Effect of gas-phase processes in argon-helium-silane plasma on amorphous-nanocrystalline transition in thin films of a-Si:H

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Abstract. The aim of the study is to increase the efficiency of solar cell elements on the basis of thin films of amorphous-nanocrystalline silicon, by incorporating silicon nanocrystals (Si-NPs) into a film of hydrogenated amorphous silicon (a-Si:H). As a result of performing the works, a two-dimensional model of the chemical composition of plasma Ar + He/SiH₄ is proposed on the basis of the system of balanced transport equations for 24 components in the discharge chamber of cylindrical geometry. It is shown that the model reasonably describes the kinetics of the chemical reactions in the PECVD reactor. Based on the calculation according to the proposed model, the densities of the main particles in the helium-argon-silane plasma of the radio-frequency capacitive (RF)-discharge are determined. It has been shown that the addition of helium to the silane plasma causes an increase in the concentration of atomic silicon.

Optimal concentration of helium in the mixture is set, and a mechanism for forming silicon nanocrystals is proposed.

1. Introduction

The impossibility of absorbing photons with energy smaller than the band gap and thermally storing photons with a larger band gap energy are the key drawbacks for increasing the efficiency of modern solar modules [1]. There are several ways to solve this problem. One of them is forming silicon nanocrystals embedded in the amorphous silicon layer [2]. Heterostructures of amorphous silicon with inclusions of nanocrystalline phase allow increasing the conductivity and anti-reflection optical properties of photoelectric converters due to absorption of high-energy photons by changing the band gap. In addition, that reduces the effect of the Steablers-Wronski also [3]. Since the band gap Si (1.1 eV) is smaller than the value of the amorphous silicon mobility gap (1.9 eV) it is possible to expect dimensional quantization of charge carriers in silicon nanocrystals on optical and electrical properties of deposited films [4]. S. Joo and co-workers in order to obtain the quantum dot structure in amorphous silicon used method of co-deposition, in which nano-crystallites are preliminarily synthesized in a separate chamber by means of laser pyrolysis from a mixture of Ar + SiH₄ + H₂ and than those by means of gas flow directed to the working area where the conventional film deposition occurs [5]. The formation of silicon nanoparticles is possible in the discharge zone of the PECVD reactor directly. It is believed that it may be advantageous for their growth to add helium to the working gas mixture, since the helium metastable species are efficiently involved in the dissociation of monosilane. The energy of the metastable state He⁺ (2S₂) is 19.81 eV, which is much higher than the ionization potential of SiH₄ (12.36 eV), so the deexcitation mechanism will occur by the route of
Penning ionization and through the reaction of breaking of all hydrogen bonds from molecule of monosilane, that is, the formation of atomic silicon [6]. The Si atoms appeared in the gas phase are the centers of formation of the silicon nanocrystals and promote their further growth.

In this work, a simulation of the plasma-chemical process of the monosilane decomposition in the glow discharge plasma is carried out. The influence of the gas pressure and the relative concentration of helium in the initial mixture of Ar + SiH\(_4\) + H\(_2\) on the kinetics of the silane radicals and atomic silicon are investigated. The presence of a crystalline phase was confirmed by Raman spectroscopy applied to samples of amorphous silicon films.

2. Problem definition

Mathematical model is based on equations of diffusion of neutral particles in cylindrical discharge chamber taking into account chemical reactions between components in vapor phase:

\[
\frac{\partial n_k}{\partial t} = D_k \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial n_k}{\partial r} \right) + \frac{\partial^2 n_k}{\partial z^2} \right) + S_k(r, z),
\]

where \(n_k\) is the density of neutral particles k-th component; \(D_k\) is diffusion coefficient, \(S_k(R, z)\) is the function which includes the source and sink terms of k-th reagents due to chemical reactions.

Boundary conditions which follow from the simplest kinetic theory are used for each equation (1). Equality of fluence falling into surface and reflecting from it gives:

\[
D_k \frac{\partial n_k}{\partial q} \bigg|_{r=r_L, z=z_L} = s_k n_k \nu_{T,k} \frac{2(2 - s_k)}{q}, \quad q = r, z.
\]

The \(s_k\) is (2) sticking coefficient characterizing the interaction of the species \(k\) species with the inner surface of the discharge chamber, \(\nu_{T,k}\) - is thermal velocity of the particles. Condition of absence of radial flow on axis of cylinder is expressed by equation:

\[
D_k \frac{\partial n_k}{\partial r} \bigg|_{r=0} = 0
\]

The set of diffusion transfer equations (1) with boundary conditions (2), (3) is approximated on a uniform spatial grid by finite difference method. Implicit two-layer scheme is used with splitting by two spatial coordinates. For all components on each time half-layer the final system of linear equations is solved by a three-point fitting method. Details of the calculation are described in [7].

With respect to the working mixture to be investigated, the specificity of the model consists in determining the components for which the system is solved (1). Because of the polymerization processes, the component composition of the plasma is expanded over time to the formation of all heavier high molecular weight compounds. In this regard, the need for inclusion in the model of those or other polymerization products and associated reactions is not always evident. In this work, the following set of reagents was used: components of the working mixture Ar + He + SiH\(_4\); metastable particles Ar* and He*; monosilane radicals SiH\(_x\) (\(x = 1-3\)); atomic silicon Si; hydrogen H and H\(_2\); as well as polymerization products: Si\(_x\)H\(_y\) (\(x = 2-5, y = 3-12\)). As shows the practice of the simulation of the silane plasma, this set is sufficient to take into account the initial stages of the polymerization of the silane [8, 9]. The diffusion coefficients \(D_k\) are calculated from molecular-kinetic theory formulas by the manner described in [9]. The values of the coefficients of adherence of the reagents indicated and the list of chemical reactions for all components of the model except for helium are also given in [9]. The reactions involving helium are presented in table 1. Most of the constant rate constants are taken from [7-9]. The electron impact rate constants necessary for modeling the electron impact rate constant are calculated in advance by the energy distribution function of the energy (EEDF), which in turn is determined by the numerical solution Boltzmann kinetic equation (in table 1 is denoted as \(\text{comp}\)). In the calculation of the kinetics of electrons, compiled data on elastic and inelastic scattering cross-sections electrons on Ar, He and SiH\(_4\) is used [10].
The value of the electronic concentration \( n_e \) and the spatial profile thereof in the model are set in an external manner. The approximation of the constant \( n_e \) along the length of the cylindrical reactor is used, and the radial junction of the concentration is approximated by the cosinusoidal shape of the cylinder. In addition to the parameters of the electronic subsystem, the initial relative population of excited atoms included in the model is also given.

### Table 1. Chemical reactions and their rate constants.

| No. | Reaction | \( k, \text{cm}^3/\text{s} \) | No. | Reaction | \( k, \text{cm}^3/\text{s} \) |
|-----|----------|----------------|-----|----------|----------------|
| 1   | \( e + \text{He} \rightarrow e + \text{He}^* \) | \( \text{comp} \) | 3   | \( \text{He}^* + \text{SiH}_4 \rightarrow \text{Si} + 2\text{H} + \text{H}_2 + \text{He} \) | \( 1.0 \times 10^{-12} \) |
| 2   | \( e + \text{He}^* \rightarrow e + \text{He}^* + e \) | \( \text{comp} \) | 4   | \( \text{He}^* + \text{He}^* \rightarrow \text{He}^* + \text{He} + e \) | \( 2.7 \times 10^{-10} \) |

3. Results and discussion

Numerical simulation of the plasma-chemical reactor working in the diffusion mode was completed. The processes in mixture of \( \text{Ar} + (1-10\%) \text{He} + 5\% \text{SiH}_4 \) were examined. The following parameters were set: radius of discharge chamber \( R = 3.5 \text{ cm} \), length of chamber \( L = 3 \text{ cm} \), pressure \( p = 0.1-0.5 \text{ Torr} \), gas temperature \( T = 500 \text{ K} \). In the EEDF calculation program, the electron impact velocity constants were calculated at the value of reduced electric field \( E/N = 1 \times 10^{-15} \text{ V}\cdot\text{cm}^2 \) and field frequency \( f = 13.56 \text{ MHz} \). The concentration of free electrons in the plasma was considered to be equal to \( n_e = 10^9 \text{ cm}^{-3} \). The relative population of metastable argon and helium particles was assumed to be \( 10^{-5} \).

The simulation was performed on the time interval \([0,\tau]\), where \( \tau = 1 \text{ sec} \). Two groups of conditions are considered: A – the variation of the pressure; B – the variation of the helium content in the working mixture.

**Conditions A:** \( \text{Ar}+1\% \text{He}+5\% \text{SiH}_4, \ p = 0.1-0.5 \text{ Torr} \), **Conditions B:** \( \text{Ar}+(1-10)\% \text{He}+5\% \text{SiH}_4, \ p = 0.1 \text{ Torr} \).

The relative densities (reduced to initial silane density) of neutral plasma components for different pressures in the gas discharge volume are shown in figures 1, 2. While pressure increase, the density of \( \text{SiH}_3 \) (figure 1a) is slightly increased. At this time, the output time to the stationary value is \( \sim 10^{-2} \) sec with the time of the output of the \( \text{SiH}_2 \) with the increase of the pressure from 0.1 Torr to 0.5 Torr, reduced by almost the order (figure 1b).

![Figure 1](image1.png)

**Figure 1.** Relative densities of radicals \( \text{SiH}_3(a) \) and \( \text{SiH}_2(b) \) in mixture \( \text{Ar}+5\% \text{He}+5\% \text{SiH}_4 \) under different gas pressures (conditions A).

Also as for \( \text{SiH}_2 \), the pressure increase reduces the content of the \( \text{SiH} \) radical (see figure 2a). The silicon bulk density varies insignificantly with increasing \( p \), going to an equilibrium value of \( \sim 10^{-1} \) sec (figure 2b).
Figures 3, 4 shows densities of the silane radicals as a function of the helium fraction in the working mixture. It can be seen that the changes in the kinetics of the SiH₃, SiH₂, and SiH radicals are practically absent. At the same time, a sharp increase in the density of atomic silicon is observed at times of 0.001 sec, with the increase of the helium fraction in the initial mixture. In summary, it should be noted that at a pressure $p = 0.1$ Torr while the helium fraction in the initial mixture of the order of 10% the yield of atomic silicon is increased.

**Figure 2.** Relative densities of radical SiH (a) and Si (b) in mixture Ar+5%He+5%SiH₄ under different gas pressures (conditions A).

**Figure 3.** Relative densities of radicals SiH₃ (a) and SiH₂ (b) under different He content in gas mixture (conditions B).
In this work, the thin films of a-Si:H deposited on a glass substrate (Corning 7059) heated to T = 250°C. The silicon-containing gas was decomposed in a chamber (plasmatron) where a plasma of radio-frequency capacitive discharge is confined. The decomposition products were then free flowing through the Laval nozzle into the chamber where the substrate is placed [11]. Gas mixtures were used in the deposition process: 1- Ar + 5% SiH₄, 2 - Ar + 5% He + 5% SiH₄. The flow of working gas was controlled within the range of 10-50 sccm by mass flow controller (T1000L with power supply and indication unit FCS-T2000-PSD-1). The effective power deposition was 30 mW/cm². After setting the pressure in the plasmatron to 100-150 mTorr, a glow discharge was ignited by the RF generator. The deposition time was 45 minutes; the substrate with the film was allowed to cool at a pressure of 1·10⁻⁵ Torr. The thin films were analyzed by Raman light scattering methods (RFS-100/s). Figure 5 shows the Raman spectra for the films of amorphous silicon obtained from different gas feed mixtures (1-Ar + 5% SiH₄, 2-Ar + 5% He + 5% SiH₄). A broad non-structural peak with a maximum in the region of 480 cm⁻¹ is observed in the spectrum, and also a peak in the vicinity of 510 cm⁻¹. \( I_{510} \) – the intensity of the Raman lines at frequencies corresponds to the thermal fluctuations of the silicon crystallite lattice (nc-Si), the position of peak \( I_{510} \) corresponds to the average size of nanocrystals on the order of 4-5 nm [12]. \( I_{480} \) is the Raman spectrum intensity at 480 cm⁻¹ corresponding to the thermal variations of the amorphous matrix (a-Si).

**Figure 4.** Relative densities of radical SiH (a) and Si (b) under different He content in gas mixture (conditions B).

**Figure 5.** Raman spectra of samples with different gas mixtures: 1 - Ar+5%SiH₄, 2 - Ar+5%He+5%SiH₄.
Conclusions

As a result of numerical simulation, it has been found that the addition of helium to Ar + SiH$_4$ plasma causes an increase in the concentration of atomic silicon (Si) due to formation of additional channel of silane decomposition through reactions of long-lived excited states of helium (He*). With decreasing plasma pressure, the relative fraction of atomic silicon increases by increasing the efficiency of the silane reactions with metastable helium atoms. As a result of the experiments carried out on the deposition of amorphous silicon films with different initial gas mixtures it has been found that there is a peak in the Raman spectrum, caused by scattering on optical phonons located in silicon nanocrystals (nc-Si). This peak has a position of 510 cm$^{-1}$, which corresponds to the average size of the nanocrystals on the order of 4-5 nm. The conditions allow generating atomic Si, which will allow controlling the formation of single-crystal silicon nanoparticles (Si-NPs).

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