Determining the Amount of Hydrogen in Thin Films Well Si$_{1-x}$Ge$_x$:H (X = 0 ÷ 1) for Electronic Devices

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Abstract

Possibilities of plasma chemical deposition of a-Si$_x$Ge$_{1-x}$:H (x=0 ÷ 1) films undoped and doped with PH$_3$ or B$_2$H$_6$ 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$_{1-x}$Ge$_x$:H films were used to fabricate three-layer solar with an element area of 13 sm$^2$ and an efficiency (η) 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 a-Si:H 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 Staebler-Wronski is weak [1]. Golikova [2] also noted the virtual absence Staebler-Wronski effect in nanostructured films a-Si:H. Crystalization 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 exceeding a few atomic distances. The resulting atomic structure in a-Si:H lead to a complete loss of the locally ordered structure on a microscopic scale and changing their conductivity type are urgent tasks. In Colder [8,9] 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$_2$H$_6$ concentration value (d) does not change, and Vc decreases. Possessing properties and hydrogen - Ge: H worse than a-Si: H, so in general the films and the optical properties - Si$_x$Ge$_{1-x}$: H (x=0 ÷ 1).

Experimental Part

Thin films of a-Si$_x$Ge$_{1-x}$: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-Si$_1$-xGe$_x$: H (x=0 ÷ 1) is determined by the method of Brodsky et al. [15,16]:

\[ N = \frac{AN_\lambda(\alpha/\omega)}{(e/2) d \omega} \]

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Where, \(N\) - Avogadro number of N- and (D/E) integral force hydride with the unit \(cm^2/mol\) (\(H/E\)) = 3.5. If the absorption width is denoted by \(AW\) and the center frequency \(\omega\), then when \(\Delta\omega/\omega_0<0.1\), after approximation with an accuracy of ± 2%, the equation (2) can be written as follows:

\[
N = \frac{AN_N}{(\frac{1}{T_e})\omega_0} \int \frac{\alpha(\omega)}{\omega} d\omega
\]

(2)

Where, \(\varepsilon\) - dielectric constant. For Si \(\varepsilon=12;\) Ge \(\varepsilon=16.\) 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:

\[
N_H = A_P J_S
\]

(3)

Ratio AS - films for a-Si: H, is in the tension mode 1.4 *10^20 cm^2. The absorption coefficient (\(\alpha\)) for said frequency (2100 cm\(^{-1}\)) is 8*10^9 + 3*10^10 cm\(^{-1}\) with NH=10^21 + 72.1*10^22 cm\(^{-3}\). For films as-Ge: H=1.7*10^20 cm\(^{2}\). Clearly, (equation 3), also described an oscillating fashion in connection stretching films as-Si: H, a-Ge: H and a-Si\(_x\) Ge\(_{1-x}\): H. Estimates of relative hydrogen bonding to the hydrogenated amorphous as-Si\(_x\) Ge\(_{1-x}\) sex: H: NSi-H.

\[
P = \left(\frac{N_{H}}{N_{Ge-H}}\right) \frac{\omega}{1-x}
\]

(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 a-Ge: H (in cm\(^{-3}\)). Equation (3) can be rewritten for (wagging mode)

\[
\frac{N_{H}}{N_{Ge-H}} = \frac{1}{1-x}
\]

(5)

Where, the total absorption rocking fashion for films and-Si: H and a-Ge: H. For these films \(A_P = 1.6*10^9\) cm\(^{-2}\) and \(A_P = 1.1*10^9\) cm\(^{-2}\), respectively. Knowing NGe-H (where, for a film-Ge: H, \(A_P = 1.6*10^9\) cm\(^{-2}\) and \(A_P = 1.5*10^9\) cm\(^{-2}\)) to calculate the concentration of hydrogen in the NH and the film-Si\(_{1-x}\) Ge\(_x\): H for expression:

\[
N_H = N_{Ge-H} \left\{ \int_{\omega=\omega_0}^{\omega=\omega_1} \frac{\alpha(\omega)}{\omega} d\omega \right\}^{-1} \left\{ \int_{\omega=\omega_0}^{\omega=\omega_1} \frac{\alpha(\omega)}{\omega} d\omega \right\}^{-1}
\]

(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\(_x\): H for expression:

\[
N_H = N_{Ge-H} \left\{ \int_{\omega=\omega_0}^{\omega=\omega_1} \frac{\alpha(\omega)}{\omega} d\omega \right\}^{-1} \left\{ \int_{\omega=\omega_0}^{\omega=\omega_1} \frac{\alpha(\omega)}{\omega} d\omega \right\}^{-1}
\]

(6)

Where, from these data we can estimate the strength of the oscillator in the film as well-Si\(_x\) Ge\(_{1-x}\): H ratio:

\[
\Gamma = J_S/J_{aw}
\]

Where, \(J_S = J_{aw} + J_{aw}^*\), \(J_{aw} = J_{aw}^* + J_{aw}^*\). The values - \(J_{aw}, J_{aw}, J_{aw}, J_{aw}\) 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\(_x\) Ge\(_{1-x}\): H. Figure 1 shows the distribution of hydrogen across the film thickness d: 1-specific method

\[
\text{Figure 1: Distribute of the hydrogen d-of the layer in the thickness: 1. Proton}\n\text{recoil method, 2. Method of red spectrum of to be swallowing.}
\]

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 hv 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:

\[
ahv = B(hv - E_0)^{1/2}
\]

(7)

Where, \(a=5*10^4 + 10^5\) cm\(^{-1}\), \(E_0\) is- optical band gap for each film, \(B\)-proportionality factor. The value is determined depending \(a(hv)^{1/2}\) on hv extrapolation for each sample. The quadratic dependence \(E_0\) 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\(_x\) Ge\(_{1-x}\): 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 [24]:

\[
T = \frac{(1 - R_j)(1 - R_j)(1 - R_j)\exp(-ad)}{(1 - R_jR_j)[1 - \frac{R_j + R_j(1 - R_j)^2\exp(-ad)}{1 - \frac{R_j + R_j(1 - R_j)^2\exp(-2ad)}{1 - \frac{R_j + R_j(1 - R_j)^2\exp(-3ad)}}]}
\]

(8)

Here we assume that

\[
R_j = \left|\frac{n - j}{n + j}\right|^2 \left(\frac{n + j}{n + j}\right)^k
\]

(9)

For weakly absorbing regions of the world, k shows slight 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:

\[
T = \frac{kx}{a(1 - bx)^2}
\]

(10)
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:
\[
\frac{\lambda_n\lambda_{n-1}}{2(\lambda_{n-1} - \lambda_n)} \Delta n = \frac{c}{2\pi} \int \frac{\alpha(v)}{v^2} dv \tag{17}
\]

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-Si0,88Ge0,12: 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 cm². 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 ZrO2 with 80% transmissivity. Covering ZrO2 simultaneously with the refractive indices is defined using or in the form of the following:
\[
\alpha = \frac{1}{d} \frac{2m}{k + \sqrt{k^2 + 4mn}} \tag{11}
\]

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:
\[
T = \left(1 - R^2\right) e^{-\alpha d};
\]
\[
x = e^{-\alpha d}, x^2 = e^{-2\alpha d}; T = \left(1 - R^2\right) x.
\]
\[
R^2 + x - 1 = 0,
\]
\[
x = \frac{\sqrt{(1-R)^2 + 4R^2T^2} - (1-R)}{2R^2T}
\]
\[
x = e^{-\alpha d} > 0.
\]
\[
x = \sqrt{(1-R)^2 + 4R^2T^2} - (1-R)
\]
\[
\alpha = \frac{1}{d} \ln \left[ \frac{1}{2T} \sqrt{(1-R)^2 + 4R^2T^2} + (1-R)^2 \right]
\]
\[
\alpha = \frac{1}{d} \ln \left[ \frac{1}{2T} \sqrt{\frac{(1-R)^2}{T} + 4R^2 + (1-R)^2} \right]
\]
\[
p = \frac{1}{T} \; \alpha = \frac{1}{d} \ln \left[ \frac{1}{2} \sqrt{R^2 + 4R^2 + p} \right]
\]
Short circuit current for sandwich elements was 8.5 mA/cm², the open circuit voltage of ~2.25 V, 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:

\[ Y(\lambda) = \frac{I_f(\lambda)}{eN(\lambda)} \]  

I, where (\lambda) is the density of the photocurrent (10 mA/cm²), N (\lambda) - 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:

\[ I_{s1} = \int_0^{\lambda_0} (1 - R N_0 \exp(-\alpha_0 W_0) \left[1 - \exp(-\alpha_1 W_1)\right] d\lambda \]  

\[ I_{s2} = \int_0^{\lambda_0} (1 - R N_0 \exp(-2\alpha_0 W_0 - \alpha_1 W_1 - \alpha_2 W_2) \left[1 - \exp(-\alpha_3 W_3)\right] d\lambda \]  

\[ I_{s3} = \int_0^{\lambda_0} (1 - R N_0 \exp(-3\alpha_0 W_0 - 2\alpha_1 W_1 - 2\alpha_2 W_2 - \alpha_3 W_3) \left[1 - \exp(-\alpha_4 W_4)\right] d\lambda \]  

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:

\[ V_{oc}(I) = 0.5(F_{occ} + E_{occ}) \]  

\[ V_{oc}(III) = 0.5(F_{occ} + E_{occ} + E_{occ}) \]  

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:

\[ \eta(I) = 0.5 \times 0.5 \times \sum E_{occ} \frac{I_f(i)}{P_m} \]  

Where, i=2 or 3 indicates the number of layers, P_m 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 \( \eta \) is required to increase the number of layers to reduce the 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 vacuum are:

\[ W = \frac{hc}{\lambda}; \quad P^* = \frac{hv}{c} = \frac{h}{\lambda}. \]

Where, \( h \) is 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:

\[ P = (1 + R)N \frac{hv}{c} = P^*/c(1 + R) \]  

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

\[ P = \frac{W}{S} = \frac{hc}{2S} \frac{N}{\lambda} \]  

\( N \)- 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:

\[ F = \frac{P \cdot S}{\lambda} \]

\[ F = \frac{h c N (1 + R)}{\lambda S c} = \frac{h N (1 + R)}{\lambda t} \]

\[ F \cdot \Delta t = h N (1 + R) \]

\[ N = \frac{F \cdot \Delta t}{h (1 + R)} \]  

\( F \)- Light pressure force (F=10⁴ H) on the surface (S=1 cm²), \( \lambda \)- the length of the incident wave, \( h \)- Planck’s constant - the fall of light for 1 sec, with energy and its value is \( Nh \) - photons, with each impulse photon is \( h/c \). On reflection radiation - and wavelength, the number of incident photons is \( 10^{17} - 10^{18} \) m⁻²s⁻¹, \( R=0.2 - 0.8; \lambda=300 - 900 \) nm. \( R \)- reflects the ability of the elements at \( \lambda=300 + 900 \) nm. It is also possible with other means to determine the number of photons:

\[ P = \frac{A}{t} \]

\( N = \frac{Nh}{t} \)
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:

\[ N = \frac{P \Delta t}{h c} \] (29)

Example:

\[ N = \frac{F \Delta t}{h c} = 10^{-8} H \times 9 \times 10^7 \times 10^{-6} M \]
\[ = 6.62 \times 10^{-34} \text{J} \cdot \text{s} \times 6.62 \times 10^{-27} \text{m} \cdot \text{s} \times 1.2 \]
\[ = 1.3 \times 10^{10} \text{photons/m}^2 \cdot \text{c} \]

\[ N = \frac{F \Delta t}{h c} = 10^{-8} H \times 3 \times 10^7 \times 10^{-6} M \]
\[ = 6.62 \times 10^{-34} \text{J} \cdot \text{s} \times 6.62 \times 10^{-27} \text{m} \cdot \text{s} \times 1.8 \]
\[ = 10^{10} \text{photons/m}^2 \cdot \text{c} \]

Conclusion

By plasma deposition using gas mixtures of H₂ + SiH₂ + H₃ + GeH₄, obtained in different proportions and thin film-Si₁₋ₓGeₓ: 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 at%. Films based on a-Si:H and a-Si₁₋ₓGeₓ: 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 region, diffuse towards the p-n junction and in 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 region, diffuse towards the p-n junction and in the electrically neutral p-type region. Hence, it is shown that the structure of the solar cells on the basis of well-Si₁₋ₓGeₓ: 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.

References

5. OA Golikova, AN Kuznetsov, VH Kudoyarova, MM Kazanin (1997) Features of the structure of amorphous hydrogenated silicon films deposited by the decomposition of silane at a constant current in the magnetic field.