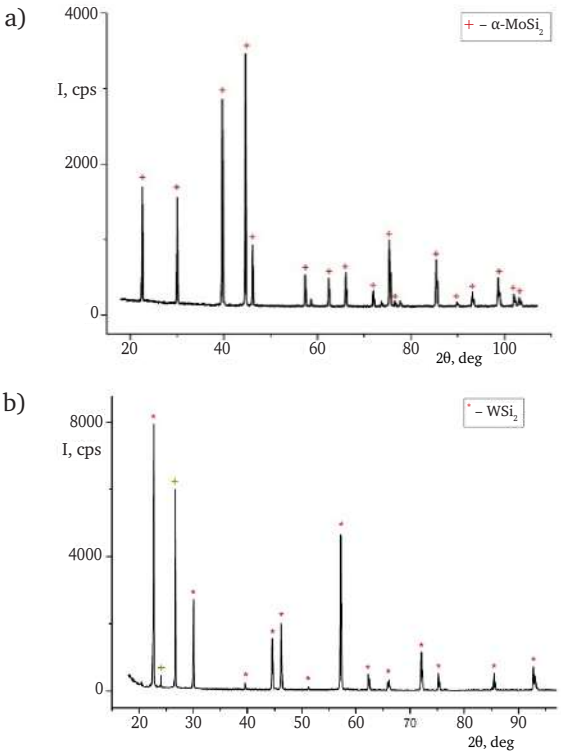

Figure 3. Diffractometric studies of samples of sublimation sources obtained by the gas-phase method: a – $MoSi_2$; b – WSi_2, where I, cps – intensity, rel. units, 2θ, deg – Bragg's reflection angle

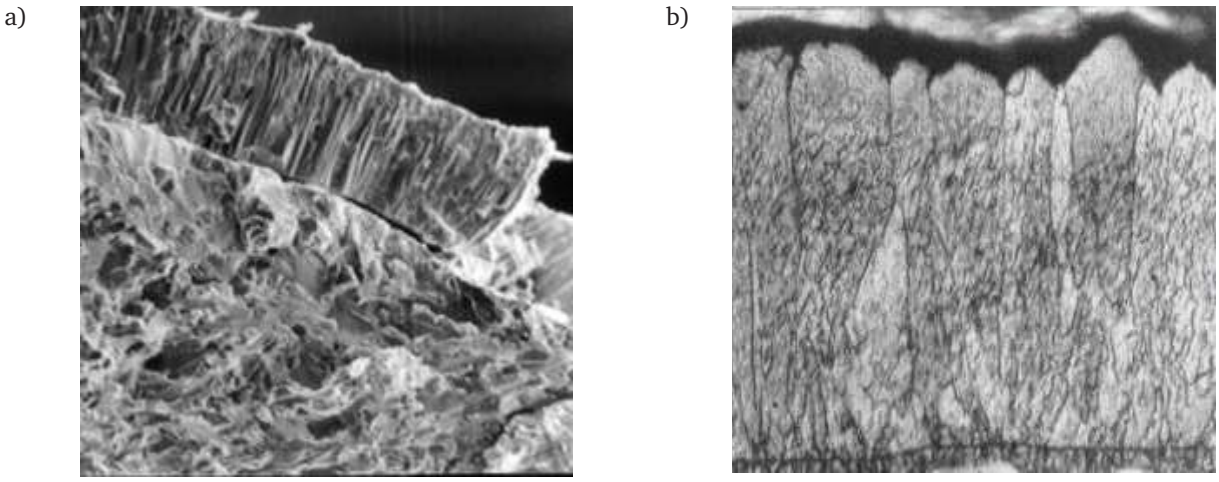

Figure 4. Metallographic sections of samples: a – $MoSi_2$; b – WSi_2, × 1200

Silicon films obtained from sublimation sources $MoSi_2$ and WSi_2 were studied by diffractometric method. Figure 5 shows a diffractogram of the sample Si obtained from the source $MoSi_2$ and WSi_2. For samples, there is only one line identified as silicon mapping (111) with the lattice parameter a=5,440 Å and a=5,458 Å (the reported values of the Silicon lattice parameters are a=5,4307 Å [10]).

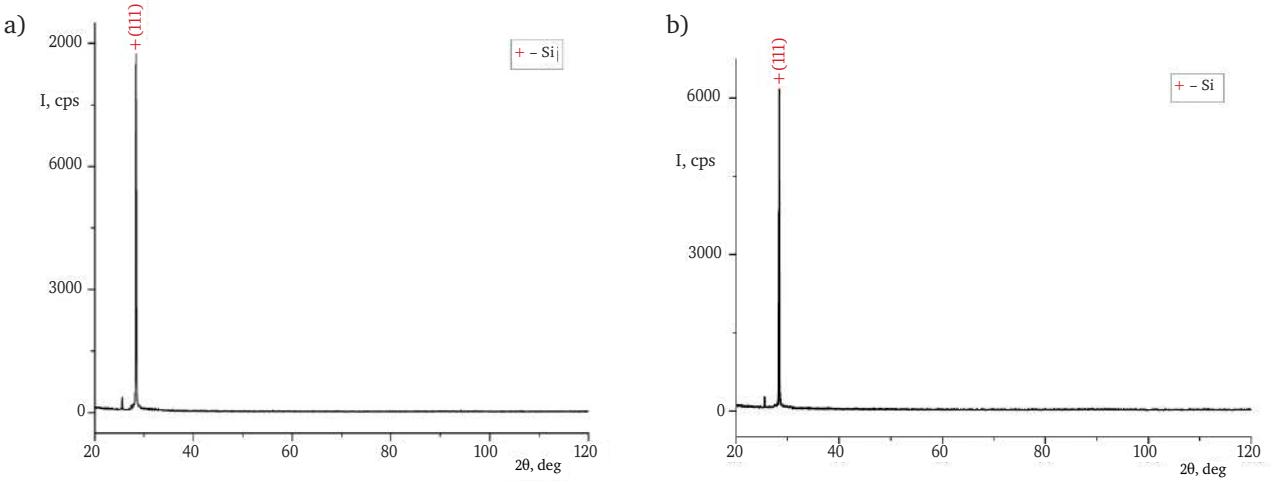

Figure 5. Diffractometric studies of samples Si obtained from sublimation sources a – Si obtained from $MoSi_2$; b – Si obtained from WSi_2, where I, cps – intensity, rel. units, 2θ, deg – Bragg's reflection angle

The method of conducting tests to determine the dependence of the evaporation rate Si on time in vacuum at different temperatures was carried out using the gravimetric method, followed by the construction of kinetic curves in the coordinates "evaporation rate – time".

The dependence of the evaporation rate Si on time in vacuum 10^{-6} Pa at different temperatures is shown in Figure 6. Figure 6a shows that the evaporation rate Si from the sublimation source $MoSi_2$ is greater than the evaporation rate of silicon at its sublimation temperature [11], and the temperature control range expands. The evaporation rate Si from the sublimation source WSi_2 is even higher than the evaporation rate of silicon (Fig. 6b).

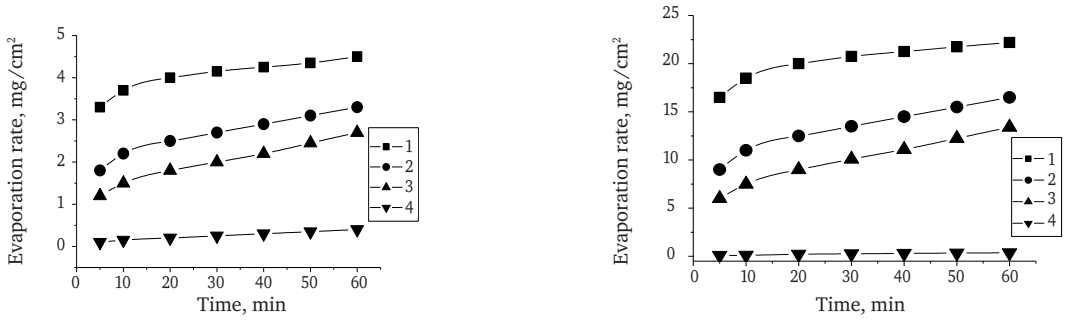

Figure 6. Dependence of the evaporation rate Si from a sublimation source a – $MoSi_2$; b – WSi_2 on time at different temperatures in vacuum in comparison with silicon: 1-2100 K; 2-2000 K; 3-1900 K; 4 – evaporation rate of silicon by temperature 1650 K

Source: compiled by the author based on [9]

It is known that silicides of refractory metals $MoSi_2$, WSi_2 when heated in air, have high heat resistance [12; 13] due to the build-up of an oxide film SiO_2 on the surface, which prevents the penetration of oxygen to the surface of metals [14]. However, when silica coatings are heated in a vacuum, due to the lack of oxygen and the build-up of a protective film SiO_2, silicon evaporates. As can be seen from Figure 7, the maximum silicon vapour pressure at its sublimation temperature ~1670 K is ~5 Pa [4], the silicon vapour pressure above $MoSi_2$ at the sublimation temperature ~2000 K is ~13 Pa, and the silicon vapour pressure above WSi_2 at the sublimation temperature ~2200 K already amounts to ~80 Pa [15]. With an increase in silicon vapour pressure, the silicon deposition rate increases [16]. For the connection $MoSi_2$, the heating can be set from to 1780, 2100⇄K, for WSi_2 – from 1900 to 2200⇄K. This simplifies the regulation and stabilisation of the silicon evaporation temperature.

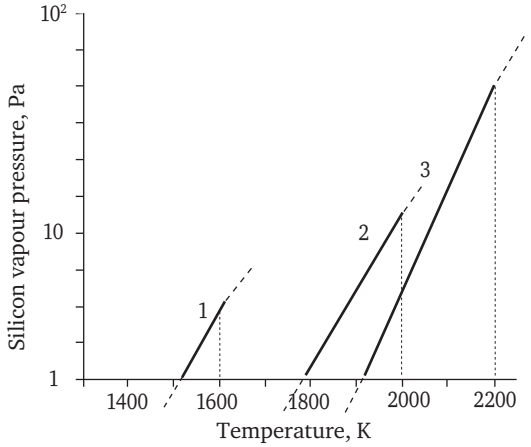

Figure 7. Temperature dependence of silicon vapour pressure: 1 – crystalline silicon Si; 2 – molybdenum disilicide $MoSi_2$; 3 – tungsten disilicide WSi_2

Source: [4; 12]

Therefore, the use of silicon compounds with refractory metals Mo, W is based on the experimental fact that the decomposition of refractory silicides during their heating in vacuum occurs by evaporation of silicon with the sequential transformation of higher silicides $(Me)Si_2$ into lower $(Me)_5Si_3$, until the silicon completely evaporates. Studies have shown that when the disilicide $MoSi_2$, WSi_2 is thermally heated, evaporation in the form of a silicon compound with Mo or W is excluded. The vapour pressure Mo, W is many orders of magnitude less than the vapour pressure of silicon by dissociation of the corresponding silicides. For example, at temperature 1920 K, the pressure of silicon above the surface WSi_2 is ~5 Pa, while the tungsten vapour pressure at the same temperature is $\sim 1.3 \cdot 10^{-9}$ Pa [17].

Therefore, sublimation sources $MoSi_2$ or WSi_2 for vacuum deposition of structures based on Si are superior to sublimational evaporation of ordinary silicon both in terms of extending the control of the evaporation temperature range and in terms of deposition rate. In addition, resistive heating of sources $MoSi_2$ and WSi_2 does not require additional heating, as in the case of heating ordinary silicon. Heating and cooling of sources $MoSi_2$ and WSi_2 occur very quickly – in a few seconds, which is very important during the creation of structures based on Si.

Conclusions

This paper proposes a source of silicon atoms for vacuum deposition of silicon-based structures by sublimation method. The source includes a solid working substance $MoSi_2$ or WSi_2 containing silicon. Such a chemical compound can be formed on a substrate of a refractory electrically conductive material in any configuration (wire, plate, curved two-turn spiral) in the form of a coating $MoSi_2$ or WSi_2 by the gas-phase method from a hydrogen reduction reaction $SiCl_4 + 2H_2 \rightarrow Si + {}_4HCl$.

It is shown that the evaporation rate Si from a sublimation source $MoSi_2$ and WSi_2 is greater than the evaporation rate of silicon (resistive evaporation, electron beam method, evaporation from an effusion cell) at its sublimation temperature.

The use of the proposed source of silicon atoms $MoSi_2$ or WSi_2 allows expanding the operating temperature range from 1780 to 2100⇄ K and increase the vapour pressure of the working substance, which significantly improves the operational properties and manufacturability of the source. The study conducted is important in the further development of vacuum deposition of silicon-based thin-film devices.

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Сублімаційний процес отримання кремнієвих плівок з дисиліцидів молібдена та вольфраму

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Анотація

Актуальність. У наявних методах сублімаційного випаровування кремнію шляхом резистивного нагрівання потрібен ретельний контроль і регулювання параметрів нагрівання. Температура сублімації обмежена в діапазоні ~1620÷1670 K. За резистивного нагрівання кремнію потрібно здійснити його додатковий розігрів електронно-променевою гарматою до температури порядку 1100 K, за якої кремній стає провідним. Крім того, швидкість осадження плівок обмежена і становить менше 1 мкм/год. Відповідно до цього, широко використовується електроно-променевий нагрів кремнію, однак недоліком такого джерела є наявність у потоці атомів кремнію крапельної фракції, через швидкий локальний перегрів. У роботі запропоновано провести дослідження сублімаційного випаровування кремнію з тугоплавких металів.

Мета. Метою роботи є розширення діапазону робочих температур випаровування кремнію для більш зручного контролю регулювання та підвищення швидкості осадження кремнію через збільшення тисків парів кремнію.

Методи. Для сублімаційного осадження структур на основі кремнію було використано газофазний метод, за допомогою якого розроблено та отримано джерело атомів $MoSi_2$ та WSi_2.

Результати. У роботі запропоновано провести дослідження сублімаційного випаровування кремнію з тугоплавких металів. Газофазним методом з реакції водневого відновлення $SiCl_4+2H_2 \rightarrow Si+4HCl$ отримано сублімаційні джерела, які являють собою сполуки $MoSi_2$, WSi_2. Визначено, що швидкість випаровування кремнію з тугоплавких металів зростає через підвищення тиску пари кремнію, а температурний діапазон випаровування розширюється для більш зручного контролю процесу осадження плівок. Показано, що швидкість випаровування Si з сублімаційного джерела $MoSi_2$ та WSi_2 більше, ніж швидкість випаровування кремнію (резистивне випаровування, електронно-променевий метод, випаровування з ефузійного вічка) за температури його сублімації. Температурний діапазон сублімаційного осадження розширено від 1780 до 2100⇄K, що значно покращує контроль регулювання температури сублімації.

Висновки. Сублімаційні джерела $MoSi_2$ та WSi_2 розширюють діапазон температур випаровування кремнію з 1780 до 2100⇄K для більш зручного контролю регулювання та підвищує швидкість осадження кремнію через збільшення тисків парів кремнію

Ключові слова: джерело атомів кремнію, силіциди тугоплавких металів, тонкоплівкові сонячні елементи, кремнієві структури