RADIATIVE PROCESSES OF AMORPHIZATION AND HYDROGENATION IN MONOCRYSTALLINE SILICON

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1 INTRODUCTION

The creation of new composition materials for the production of the highly-efficient silicon photo-converters with modified optical and electrophysical properties of Si-materials is achieved due to the amorphous-crystalline phase transformation (a-Si/c-Si) and formation of a wide-zone cluster structure (a-Si:H). Strong and sharp electric fields $(\delta - BSF)\nabla E_g$ are necessary for the control of charge-carrier fluxes during their photo-generation in the semiconductor's bulk, are formed by a-Si:H(B,Al)/c-Si:H(B,Al) interface structures. The method of amorphous-crystalline transformation and hydrogen-stimulated amorphization in the bulk mono-crystalline Si structure enables the development of a new technology for the creation of Si-photo-converters with a high conversion efficiency in a wide range of solar radiation wavelengths [1]. The main difficulties in the realization of this method are connected with a week migration of hydrogen at a great depth in the Si semiconductor. The processes described will form the H-concentration at the required depth of Si semiconductor due spin splitting of Si:H compounds with the intensive electron beams and processes of the photo-stimulation of the volume diffusion. This will provide a continuous migration of hydrogen into the bulk material.

2 FORMATION OF THE AMORPHOUS-CLUSTER STRUCTURES

Amorphization of the c-Si structure is performed under irradiation with the intensive electron beam up to a doze of about 10^{-3} displacements per atom (d.p.a) in the dense $He^4 + H^+_x$-plasma when the primary knocked-out atom acquires the energy $\varepsilon \geq 5$ keV. For the electron irradiation the primary energy of particles should be $\varepsilon_0 \geq 10$ MeV. Disordered domains are local defect clusters (50 to 1000 Å) surrounded by a space charge layer and blocking the flows of charge carriers (CC). At recoil energy less than 5 keV (the threshold energy of forming the disordered structures) only the point defects are injected into the crystal. At point disordering of lattice atoms the Frenkel pair components are being spaced for a distance r_{min}, with $r_{min} \geq a_0$ (a_0 is the lattice constant). The threshold energy E_d of a primary knocked-out atom in silicon equals 140±5 keV. The concentration of the amorphous phase is defined by correlation

$$N_{dr} = n_0 \Phi \sigma_{dr}(\varepsilon_0), \qquad (1)$$

where $n_0 = 55.19 \cdot 10^{22}$ cm^{-3}, Φ is the integral flux of the bombarding electrons with an energy of ε_0,

$$\sigma_{dr}(\varepsilon_0) = \int_{\varepsilon_{dr}}^{\varepsilon_{max}} \frac{d\sigma(\varepsilon_0 \varepsilon)}{d\varepsilon} d\varepsilon . \qquad (2)$$

The differential cross sections of the electron scattering on Si for different energies are calculated in [2]. Under one-pulse material irradiation with an intense electron beam [3] the temperature (T) of the material increases linearly and than falls down to the initial value
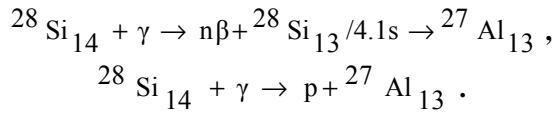
$$T = \frac{2P_0 \tau}{\rho_0 C_p S_0} \cdot F(x) , \qquad (3)$$

where P_0 is the electron beam power, τ is the duration of the current pulse, ρ_0 and C_p are the density and heat capacity of the material respectively, S_0 is the electron beam area, $F(x) = \frac{1}{\sqrt{2\pi l}} \exp\left(- x^2/2l^2\right)$ is the energy release profile, and l is the depth of beam electron penetration into the material. The re-crystallization of the structure is caused by the combinations of thermal effects which heat the material up to the melting point $\propto 0.8$ corresponding to the maximum crystallization rate. The metastability of the amorphous state weakens when free charge carriers are created due to splitting of covalent bonds. The annealing of point defects takes place at a temperature of $T \propto 300^\circ C$. The partial crystallization of the amorphous Si takes place at a temperature of the order of $T \propto 600^\circ C$. To study the structure of a-Si, and a-Si:H materials, the methods of X-ray and electron diffraction as well as the combination scattering of laser radiation are used. The IR spectroscopy is used for the determination of the local configuration bonds of hydrogen. The abundance of chemically bonded hydrogen atom influences on the degree of structure disordering, hence the energy value of the optical gap E_g in a-Si. On entering from 10 to 20 at. % of H into the a-Si structure, the value of E_g grows up to $(1.7 \div 1.8)$eV. The c-Si(Al)-structure forming is performed by the method of nuclear doping of Si<Al> using the bremsstrahlung gamma-quanta with energy $E_\gamma \geq 25$MeV and irradiation doses 10^{-5} displacements per atom.

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ВОПРОСЫ АТОМНОЙ НАУКИ И ТЕХНИКИ. 2001. №5.
Серия: Ядерно-физические исследования (39), с. 214-216.

$$^{28}Si_{14} + \gamma \rightarrow n\beta + ^{28}Si_{13}/4.1s \rightarrow ^{27}Al_{13} \, ,$$

$$^{28}Si_{14} + \gamma \rightarrow p + ^{27}Al_{13} \, .$$

3 HYDROGENATION OF SILICON

The c-Si matrix hydrogenation needed for the amorphous phase stabilization and recombination center neutralization is carried out in the course of the semiconductor irradiation with beam electrons in a hydrogen-helium plasma. The spatial hydrogen distribution over the semiconductor volume forms the profile of the a-Si/c-Si interface structure distribution in the matrix while the hydrogen concentration determines the value of electric field intensity. The diffusion is described in terms of hydrogen atom capture and release by energy-bonded states defined as H traps. The capture of H leads to the creation of Si:H cluster structures. The density of the bond states changes depending on the H concentration, temperature and time. The average length of atom displacement is proportional to the distance between the regions of hydrogen capture. Point defects (vacancies, di-vacancies), the domains of the disordered structure, grain boundaries, and impurity atoms all they are traps. The diffusion of H takes place at the grain boundaries and between the lattice planes. At a low H concentration, the cluster dimensions are restricted. At high H concentration the effective diffusion is determined by the capture of hydrogen atoms and their release from the cluster structures. The hydrogen migration in silicon and the profile of H concentration with the depth of material $C_n(x,t)$ is described [4] by the formula:

$$C_n(x,t) = C_0[erfc(x/S(t))], \qquad (4)$$

where C_0 is the H concentration at the sample surface (x=0), x is the running coordinate, $S(t) = (4D_{eff}t)^{1/2}$, t is the diffusion time, and D_{eff} is the effective diffusion coefficient. At high H concentration, the diffusion is independent on the degree of lattice disorder, and the atom arrangement in the lattice does not depend on the lattice structure. Weak Si-Si bonds will be splitted by H atoms, and only strong bonds will remain. As a result of the hydrogenation, the density of splitted spin couplings in silicon decreases. When splitting the weak bonds, the generation of spin-active defects takes place, and the defects by their passivation with H atoms form additional Si:H cluster structures. The Si(B) hydrogenation leads to the decrease of the electric conductivity of the structure because of the neutralization of doped (B) atoms. The recovery of the electric conductivity occurs due to of Al atom production in the process of the nuclear transmutation of Si atoms. With increasing the sample thickness up to 1 μm and at high H concentration, a good agreement is observed between the calculated and experimentally measured values of the cluster structure density. However, for the H concentration less than $4 \cdot 10^{18}$ cm^{-3} the diffusion concentration profile is already described by the damped exponent. The discrepancy between the exponent and *erfc* begins in the region where the H concentration equals to the density

of traps. The process of H migration into the solid-state Si is of activation nature, and the diffusion coefficient of the process is determined by the expression

$$D_{eff} = D_0 \exp(-E_a/kT) \, . \qquad (5)$$

The time (t) of the neutralization (passivation) of the splitted spin couplings and of the formation of Si:H cluster structures is determined by the expression

$$t = t_0 \exp(E_a/kT) \, , \qquad (6)$$

where E_a is the activation energy, k and T are the Boltzmann constant and the temperature of the sample, respectively, and $t_0 = 10^{-11}$ s for Si: H compounds. At low H concentration, the energy level of deep traps is approx. 1.7 eV and their concentration can reach approx. 10^{18} cm^{-3}. As the H concentration increases, the activation energy shifts to the neighboring peak of the density of states. The energy corresponds to the deep-occurring trap level of approximately 0.5 eV. The hydrogen migrates at the minimum of the concentration of the traps in the material determined by their energy state being between 0.5 and 1.7 eV. On capture of H by Si-Si bond centers, its diffusion into the depth of material ceases. In the material structure initially the deep-occurring traps and then the shallow-occurring ones are filled. The equilibrium H distribution in the shallow-occurring traps is established in the course of the diffusion. The higher times and temperatures are needed for a greater change of the H concentration. The H concentration change in the capturing regions is equivalent to the change of hydrogen solubility and is determined by the chemical H potential between 1.2 and 1.3 eV. According to the data of [4], the H concentration distribution drops from 10^{20} to 10^{18}cm^{-3} in the thickness interval up to 0.3 μm. But as is shown in [2], the c-Si material thickness of approx. 500 μm is needed for the full capture of the solar spectrum radiation. Therefore, it is impossible to solve by the existing means the problem of the H concentration diffusion for photocells. The formation of the H concentration at the required depth in the Si material can be achieved only by the forced destruction of the spin couplings of the compounds with the help of an intense electron beam thereby ensuring the continuous migration of hydrogen into the material. For this purpose the Si material is irradiated with the intense electron beam in the dense ^{4}He + H$_x^+$ plasma. The beam electrons shift the lattice and form additional radiation H traps while the ions ^{4}He and H$_x^+$ diffuse into the Si material. The ^{4}He prevents from the recombination of the shifted lattice atoms with vacancies and intensify the c-Si structure amorphization process. The primary defects and radiation defects of the structure are neutralized by the hydrogen atoms with the formation of Si:H and H$_2$ bounded states. The beam electrons destroy the spin couplings of the created structures, and released hydrogen migrates into the material depth until it will be subsequently captured by H traps. The hydrogen-release process takes place only on the radiation treatment of the material by the electron beam. With the termination of the irradiation process, the H migration into the Si material stops. In this way, it is possible to form the desired profile of the H concentration distribution over the Si material depth for the creation of the required distri-

bution shape of the pulling (δ -BSF) ΔE_g electric field in the semiconductor [5].

4 PHOTOSTIMULATION OF THE BULK DIFFUSION

One of the possible methods of exciting the phonons which stimulates the diffusion in solids is electromagnetic (laser) irradiation. The photon-to-phonon energy transfer can be realized by IR-absorption or stimulated combination scattering. Besides, the direct or indirect absorption at defect centres is possible. The process of the photon-phonon interaction that leads to the stimulation of migration of atoms or ions consists of three stages [6]:

- Photon conversion into the optical phonon;
- Nonharmonic interaction that leads to the decay of long-wave longitudinal phonons created by relaxation of hot charge carriers on longitudinal and transversal acoustic phonons with energy-momentum conservation in each event;
- Transfer of the pseudo-momentum from acoustical phonons to atoms or ions in the longitudinal and transversal directions.

The amplitude of the lattice atom vibrations caused by photon-phonon interaction and photon-to-phonon energy transfer increases, and, therefore, the probability of doped atom migration increases. Acceleration of the atomic migration results in increasing the temperature of solids from T to T_{eff}, where T_{eff} is the effective temperature that is created by photoexited and thermoexited phonons. As is known the temperature dependence of the coefficient of atom diffusion in solids is defined by Arrenius correlation (5). In the case of one-photon absorption with subsequent decay of the optical phonon into acoustic ones, the exponent in eq. (5) can be represented in the form [7]:

$$\frac{E_a}{kT_{eff}} = \frac{1}{\sum_S \hbar [2(n_s + n_e)+1]}, \qquad (7)$$

where n_s and n_e are the numbers of thermal and photo-excited photon, respectively. One can see from formula (7) that excitation by photons n_e increases T_{eff} and, consequently, increases the diffusion coefficient of atoms. The formula of the diffusion coefficients with photoexcited phonons (D_e) and without them (D) is defined by the formula:

$$\frac{D_e}{D} = \exp \frac{E_a}{k}\left(\frac{1}{T} - \frac{1}{T_{eff}}\right) \qquad (8)$$

The intensity of the required flux (N_e) of the laser radiation, that is necessary for observation of IR-absorption influence on the diffusion of doping atoms in Si, is defined by the value $N_e = n_e^c c_S / V =$ $=10^{27}$ photon/cm^2, where n_e^c is the critical number of phonons excited by laser radiation, in the range of an

elementary cell, c_S is the velocity of sound. In the thin silicon rod the velocity of sound is $c_S = \sqrt{\dfrac{E}{\rho}} = 1.1 \cdot 10^6$ cm/sec, where E is the Young's modulus, ρ is the density of the material, V is the volume of the Si atom (for the Si atom radius $r_0 = 1.34$ Å, $V = 1.03 \cdot 10^{-23}$ cm^3). The focused laser $AIG : Nd^{3+}$ beam of 10^8 W/cm^2 produces the flux of the order of 10^{31} photon/cm^2 and the flux of the order of $5 \cdot 10^{26}$ photon/cm^2 without focusing. Thus using IR-lasers one can excite acoustic phonons and stimulate migration of doping atoms into the crystal in the bulk of Si. Developed processes of radiation disordening of lattice atoms and laser photo-stimulation of the hydrogen migration in the bulk of Si semiconductor allow to form amorphous-crystal structures of high effective photocells for solar energetics.

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