The role of SiHn radicals generation in the mechanisms of formation of thin films of amorphous silicon.

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Abstract. In this research, we studied the processes of configuration changes to the structural elements of amorphous silicon thin films created by the decomposition of reacting gas mixture (silane and argon) in low-frequency glow discharge plasma. We analyzed how concentrations of various local atomic groups and their links depend on deposition parameters. We also defined phase composition and the role of SiHn radicals generation in the mechanisms of formation of hydrogenated amorphous silicon thin films deposited on glass and Sitall substrates.

1. Introduction
Amorphous silicon, which proved to be a very promising material, has been widely used in modern optoelectronics and integrated optics when creating element bases. Solar elements, memory elements, and large area transistor matrices based on amorphous silicon have become highly competitive compared to semiconductor materials. The most successful application of amorphous silicon thin films is connected with the solution of energy problems by using alternative everlasting energy sources, including solar energy. Thus the research of production of amorphous hydrogenated and crystalline silicon thin films used to create thin-film solar cells is becoming more relevant. The technology based on using thin films of amorphous silicon is significantly cheaper compared to more expensive crystalline silicon technology. It also proved to be useful in situations, when crystalline semiconductors (flexible, semi-transparent modules) cannot be used at all, for example in the case of low temperatures and large sprayed surfaces [1].

If we find a solution to the problem of defining optimum modes of a-Si:H thin film forming, of controlling and managing the properties of thin films obtained, and of finding correlations between the properties of thin films and the processes of generation and deposition of silane "target" radicals along with technological parameters of plasma deposition, we can change a-Si:H technology of solar cells production and increase the efficiency of technological processes. The major interest of the study concerned with mechanisms of amorphous silicon thin films formation lies in defining the behaviour of silane radicals and buffer gas atoms on the substrate surface during the deposition process.

Formation of amorphous silicon thin films runs in accordance with the cluster model in which thin film formation occurs continuously throughout the deposition process. Atoms of silicon gases adsorbed and diffusing on the substrate form metastable or stable islands of growth. The sizes thereof are limited by the speed of atoms’ diffusion on the substrate surface, the substrate temperature, sedimentation velocity, which depends on the partial pressure of the gas.

Size of such groups of atoms formed during thin films growth and packing density of the atoms depends on the energy of the lattice [1].
Oscillatory spectroscopy carried out in the middle infrared area showed that hydrogen atoms in a-Si:H are linked covalently and form one of the four links: monohydride (Si-H), dihydride (-SiH₂-), trihydride (-SiH₃-), and polymer (-SiH₂)n. Their availability is determined by coating conditions [2]. By using methods of Raman and FTIR spectroscopy, it was determined that, in the conditions given, atoms of silicon and hydrogen in thin films form the following groups of links: monohydride (Si-H), dihydride (-SiH₂-), trihydride (-SiH₃-), and polymer (-SiH₂)n. Presence and number of these links in the structure of thin films are determined by coating conditions [2]. According to experimental data, amorphous silicon created by the decomposition of a gas mixture containing silicon comprises significant amounts of hydrogen, mainly linked with silicon atoms. The hydrogen concentration in thin films ranges from 10 to 50% [3].

2. Results and discussion

In the framework of this research, we studied thin films of amorphous silicon obtained by the method in which gas mixture decomposition products containing silane were deposited on a heated substrate with the preliminary decomposition of gas in HF capacitive discharge and subsequent formation of supersonic streams flowing to deposition chamber through a system of supersonic nozzles [4]. The thin films obtained were analyzed by methods of Raman scattering (RFS-100/s) and FTIR spectroscopy (FT-801). We defined phase, quantitative, and qualitative composition of the thin films deposited on glass and Sitall substrates. Capacitive discharge parameters (discharge power 

$P$, pressure in discharge chamber and gas mass flow $Q$) remained unchanged. Substrate temperature $T_d$ of analyzed samples varied from 100 to 250°C. Analysis of infrared absorption spectra showed that the areas of approximately 600-700 cm⁻¹ and 2100-2300 cm⁻¹ presented fluctuations SiH of groups as well as groups of Si-O-Si and Si-CH (figure 1) [5].

![Figure 1. FTIR spectra of a thin film of hydrogenated amorphous silicon.](image)

Then we analyzed a combined light scattering spectra obtained from thin films of amorphous silicon deposited in accordance with the conditions described above. Figure 2 shows the Raman spectra for films deposited under different conditions ($T_d$=100-250°C). Here we can clearly see the peaks at 470 cm⁻¹, $I_{470}$ is an intensity of Raman bands at a frequency of 470 cm⁻¹, that corresponds to thermal fluctuations of amorphous matrix.
Figure 2. Raman spectra of samples with different conditions.

Figure 3 shows one of Raman spectra typical for these thin films.

Figure 3. Raman spectra of a thin film of amorphous silicon obtained by jet plasma chemical method.

As you can see, Raman scattering data correspond to the data obtained by FTIR-spectroscopy. There is no Raman scattering signal from crystalline phase at 510-520 cm\(^{-1}\), although there is an amorphous band at 470 cm\(^{-1}\). This suggests that the thin film is amorphous, but does not contain nano- and microcrystalline inclusions in the amorphous phase.

Analysis of width and shape of the band that corresponds to local fluctuations of Si-Si linkages’ valence vibrations allowed us to calculate an average bond angle deviation \(\Delta \Theta_b\) from the tetrahedral bond arrangement and to draw a conclusion about the structure of amorphous matrix [5].

The calculated value of the parameter \(\Delta \Theta_b\), measured according to Raman band semi-breadth was \(~7.3^\circ\). This corresponds to a random model ideal network with an average bond angle deviation up to 10\(^\circ\).

Scattering intensity of the bands corresponding to valence vibrations of structural groups Si-H, Si-H\(_2\), (Si-H\(_2\))\(_n\), Si-H\(_3\), Si-O-Si and to deformation vibration of groups C-H\(_2\), C-H\(_3\), C-C, which are not
linked with silicon though can be seen in Raman spectrum, show that thin films include a significant amount of hydrogen atoms, which saturate the dangling links of silicon, mostly in configurations \((\text{Si-H})\), \((\text{Si-H}_2)\), \((\text{Si-H}_3)\), and polymer \((-\text{SiH}_2)_n\).

There is also a noticeable amount of oxygen and carbon which is not liked to silicon. Random impurities in the thin film can be explained by the presence of water vapour in the working atmosphere and hydrocarbon compounds adsorbed on the walls of the chamber [6].

The concentration of hydrogen in thin films was determined for different temperatures of the substrate according to the width of the bandgap. The single-beam spectrophotometer CF-56 was used to measure spectral dependence of silicon thin films transmittance. The energy of fundamental absorption edge was measured according to the dependence of the absorption coefficient of a film on the incident radiation energy \(h\nu\). The width of bandgap was calculated according to the measured dependence of thin films absorption coefficient on optical radiation energy. Hydrogen concentrations in sputtered films were calculated according to the value of the bandgap [7], see. table 1.

### Table 1. Parameter values of thin films studied.

| No | Sample | \(T_d\), °C | \(E_g\), eV | \(C_H\), at.% | \(E_g\), eV, after annealing | \(C_H\), at.%, after annealing |
|----|--------|-------------|-------------|---------------|------------------------------|-----------------------------|
| 1  | 100    | 1.98        | 31          | 1.89          | 25                           |
| 2  | 100    | 1.92        | 28          | 1.87          | 25                           |
| 3  | 100    | 1.91        | 27          | 1.72          | 15                           |
| 4  | 100    | 1.90        | 26          | 1.6           | 7                            |
| 5  | 150    | 1.82        | 21          | 1.73          | 15                           |
| 6  | 150    | 1.79        | 19          | 1.72          | 13                           |
| 7  | 150    | 1.79        | 19          | 1.50          | <1%                          |
| 8  | 200    | 1.78        | 19.2        | 1.73          | 15                           |
| 9  | 200    | 1.73        | 15          | 1.65          | 10                           |
| 10 | 200    | 1.72        | 14          | 1.40          | <1%                          |
| 11 | 250    | 1.72        | 14          | 1.63          | 8                            |
| 12 | 250    | 1.70        | 13          | 1.63          | 8                            |
| 13 | 250    | 1.63        | 9           | 1.50          | <1%                          |

Calculations suggest there is a high hydrogen content in the thin films. Its concentration varies from 9% to 31%, which in turn leads to greater bandgap values (compared with the width of amorphous silicon bandgap described by scholars as ~ 1.7 eV). This leads to changes in the optical properties of obtained thin films.

Higher values of bandgap width can be explained both by hydrogenation of thin films, along with Si-Si links substituted by stronger Si-H links and maximum valence band offset, and passivation of dangling links by hydrogen atoms that leads to the reduction of bond charge.

Another property connected to hydrogen in hydrogenated amorphous silicon films is the edge of interband optical absorption, like Tauc gap \(E_{opt}^g\) in thin films of silicon [8]. As shown in figure 4, the energy \(E_{opt}^g\) decreases with an increase in the content of atomic silicon in films. An empirical expression for finding energy \(E_{opt}^g\) can be written as follows:

\[
E_{opt}^g = 2.098 - 1.556 \cdot C_H
\]

Thus substrate temperature decreases with an increase in the width of the bandgap. It can be explained by an increase in the amplitude of thermal vibrations of atoms of the lattice, as well as by change of interatomic spacing, affecting the width of the bandgap. Thus annealing of the source amorphous films may help to smooth out their original features associated with different structural
macro- and micro-imperfections and to reconstruct structural net by the loss of hydrogen (when temperature grows, the bonds between silicon atoms and hydrogen become weaker and partially destroyed, so some part of hydrogen leaves the film).

Figure 4. The Tauc gap $E_g^{opt}$ vs $C_{H_2}$ of silicon films.

To study the dependence of hydrogen concentration in films, as well as their optical parameters, on temperature, the films obtained may be annealed. The films were annealed at a temperature of 300°C. After that, we measured transmittance coefficient, calculated the width of the bandgap and hydrogen concentration once again. Values of bandgap width and hydrogen concentration before and after annealing are shown in table 1. As a result of annealing, bandgap width and hydrogen concentration in films were reduced. Consequently, we can conclude that the annealing process changes the film’s structural net and its optical properties [8].

Analyzing the results, we can draw some conclusions concerning the mechanisms of thin films of amorphous silicon formation. When the mixture of monosilane and argon decomposes in the plasma glow discharge, the rate at which atoms come to the surface of the emerging film significantly exceeds the speed of diffusion of atoms into the structural net. The concentration of atoms on the surface becomes higher than in the whole volume, so new local islands of growth formed by the links of Si-H and Si-Si appear on the surface. Due to the fact that Si-Si links are weaker, the concentration of hydrogen atoms on the borders of individual islands is higher than the concentration of silicon atoms; thus such points of growth hinder the formation of a solid amorphous net. It results in the creation of a heterogeneous structure with columnar inclusions, saturated with hydrogen. It is the existence of such inclusions that explains the change in properties of the films obtained as a result of their annealing. When the temperature of the film surface rises, the diffusion coefficient rises as well. Thus hydrogen atoms diffuse deep into the grains and along the borders more efficiently.

Conclusions
The data obtained in this work allow us to draw a conclusion about the role of generating SiHn radicals in the mechanisms of hydrogenated amorphous silicon films formed in deposition systems studied.

The results of Raman and FTIR spectroscopy have lead to some conclusions concerning the structure of the amorphous matrix of generated thin films. Its bond arrangement remains tetrahedral. The area under the first maximum of distribution function determines the number of nearest neighbours, which in the case of the tetrahedral arrangement of atoms equals 4. Valence angles are
approximately $09^\circ 28' \pm 7^\circ 3' $ (normal tetrahedral angle is $109^\circ 28' $). The obtained values, with average bond angle deviation to $10^\circ$, characterize random model ideal networks. After adsorption on the surface of the growing film on a substrate, structural groups of Si-H, Si-H$_2$, (Si-H$_2$)$_n$, Si-H$_3$ - as a result of a subsequent diffusion - either are embedded directly into the structure of the film by joining in one of the islands or form new points of growth. Diffusion processes in silicon-hydrogen radicals on the substrate are defined not only by the temperature of the substrate but also by gas pressure, on which deposition velocity depends. High pressure makes hydrogen atoms that did not have time to diffuse get "locked" in the fast-growing amorphous structural net. When spraying films to a substrate at temperatures below 200°C, the surface of a growing film is saturated with hydrogen bonds almost completely. The hydrogen concentration in the near-surface area of obtained films ranges from 30 to 50%. Adding hydrogen into the structure of films moves the vertices of valence band down so that the width of the bandgap increases. Such a mechanism of growth of hydrogenated amorphous silicon films can be confirmed by a change in their optical properties and concentration of hydrogen in the process of annealing. When the film is formed on a substrate at temperatures below 200°C, it mainly has dangling and weak Si-Si links. In the process of annealing, dangling links become passive due to hydrogen atoms, a part of weak Si-Si links is replaced by Si-H bonds, resulting in elimination of defects, disappearance of columnar structures and formation of continuous thin film of amorphous silicon.

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