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SOLAR ENERGY CONVERTERS BASED ON a- $Si_{0.80}$ $Ge_{0.20}$:H FILMS

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Abstract. In the work, the spectral dependence of the photoconductivity, ESR and IR absorption spectra of a- $Si_{0.80}$ $Ge_{0.20}$:H films, and also based on a- $Si_{0.80}$ $Ge_{0.20}$:H solar cell structures of the p-i-n junction and Pt/ a- $Si_{0.80}$ $Ge_{0.20}$:H Schottky-barrier types are examined. The results of the carried out studies makes it possible to maintain that a- $Si_{0.80}Ge_{0.20}$:H material involved is thermodynamically stable and it is of important for manufacturing solar energy converters. Solar cells with the energy conversion efficiency of 5.9 and 4.2% for p-i-n and Pt/ a- $Si_{0.80}$ $Ge_{0.20}$:H structures, respectively, have been obtained.

1. INTRODUCTION

At present it is extensively studied hydrogenated films of a-Si_{1-x}: H $_x$, a-$Si_{1-x}N_x$:H, a-$Si_{1-x}C_x$:H, a-$Ge_{1-x}C_x$:H, a-$Si_{1-x}O_x$:H, and a-$Si_{1-x}Ge_x$:H solid solutions. Amorphous silicon is gradually degraded by exposure to light through the Staebler-Wronski effect and hydrogen passivation and alloying with germanium can reduce (with the germanium content which does not exceed 20mole%, $x \leq 0.20$) both the presence of the high density localized states in the energy gap and the film band gap itself and hence further improve light absorption and stabilized efficiency [1-8]. At the same time investigations of H-Si and H-Ge bond concentrations by ESR and IR absorption methods display that hydrogen passivating properties in a-Ge far worse than those in a-Si and therefore as a whole the a- $Si_{0.80}$ $Ge_{0.20}$:H film photoefficiency turn out to be somewhat lower than that of a-Si:H [5].

In the work, the ESR and IR absorption spectra of a- $Si_{0.80}$ $Ge_{0.20}$:H films, and also based on a- $Si_{0.80}$ $Ge_{0.20}$:H solar cell structures of the p-i-n junction and Pt/ a- $Si_{0.80}$ $Ge_{0.20}$:H Schottky-barrier types are examined. Solar cells with energy conversion efficiencies of 5.9 and 4.2% for p-i-n and Pt/ a- $Si_{0.80}$ $Ge_{0.20}$: H structures, respectively, in 90mW/cm^2 sunlight have been obtained.

2. EXPERIMENTAL

a-$Si_{0.80}Ge_{0.20}$:H thin films were fabricated by the plasmochemical deposition method 0.8μm thick, at the substrate temperature of 200°C, the rate of deposition of the material on the substrate was $3\,\mathring{A}$/s, and the distance between the target and the substrate was L ≈25cm. The film growing was carried out for about an hour. The electric field strength at measurements of film electrical properties did not exceed 10^4V/cm. At measurements of the electrical property temperature dependence an aluminum-chrome thermocouple was used. The thickness of the a-$Si_{0.80}Ge_{0.20}$: H films was determined by the optical method in conditions of rise of transport phenomena. The hydrogen concentration in the films was calculated by the effusion method and the use of absorption spectra, and its value amounted to 1.7÷17.3at%. The deposition process was executed at different partial pressures in a hydrogeneous plasmic medium that had been obtained by means of a permanent magnet, magnetron and a RF field. $Si_{0.80}Ge_{0.20}$ crystalline alloy plates 60-63mm in diameter served as a target. The film amorphity was checked by electronographic methods. As a substrate crystalline Si for IR measurements and an aluminum foil for ESR measurements were used. The ESR and IR measurements were performed with a JEOL PE 3X spectrometer and a HITACHI 260-50 spectrometer with work frequency of 0.4 Hz (λ=3.2cm) at temperature of 80K. ESR spectrum parameters and the paramagnetic centers concentration were determined by M_n^{2+} pattern in the MgO lattice. At

film fabrication the RF frequency was 230 MHz (or 50W). The relative error at determination of the hydrogen concentration made up 10-12at. %. For thin film solar cells in the visible range of the absorption spectrum it was held true a condition $\alpha d \geq 1$, where d is the active layer thickness, the absorption coefficient was $\alpha = 8 \cdot 10^4 cm^{-1}$ for a-$Si_{0.80}Ge_{0.20}$: H films.

3. RESULTS AND DISCUSSION

ESR and IR absorption spectra of a-$Si_{0.80}Ge_{0.20}$: H solid solution films. Taken ESR spectra of a-Si_{1-x} Ge_x: H (with H=17,3at.%) at 80K were asymmetric in form, inasmuch as they were composed of two kinds relating to dangling bonds of Si and Ge, respectively (Fig. 1). At the same time the observed signal was not a simple superposition of the two signals (for Si and for Ge), since they violently interacted with each other and the resulting signal in the intervening interval aimed to assume the form of a sole line. Because of this the observed spectrum on its left and on its right could be depicted by a superposition of the two signal: with g-factor of g=2.004 ÷ 2.006 and the line width of 51-65 G and with g=2.018 ÷ 2.022 and 73-86 G relating to the silicon and germanium dangling bonds, respectively. In this way it could be evaluted densities of Si and Ge dagling bonds, taken separately. But in accordance with the computation of molecular orbitals in a-Si_{1-x} Ge_x : H , the presence of atoms, adjacent to the orbitals, almost does not alter g-value of ESR-signals from both Si and Ge dangling bonds [11]. By the IR absorption spectrum determining a number of Si-H bonds, and also a number of Ge-H bonds, it may affirm that a number of Ge dangling bonds is 8-10 times larger than that of Si [8]. It is proved that in a-$Si_{1-x}Ge_x$: H films H atoms are mainly bound to Si atoms. This fact is also confirmed by ESR investigations. The localized centres are paramagnetic, and they probably define also the form of dependence of electrophysical properties of the material, σ (T) vs.$T^{-1/4}$, in low temperature ranges. Hence in a-Si_{1-x} Ge_x : H films by the signal intensity, it can be found the paramagnetic centre concentration, N_s,

$$N_s = \alpha N(\varepsilon_F)kT, \qquad (1)$$

which unambiguously give a value of the density of states provided that the effective energy of correlation between two electrons in the band gap, U, is much less than kT (U << kT), N (ε_F) is the density of states near the Fermi level of 10^{18} $cm^{-3}eV^{-1}$ order, and $\alpha \approx 3$ [12]. In case of U >> kT, states lying below ε_F in U magnitude are paramagnetic independent of temperature. Connel and Pawlik [13] disclosed that H atoms in the a-Ge:H film subsist in two different environments : single H atoms on isolated defect states and single H joinings to Ge defect states on the inner surface of the pore. Such an interpretation proceeded from that in the spectrum range of 700 to 900cm^{-1} the IR absorption vanishes. The joining of several H atoms to Ge in the form of GeH_2 and GeH_3 yields the bending mode in the above-mentioned range. The similar occurence was evident by authors of papers [8, 13, 14] at the spectroscopic investigation into the local atomic structure in a-$Si_{1-x}H_x$ alloys, i.e. it is possible the formation of compounds of SiH, SiH_2, SiH_3 types. Authors of papers [13, 15] revealed that the germanium monohydrid GeH gives absorption strips at 1880cm^{-1} and the germanium dihydrid GeH_2 does those at 1980cm^{-1} and 830cm^{-1}.

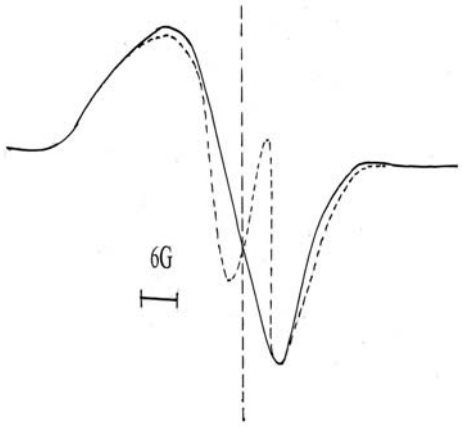


Fig. 1. ESR spectra taken at 80K on a- $Si_{0.80}Ge_{0.20}$:H films (H=17.3at.%).

The absorption strip for the SiH monohydrid complies with 2000cm^{-1} and the SiH_2 dihydrid is in conformity with 2100cm^{-1} and 875cm^{-1}. It should be emphasized that the bending vibration for GeH and GeH_2 groups complies with the frequency of 570cm^{-1} and the bendind vibration for the SiH_2 group is observed at 630cm^{-1} [16].

As is seen from Fig.3a peaks complying with the absorption strips of 1880cm^{-1} and 2000cm^{-1} are related to GeH, SiH valence oscillations (stretching) and the absorption strip peaks at 830 and 875cm^{-1} correspond to deformation oscillations of GeH and SiH bonds. In accordance with Ref.17 in the a-GeH film the absorption at 1980cm^{-1} is connected with the presence of GeH_2 and for a-$Si_{0.80}Ge_{0.20}$:H films the absorption results from the presence of GeH bounds. Consequently in a-GeH and a-Si:H films the absorption at 2000cm^{-1} and 1980cm^{-1} results from valence oscillations and the absorption at 630cm^{-1} and 570cm^{-1} does from oscillations of the bond bending type (Fig.2b,2c). Thus for a-$Si_{0.80}Ge_{0.20}$:H the significant overlapping occurs which is observed from IR absorption spectra for both GeH (1980cm^{-1}) and SiH (2000cm^{-1}) stretching strips and bending strips nearby the frequency of 600cm^{-1} (Fig.2b) .

The study of influence of the γ- radiation on properties of the amorphous hydrogenated a-$Si_{0.80}Ge_{0.20}$: H enables one to get the valuable information on defects in the material. The investigation after γ- irradiation from a source with a radiation dose of $10^{17} \div 10^{18}$ photon/cm^2 has revealed that quanta, passing through the a-Si_{1-x} Ge_x :H film, do not produce ruptured bonds (as it would occur ,e.g., under irradiation by the visible light).

2.3. Solar cells on the basis of a-$Si_{0.80}Ge_{0.20}$:H thin films

In the subsection it is considered some physical parameters of solar cells of Pt-barriers formed on a-SiGe:H samples (with H=17.3at.%) as well as the cell structure in its simplest form, a single sequence of p-i-n layers. In order to obtain the galvanomagnetic effect the film was illuminated by power of ~90mWatts·cm^2. For utilizing the p-i-n structure it was chosen a glass substrate, the indium–tin oxide (ITO) coating with the thickness of about 500 $\overset{\circ}{A}$ which transmitted light up to 80%. The i-layer was undoped and the optical absorption coefficient,

α, reaches the value of $8\cdot10^4 cm^{-1}$ in the visible region of the spectrum and satisfied the relation (Fig.3a,3b) he B value was determined by extrapolation of the dependence $(\alpha h\nu)^{1/2}$ on $h\nu$ and came to $539 eV^{-1}cm^{-1/2}$. E_g is the band gap width amounted to 1.72 eV. The value of $\mu\tau$ for the i-layer amounted $10^{-7}cm^2B^{-1}$. The generation process efficiency in the given case was close to unity ($\nu\approx1$). Thin p^+ and n^+ layers were 200-350 $\mathring{A}$ thick and produced in the discharge of SiH_4 having contained ~1% of B_2H_6 and PH_3.

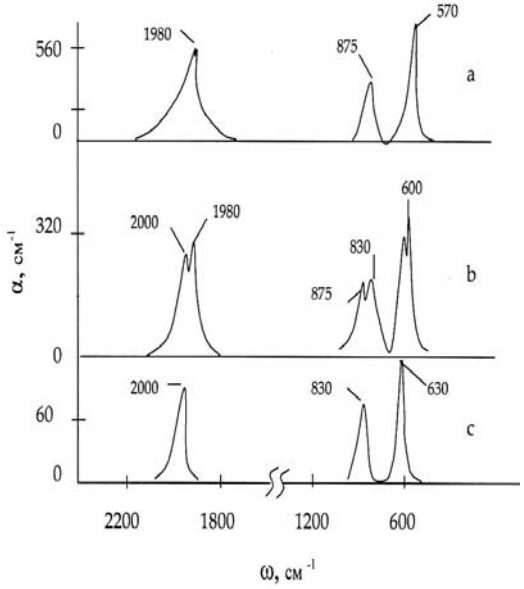


Fig.2 IR absorption spectra taken at 300K on a-Si:H (a),a- $Si_{0.80}Ge_{0.20}$:H (b), and a-Ge:H (c) films.

Doping levels of B_2H_6/ SiH_4 and PH_3/ SiH_4 were $\leq10^{-4}$. Since the resistivity of the doped a-Si:H $\geq10^2$ Om·cm, as a contact electrode on the illumined side of the cell an ITO semitransparent conductive layer was used, furthermore on the cell reverse side an Al layer was applied. At that the maximal efficiency was as high as 5.9% and the largest magnitude values of the short-circuit current, j_{sc}, open-circuit voltage, V_{oc}, and the curve fill factor, ξ, were equal to $12.4 mA\cdot cm^2$, 790mV, 0.55, respectively. Making use of the dependence j_{sc} on V_{oc} from the expression

$$V_{oc}=n'kT/q\cdot\ln(j_{sc}/j_{oc}+1), \quad (3)$$

one finds the diode quality factor n′under illumination and its value amounts to 1.6.

In a similar manner the solar cells of the Pt/ a-$Si_{0.80}Ge_{0.20}$:H type were fabricated. The substrate was chosen stainless steel and the ZrO_2 coating was used with the light transmittance of ~80%. In order to improve the performance over time and run of the cell, on the substrate it was deposited a thin n^+ layer with the thickness of 200 $\mathring{A}$, that had been produced from SiH_4.

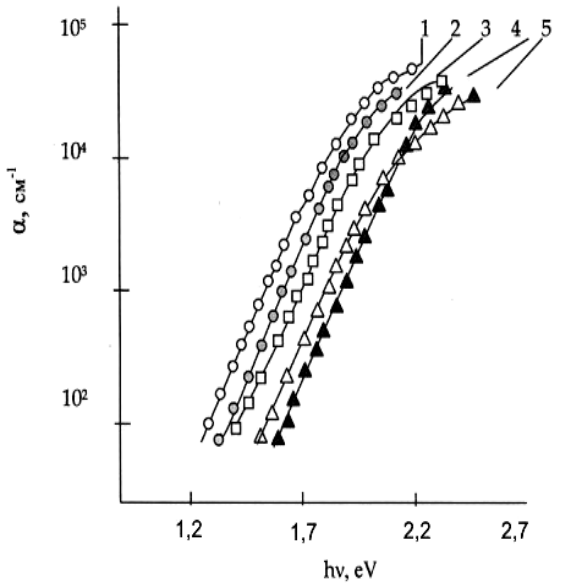
Parameters of the active layer have been considered above. Using the dark volt-amperic characteristics the saturation current density is determined [12]

$$j_{oc}=q\mu_c N_c E_s \exp(-\varphi_B/kT), \quad (4)$$

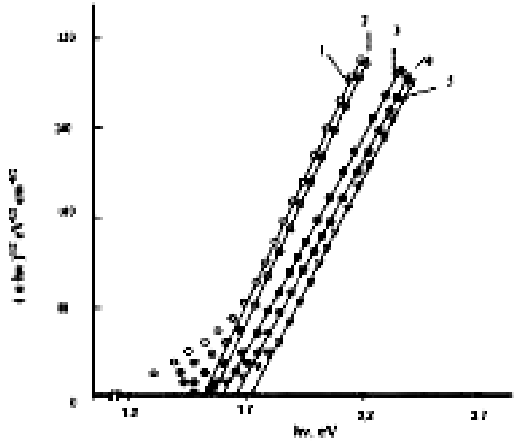
where μ_c is the electron mobility in the conduction band, from which one deduces the dependence $\sigma(T)$ on 1/T and its value equals $6cm^2/V\cdot s$, N_c is the effective density of states in the conduction band and its value, $10^{21}cm^{-3}$, has taken from Ref.[18] and $E_s=10^4 V/cm$. Knowing the experimental value for $j_{oc}=10^{-10}A/cm^2$, from the relation discover that the barrier height $\varphi_B=1.2eV$ and the diode quality factor n′=1.4. From capacitance-voltage (C-V) characteristics one finds the internal potential value, 0.42, and charge spatial density, $\sim3\cdot10^{17}cm^{-3}$, then from the equation [12]

$$W_B=(\varepsilon/2\pi q)^{1/2}(V_{oc}/N_c)^{1/2}, \quad (5)$$

the impoverished region width, W_B, equals to 0.35μm.



a)



b)

Fig.3 Dependences of absorption characteristics, α (a) and $(\alpha h\nu)^{1/2}$ (b), as functions of $h\nu$ for a-$Si_{0.80}Ge_{0.20}$:H films (H=1.7; 3.9; 7.1; 12.1; 17.3at.%).

$$\alpha h\nu=B(h\nu-E_g)^2, \quad (2)$$

In Fig.4 (Curve1 and Curve2) current-voltage (I-V) characteristics for the solar cell with the Pt/ a- $Si_{0.80}Ge_{0.20}$: H and p-i-n structures after illumination of a light source of $90 mWatt/cm^2$ are plotted. Using the dependence j_{sc} on V_{oc} one finds the diode quality factor n′ at illumination and it is equal to 1.52. From Fig.4 (Curve1) it is determined that the maximal efficiency comes to 4.2%. It is found that the largest magnitude values of the short-

circuit current, j_{sc}, open-circuit voltage, V_{oc}, and the curve fill factor,ξ, were equal to 11.2mA/cm^2, 650mV, 0.52, respectively. Fig.5 presents the dependence of the collection efficiency on a wave length of light with the falling photon flow of $10^{13}\div10^{14}$cm^{2}s^{-1} in the short-circuit regime, computed by data of the optical absorption for a film 0.5 thick; when computed, the photon flow is diminished by 80% to accommodate the limited optical transmittance of the metallic film (Curve1), in the same way the collection efficiency for the p-i-n structure is shown (Curve2).

In the case of the photocurrent saturation, when all carriers excited by light are collected in the short-circuit regime, the measured collection efficiency does not depend on the reverse displacement of the voltage. A maximum of the collection efficiency corresponds the wave length of λ≤0.7 μm. A decrease of the collection efficiency in the large wavelength range in general is explained by the absorption coefficient reduction for the active i-layer.

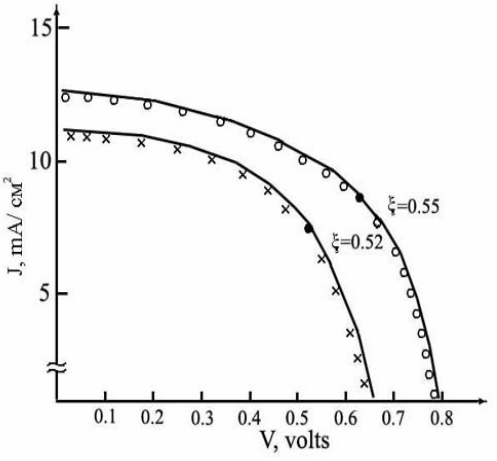


Fig.4 I-V characteristics for the solar cells of the Schottky barrier type used in the study (Curve1) and p-i-n structure (Curve 2).

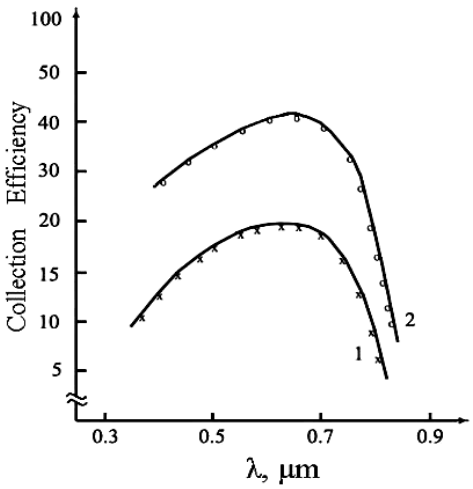


Fig.5 Dependence of the collection coefficient on a wave length of light for the solar cells of the Schottky barrier type (Curve1) and p-i-n structure (Curve 2).

4. CONCLUSIONS

The results of the carried out studies makes it possible to maintain that a- $Si_{0.80}Ge_{0.20}$:H material involved is thermodynamically stable and it is of important for manufacturing solar energy converters.

The obtained results allow to assert that for manufacturing solar cells on base of a-$Si_{0.80}Ge_{0.20}$:H it is needed thin films with a minimum paramagnetic centers concentration N_S, maximum hopping activation energy and efficiency of the generation process of electron-hole pair carriers, η≈1, and also optical absorption coefficient, α, in the visible region of the spectrum. It has been shown that solar cells with the largest short-circuit photocurrent density, j_{sc}, open-circuit voltage, V_{oc}, and the curve fill factor in cells, ξ, possess the best properties.

It might be emphasized that for improving the quality of solar cells, the development of new technological installations and a further modification of properties of the active i-layer is demanded, it also requires new combinatorial approaches to device optimization in order to reach the best compromise on the thermodynamical stability, manufacturing cost, long run and conversion efficiency.

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