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Determining the Amount of Hydrogen in Thin Films Well $Si_{1-X}g_{ex}$: H (X = 0 ÷ 1) for Electronic Devices

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Abstract

Possibilities of plasma chemical deposition of *a*-$Si_{1-x}Ge_x$:H (x=0 ÷ 1) films undoped and doped with PH_3 or B_2H_6 have been analyzed from the viewpoint of their application in *p-i-n* structures of solar cell. The optical properties are considered, and the amount of hydrogen contained in those films is determined. The film properties are found to strongly depend on the film composition and the hydrogenation level. The number of hydrogen atoms in the films is varied by changing the gas mixture composition, and IR absorption in *a*-Si:H and *a*-Ge:H films is measured. The *a*-Si:H and *a*-$Si_{0,88}Ge_{1,2}$:H films were used to fabricate three-layer solar with an element area of 13 sm^2 and an efficiency (ξ) of 9.5%.

Keywords: Thin film; Amorphous silicon; Solar cells; Efficiency; Optical properties

Introduction

Si alloy film and have different structural phases. The most interesting, are in an amorphous matrix of them are crystalline grains. Such alloys a0072e manufactured by various methods and under various process conditions. For films of amorphous hydrogenated silicon a-Si: H, formed by cyclic deposition annealing in hydrogen plasma, the effect Staeblera-Wronski is weak [1]. Golikova [2] also noted the virtual absence Staeblera-Wronski effect in nanostructured films as-Si: H. Crystallization films and silicon-Si: H is carried out by various methods: prolonged annealing in vacuum at 600°C, rapid thermal processing [3], the laser annealing [4] and ion implantation [5].

This single junction p-i-n a-Si: H solar cell deposited on a glass substrate coated with transparent conductive oxide (TCO) and aluminium back contact exhibited 2.4% conversion efficiency. In order to increase the output voltage of a-Si:H solar cells the concept of a stacked (also called multi-junction) solar cell structure was introduced.

Due to a high absorption coefficient of a-Si:H in the visible range of the solar spectrum, 1 micrometer (μm) thick a-Si:H layer is sufficient to absorb 90% of usable solar light energy. Low processing temperature allows using a wide range of low-cost substrates such as glass sheet, metal or polymer foil. These features has made a-Si:H a promising candidate for low-cost thin-film solar cells.

The a-Si:H has the same short-range order as the single crystal silicon but it lacks the long range order. The small deviations in bonding angles and bonding lengths between the neighbouring atoms in a-Si:H lead to a complete loss of the locally ordered structure on a scale exceeding a few atomic distances. The resulting atomic structure of aSi:H is called the continuous random network. Due to the short-range order in the continuous random network of a-Si:H, the common semiconductor concept of the energy states bands, represented by the conduction and valence bands, can still be used.

Mobility of charge carriers and the efficiency of doping in these films is higher than in the a-Si: H, and the optical absorption coefficient higher than that of crystalline silicon. Films and $Si_{1-x}Ge_x$: H, a-$Si_{1-x}S_x$: H are effective and cheap material for the manufacture of solar cells and other electronic devices [6,7]. Therefore these films of receiving and changing their conductivity type are urgent tasks. In Colder [8,9] with the change that the substrate temperature is increased nanocrystal growth. It was found that the average grain size (d) and the proportion of crystal grain volume (Vc) decreases with increasing concentration of PH_3. When doped with boron, increasing B_2H_6 concentration value (d) does not change, and Vc decreases. Passivating properties and hydrogen - Ge: H worse than a-Si: H, so in general the films and fotoeffektivnity- $Si_{1-x}Ge_x$: H, somewhat lower than in a-Si: H [10,11].

Hydrogen atoms, and play an important major role in the structure of the film. The purpose of this work - is to determine the amount of hydrogen in the film and measuring its electro-physical properties, as well as the creation of electronic devices based on the films and $Si_{1-x}Ge_x$: H (x=0 ÷ 1).

Experimental Part

Thin films of a-$Si_{1-x}Ge_x$: H (x=0 ÷ 1) obtained by plasma deposition using gaseous mixtures of H_2 + SiH_4, He + GeH_4 in various proportions. The details for the preparation of films are shown in the above mentioned theory [12,13]. The plasma is created by RF field mainly inductive coupling. The film thickness was 0,1 ÷ 1,0 mm. Measured absorption coefficient (α), refraction (n), reflection (R), transmission (T), the band gap (E) for each sample, using the Tauc model [14]. The optical absorption was studied at room temperature as described in [15,16] 21-IR spectrometer.

Results and Discussion

The concentration of hydrogen in the films as-Si1-xGex: H, (x=0 ÷ 1) is determined by the method of Brodsky et al. [15,16]:

$$N = \frac{AN_A}{(\Gamma/\xi)}\int\frac{\alpha(\omega)}{\omega}d\omega \tag{1}$$

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Where, Avogadro number of N- and (D/£) integral force hydride with the unit cm^2/mol (H/ξ)=3,5. If the absorption width is denoted by Aw and the center frequency ω_0, then when $\Delta\omega/\omega_0 \le 0{,}1$, after approximation with an accuracy of ± 2%, the equation (2) can be written as follows:

$$N = \frac{AN_A}{(\Gamma/\xi)\omega_0}\int\frac{\alpha(\omega)}{\omega}d\omega \tag{2}$$

Where, ε- dielectric constant. For Si ε=12; Ge ε=16. In equation (3) before the integral expression denoted by AS, and - the total absorption of stretching modes for each film, then in determining the concentration of hydrogen (NH) obtain a general expression in abbreviated form:

$$N_H = A_S J_S \tag{3}$$

Ratio AS - films for a-Si: H, is in the tension mode 1.4 $*10^{20}$ cm^{-2}. The absorption coefficient (α) for said frequency (2100 cm^{-1}) is $8*10^{-1} \div 3*10^2$ cm^{-1} with NH=$10^{21} \div 72.1*10^{22}$ cm^{-3}. For films as-Ge: H=1.7*10^{20} cm^{-2}. Clearly, equation (3), also describes an oscillating fashion in connection stretching films as-Si: H, a-Ge: H and a-$Si_{1-x}Ge_x$: H. Estimates of relative hydrogen bonding to the hydrogenated amorphous as-Si_{1-x}Gex: H: NSi-H.

$$P = \left\{\frac{N_{Si-H}}{N_{Ge-H}}\right\}\frac{x}{1-x} \tag{4}$$

Where, NGe-H - the hydrogen concentration in the a-Si: H and a-Ge: H (in cm^3). Equation (3) can be rewritten for (wagging mode) films and rocking fashion-Si: H and a-Ge: H [17,18]. Thus the value of NSi-H and NGe-H determined from the equation (3) for the fashion swing in the following form:

$$N_H = A_W J_W \tag{5}$$

Where, the total absorption rocking fashion for films and-Si: H and a-Ge: H. For these films A_w=1.6* 10^{19} cm^{-2} and A_w=1.1*10^{19} cm^{-3}, respectively. Knowing NGe-H (where, for a film-Ge: H, A_w = 1.6*10^{19} cm^{-2} and α=5 *10^1 cm^{-1}) to calculate the concentration of hydrogen in the NH and the film-$Si_{1-x}Ge_x$: H for expression:

$$N_H = N_{Ge-H}^{wag}\left\{\frac{\int\limits_{streets}\left(\frac{\alpha_1(\omega)}{\omega}\right)d\omega}{\int\limits_{streets}\left(\frac{\alpha_2(\omega)}{\omega}\right)d\omega}\right\} \tag{6}$$

Where, number of connections defined by modes of oscillation in a clean well-Ge: H, whose value is calculated according to the equation (5). The second factor in the expression for NH (integral ratio of infrared absorption maxima) is stretching vibrational mode of the sample in a clean and well-Ge: H. To calculate the ratio using integrated peak corresponding Ge-H (2000 cm^{-1}) and a film-$Si_{1-x}Ge_x$ stretching vibrational mode: H.

From these data we can estimate the strength of the oscillator in the film as well-$Si_{1-x}Ge_x$: H ratio:

$$\Gamma = J_S/J_W,$$

Where, $J_S \approx J_S^{Ge} + J_S^{Si}$, $J_W \approx J_W^{Ge} + J_W^{Si}$. The values - $J_S^{Ge}, J_S^{Si}, J_W^{Ge}, J_W^{Si}$ are integral acquisitions fashion stretching and rocking fashion, respectively oscillator strength f=0.51 (x=0) and r=0.13 (x=1). The maximum value of P=4.16 to x=0.40. Table 1 shows the characteristic parameters of amorphous films a-$Si_{0{,}60}Ge_{0{,}40}$:H. Figure 1 shows the distribution of hydrogen across the film thickness d: 1-specific method

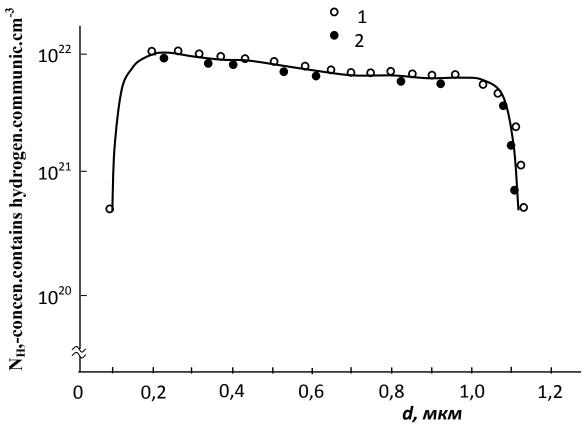

Figure 1: Distribute of the hydrogen d-of the layer in the thickness: 1. Proton recoil method, 2. Method of red spectrum of to be swallowing.

of recoil protons 2 by infrared absorption spectrum. It can be seen that sufficiently uniform distribution of hydrogen. Note that the value of NH, defined by recoil protons (MOS) and IR spectroscopy agree within 2-3 atm. %.

The optical properties of the films

Dependence on hν makes it possible to determine the width of the band gap [14,16] for each film.

In all the studied films of the optical absorption coefficient of the edge is described by the relation:

$$\alpha h\nu = B(h\nu - E_0)^2 \tag{7}$$

Where, α=5·10^4 ÷ 10^5 cm^{-1}, E_0 is- optical band gap for each film, B- proportionality factor. The value is determined depending $(\alpha h\nu)^{1/2}$ on hν extrapolation for each sample. The quadratic dependence [7] obtained theoretically for Tauc model [14], which describes the density of states of the mobility gap. The value for x=0 ÷ 1 is from 527 to 343 eV 1 $sm^{1/2}$, respectively, and for films-$Si_{1-x}Ge_x$: H (x=0 ÷ 1), E_0=1.14 ÷ 1.86 eV. We use the well-known relation, the absorption coefficient - is determined by the following equation [2,4]:

$$T = \frac{(1-R_1)(1-R_2)(1-R_3)\exp(-\alpha d)}{(1-R_2R_3)\left\{1-\left[R_1R_2 + R_1R_2(1-R_2)^2\right]\right\}\exp(-2\alpha d)} \tag{8}$$

Here we assume that

$$\begin{aligned} R_1 &= \left|(n-1)^2 + k_0^2\right| / \left|(n+1)^2 + k_0^2\right| \\ R_2 &= \left|(n-n_1)^2 + k_0^2\right| / \left|(n+n_1)^2 + k_0^2\right| \\ R_3 &= \left|(n_1-1)\right| / \left|(n_1+1)\right|^2 \end{aligned} \tag{9}$$

For weakly absorbing regions of the world, k_0 shows light attenuation in the substrate. Note that the film thickness d, is determined in this case from the respective extrema transmission or reflection of the interference fringes.

From equation (8), the absorption coefficients are defined as follows:

$$T = \frac{kx}{a(1-bx)^2} \tag{10}$$

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$$aT\left(1-bx\right)^2 = kx,$$
$$k\left(1-R_1\right)\left(1-R_2\right)\left(1-R_3\right),$$
$$a = 1 - R_2R_3,$$
$$b = R_1R_2 + R_1R_3\left(1-R_2\right)^3,$$
$$m = aTb,\ n = aT,$$
$$mx^2 + kx - n = 0,$$
$$e^{-\alpha d} = \alpha = \frac{-k \pm \sqrt{k^2+4mn}}{2m};\frac{-k \pm \sqrt{k^2+4mn}}{2m} > 0.$$

Then,

$$e^{-\alpha d} = \alpha = \frac{2m}{k \pm \sqrt{k^2+4mn}},$$
$$\alpha d = \ln\frac{2m}{k \pm \sqrt{k^2+4mn}}, \qquad (11)$$
$$\alpha = \frac{1}{d}\cdot\frac{2m}{k \pm \sqrt{k^2+4mn}}.$$

Equation (11) is a working formula to determine the optical absorption coefficients for the films in weakly absorbing regions of the spectrum [19].

In a strongly-absorbing regions of the spectrum, and. Then the equation (8) can be rewritten as follows:

$$T = \frac{\left(1-R\right)^2 e^{-\alpha d}}{1-R^2e^{-2\alpha d}}; \qquad (12)$$

$$x = e^{-\alpha d};\ x^2 = e^{-2\alpha d};\ T = \frac{\left(1-R\right)^2 x}{1-R^2x^2};$$

Then,

$$T - R^2Tx^2 = \left(1-R^2\right)x, \qquad (13)$$

$$R^2Tx^2 + \left(1-R^2\right)x - T = 0, \qquad (14)$$

$$x = -\frac{\left(1-R^2\right) \pm \sqrt{\left(1-R\right)^4 + 4R^2T^2}}{2R^2T},$$
$$x = e^{-\alpha d} > 0.$$

$$x = \frac{\sqrt{\left(1-R\right)^4 + 4R^2T^2} - \left(1-R\right)^2}{2R^2T},$$
$$e^{-\alpha d} = \frac{\sqrt{\left(1-R\right)^4 + 4R^2T^2} - \left(1-R\right)^2}{2R^2T},$$

$$e^{\alpha d} = \frac{2R^2T}{\sqrt{\left(1-R\right)^4 + 4R^2T^2} - \left(1-R\right)^2}, \qquad (15)$$

$$\alpha = \frac{1}{d}\ln\left[\frac{1}{2T}\sqrt{\left(1-R\right)^4 + 4R^2T^2} + \left(1-R\right)^2\right],$$

$$\alpha = \frac{1}{d}\ln\frac{1}{2}\left(\sqrt{\left[\frac{\left(1-R\right)^2}{T}\right]^2 + 4R^2} + \left[\left(1-R\right)^2\right]\right),$$

$$p = \frac{\left(1-R\right)^2}{T};\ \alpha = \frac{1}{d}\ln\left[\frac{1}{2}\left(\sqrt{p^2+4R^2} + p\right)\right] \qquad (16)$$

This formula is working to determine the optical absorption coefficient in strongly absorbing regions of the spectrum. Accordingly, the refractive indices are defined using or in the form of the following:

$$nd = \frac{\lambda_m\lambda_{m-1}}{2\left(\lambda_{m-1} - \lambda_m\right)}$$

$$\Delta n = \frac{c}{2\pi^2}\int\left[\frac{\alpha\left(\nu\right)}{\nu^2}\right]d\nu \qquad (17)$$

Creating a solar cell

The research results show that the film and-Si1-xGex: H (x≥0,20) can be used as high-quality material in semiconductor electronics. For this purpose, we have developed a three-layer element based on cascade-type dual-layer elements. The three-layer element is made of two-layer element consisting of two elements based on a-Si: H with p-i-n junction and the p-i-n element i- layer of a film-$Si_{0,88}Ge_{0,12}$: H (Figure 2). The thicknesses of the i- layers to the upper two transitions were selected so as to comply with the conditions of equality of short-circuit current of the lower element. Short-circuit current was about half the value for the element with one p-i-n junction. Open-circuit voltage is increased, and short circuit current is reduced with increasing number of superimposed layers. This method can increase the number of layers (create an n-layered element). Note that for each item produced i- layer 0.5 microns thick. The area of each element was 1.3 cm^2. When a three-layer solar cells must be observed uniform thickness and area of each element. The material of the substrate steel was chosen and used as a coating ZrO_2 with 80% transmissivity. Covering ZrO_2 simultaneously plays the role of the upper (front) contact. The thickness of the layers a-Si: H p- and n- type was about 300 and 400 Å, respectively [20].

For films doping amount of B_2H_6 and PH_3 gas mixtures was varied between 0.1 and 0.5%, respectively. After deposition of the amorphous semiconductor layers deposited by evaporation ZrO_2 film thickness of about 500 Å. Upper contacts used for Ni/Ag, to lower - stainless steel substrate. Items covered sunlight source provided AM-1 (100 mW/

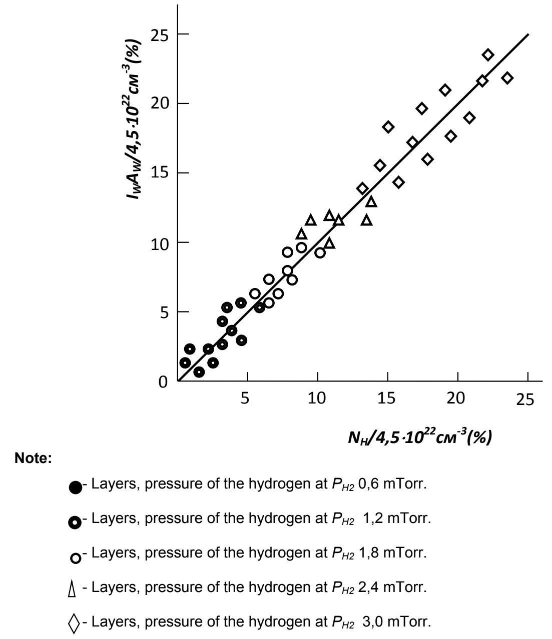

Figure 2: *a*-$Si_{0,60}Ge_{0,40}$:H correlation of the quantity (amount, number) of the hydrogen specified with effusion method for layers correlation dependence.

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cm²). Short circuit current for sandwich elements was 8.5 mA/cm², the open circuit voltage of ~2.25 B, the filling factor of ~ 0.50 and n (efficiency) ~ 9.5% (Figure 3). Efficiency for single-layer and two-layer element is 7% and 8.9%, respectively. Collection efficiency of carriers at different wavelengths is defined as:

$$Y(\lambda) = \frac{J_f(\lambda)}{eN(\lambda)} \quad (18)$$

J_f where (λ) is the density of the photocurrent (10 mA/cm²), N (λ) - the number of photons incident on a unit area per second, e- free charge carriers. For elements with the above structures is calculated short-circuit current in the assumption of complete exhaustion of all-shells, in the absence of forward bias. Thus, the short-circuit current for the first, second and third elements are given by the following expressions:

$$I_{Sc1} = q\int_0^{1,24/E_{01}} (1-R)N_{ph}\exp(-\alpha_n W_n)\left[1-\exp(-\alpha_1 W_1)\right]d\lambda \quad (19)$$

$$I_{Sc2} = q\int_0^{1,24/E_{02}} (1-R)N_{ph}\exp(-2\alpha_n W_n - \alpha_1 W_1 - \alpha_p W_p)\left[1-\exp(-\alpha_2 W_2)\right]d\lambda \quad (20)$$

$$I_{Sc3} = q\int_0^{1,24/E_{03}} (1-R)N_{ph}\exp(-3\alpha_n W_n - 2\alpha_n W_n - 2\alpha_p W_p - \alpha_1 W_1 - \alpha_2 W_2)\left[1-\exp(-\alpha_3 W_3)\right]d\lambda \quad (21)$$

Here, the field distribution within the layer, respectively, - the number of photons incident on the surface of the elements, - the reflectance of the film, - the absorption coefficient for each layer elements. The open circuit voltage for the cascade elements with two and three transitions represented in the form:

$$V_{oc}(//) = 0.5(E_{01} + E_{02}) \quad (22)$$

$$V_{oc}(III) = 0.5(E_{01} + E_{02} + E_{03}) \quad (23)$$

The duty cycle for all elements specified by the value of 0.5. Short-circuit current of the cascade element with two transitions is given by the smaller of the values or Short-circuit current of the cascade element with three transitions is determined by the smallest value of, or Efficiency multijunction cascade elements is given by:

$$\eta(i) = 0.5 \times 0.5\left(\sum_i E_{0i}\right)\frac{I_{sc}(i)}{P_{in}} \quad (24)$$

Where, i=2 or 3 indicates the number of layers, P_{in} the power of the incident light on the surface of the elements, its value is 100 mV/cm² [10] - respectively, the band gap for each *I* th layer. To improve the solar cell to η is required to increase the number of layers to reduce the

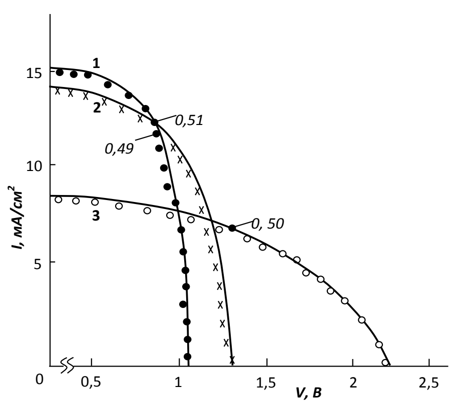

Figure 3: The current-voltage characteristics of solar cells: 1. cascade type УН/*a*-Si:H *a*-$Si_{0,60}Ge_{0,40}$:H; 2. *a*-$Si_{1-x}C_x$:H/*a*-Si:H; 3. нк-*a*-Si:H.

area of the elements, the choice of metal wires, metal contacts to reduce resistance and others.

Measurements of spectral sensitivity are usually produced with a constant white light illumination, the intensity of which corresponds to normal operating conditions (AM-100 ~ 1 MW/cm²), simultaneously modulating element falls calibrated monochromatic radiation. The photo-current, and its dependence on the wavelength of monochromatic radiation are measured in the shorted circuit with the help of a synchronized amp.

To determine the effectiveness of gathering important knowledge of the electric field that is transmitted to the element. It has been observed that the device configuration dependent collection efficiency is shifted from the red light in the blue region of the spectrum.

The wavelength dependence of the number of photons is calculated using equation (27). It is known that the photon energy and momentum of the corresponding electromagnetic waves with a frequency and wavelength in a vaccum are:

$$W = h\nu = \frac{hc}{\lambda}\ ;\ P^* = \frac{h\nu}{c} = \frac{h}{\lambda},$$

Where, h is equal to Planck's constant. Malia frequencies - the predominant role played by the wave properties at high - corpuscular properties of light. Photoelectric effect (photoelectric effect) is the process of interaction of electromagnetic radiation with matter, in which the energy of the photon is transferred to an electron of an atom of matter. In addition, these properties of substances exist mechanical action produced by electromagnetic waves in the fall for what is called a surface pressure of light. If - energy electromagnetic radiation normally feed on a surface of unit area per 1 sec, c is the velocity of propagation of light waves in a vacuum, R- coefficient of surface reflection of light, the pressure P - light on the surface is equal to:

$$P = (1+R)N\frac{h\nu}{c} = P^*/c\ (1+R) \quad (25)$$

Light pressure (P) is given by equation (19) and is denoted in the following form:

$$P^* = \frac{W}{S} = \frac{hc}{\lambda S}\frac{N}{t}, \quad (26)$$

N- number of incident photons at the time. W- energy photon incident on all the wavelengths of the body surface. P * - a pulse of light falling on the surface of 1 cm² for 1 sec. Then the force of the incident light is determined by the pressure in the following form:

$$F = P \cdot S$$

$$F = \frac{hcNS(1+R)}{\lambda St} = \frac{hN(1+R)}{\lambda t}$$

$$F\lambda t = hN(1+R)$$

$$N = \frac{F\lambda t}{h(1+R)}, \quad (27)$$

F - Light pressure force ($F=10^{-8}$H) on the surface (S=1 cm²), λ- the length of the incident wave, h - Planck's constant - the fall of light for 1 sec, with energy and its value is $Nh\nu$ - photons, with each impulse photon is hn/c. On reflection radiation - and wavelength, the number of incident photons is $10^{17} \div 10^{18}$ $m^{-2}s^{-1}$, $R=0.2 \div 0.8$; $\lambda=300 \div 900$ nm. R- reflects the ability of the elements at $\lambda=300 \div 900$ nm. It is also possible with other means to determine the number of photons:

$$P = \frac{A}{t} = \frac{Nh\gamma}{t} \quad (28)$$

Here, the work function of the A-rays of light in the fall and is, the P power light radiation and is 100 mW/cm². From (22) we can determine the number of photons in the following form:

$$N = \frac{P\lambda t}{hc} \tag{29}$$

Example:

$$N = \frac{F\lambda t}{h(1+0.2)} = \frac{10^{-8}H \times 9 \times 10^{2} \times 10^{-9}M}{6.62 \times 10^{-34}dj.cek \times 1.2} = 1.3 \times 10^{17}\ fot / M^2c$$

$$N = \frac{F\lambda t}{h(1+0.8)} = \frac{10^{-8}H \times 3 \times 10^{2} \times 10^{-9}M}{6.62 \times 10^{-34}dj.cek \times 1.8} = 10^{18} fot / M^2c$$

Conclusion

By plasma deposition using gas mixtures H_2 + SiH_4; H_2 + GeH_4 obtained in different proportions and thin film-$Si_{1-x}Ge_x$: H (x=0 ÷ 1). It is shown that the absorption coefficient for visible light and the band gap increases with increasing silicon content. The carrier mobility in the film photoconductivity and a-Si: H is greatly reduced when a germanium content of 40 atm. %. Films based on a-Si: H and a-$Si_{0,88}Ge_{0,12}$: H solar cells are made and established monolayer, two-layer and three-layer structure; measure their performance. It was found that for single, double and triple layer structures with an area of 1.3 cm² element η is 7; 8.9; 9.5%, respectively. For the three-layer cell collection efficiency peaks shifted to longer wavelengths. The structures obtained when illuminated by light in the wavelength range 0.3 ÷ 1.1 micron for 120 hour, no degradation was observed. The depletion region, where an internal electric field is created, represents only a tiny part of the wafer. Most electron-hole pairs are generated in the bulk of the electrically neutral p-type region. Electrons, which are the minority carriers in the p-type region, diffuse towards the p-n junction and in the depletion region of the junction the electrons drift to the n-type layer under the influence of the internal electric field. Hence, it is shown that the structure of the solar cells on the basis of well-$Si_{0,88}Ge_{0,12}$: H and a-Si: H are effective and further efforts to improve the quality of films and higher-efficiency of the efficiency they are urgent tasks. So, we can conclude that the above study is very useful in various applications like hydrogenated amorphous silicon, hydrogenated microcrystalline silicon, deposition of thin-film silicon.

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