HYDROGEN REDUCTION OF SILICON TETRACHLORIDE IN LOW TEMPERATURE NON-EQUILIBRIUM PLASMA OF INDUCTION RF DISCHARGE

A.N. Deryzemlia, A.I. Yevsiukov, V.I. Radchenko, D.A. Khizhnyak, P.G. Kryshtal, A.Yu. Zhuravlov, A.V. Shijan, S.V. Strigunovskiy, Yu.A. Pelypets, B.M. Shirokov

National Science Center "Kharkov Institute of Physics and Technology", Kharkiv, Ukraine

E-mail: shirokov@kipt.kharkov.ua

In this work, silicon is obtained by plasma-chemical reduction of silicon tetrachloride in an argon-hydrogen low-temperature nonequilibrium plasma. It is shown that in the investigated range of process parameters, the energy cost of producing one kilogram of silicon is in the range of 150…190 kW/h with a silicon yield of ~ 85 %. This cost reduction in the plasma-chemical process is associated with the transfer of electricity directly into the gas-vapor mixture. In addition, carrying out the recovery process under nonequilibrium conditions leads to the formation of atomic hydrogen in the discharge.

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INTRODUCTION

Majority of polycrystalline silicon in the world – up to 80 % – is obtained by hydrogen reduction of trichlorosilane $SiHCl_3$ by the so – called "Siemens-Process". uch production requires significant material and energy expenses. In "Siemens-Process" the share of raw materials is about 35…40 % in the cost of production. Up to 30…35 % of the cost falls on energy resources. Hydrogen, obtained by electrolysis, is another 8…10 % of the cost – it is also a rather energy-consuming process. Energy consumption of a silicon reduction reaction makes up 250 kW h/kg, with the yield of silicon 10…15 % [1].

Industrial method's disadvantage is utilization of the processes of synthesis and purification of $SiHCl_3$, which is obtained from metallurgical silicon by chlorination with hydrochloric acid using catalysts. Such disadvantage becomes essential for solar energetics, where further prospects of wide development are directly depend on the cost of solar cells made from "solar" silicon. Search of new technologies is aimed primarily to reduce the cost of polycrystalline silicon of "solar purity" to 5…10 kg. In addition, production of every ton of silicon in the "Siemens-Process", leads to forming of 11 tons of silicon tetrachloride. These waste of trichlorosilane reduction, being returned to the process of obtaining silicon by hydrogenation to trichlorosilane, which requires significant additional energy costs. Therefore, the development of a new highly effective and energy-saving method becomes very important.

EXPERIMENTAL EQUIPMENT

Processes and installations, based on the application of low-temperature plasma, have increased importance in recent time. High-frequency induction discharges are widely used, both for studying of low-temperature plasma, and for industrial use in various plasma technologies [2]. There is a lot of literature dedicated to the experimental and theoretical study of discharges in induction-plasma devices, including the works about direct numerical simulation as well. However, the presence of a large number of works on the subject under discussion is not yet an indication that all questions of theory and practical use have been successfully solved, but rather only indicating the existence of a strong interest to the topic.

In this study, an experimental installation, consisting of reactor, pumping system, reagent supply system and excitation system of high-frequency discharge, was created for research on the process of polycrystalline silicon obtaining in a low-temperature non-equilibrium plasma of high-frequency induction discharge. Silicon tetrachloride $SiCl_4$, hydrogen H_2 and argon Ar were used as starting reagents. The deposition was carried out on carbon plates.

Diagnostic studies of low-temperature plasma (Fig. 1) shows, that the atomic hydrogen acts as the main reason of silicon tetrachloride reduction in high-frequency discharges (spectral lines H_α and H_β in Fig. 1), it was formed in the high-frequency discharge as a result of the impact of electronic shock H_2. The spectra were took by the SL40-2 spectrograph.

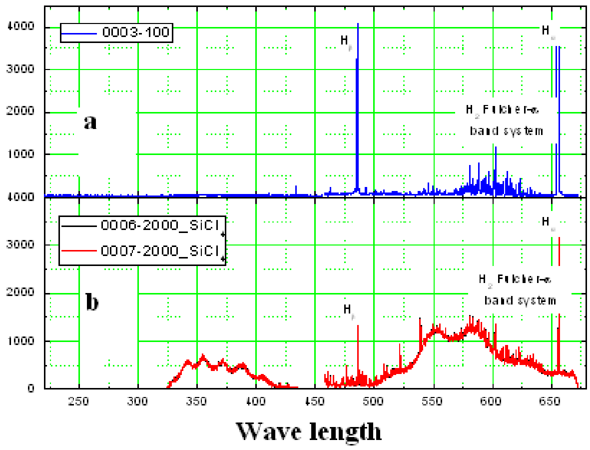

Fig. 1. Plasma spectra: a – H_2 + Ar; b – H_2 + Ar + $SiCl_4$

Presence of atomic hydrogen in the discharge has a significant impact during supply of $SiCl_4$ to the reaction chamber. A chart with the temperature dependence of the reduction of silicon tetrachloride by molecular and atomic hydrogen is shown in Fig. 2. It is clear from the chart that the Gibbs energy has lower values at reduction of silicon tetrachloride by atomic hydrogen.

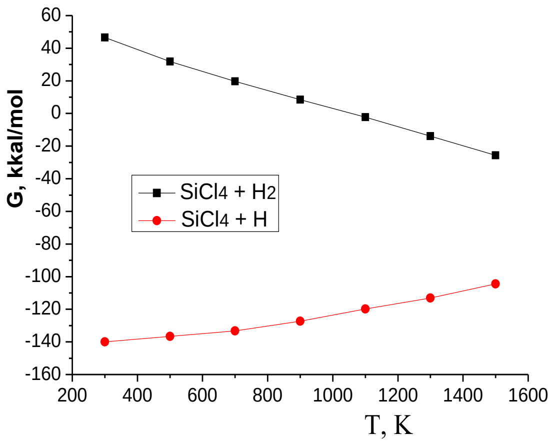

Fig. 2. The temperature dependence of the reduction of silicon tetrachloride by molecular and atomic hydrogen

Visually all obtained samples had a smooth surface. Films thickness measured by the interference method was 2…17 µm. The surface structure of the silicon film is shown in Fig. 3.

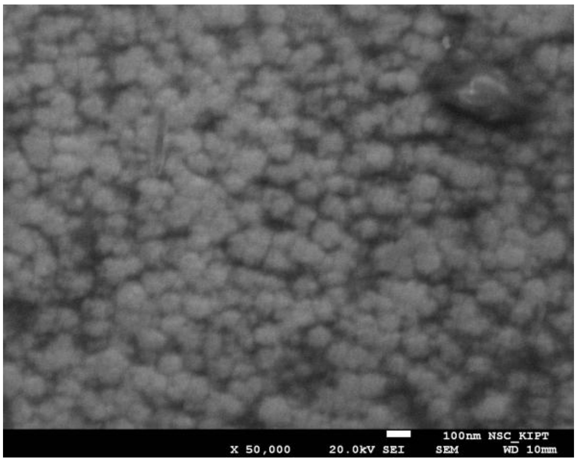

Fig. 3. The surface structure of the silicon film

X-ray crystallography-phase analysis was performed to determine parameters of the crystal lattice of the obtained silicon. The scanning was carried out on an X-ray diffractometer "DRON 4-07" at C Cu K_{α} radiation according to the Bragg-Brentano X-ray-optical method. Based on the reference data the areas of the X-ray chart, in which the reflection from crystalline silicon is expected in the first X-ray lines, were researched: (111), (220), and (311). Above mentioned values of the periods of condensate lattice were given according position of these lines Table 1. The diffractogram of the sample is presented in Fig. 4.

Average film growth rate is R_0 = 2.41 nm/s at a film thickness of 11.6 µm. This is considerably higher than deposition rate obtained in capacitive high- frequency discharges [3].

Table 1

Periods of condensate lattice

(hkl)	2θ		*f(θ)*
	Experimental data	Reference data	
(111)	28.58	28.44	7.57
(220)	47.48	47.30	4.104
(311)	56.30	56.12	3.230

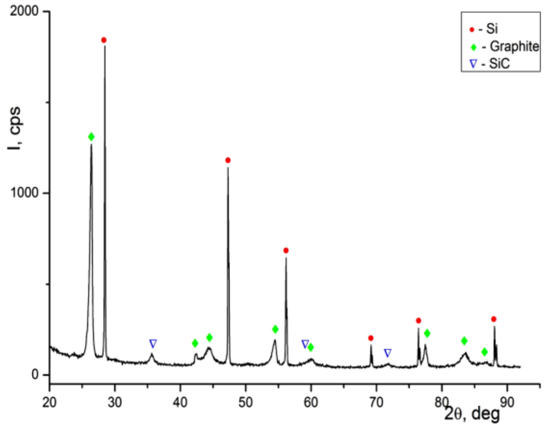

Fig. 4. Characteristic X-ray spectrum of obtained silicon film

Consumption of electrical energy per kilogram of silicon, obtained by plasma-chemical reduction, is shown in Table 2, here P – discharge power, E – energy costs, t – time.

Table 2

Consumption of electrical energy per kilogram of silicon, obtained by plasma-chemical reduction

$SiCl_4$, g	85% $SiCl_4$, g	Si, g	t, h	P, W	E, kW/h
28.0	23.8	3.1	1	0.20	64.5
14.9	12.7	2.0	1	0.28	140.0
25.0	21.2	3.4	1	0.39	134.0
38.5	32.7	5.2	1	1.00	192.3

Electricity consumption per kilogram of deposited silicon via plasma-chemical method was also calculated in the work. It is shown that in studied range of process parameters, the energy costs of obtaining one kilogram of silicon are lying in the range of 150… 190 kW/h with a silicon yield ~ 85 %.

CONCLUSIONS

Research on plasma-chemical reduction of silicon tetrachloride in a hydrogen low-temperature non-equilibrium plasma was carried out. It is shown that in studied range of process parameters, the energy costs of obtaining one kilogram of silicon are much lower than in existing "Siemens-Process". Such cost reduction of the plasma-chemical method is possible due to transfer of electrical energy directly into the gas-vapor mixture. In addition, reduction process in non-equilibrium conditions leads to a formation of atomic hydrogen in the discharge. In according to thermodynamic data, such substance is more reactive in comparison with molecular one.

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ВОДОРОДНОЕ ВОССТАНОВЛЕНИЕ ТЕТРАХЛОРИДА КРЕМНИЯ В НИЗКОТЕМПЕРАТУРНОЙ НЕРАВНОВЕСНОЙ ПЛАЗМЕ ВЫСОКОЧАСТОТНОГО ИНДУКЦИОННОГО РАЗРЯДА

А.Н. Дериземля, А.И. Евсюков, В.И. Радченко, Д.А. Хижняк, П.Г. Крышталь, А.Ю. Журавлев, А.В. Шиян, С.В. Стригуновский, Ю.А. Пелипец, Б.М. Широков

Получен кремний путем плазмохимического восстановления тетрахлорида кремния в аргон-водородной низкотемпературной неравновесной плазме. Показано, что в исследуемом диапазоне параметров процесса энергетические затраты на получение одного килограмма кремния находятся в пределах 150…190 кВт/ч при выходе кремния ~ 85 %. Такое снижение затрат в плазмохимическом процессе связано с введением электроэнергии непосредственно в парогазовую смесь. Кроме того, проведение процесса восстановления в неравновесных условиях приводит к образованию в разряде атомарного водорода.

ВОДНЕВЕ ВІДНОВЛЕННЯ ТЕТРАХЛОРИДУ КРЕМНІЮ В НИЗЬКОТЕМПЕРАТУРНІЙ НЕРІВНОВАЖНІЙ ПЛАЗМІ ВИСОКОЧАСТОТНОГО ІНДУКЦІЙНОГО РОЗРЯДУ

А.М. Дериземля, О.І. Євсюков, В.І. Радченко, Д.О. Хіжняк, П.Г. Кришталь, О.Ю. Журавльов, О.В. Шиян, С.В. Стригуновський, Ю.О. Пелипець, Б.М. Широков

Отримано кремній шляхом плазмохімічного відновлення тетрахлориду кремнію в аргон-водневій низькотемпературній нерівноважній плазмі. Показано, що в дослідженому диапазоні параметрів процесу енергетичні витрати на отримання одного кілограма кремнію знаходиться в межах 150…190 кВт/ч при виході кремнію ~ 85 %. Таке зниження витрат у плазмохімічному процесі пов'язане з введенням електроенергії безпосередньо в парогазову суміш. Крім того, проведення процесу відновлення в нерівноважних умовах призводить до утворення в розряді атомарного водню.