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# Influence of Substrate Temperature on the Optical Properties and the Deposition Rate of Amorphous Silicon Films

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Layers of intrinsic hydrogenated amorphous silicon (a-Si:H) films were deposited using Gas-Jet Electron Beam Plasma Chemical Vapor Deposition (GJ-EBP-CVD) technique. The optical parameters (refraction index (n), absorption coefficient ($\alpha$)) and the thickness were determined from the extremes of the interference fringes of transmission spectrum in the range of 500 – 1000 nm using the envelope method and method PUMA. The spectral dependence of the refractive index and absorption coefficient was obtained by varying the substrate temperature ($T_s$). The optical band gap ($E_g$) was determined using Tauc method and the estimated values were in range 1.88 – 1.78 eV for various substrate temperatures. The calculated thicknesses for all samples were about 1 micrometer. The film's deposition rate as a function of the substrate temperature was found.

**Keywords:** Hydrogenated amorphous silicon films, Optical properties, Optical band gap, Deposition rate, Chemical Vapor Deposition, Electron beam plasma.

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## 1. INTRODUCTION

Currently, thin films of amorphous hydrogenated silicon (a-Si:H) are widely used in solar cells, thin film transistor, liquid crystal displays, etc. [1,2]. One of the promising techniques for synthesizing thin films of silicon is GJ-EBP-CVD. This method provides a high rate of growth of the main light-absorbing layer of silicon for solar cell with low energy consumption in a standard vacuum chamber [3].

The optical parameters and the thickness of a-Si:H films have significant influence on the characteristics of semiconductor devices. Accurate determination of the complex refractive index of thin films is very important both from a fundamental and a technological point of view. This dependence can provide information about the optical band gap for semiconductor materials, defect density, the phonon and plasma frequencies.

Various methods have been used to determine the optical parameters and the thickness of films. One of the widely used techniques to calculate the optical properties and thickness of films was put forth by Swanepoel [4]. This is relatively a simple procedure that depends on the method suggested by Manifacier et al [5] to calculate the optical parameters and the thickness of films using only the transmission spectrum.

In this paper, we report the systematic investigation of the determination of optical properties (refractive index, absorption coefficient, optical band gap) and thickness proposed by Swanepoel [4] and computer code PUMA [6] for set of a-Si:H thin-films samples prepared by GJ-EBP-CVD technique. The set was synthesized from a mixture of silane with argon (5% $SiH_4$ + 95% Ar) at different substrate temperatures, 25 - 300 °C.

## 2. EXPERIMENTAL DETAILS

Amorphous silicon samples have been prepared by GJ-EBP – CVD. The method is based on the activation of a gas mixture jet by electron beam plasma and fast convective transfer of generated radicals by the supersonic free jet to a substrate (Fig. 1). The method has the following main features. Firstly, the electron beam plasma, in comparison with the discharge plasma, contains much more electrons with an effective energy enough for generation of radicals and ions. Secondly, a fast convective transfer of active particles from the activation zone to the substrate by the jet inhibits undesirable gas-phase processes. With the expansion of gas (a mixture of silane with argon) from a gas source through the nozzle diameter $d_0$ is formed free, low-density supersonic jet.

The pressure in the vacuum chamber $P_H$ = 0.1 Torr. The electron beam with energy 1600 eV was created by electron gun with a plasma cathode. The activation with the formation of radicals, atoms, molecules and ions takes place in the generated electron-beam plasma. Films' deposition occurs on the substrate which is placed downstream of the jet and the electron beam intersection zone. The substrate is placed on the heater which is located on the coordinate mechanism that allows movement of the substrate. All samples were deposited on Corning Eagle XG aluminoborosilicate glass substrates. Before synthesis substrates was treated for 30 minutes in an ultrasonic bath with a 0.1% sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$) distilled water solution than 30 minutes in isopropyl ultrasonic bath.

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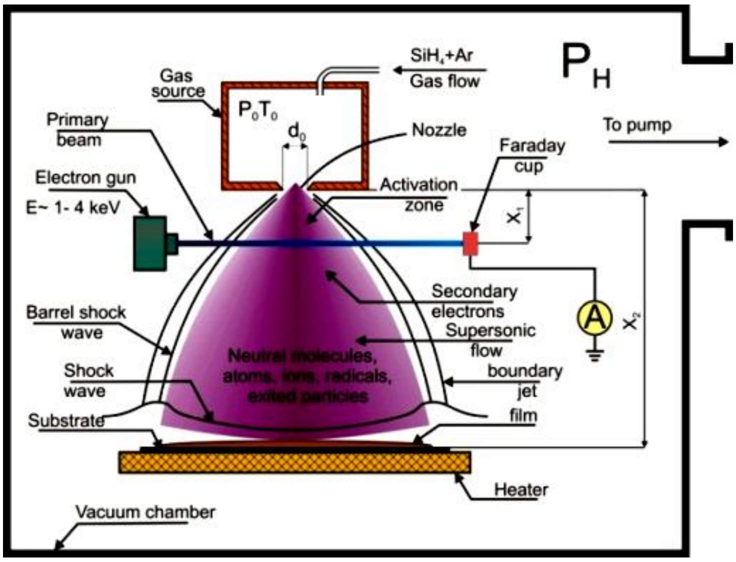



**Fig. 1** – Schematic diagram of the method and electron-beam reactor

Then substrates were dried by a stream of pure nitrogen. Substrate's surface treatment was carried out in a hydrogen plasma jet for three minutes immediately before synthesis.

The silicon films were synthesized from a mixture of silane with argon (5% $SiH_4$ + 95% Ar) at different substrate temperatures, 25 – 300 °C. Mixture's flow rate was 185 sccm.

According to Swanepoel [4] envelope method includes determination the values of the transmission coefficient on the envelope curves $T_m(\lambda)$ and $T_M(\lambda)$ with subsequent calculation of the refractive index by the following formula:

$$n = \left[ N + \left( N^2 - s^2 \right)^{0.5} \right]^{0.5},$$

where

$$N = 2s\left( T_M - T_m \right) / T_M T_m + \left( s^2 + 1 \right) / 2.$$

This formula is valid in the area of medium and weak absorption (λ = 600 – 800 nm.). After calculation the spectral refractive index of the film, from the basic equation for interference extremuma (1) the thickness of the film can be determined.

$$2nd = m\lambda \qquad (1)$$

Where m – an integer value for the maxima and half-integer for the minima. We selected two adjacent extrema to determine the thickness of the film. In this case the expression for the film thickness is given by:

$$d = \lambda_1 \lambda_2 / 2\left( \lambda_1 n_2 - \lambda_2 n_1 \right)$$

$n_1$ and $n_2$ are the refractive indices at two adjacent maxima (or minima) at $\lambda_1$ and $\lambda_2$. Substituting the average value of $d_1$ obtained for all extremuma in equation (1), we find the values m, which are rounded to integer and half-integer. These values are again substituted in equation (1), thus, is more accurate film thickness $d_2$. The final step, substituting $d_2$ in equation (1), we have more accurate values of the refractive index. In [6] proposed a nonlinear model for finding films' thickness and optical parameters which is based on spectral transmittance. This problem was solved with a package PUMA (Pointwise Unconstrained Minimization Method). The proposed procedure is a very reliable method to assess the true thickness of the film. Also, using this method it is possible to determine the thickness of very thin films (75 nm). The optical band gap of amorphous semiconductors can be found from the dependence of the absorption coefficient on photon energy with Tauc method [7]. The value $(\alpha h\nu)^{0.5}$ is proportional $h\nu$ in the area where photons' energy much more optical band gap.

Thus,

$$(\alpha h\nu)^{0.5} = B(h\nu - E_g),$$

where B is prefactor. The value of $E_g$ was defined as the point of intersection the abscissa with the line, which approximates the high-energy part of the Tauc curve.

## 3. RESULTS AND DISCUSSION

The spectral transmittance of the films, show in Fig. 2, synthesized from mixture of silane in argon (5% $SiH_4$ + 95% Ar) at different substrate temperatures. Dependencies are a sequence of alternating interference maxima and minimal. The dependence of the refractive index on wavelength for silicon films synthesized at different substrate temperatures shows In Fig. 3a. Values obtained by both methods (the envelope and using the package PUMA).

The refractive index decreases with increasing wavelength, due to the dispersion phenomenon (red light has maximum speed in the medium and minimum degree of refraction, the purple light - on the contrary). The value of the refractive index increases with increasing substrate temperature at a fixed wavelength

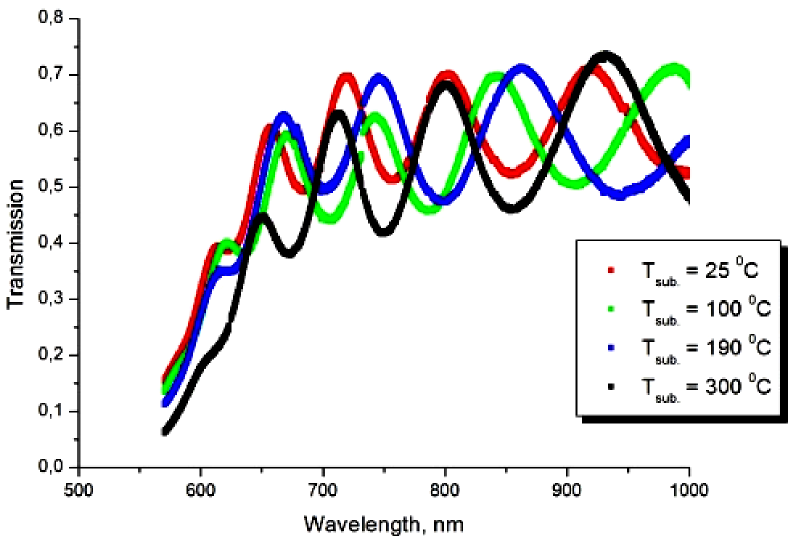



**Fig. 2** – The spectral transmittance of amorphous silicon films synthesized at different substrate temperatures

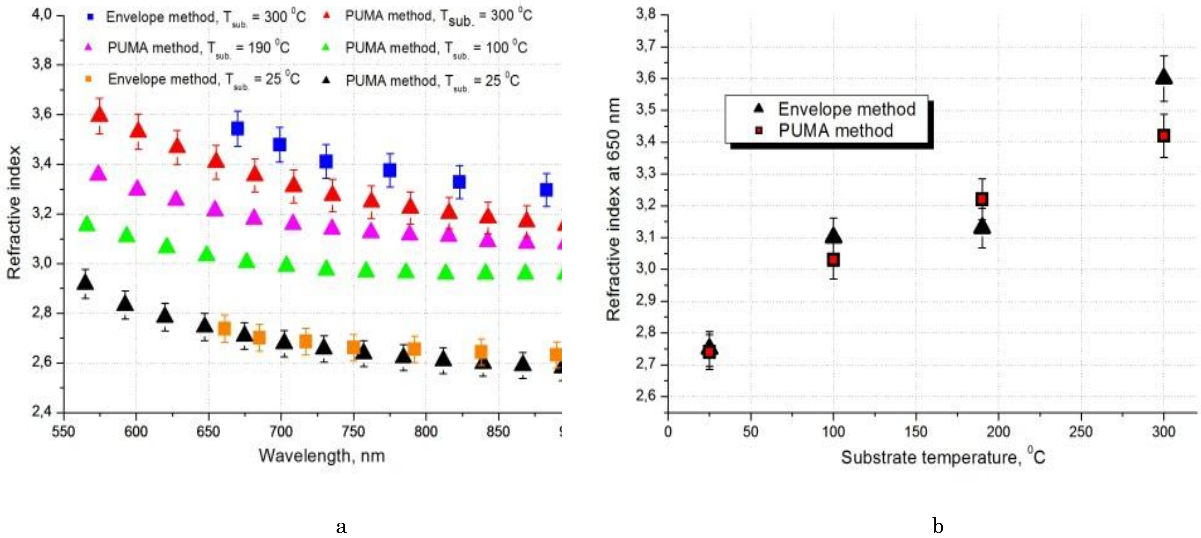
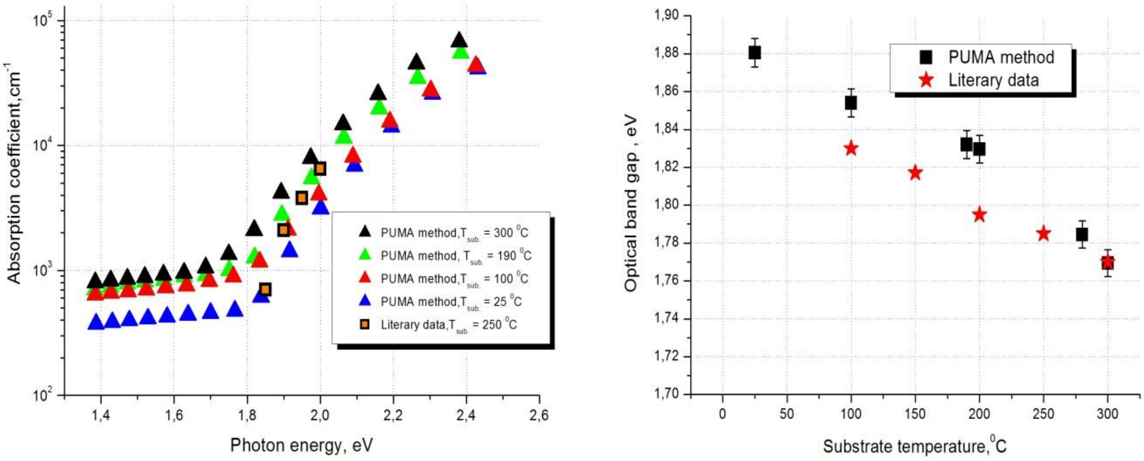



**Fig. 3** – The spectral dependence of the refractive index of silicon films synthesized at substrate temperatures of 25 - 300 0C, envelope and PUMA methods (a) and the dependence of the refractive index (at wavelength 650 nm) films of silicon on the substrate temperature (b)

(Fig. 3b). Apparently this is due to hydrogen concentration decrease in the films and, consequently, a decrease in the films of the bulk concentration of voids [8]. These results agree well with each other (methods envelopes and PUMA). The measurement error was 2%.

Using the package PUMA the dependence of the silicon films' absorption coefficient on the photon energy was obtained emission (Fig. 4a). The boundary of the regions of weak and strong absorption (1.7 – 1.8 eV) is clearly discernible on the graph. The value of the absorption coefficient increases with increasing substrate temperature, which is associated with a decrease in the optical band gap a-Si: H with heating the substrate. The obtained dependences are consistent with published data [9]. The measurement error was 5%. The dependence of the optical band gap at the different substrate temperature, show in Fig. 4b, was determined by Tauc method. The optical band gap values decrease with the heating of the substrate due to the reduction of hydrogen content in the film [10]. In this paper was showed that with hydrogen concentration increasing in amorphous silicon valence band edge moves down, which leads to an increase in the band gap. These results are in good agreement with literature data [11]. The measurement error was 0.4%.

Both methods (the method of envelopes, and PUMA) were also used to determine the thickness and the growth rate of the films. The film thickness was about 1 micrometer. The behavior of the deposition rate during the heating of the substrate correlated with the value of the refractive index. According Fig. 5 the deposition rate decreases by increasing the density of the film (reduction of voids in it) with increasing substrate temperature and the refractive index increases for the same reason. The values which was obtained by different methods, agree well with each other. The measurement error was 3.4%.




a b

**Fig. 4** – Absorption coefficient of silicon films synthesized at substrate temperatures of 25 - 300 0C versus the photon energy in comparison with literary data [9] (a) and the dependence of the optical band gap versus the substrate temperature in comparison with literature data [10] (b)

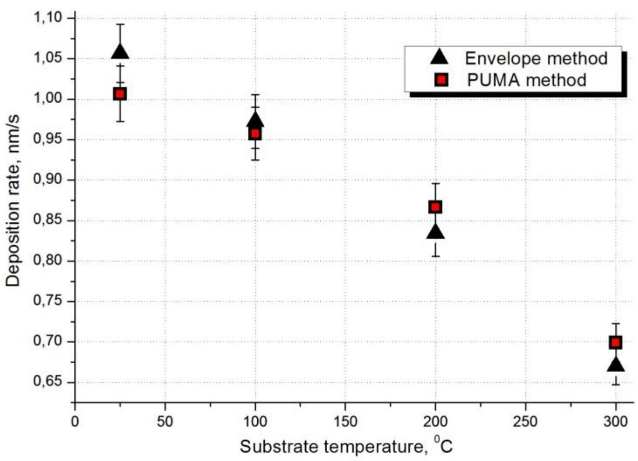



**Fig. 5** – The dependence of film deposition rate versus substrate temperature

## 4. CONCLUSIONS

The series of experiments on the synthesis of thin films of silicon were conducted. Films were synthesized from a mixture of silane with argon (5% $SiH_4$ + 95% Ar) at substrate temperatures from 25 to 300 °C.

Spectral dependence of the refractive index and absorption coefficient of the films as well as their dependence on substrate temperature was found based on the measured spectral transmittance of silicon films by envelope and PUMA methods. The refractive index decreases with increasing wavelength, due to the dispersion phenomenon (red light has maximum speed in the medium and minimum degree of refraction, the purple light – on the contrary). The value of the refractive index increases with increasing substrate temperature at a fixed wavelength. Apparently this is due to hydrogen concentration decrease in the films and, consequently, a decrease in the films of the bulk concentration of voids.

The value of the absorption coefficient increases with increasing substrate temperature, which is associated with a decrease in the optical band gap a-Si: H with heating the substrate.

The optical band gap was determined from the spectral dependence of the absorption coefficient by high-energy part of the curve Tauc. The value of optical band gap decreases with increasing substrate temperature, which is associated with a decrease the concentration of hydrogen in the film. The data obtained are in good agreement with literature sources.

Both methods (the method of envelopes, and PUMA) were also used to determine the thickness and the growth rate of the films. The film thickness was about 1 micrometer. The behavior of the deposition rate during the heating of the substrate correlated with the value of the refractive index. The deposition rate decreases by increasing the density of the film (reduction of voids in it) with increasing substrate temperature and the refractive index increases for the same reason. The values which was obtained by different methods, agree well with each other.

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**REFERENCES**

1. S.D. Brotherton, *Semicond.Sci. Technol.* **10**, 721 (1995).
2. V.P. Afanasyev, E.I. Terukov, *Thin film solar cells based on silicon* (St. Petersburg: ETU "LETI": 2011) (in Russian).
3. R.G. Sharafutdinov, S.Ya. Khmel, V.G. Shchukin, *Sol. Energ. Mat. Sol. C.* **89**, 99 (2005).
4. R. Swanepoel, *J. Phps. E: Sci. Instrum.* **16**, (1983).
5. J.C. Manifacier, J. Gasiot, J.P. Fillard, *J. Phys. E: Sci. Instrum.* **9**, 1002 (1976).
6. E.G. Birgin, I. Chambouleyron, J.M. Martínez, *J. Comp. Phys.* **151**, 862 (1999).
7. J. Tauc, *The optical properties of solids*, (North. Holland, Amsterdam: Ed. F. Abeles, 1970).
8. T. Haage, U.I. Schmidt, H. Fath, P. Hess, B. Schrijder, H. Oechsner, *J. Appl. Phys.* **76**, 4894 (1994).
9. J. Müllerová, L. Prusáková, M. Netrvalová, V. Vavrunková, P. Sutta, *Appl. Surf. Sci.* **256**, 5667 (2010).
10. B.V. Roedern, L. Ley, M. Cardona, *Phys. Rev. Let.* **39**, 1576 (1977).
11. P.R. Cabarrocas, Y. Bouizem, M.L. Theye, *Phil. M.* **65**, 1025 (1992).