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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

GENERAL CHARACTERISTICS OF THE RESEARCH WORK STUDY OF RADIATION-HETEROGENEOUS PROCESSES IN THE NANO-Si+H_2O SYSTEM

Specialty: **2225.01 – Radiation Materials Science**

Field of science: **Physics**

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BAKU – 2021

The dissertation work was carried out according to the scientific research plan of the laboratory "Radiation chemistry of heterogeneous processes" of the Institute of Radiation Problems of the Azerbaijan National Academy of Sciences and "Control-measurement devices of radioactive pollution" department of the National Aerospace Agency of the Ministry of Defense Industry of Azerbaijan.

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GENERAL DESCRIPTION OF WORK

Relevance of the topic. Recently, the demand for oil and gas from natural energy resources is growing day by day due to the rapid development of industry. As the use of oil and gas does not meet modern requirements both economically and environmentally, the transition to the use of new type energy remains one of the most pressing issues today. One of the solutions to these problems is the use of alternative energy sources (water, wind, solar, bio, hydrothermal, nuclear, etc.). Of these energy sources, nuclear energy has the largest reserve and is considered environmentally friendly. One of the ways to obtain and efficiently use nuclear energy is the transition to hydrogen energy.

For this purpose, it was used the method of obtaining molecular hydrogen from radiation-heterogeneous decomposition of water in systems created in the contact of porous materials with different particle size (metals, metal oxides, etc.) with water under the influence of ionizing radiation. Analysis of the results of scientific research conducted in our Republic and in other countries to select the optimal mode for mentioned system allows us to say that this area is the focus of researchers. At the same time, there is a need to study the mechanism of production of intermediate products and products formed in both phases in the physical, physicochemical and chemical stages of the processes under the influence of ionizing radiation in these systems.

The safety of nuclear reactors using water as a cooler, retarder and energy carrier is ensured by the study of molecular products H_2, O_2 and H_2O_2 obtained from its thermal and radiation-thermal decomposition by preparing the scientific basis for radiation-heterogeneous decomposition of water. Molecular products H_2, O_2 and H_2O_2, which are considered hazardous to the given system, are obtained under the combined influence of ionizing radiation and temperature from nuclear conversion inside a container used to store nuclear fuel waste. The safety of these systems is one of the most pressing issues today.

Aims and objectives of the research. The main aim of the dissertation work is to define the obtaining regularity of molecular

hydrogen from radiation-heterogeneous decomposition of water in created Si/H_2O system with the particle size of d = 50, 100 and 300÷500 nm.

The following issues have been resolved to achieve this goal:

- The calculation of energy yields of active intermediate products that have a role in water decomposition, such as different electron-exicition states and electron-hole pairs obtained from direct single ionization of different molecular orbitals (MO) - in physical stages of non-elastic collision between low-energy electrons and silicon atoms, on the basis of mathematical model by Mathcad program, using single-collision, stepping, and Monte-Carlo methods.
- On the basis of that model, the dependence of the percentage of emission of electrons with different energies formed inside the nanoparticle under γ-quanta influence, from particle surface to liquid phase (into water) on the particle size and its kinetic energy.
- Dependence of the formation rate and energy yield of molecular hydrogen obtained from radiation-heteregenous decomposition of water in absorbed Si/H_2O system with the particle size of 50, 100 and 300÷500 nm under the γ-quanta influence, on the particle size and filling degree of water absorbed in particle surface;
- Influence of mass and particle size of Si on the formation rate and energy yield of molecular hydrogen obtained from the radiation-heteregenous decomposition of water in the systems created by the addition of Si with the particle size of 50, 100 and 300÷500 nm suspended via vibrator inside V=5ml water under γ-quanta influence;
- Determination of dependence of the formation rate and energy yield of molecular hydrogen obtained from thermal and radiation-thermal decomposition of water in created nano Si/H_2O system with the particle size d=50 nm, on the temperature of system and density of water vapour in reaction medium.

Research methods. The dissertation results were obtained using high-accuracy and high-sensitive gas chromatographs “Agilent-7890” and “Tsvet-102”, infrared (IR) spectrophotometer, atomic force microscope (AFM), physicochemical and chemical analysis methods. Theoretical calculations (kinetic analysis,

mathematical modeling) were carried out on the basis of the modern computer program Mathcad. The correspondence between the values of physical quantities obtained from calculations on the basis of the experiment and model proved that mathematical modeling is sufficient.

The main provisions of the defense:

1. Determination of unbalanced energy carriers (electrons, holes and excitons) obtained from inelastic collision between low-energy electrons and Si atoms, which play a role in the production of molecular hydrogen from the radiation-heterogeneous decomposition of water in the created nano-Si/H_2O systems;
2. Determination of a role of electrons formed inside the particle in the created nano-Si/H_2O suspension systems under the influence of γ-quanta, and emitted from its surface into the water in the acquisition of molecular hydrogen obtained from water decomposition;
3. Determination of the mechanisms of the influence of mass, size, filling degree of water and temperature on the energy yield of molecular hydrogen obtained from the water decomposition in created nano-Si/H_2O systems under the influence of γ-quanta.

Scientific innovation of the research:

1. Using stepping, single-collision and Monte-Carlo methods, it has been calculated the energy yields of unbalanced energy carriers, such as electron-hole pairs and electron excitation states formed from direct single ionization of different MOs that are formed in inelastic collision between low-energy electrons and Si atoms at physical stages of process and have a role in the radiation-heterogeneous decomposition of water by the model based on the Mathcad program.
2. On the basis of that model, it has been determined the dependence of the emission percentage of electrons formed inside the nanoparticle under γ-quanta influence from particle surface into water, on the particle size and its kinetic energy.
3. It has been defined the increase of formation rate and energy yield of molecular hydrogen obtained from radiation-heteregenous decomposition of water in nano-Si/H_2O systems with a particle size of d=50 nm under the influence of γ-quanta directly proportion to the

filling degree (θ) of water on particle surface and the decrease in an inclination angle after the certain values.

4. It was revealed the dependence of formation rate and energy yield of molecular hydrogen obtained from radiation-heterogeneous decomposition of water in created Si/H_2O systems $(\theta=4)$ with particle size of d = 50, 100 and 300÷500 nm under the γ - quanta influence, on its particle size.

5. It was determined a directly proportional increase in the formation rate and energy yield of molecular hydrogen obtained from the water decomposition in the systems created by the addition of Si with the particle sizes d=50, 100 and 300÷500 nm suspended via vibrator in the water V=5 ml under the influence of γ-quanta, up to the certain values of the Si mass depending on then particle sizes and then a decrease in the inclination angle.

6. It has been identified the dependence of formation rate and energy yield of molecular hydrogen obtained from thermal and radiation-thermal decomposition of water under the influence γ-quanta in nano-Si/H_2O system with the particle size d=50 nm on the temperature of system and the density of water vapour in the reaction medium.

Theoretical and practical significance of the research:

Dissertation results can be used in aerospace research, aerospace technology, in nuclear reactors, where light water is used as a retarder, coolant, and energy carrier, in high energy physics and chemistry, in the use and storage of nuclear fuel waste, in hydrogen energy, which is a source of environmentally friendly energy from radiation-heterogeneous processes.

Approbation and application.

The main results of the dissertation were reported at the following national and international events:

- "Academic Science Week-2015" - International Multidisciplinary Forum, ANAS, November 2-5, 2015, Baku;
- Dedicated to the 93rd Anniversary of the National leader of Azerbaijan, Heydar Aliyev IV International Scientific Conference of Young Researchers, April 29-30, 2016, Baku;

- Materials of "Khazarneftgazyatag-2016" scientific-practical conference, ASOIU, 2016, Baku;
- Republican scientific and technical conference of students and young researchers on "Youth and scientific innovations", dedicated to the 94th anniversary of the national leader of the Azerbaijani people Heydar Aliyev, AzTU, May 3-5, 2017, Baku;
- International scientific conference on "Chemistry of coordination compounds: current problems of analytical chemistry", BSU, November 16-17, 2017, Baku;
- III International Scientific Conference on "Ecology: Problems of Nature and Society", BSU, December 7-8, 2017, Baku;
- Dedicated to the 95rd Anniversary of the National leader of Azerbaijan, Heydar Aliyev II International Scientific Conference of Young Researchers, BEU, April 27-28, 2018, Baku;
- "Radiation processes and their applications" international conference dedicated to the 70th Anniversary of Academician M.K. Karimov, Institute of Radiation Problems ANAS, November 13-14, 2018, Baku;
- "EurasiaScience" XXV International Scientific and Practical Conference, Scientific Publishing Center "Actuality.RF", 2019, Moscow.

Published scientific works: 19 scientific works, including 10 articles, 9 theses were published in the Republican and foreign journals on the topic of the dissertation. 2 of the articles were published abroad, in journals included in International databases, and 3 of them were published as single-author articles.

The structure, volume and main content of the dissertation.

The dissertation consists of an introduction, four chapters, results and a list of 157 references. The total volume of the work is 137 pages, including: 41 figures and 20 tables.

Name of the organization where the dissertation work was carried out:

The dissertation work was carried out according to the scientific research plan of the laboratory "Radiation chemistry of heterogeneous processes" of the Institute of Radiation Problems of

the Azerbaijan National Academy of Sciences and "Control-measurement devices of radioactive pollution" department of the National Aerospace Agency of the Ministry of Defense Industry of Azerbaijan

CONTENT OF THE RESEARCH WORK

The introduction substantiates the relevance of the topic and provides information on research methods, scientific novelty and practical significance of the work, information about the purpose, structure and content of the work, the main provisions to be defended and the approbation of the work.

The first chapter provides the information about the literature on the dissertation topic and their analysis. Active intermediate particles such as non-balanced energy carriers (electron-hole pairs, electron-excitation states and various type radiation defects) occur from the interaction of ionizing rays (γ- quanta, electrons, protons, neutrons, α-particles, high-energy ions, etc.) with atoms or molecules that make up the matter while passing through it. These particles play an important role in the processes of obtaining molecular hydrogen from water decomposition in created Me(MeO)/H_2O adsorption and suspension systems. At present, the role of these active intermediate particles in the products obtained from water decomposition in homogeneous and heterogeneous systems has not been fully studied, either experimentally or theoretically. Thus, the dependence of the energy yield of products obtained from radiation-heterogeneous processes: on the mass of the used Me or Me_xO_y, particle size, filling degree of the water adsorbed on the particle surface, system temperature and density of water vapour in the reaction medium at high temperatures has not been sufficiently studied.

The second chapter provides the practical part of the dissertation. In this chapter, it has been given the methods of the formation of nano-Si/H_2O systems by the methods of cleaning the surface of different size Si by thermal treatment, air purification of water and expelling water to the silicon surface. The ^{60}Co isotope was used as a source of γ-radiation in this study. In order to determine the dose strength of source, the dosimetric ferrosulfate, the

acquisition of molecular hydrogen from the decomposition of pure methane, and theoretical calculation methods were used. Products and intermediate products obtained after irradiation were studied using Gas Chromatography, IR-spectroscopy and AFM. Theoretical calculations (kinetic analysis, mathematical modeling) were performed on the basis of the computer program Mathcad.

In the third chapter, low-energy electrons are mainly formed within the track in the physical stage of the process in the nano-Si, H_2O, nano-Si/H_2O systems under the influence of γ-quanta. Energy yields of the products of inelastic collision between low-energy electrons (E=0.1-10.0 keV) and Si atoms: - different electron-excitation states (L_{1v}, Γ_2, L_3, Γ_{15}, L_{1c}, X_{1c}) and electron-hole pair formed from direct single ionization of MOs (K-(1s), L-I (2s), L-II (2p ½), L-III (2p 3/2), M-I (3s), M-II (3p)) have been calculated using single collision, stepping and Monte-Carlo methods and forming mathematical model on the basis of Matchad program. In the calculation, the initial electrons and each new generation δ-electrons they create, lose some of their kinetic energy in an inelastic collision, and this process continues until the kinetic energy of the electron can re-create an inelastic collision. Obtained unbalanced energy carriers: -electrons, holes and electron-excitation states (excitons) play a direct role in the process of obtaining molecular hydrogen from the heterogeneous decomposition of water.

If we accept Si as immobile before and after the collision, then the energy balance in the inelastic collision between the initial electrons and the Si atoms can be written as simple as (1):

$$E = E_K + \Delta E \qquad (1)$$

Here, E - is kinetic energy of initial, E_K–of scattered electrons, ΔE – energy transferred to Si atom by the initial electon during the collision. The energy transferred in the ionization process is used to create an electron-hole pair (2) formed from the direct ionization of different MOs:

$$e_0 + Si \rightarrow Si_j^+ + e_s + e_e \left(\Delta E = E_k + B_j\right) \qquad (2)$$

Here, e_0, e_s, e_e – are initial, scattered and recoil electrons, respectively, Si_j^+ – state of direct single ionization of J[th] MO of Si atom. The energy ΔE transferred during this process (2) is equal to the sum of the kinetic energy E_K of the recoil electron from the J[th] orbital and the binding energy – B_j corresponding to that MO (Table 1). According to the laws of energy and momentum conservation, the energy ΔE transferred in the ionization process can vary in range of $\Delta E_{\min} = B_i$, $\Delta E_{\max} = \frac{E + B_i}{2}$. The differential equation (3) proposed by Grizinski was used to calculate the effective cross section of the direct single ionization processes of MOs in an inelastic collision between low-energy electrons and Si atoms:

$$\frac{d\sigma_{i,j}(\Delta E, E, B_{i,j})}{d\Delta E} = \frac{\pi e^4}{\Delta E^3}\frac{B_{i,j}}{E}\left(\frac{E}{E+B_{i,j}}\right)^{\frac{3}{2}}\left(1-\frac{\Delta E}{E}\right)^{\frac{B_{i,j}}{B_{i,j}+\Delta E}}\left\{\frac{\Delta E}{B_{i,j}}\left(1-\frac{B_{i,j}}{E}\right)+\frac{4}{3}\ln\left[2.7+\left(\frac{E-\Delta E}{B_{i,j}}\right)^{\frac{1}{2}}\right]\right\} \quad (3)$$

Here, e – is a charge of electron. If we integrate expression (3), the differential equation, correspomding to the J[th] MO, according to all possible values of transmitted energy, ie from $\Delta E_{\min}$ to $\Delta E_{\max}$, and multiply the result by the number of electrons (n_j) in the MO (Table 1), we get the dependence of the effective cross section of the ionization of that MO on the kinetic energy of the initial electron (4) in inelastic collision:

$$\sigma_j(E, B_j) = n_j \int_{\Delta E_{\min}}^{\Delta E_{\max}} \frac{d\sigma_j(\Delta E, E, B_j)}{d\Delta E} d\Delta E \quad (4)$$

The sum of the effective cros-sections of ionization (4) corresponding to different MOs gives the full effective cross-sections of ionization (5) (Figure 1(2)):

$$\sigma_{ion}(E) = \sum_j \sigma_j(E, B_j) \quad (5)$$

The process of electron excitation in an inelastic collision between initial electrons and Si atoms can be symbolically described as follows (6):

$$e_0^- + Si \rightarrow Si_i^* + e_s^- \quad (\Delta E = W_{0,i}) \quad (6)$$

In this process, Cobut's improved equation (7) of the equation proposed by Kutcher and Green was used for the differential value of the effective cross-section of the transition of electron from the main state 0 to the i^{th} excitation state:

$$\frac{d\sigma_{0,i}(E,W)}{dW} = \rho(W)Wf_i(W)\ln\left[\frac{4E}{Q_{\min}}\right] \quad (7)$$

Here, Q_{min} – is the minimal energy loss in electron-excitation in electron-electron interaction, $\rho(W) = \frac{4\pi a_0^2}{E}\left(\frac{R}{W}\right)^2$, $f_i(W)$ - the strength of osilator, R=13.6 eV - Ridberg energy, a_0- Bohr radius. In this case, in order to find the effective cross section of the transition of the electron from the main state 0 to the i^{th} excitation state *(L_{1v}, Γ_2, L_3, Γ_{15}, L_{1c}, X_{1c})*, we need to integrate expression (7) according to the width of the peak (8) corresponding to that electron-excitation:

$$\sigma_{0,i}(E) = \int_{W_{\min}}^{W_{\max}} \frac{d\sigma_{0,i}(E,W)}{dW} dW \quad (8)$$

The sum of the effective cross-sections of the various electron-excitations (excitons) gives the full effective (9) cross-sections of the electron-excitation states (Figure 1 (1)):

$$\sigma_{exc}(E) = \sum_i \sigma_{0,i}(E) \quad (9)$$

The sum of the full effective cross-sections of the ionization (5) and electron-excitation (9) states gives us the full effective (10) cross section in inelastic collision:

$$\sigma_{tot}(E) = \sigma_{ion}(E) + \sigma_{exc}(E) \quad (10)$$

Figure 1 shows a dependence graph of the electron-excitation (curve 1) and direct single ionization of the MOs (curve 2) and the full effective cross section (curve 3) on the kinetic energy of the electron.

The values obtained from the calculation based on model for energy yields of the products of inelastic collision between low-energy electrons and Si atoms: - electron-hole pair formed from direct single ionization of different MOs was given in table 1 and electron-excitation states in table 2.

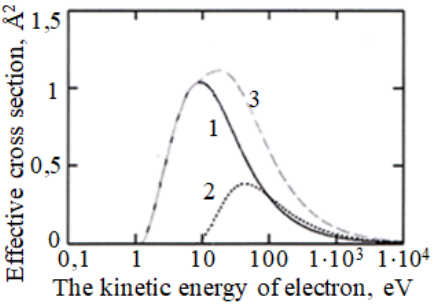

Figure 1. Dependence of the products of inelastic collision between low-energy electrons and Si atoms: electron-excitation - σ_{exc}(E) (1), ionization σ_{ion}(E) (2) states and full effective cross sections σ_{tot}(E) (3), on the kinetic energy of electron

Table 1.

Energy yields of electron-hole pairs ($S_j^+ - e^-$) formed from direct single ionization of different MOs *(K (1s), L-I (2s), L-II (2p ½), L-III (2p 3/2), M-I (3s), M-II (3p))* obtained from inelastic collision between low-energy electrons and Si atoms

Levels	Marking	Number of electrons, n_i	Binding energy, B_i, eV	Kinetic energy of electron, keV				
				0.1	0.5	1	5	10
K	1s	2	1844	0	0	0	0	0.01
L-I	2s	2	154	0	0.01	0.03	0.06	0.07
L-II	2p 1/2	3	104	0	0.06	0.1	0.15	0.16
L-III	2p 3/2	3	104	0	0.06	0.1	0.15	0.16
M-I	3s	2	13.46	2.28	1.62	1.48	1.25	1.18
M-II	3p	2	8.15	3.69	3.21	2.81	2.23	2.08

In the calculation based on model, the energy yields of electron-hole pair get the value of $G(h^+\text{-}e^-)$ = 6.06÷3.66 electron-hole pair/(100 eV) and energy yields of electron-excitation states-G(exc)=18.9÷9.55 electron-excitation state/(100 eV) at the physical stage of process in inelastic collision between low energy electrons and Si atoms. Then, at the physicochemical stage of the process (10^{-11}-10^{-6} sec), electron-excitation energy of the atoms higher than the width of the band gap

of the Si atom dissociate $(Si^* \rightarrow Si^+(h^+)+e^-)$ to form an electron-hole pair again, in this case, the energy yield of the electron-hole pair is $G(h^+\text{-}e^-)$=24.97-13.21 electron-hole pair/(100 eV).

Table 2.

Energy yields of different electon-excitation states (L_{1v}, Γ_2, L_3, Γ_{15}, L_{1c}, X_{1c}) obtained from inelastic collision between low-energy electrons and Si atoms

Excitation levels	Excitation energy, $W_{0,i}$, eV	Kinetic energy of electron, *keV*				
		0.1	0.5	1	5	10
L_{1v}	6.7	1.12	0.63	0.51	0.39	0.36
$\Gamma_2^{'}$	4.23	2.85	1.94	1.66	1.24	1.15
L_3	4.15	0.22	0.13	0.10	0.08	0.07
Γ_{15}	3.4	2	1.36	1.14	0.85	0.79
L_{1c}	2.4	3.39	2.88	2.64	1.95	1.72
X_{1c}	1.25	9.34	8.91	8.42	5.99	5.46

Assume that in the model nano-silicon particle is in the form of a sphere with radius R. Assume that electrons, holes and excitons, which are the energy carriers that formed at the physical stage of the process within the sphere under the influence of γ-quanta, are equally distributed throughout the volume and transported with the same probability in all directions. The obtained hole centers can be transported as a result of drift and and some of them can be localized in the internal structural defects of the particle and some in the surface centers by migrating to the surface. Some of the excitons formed inside the particle can also be captured in volume, and some can be transferred to another phase through the centers connected to the particle surface. The Compton electrons formed within the nano-Si under the influence of radiation and each new generation δ-electrons they create, gradually lose their kinetic energies in the elastic and inelastic collisions inside the particle during the physical stage of the process, and some of them are captured by structural defects inside the particle and some are transported up to the particle

surface. Of the electrons transported up to the surface, some of them whose kinetic energies are lower than the surface potential are localized on the surface, some return to the particle, and some whose energy are higher are emitted into the water beyond the particle surface. Based on the model, the trajectories of the electrons were tracked and the emission percentage of electrons emitted from the nanoparticle surface into the water was calculated. Figure 2 shows a dependence graph of the emission percentage on the kinetic energy of the electron and the particle size of the nanoparticles.

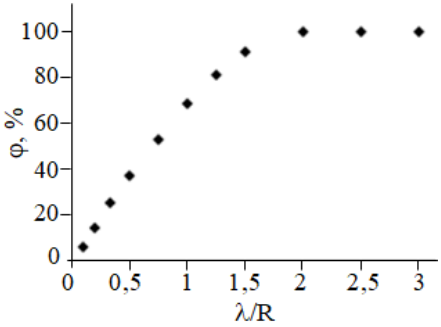

Figure 2. Dependence of the emission percentage of electrons emitted from the surface of a nanoparticle on its particle size

It was calculated on the bases of model that the percentage of electron emission from the nanoparticle surface to the liquid phase varies depending on its particle size and the kinetic energy of the electrons. All electrons that meet the average free running distance $\lambda \geq 2R$ are emitted from the nanoparticle surface into the water.

In the fourth chapter, it was studied the processes of obtaining molecular hydrogen from thermal *(T = 373, 473, 573, 623 and 673K)* and radiation-thermal *(T = 300, 373, 473, 573, 623 and 673K)* decomposition of water by γ-quanta influence (^{60}Co, P = 18.17 rad/sec) in the systems of Si/H_2O with particle size of d = 50, 100, 300÷500 nm. These processes were carried out in three directions.

In the first direction, kinetic curves of the dependence of molecular hydrogen amount obtained from radiation-heteregenous decomposition of water in *nano-Si/H_2O* systems created by the

adsoption of nano-Si surface with the particle size d=50 nm in the different filling degree of water θ=0.25(1); 0.5(2); 1(3); 2(4); 4(5); 10(6) by the influence of γ-quanta (^{60}Co, P=18.17 rad/sec, T=300K), on the duration of radiation were given in the Figure 3.

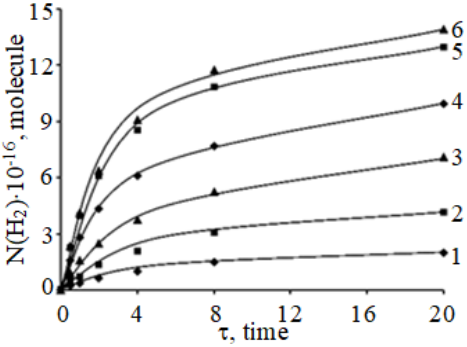

Figure 3. Dependence of molecular hydrogen amount obtained from radiation-heteregenous decomposition of water in nano-Si/H_2O systems created by the adsorption of nano-*Si* surface with the particle size of d=50 nm in the different filling degrees of water θ=0.25(1); 0.5(2); 1(3); 2(4); 4(5); 10(6) by the influence of γ-quanta, on the duration of radiation

The formation rates - $w(H_2)$ and energy yields -$G(H_2)$ of molecular hydrogen defined for nano-Si from the obtained kinetic parts of the curves (1-6) in Figure 3, are given in Table 3.

$$[Si-H_2O_s]^+ + e^- \rightarrow [Si-H_2O_s]^* \qquad (12)$$

On the other hand, these processes was performed in the θ=4 value of filling degree of the surface with d=100,300÷500 nm size Si.

The holes formed inside the Si particle under the influence of γ-quanta and migrating to the particle-water boundary are captured by the water $[Si-H_2O_s]$ complex adsorbed on the surface and form the ion-complex (11):

$$[Si-H_2O_s] + h^+ \rightarrow [Si-H_2O_s]^+ \qquad (11)$$

The ion-complex recombines with heat or tunneling electrons and forms an electron-excitation $[Si-H_2O_s]^*$ complex (12):

On the other hand, excitons (only L_{1v}) formed under the influence of ionizing radiation create complex electron-excitation (13), transmiting their energy (6.7 eV) to the water complex adsorbed on the surface.

$$exc + [Si - H_2O_s] \rightarrow [Si - H_2O_s]^* \qquad (13)$$

Table 3.

Dependence of formation rate - $w(H_2)$ and energy yield - $G(H_2)$ of molecular hydrogen obtained fom radiation-heteregenous decomposition of water adsorbed on the surface of nano-Si with the particle size of d=50 under the influence of γ-quanta (^{60}Co, P=18.17 rad/sec, T=300K), on the filling degree of its surface

Formation rates and energy yields of H_2	Filling degree of surface, θ					
	0.25	0.5	1	2	4	10
$w(H_2)\cdot 10^{-13}$, molecule/(g·sec)	0.33	0.63	1.23	2.2	3.1	3.25
$G(H_2)$, molecule/(100 eV)	0.29	0.55	1.08	1.92	2.7	2.87

In both cases, the electron-excitation $[Si - H_2O_s]^*$ energy of the complex is transmitted to the adsorbed water molecule, causing its decomposition, and as a result, an OH group and an H atom are formed on the nanoparticle surface (14).

$$[Si - H_2O_s]^* \rightarrow Si - OH + H \qquad (14)$$

Finally, molecular hydrogen is obtained from the radiation-heterogeneous decomposition of water $(H+H \rightarrow H_2)$. As a result of the combination of adjacent OH groups, dose-dependent oxidation of the surface occurs (15):

$$2SiOH \rightarrow Si - O - Si + H_2O \qquad (15)$$

In this case, the electron-excitation energy (E_{exc}) transferred to the water must be higher ($E_{exc} \geq E_{rab}$) than or equal (E_{rab}=5.1eV) to the binding energy required for the water decomposition ($H_2O \rightarrow OH+H$).

Thus, in order water decomposition to occur in the reactions occurring by the transfer of non-balanced energy carriers (electrons, holes, excitons) formed inside the particle under γ-quanta influence on Si/H_2O system, to the water molecule absorbed on the surface,

they need to migrate to surface absorption levels. The migration of particles to the surface level can occur by the mechanism of diffusion and drift, and their migration distance is limited. From these mechanisms (11-15) it is clear that two electron-hole pairs and two excitons must be used for obtaining each hydrogen molecule from the radiation-heterogeneous decomposition of water. If we assume that all energy carriers formed under of γ-quanta influence are involved in the production of molecular hydrogen, then according to reactions (11-15) the energy yield of molecular hydrogen obtained from the radiation-heterogeneous decomposition of water adsorbed on the Si surface must obey the relation (16):

$$G_n(H_2) = \frac{1}{2}\left[G_n(h^+ - e^-) + G_n(L_{1v})\right] \qquad (16)$$

That is, the energy yield of the molecular hydrogen obtained from the experiments must be equal to half the sum of the energy yields of the working exciton (L_{1v}) and the electron holes pair obtained from the theoretical calculation. Table 4 compares the energy yields of molecular hydrogen obtained from the radiolysis process in systems formed by adsorption (θ=4) of water on the surface of Si with particle size d = 50, 100, 300÷500 nm with values obtained from calculation based on the model.

Table 4.

Comparison of values of energy yield of molecular hydrogen obtained from radiation-heterogeneous decomposition of water in systems created by adsorption of water on the particle surface of Si (θ=4) from the calculation based on experience and model

50 nm	100 nm	300÷500 nm	$G_n(h^+\text{-}e^-)$	$G_n(L_{1v})$	$G_n(H_2)$
Energy yield of H_2, $G_t(H_2)$ molecule/(100eV)			Values defined on the basis of model		
2.7	1.7	1.15	6.06-3.66	1.12-0.36	3.6-2.01

As can be seen, as the particle size increases, the energy yield of molecular hydrogen decreases. This proves that some of the energy carriers are recombined and some do not reach the surface.

In the second direction, it was considered the dependence of the molecular hydrogen amount obtained from water decomposition in the suspension systems created by changing the mass (m= 0.01÷0.12 g) and particle size (d=50, 100, 300÷500 nm) of 5ml pure water and Si added to the same amount of water and suspended through vibrator during radiation under the influence of γ-quanta (^{60}Co, P = 22 rad /sec, T = 300K), on the duration of radiation. From the kinetic parts of the obtained graphs, the formation rates -*w (H_2)* and energy yields - *G (H_2)* of molecular hydrogen defined for water were determined. The obtained results were given in Table 5.

Table 5.

The mass dependence of formation rate - w(H_2) and energy yield - G(H_2) of molecular hydrogen obtained from water decomposition in the systems created with 5ml pure water and d=50, 100 və 300÷500 nm size Si suspended via vibrator in the same amount water during irradiation under γ- quanta influence and defined by water

m_{Si}, q	50 nm		100 nm		300 ÷ 500 nm	
	w(H_2)·10^{-13}, molec./(g·sec)	G(H_2), molec./100eV	w(H_2)·10^{-13}, molec./(g·sec)	G(H_2), molec./100eV	w(H_2)·10^{-13}, molec./(g·sec)	G(H_2), molec./100eV
0	-	-	0.61	0.436	-	-
0.01	5	3.64	3.4	2.77	2.53	1.84
0.02	9.67	7.03	7.97	5.48	5.15	3.75
0.06	13.4	9.05	9.67	7.03	6.3	4.58
0.12	15	10.9	11.1	8.07	7.21	5.24

Due to the electrons emmited from the particle surafce into water in created nano-Si/H_2O suspension systems under γ-quanta influence, the concentration of electrons of a certain thickness in the phase around the particle is higher than in pure water. As the particle size increases the emission percentage of emitted electrons decreases. The electrons emitted into the water gradually lose their kinetic energy as a result of dipole relaxation, elastic and inelastic collisions, and are first converted into thermal and then solvated electrons. Molecular and atomic hydrogen obtained from the reactions between

the solvated electrons $\left(e_{aq}^{-}\right)$ and the water and protonated water molecules (H_3O^+) can be described as follows (17-19):

$$2e_{aq}^{-} + 2H_2O \rightarrow H_2 + 2OH^- \quad (17)$$

$$e_{aq}^{-} + H + H_2O \rightarrow H_2 + OH^- \quad (18)$$

$$e_{aq}^{-} + H_3O^+ \rightarrow H + H_2O \quad (19)$$

Table 6 compares the values of energy yields of molecular hydrogen obtained from the water decomposition in suspension systems with d= 50, 100, 300 ÷ 500 nm particle size Si/H_2O under the influence of γ-quanta from experiments and model calculations. Based on the model, the energy yield of molecular hydrogen was calculated based on the expression (20).

$$G_n(H_2) = \frac{1}{2}\left[G_n(h^+ - e^-) + G_n(L_{1v}) + G(e_{aq}^-)\right] \quad (20)$$

Table 6.

Comparison of the values of energy yields of molecular hydrogen obtained from the water decomposition in created suspension systems of Si/H_2O under the influence of γ-quanta from calculations based on experiment and model

Energy yield of molecular hydrogen	Results from experiment			Theoretical results
	50 nm	100 nm	300÷500 nm	
$G(H_2)$, molecule/10eV	10.9	8.07	5.24	12.5-6.6

As can be seen, as the particle size increases, the energy yield of molecular hydrogen decreases. This proves that some of the energy carriers are recombined and some cannot be transported to the surface. The process of obtaining molecular hydrogen in suspension systems under the influence of γ-quanta occurs through both the recombination mechanism (11-14), the direct exciton transfer (13-14) and the electrons emitted from the solid surface and solvated in water (17-19).

In the third direction, it was considered, the dependence of molecular hydrogen amount obtained from thermal and radiation-

thermal decomposition under γ-quanta influence (^{60}Co, P=18.17 rad/sec) in the contact of nano-Si with d=50 nm particle size with the water vapour at ρ=0.25; 0.5; 1, 3 and 8 mg/cm^{3}density at the temperature T=673K, on the irradiation period. From the obtained graphs, it was defined the formation rates on the basis of expression of thermal -$w_T(H_2)$ and radiation-thermal -$w_{RT}(H_2)$ and radiation share $w_R(H_2)=w_{RT}(H_2)-w_T(H_2)$). Energy yield - $G_R(H_2)$ of molecular hydrogen has been determined according to the rate difference - $w_R(H_2)$ (Table 7).

Table 7.

Formation rates ($w_T(H_2)$, $w_{RT}(H_2)$, $w_R(H_2)$ and energy yields $G_R(H_2)$ of molecular hydrogen obtained from thermal and radiation-thermal decomposition of water under γ-quanta influence in the contact of nano-Si with d=50 nm size with the water vapour at ρ=0.25; 0.5; 1, 3 and 8 mg/cm^3 density at T=673K temperature

Formation rates ($w_T(H_2)$, $w_{RT}(H_2)$, $w_R(H_2)$) and energy yields $G_R(H_2)$ of molecular hydrogen	density of water vapour, mg/cm^3				
	0.25	0.5	1	3	8
$w_T(H_2)10^{-14}$, molecule/g·sec	1.68	3.34	6.49	18.74	20.1
$w_{RT}(H_2)\cdot10^{-14}$, molecule/g·sec	1.73	3.45	6.7	19.15	20.6
$w_R(H_2)\cdot10^{-14}$, molecule/g·sec	0.05	0.1	0.21	0.41	0.5
$G_R(H_2)$, molecule /100eV	0.45	0.89	1.85	3.6	4.4

On the other hand, it was studied the temperature (T=300, 373, 473, 573, 623, 673K) dependence regularity of the amount, formation rate and energy yields of molecular hydrogen obtained from thermal and radiation-thermal decomposition of water under γ-quanta (^{60}Co, P=18.17 rad/sec) influence in the contact of nano-Si with d=50 nm size with the water vapour at ρ=8 mg/cm^3 density.

The activation energies of processes were defined from the 1/T dependence of the lgw formation rate of molecular hydrogen obtained from thermal and radiation-thermal decomposition of water under γ-quanta influence in the contact of nano-Si with water vapour

at ρ=8 mg/cm^3 density in the reaction medium using Arrhenius coordinates (lgw(H_2), 1/T)).

Table 8.

The temperature influence of the formation rate and energy yield of molecular hydrogen obtained from the thermal and radiation-thermal decomposition of water under the influence of γ-quanta in the contact of nano-Si with a particle size d=50 nm with water vapor at a density of ρ=8 mg/cm^3 in the reaction medium at the temperature T = 673K

T, K	$w_T(H_2)$, molecule/ g·sec	$w_{RT}(H_2)$, molecule /g·sec	$w_R(H_2)$, molecule /g·sec	$G_R(H_2)$, molecule /(100·eV)
300	-	$0.325 \cdot 10^{14}$	$0.325 \cdot 10^{14}$	2.87
373	-	$0.332 \cdot 10^{14}$	$0.332 \cdot 10^{14}$	2.9
473	-	$0.363 \cdot 10^{14}$	$0.363 \cdot 10^{14}$	3.2
573	$2.40 \cdot 10^{14}$	$2.88 \cdot 10^{14}$	$0.48 \cdot 10^{14}$	4.2
623	$7.22 \cdot 10^{14}$	$7.71 \cdot 10^{14}$	$0.49 \cdot 10^{14}$	4.32
673	$2.01 \cdot 10^{15}$	$2.06 \cdot 10^{15}$	$0.50 \cdot 10^{14}$	4.4

At a temperature range T = 300-473K, molecular hydrogen is obtained from the nano-Si/H_2O system by radiation-thermal decomposition of water, and the activation energy of this process is determined to be 1.07 kC/mol (Figure 4 (1a)). In the temperature range T = 573-673K, molecular hydrogen is obtained from both radiation-thermal (Figure 4 (1b)) and thermal (Figure 4 (2)) decomposition of water, so that the activation energies corresponding to both processes were defined as 53.83 kC/mol and 68.6 kC/mol.

It was determined by IR spectroscopy that during the radiation-thermal and thermal decomposition of water in the nano-Si/H_2O system, the rates of separation of H-bond groups from the surface and the formation rates of isolated OH – groups on the surface are higher in the radiation-thermal process. This shows the stimulating role of radiation and is consistent with the values of the formation rate and energy yield of molecular hydrogen. At the same time, under the influence of γ-quanta, active intermediates (Si-O, Si-H, Si-OH, Si-H_2) are formed during the water decomposition in the nano-Si/H_2O heterosystem in the temperature range T = 300-673K.

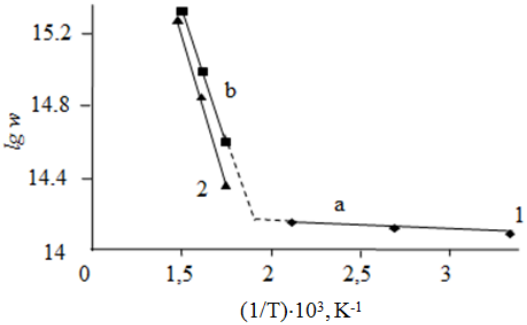

Figure 4. 1/T dependence of the lgw formation rates of molecular hydrogen obtained from thermal and radiation-thermal decomposition of water under γ-quanta influence in the contact of nano-Si of a particle size d=50 with water vapour at ρ=8 mg/cm^3 density in the reaction medium

Comparative AGM analysis of initial and radiation-thermal oxidized silicon surfaces gives the following results: 1)The oxidized surface has a relatively more regular structure, 2)Radiation-thermally oxidized layers are characterized by the presence of smaller particles (1.5 times smaller, maximum distribution 100-150 nm) In this case, the number of particles increases ~2 times (14000: 650).

MAIN RESULTS

1. From the calculation based on model, the value of energy yields of products of inelastic collision between low energy electrons and Si atoms in the physical stage of the process is defined as G(h^+-e^-)=3.66-6.06 electron-hole pair/(100 eV) for electron-hole pair, G(Si^*)=9.55-18.9 excitation state/(100 eV) for electron-excitation states, while it is G(h^+-e^-)=13.21-24.97 electron-hole pair/(100 eV) for electron-hole pair in the next physical-chemical stage.

2. It has been established that the energy yield of electrons formed within nano-Si under the influence of γ-quanta and emitted from the particle surface into water and solvated there varies depending on the particle size and the kinetic energy of the electron. All electrons that meet the average free running distance $\lambda \geq 2R$ are emitted from the nanoparticle surface into the water.

3. It has been determined that the energy yield of molecular hydrogen obtained from water decomposition in nano-Si(d=50 nm)/H_2O system increases directly proportional with surface filling degree when $\theta \leq 2$, and inclination angle sharply decreases when $\theta > 2$. Energy yields of molecular hydrogen defined for the silicon obtained from radiation-heterogeneous decomposition of water in the Si/H_2O adsorption ($\theta=4$) systems with the particle size of d=50, 100, 300÷500 nm got the values $G(H_2)$=2.7; 1.7 and 1.15 molecule/(100 eV), respectively. In the adsorption system, the energy yield of molecular hydrogen obtained from the transfer of energy calculated on the basis of the model by recombination and exciton mechanisms was $G_n(H_2)$=2-3.6 molecule/100 eV.

4. In the created Si/H_2O suspension systems with the particle size d=50, 100 and 300÷500 nm under γ-quanta influence, maximum energy yields of molecular hydrogen obtained from water decomposition and defined for water were $G(H_2)$=10.9; 8.07 and 5.24 molecule/100eV, respectively. In this system, there is observed an increase in the energy yield of molecular hydrogen directly proportional to the mass of Si at $m_{Si} \leq 0.02$g, and a sharp decrease in the inclination angle at $m_{Si} > 0.02$g depending on the particle size. The energy yield of molecular hydrogen calculated based on the model by transfer of energy according to the mechanisms of recombination and exciton and by the electrons emitted from the particle surface into water and solvated there was $G_n(H_2)$=6.6-12.5 molecule/100 eV.

5. In the nano-Si(d=50nm)/H_2O systems at T=673K temperature, in ρ=0.25; 0.5; 1; 3 and 8 mg/cm^3 density of water vapour in reaction medium, the energy yield of molecular hydrogen obtained from thermal and radiation-thermal decomposition of water under γ-quanta influence increases directly proportional with it at $0<\rho<3$ mg/cm^3 density, and the increase rate sharply decreases at $\rho \geq 3$ mg/cm^3.

6. In the nano-Si/H_2O system, at a water density of ρ=8 mg/cm^3 in the reaction medium the molecular hydrogen obtained from the thermal and radiation-thermal decomposition of water under the γ-

quanta influence is obtained only from radiation-thermal processes at a temperature range of 300K≤T≤473K and the activation energy of these processes is 1.07 kC /mol, while in the temperature range of 573K≤T≤673K it is obtained from both thermal and radiation-thermal processes and the activation energies of these processes were 68.6 kC/mol and 53.83 kC/mol, respectively. The energy yield of molecular hydrogen calculated according to radiation share of molecular hydrogen obtained in those systems was $G(H_2)$=2.7-4.4 molecule/100·eV

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The defense will be held on « 17 » december 2021, at 15:00 in the meeting of the Dissertation council FD1.21 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the Institute of Radiation Problems of Azerbaijan National Academy of Sciences

Address: AZ1143, Baku, B.Vahabzadeh str., 9.

Dissertation is accessible at the Institute of Radiation Problems of Azerbaijan National Academy of Sciences.

Electronic versions of dissertation and its abstract are available on the official website of the Institute of Radiation Problems of Azerbaijan National Academy of Sciences.

Abstract was sent to the required addresses on «15» noyabr 2021.

Signed for print: 11.11.2021

Paper format: A5

Volume: 38364 characters

Number of hard copies: 30