Determination of optimum deposition conditions amorphous silicon thin films

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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). The purpose of the operation is to work out optimum deposition modes of amorphous silicon films. An obstacle here is the occurrence of dust particles affecting the properties of the resulting films. As well as increasing the overall efficiency of photovoltaics due to the creation of single-crystal quantum dots (nanocrystals), which will play the role of centers of flow of parasitic currents. The obtained samples were studied using physical methods of analysis (Raman light scattering, study of the band gap).

1. Introduction

The main mechanisms of power loss of modern solar cells are: inability to absorb photons with energy less than a band gap and thermalization of photon with energy more than it. A solution to this problem is to create a structure consisting of single crystal nano-particles of silicon (Si-NPs) embedded in different coatings [1]. Silicon nano particles form the structure of quantum dots. The quantum dot matrix acts as an additional layer of absorption of high-energy photons, which allows to regulate the band gap, reduce the influence of the Steablers-Wronski effect, as a result, increase the efficiency of solar cells [2, 3].

One mechanism for the synthesis of the nano-crystal structure within the amorphous silicon matrix is the decomposition of silane molecules followed by the formation of nano-crystallites in the discharge core. However, this deposition technique is accompanied by significant spraying of the surface of the growing film with high-energy ions. The film surface will contain dust microparticles, microstructural defects, and a columnar structure. It is important to note that a low deposition rate prevents the start-up of industrial production of amorphous silicon-based devices (1-3 Å/s). The increase in deposition rate leads to microstructural inhomogeneities which cause deterioration of the electronic properties of the films. However, the role of microstructural heterogeneity currently remains unclear, although it is known that the material produced under "favorable" process conditions contains microstructural heterogeneities (micropores, colons, cluster hydrogen) [4-8].

Deposition of thin films of amorphous silicon on glass substrate was carried out by jet plasma-chemical method, which is based on generation of "target" radicals in process of plasma-chemical decomposition of silane and their subsequent delivery to substrate surface by jet flowing from plasmatron into vacuum space. Gas jet flows freely from plasmatron chamber with further deposition of silane decomposition products onto substrate, working gas (He, Ar/He) is introduced into...
plasmatron volume, and gas containing silicon is introduced through tube having holes for radial supply of mixture [9]. The tube is electrically connected to the grounded electrode. The working gas heated by the RF discharge will flow freely through the nozzle where it will be mixed with the argon-silane mixture. Presence of helium in working mixture of gas will allow controlling growth of nanocrystallites in amorphous matrix of silicon. In the core, together with the decomposition of silane, various reactions occur between radicals in the discharge zone, which can lead to the formation of higher silanes as well as a condensed dispersed phase (CDP or dust particles). This will change the composition of the plasma and the quality of the growing film. Development of modes and conditions of gas discharge maintenance will allow producing silicon films of instrument quality.

2. Experimental setup

Glow RF capacitive discharge in argon-silane mixture was excited in plasmatron (Ar+5%H₂+5%SiH₄). The distance from the nozzle cut to the substrate was 8 cm. The pressure in the plasmatron chamber was monitored by a capacitive vacuum sensor SETRA 730. The capacitive radio frequency glow discharge was driven by a 600 W oscillating generator ACG-6b (field strength was E = 50 V/cm). The limiting residual pressure was 5·10⁻⁶ Torr. Prior to deposition, the substrate was annealed in a vacuum chamber at a temperature of 200 °C. The gas flow regulator controlled the flow of working gas within 10–50 sccm. After increasing the pressure in the plasmatron chamber to 100-300 mTorr, the glow RF discharge was excited. The deposition time was 45 minutes. After deposited the film, the substrate was cooled in a vacuum chamber at a pressure of 1·10⁻⁵ Torr.

3. Results and discussion

Figure 1 shows the dependence of the growth rate of amorphous silicon films on the pressure in the plasmatron chamber at a constant power applied to the discharge. Growth rate of films has a local maximum at ~220 mTorr value. This value should be considered optimal for deposition of amorphous silicon films, which has been indirectly confirmed before [10].

The increase in power, under constant pressure, does not lead to an increase in the growth rate of the films (figure 2), which is due to the rapid increase in the frequency of molecular collisions, which in turn lead to the formation of higher silanes, which is confirmed by the presence of dust particles on the surface of the substrate as a consequence of their formation in the plasmatron. In order to avoid the occurrence of dust particles on the surface of the films, it is necessary to maintain optimal "anti-dust" processes in the plasmatron.

Microparticles formed in the gas phase can reach the surface of the film; there are two ways to solve their formation. The first is to reduce the total volume fraction of silane in the working gas. The second, more correct - reduction of gas time in the discharge core. Gas residence time is an important parameter in the process of deposition of thin films, since the more gas is in the active phase of discharge; the more likely it is to form microparticles of dust.

Results of modeling argon-silane of plasma foretell that concentration of radicals (SiH₃, SiH₂ SiH) reaches an equilibrium state during less t=1 ms, and practically does not change after achievement of equilibrium level [11]. Knowing the pressure in the plasmatron chamber P and the residence time of the gas in the core can be estimated \( \tau \)

\[ \tau = \frac{PV}{Q}, \]

where \( Q \) is volumetric gas flow rate, [Torr·cm⁻³·s⁻¹]. The ratio between gas flow rate and pressure is not so clear, it depends on many parameters: nozzle size, pumping rate, etc.
Figure 1. Growth rate of amorphous silicon films depending on the pressure in the plasmatron. 1 – power 45 W, 2 – power 30 W, 3 – power 15 W.

Figure 2. Growth rate of amorphous silicon films depending on discharge power. Pressure in plasmatron $P=220$ mTorr.

Expression (1) gives the assessment based on measurement of the $Q, P$ parameters. The volume of the camera of the plasmatron used in $V=600$ cm$^3$ experiments. The result of calculations of the $\tau$ parameter is shown in table 1:

| No | P, Torr | Q, sccm | $\tau$, s | dust particles |
|----|---------|---------|-----------|---------------|
| 1  | 0.1     | 4       | 1.12      | present       |
| 2  | 0.2     | 38      | 0.24      | not present   |
| 3  | 0.5     | 20      | 1.14      | present       |

As can be seen from table 1, the residence time of the working gas in the discharge zone should be less than 0.2 s. Thus, in order to reduce the probability of the microparticles depositing on the surface of the growing film, it is necessary to reduce the residence time of the gas in the discharge core. This result can be achieved by reducing the pressure in the plasmatron, decreasing the volume of the plasmatron, and increasing the gas pumping rate. A 1.7-fold reduction in the volume of the plasmatron ($V=350$ cm$^3$) reduced the residence time of the gas by 2 times. It is difficult to increase the gas pumping rate, since for the same conditions; the capacity of diffusion and pre-vacuum pumps is limited.

Various working gas ratios (Ar/SiH$_4$ + He) were tested during the experiments. The deposition parameters are shown in table 2.

The result of the experimental deposition showed that a 2:3 ratio of working gases should be used to obtain quality films. No dust particles were observed at this ratio, and dust was present at other ratios.

Table 2. The deposition parameters.

| Ar + SiH$_4$, sccm | He, sccm | P, mTorr | $T$, °C | t, min | Power, W | ratio |
|--------------------|----------|----------|---------|--------|----------|-------|
| 10                 | 10       | 220      | 200     | 45     | 15       | 1:1   |
| 15                 | 5        | 220      | 200     | 45     | 15       | 3:1   |
| 12                 | 8        | 220      | 200     | 45     | 15       | 3:2   |
| 8                  | 12       | 220      | 200     | 45     | 15       | 2:3   |
Raman spectroscopy (RFS-100/s) and spectrophotometry (Agilent Carry-100) were used. In the combination scattering spectra (CSS) of amorphous silicon, there is a wide structural peak with a maximum of ~ 480 cm$^{-1}$, while crystalline silicon has a narrow peak at ~ 522 cm$^{-1}$ corresponding to transitions in the center of the zone involving LO- and TO-phonons, so combination scattering techniques can be used to determine the phase composition of films and the crystalline state of silicon therein.

Typical Raman spectra typical of those deposited under the described conditions: at different substrate temperatures (table 3.1), power (table 3.2.) and gas volume flow (table 3.3) of amorphous silicon films are shown in figures 3-5. Analysis of the Raman spectra revealed that the film did not contain nano- or microcrystalline inclusions in the amorphous phase because there was no CSS signal from the crystalline phase in the range of 510 - 520 cm$^{-1}$ in the spectrum. A band at 470 cm$^{-1}$ of the amorphous phase is observed in the spectrum.

As can be seen from figure 6 at different volume flow rates, but retained ratio of helium to Ar/SiH$_4$ mixture, there are also no peaks of corresponding nano- and microcrystalline phase in the Raman spectra. Figure 6 shows the Raman spectra of silicon films obtained from a mixture of He, Ar, H$_2$+5% SiH$_4$ under different deposition conditions (table 4).

| No. | Ar $+$ SiH$_4$, sccm | He, sccm | P, mTorr | T,°C | T, min | Power,W |
|-----|----------------------|---------|----------|------|--------|---------|
| 1   | 6.7                  | 10      | 220      | 100  | 45     | 35      |
| 2   | 6.7                  | 10      | 220      | 150  | 45     | 35      |
| 3   | 6.7                  | 10      | 220      | 200  | 45     | 35      |

| No. | Ar $+$ SiH$_4$, sccm | He, sccm | P, mTorr | T,°C | T, min | Power,W |
|-----|----------------------|---------|----------|------|--------|---------|
| 4   | 6.7                  | 10      | 220      | 200  | 45     | 25      |
| 5   | 6.7                  | 10      | 220      | 200  | 45     | 45      |
| 6   | 6.7                  | 10      | 220      | 200  | 45     | 55      |

| No. | Ar $+$ SiH$_4$, sccm | He, sccm | P, mTorr | T,°C | T, min | Power,W |
|-----|----------------------|---------|----------|------|--------|---------|
| 7   | 8                    | 12      | 220      | 200  | 45     | 35      |
| 8   | 6.7                  | 10      | 220      | 200  | 45     | 35      |
| 9   | 5.3                  | 8       | 220      | 200  | 45     | 35      |

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Figure 3. Typical Raman spectra obtained in the TO-like mode, for amorphous silicon films, at different substrate temperatures. 1 – T = 100 °C, 2 – T = 150 °C, 3 – T = 200 °C.

Figure 4. Typical Raman spectra obtained in the TO-like mode, for amorphous silicon films, at different discharge power. 1 – P = 25 W, 2 – P = 45 W, 3 – P = 55 W.

Figure 5. Typical Raman spectra obtained in the TO-like mode, for amorphous silicon films, at different volume flow rate of working gas. 1 – Q = 20 sccm, 2 – Q = 16.7 sccm, 3 – Q = 13.3 sccm.

Figure 6. Typical Raman spectra obtained in the TO-like mode, for amorphous silicon films. 1 – sample #1, 2 – sample #2. 3 – sample #3, 4 – sample #4, 5 – sample #5.

Figure 6 shows peaks around 480 nm and 510 nm. $I_{510}$ - intensity of combination scattering lines at frequencies corresponds to thermal oscillations of silicon crystallite array, $I_{480}$ - intensity of combination scattering band at frequency 480 cm$^{-1}$, corresponding to thermal oscillations of amorphous matrix. The presence of peak $I_{510}$ indicates the presence of crystalline phase or crystalline inclusions, no peak at 520 nm, and then the degree of micro-crystallinity of the film could be determined. From figure 7, it can be concluded that sample #2 contains, in addition to the amorphous phase, crystalline inclusions.

Data on absorption spectra of samples #1, #2 in the area of 300-900 nm are shown on figure 8.
Figure 7. Spectra of optical absorption of silicon films produced by jet plasma chemical method. 1 – substrate, 2 – sample #1, 3 – sample #2.

For sample #1 $E_g = 1.82$ eV, for sample #2 $E_g = 1.95$ eV, the presence of the crystalline phase slightly increased the gap width (figure 8). As a result, it can be seen that only sample #2, for which the ratio of the volume flow rate of He Ar to H$_2$+SiH$_4$ gas is 1:2, has Raman spectra from crystal phase, under all equal conditions. More research should be done to identify this pattern.

Conclusions

As a result of the studies carried out, it was found that effective deposition of amorphous silicon films should be carried out at a pressure in the chamber of plasmatron equal to 200-220 mTorr. Increasing the discharge power at constant pressure does not increase the growth rate of the films.

It has been found that a working gas ratio of 2:3 should be used to produce amorphous silicon films without condensed dispersion phase. Time of working gas stay in the discharge zone must be less than 0.2 s. The results of the film studies by Raman spectroscopy confirmed the absence of microcrystalline phase in the amorphous matrix under different deposition conditions but with a 2:3 working gas ratio.

Parameters of deposition of fine films of amorphous silicon with presence of microcrystalline inclusions are determined. Results were obtained on absorption spectra of samples #1, #2 in the area of 300-900 nm, the band gap of these samples was measured. It has been found that crystalline inclusions are present in amorphous silicon films at a 1:2 flow rate, possibly suggesting an amorphous nanocrystal transition in thin silicon films [12].

As a result of the sample studies carried out, optimal deposition parameters were established in which amorphous silicon films met the requirements for such coatings.

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