PACS: 78.67.Bf

DEPENDENCE OF THE YIELD OF MOLECULAR HYDROGEN OBTAINED FROM RADIATION-HETEROGENEOUS DECOMPOSITION OF WATER ON PARTICLE SIZE OF SILICA AND FILLING RATE OF PARTICLE SURFACE OF WATER IN Si+H_2O SYSTEM BY THE INFLUENCE OF GAMMA-QUANTA

Y.D. Jafarov[1], S.M. Bashirova[2], S.M. Aliyev[1]
[1]Institute of Radiation Problems of ANAS
[2]NASA-Research Institute of Aerospace Informatics
yadjafarov@rambler.ru

Abstract: It has been studied the dependence of amount, formation rate and radiation-chemical yield of molecular hydrogen obtained from radiation-heterogeneous decomposition of water on particle size of silica and filling rate (θ) of silica surface of water in the system of d=50, 100, 300÷500 nm size silica + water absorbed in different filling rate of silica surface by the influence of gamma-quanta (^{60}Co, P=18.17 rad/sec, T=300K). Maximum radiation-chemical yields of molecular hydrogen, corresponding to those particle sizes (d=50, 100, 300÷500 nm) have got the values of $G(H_2)$=10.85; 6.97 and 4.6 molecule/(100·eV), respectively. The researches conducted in different values *(θ=0.5; 1; 2; 4; 10)* of filling rate of particle surface of water in the system of nano-silica with d=50nm particle size + H_2O show that, radiation-chemical yield of molecular hydrogen is directly proportional to filling rate of surface at θ<4, but there is observed saturation state at θ ≥ 4. The mechanisms and explanations have been given below.

Key words: nanoparticle, radiolysis, radiation-chemical yield

1. Introduction

Predicting the changes that may occur inside, on the surface and in a surrounding environment of metal and various metal compounds used as a construction material in atomic, nuclear and thermonuclear energy by the influence of ionizing rays (γ-quanta, electrons, protons, neutrons, α-particles, high energy ions), is one of the main problems of science and technology workers. Therefore, radiolysis process of liquids, especially water in nano- and micro-heterogeneous systems by the influence of ionizing rays has remained an actual problem of the day. The authors of [1-10] have conducted the research of products of radiation-heterogeneous decomposition of water, occurring in the systems of metal or metal oxides + water by the influence of γ-quanta, in two conditions. The first is water suspension of particles, constituting these substances, the second – analyzing some of the products obtained from water radiation-heterogeneous decomposition, occurring during water adsorption at different filling rate, on the surface of these materials. It turns out from the researchers' results that, the amount, formation rate and radiation-chemical yield of molecular hydrogen obtained from radiation-heterogeneous decomposition of water in metal or metal oxides + H_2O systems change depending on:

- the type of solids
- band gap width
- size of particles that form it
- filling rate of particle surface of water
- overall system temperature

- water density in the system at high temperature
- mass of solid suspended in water
- nature of substances dissolved in water

According to different researchers' and our results it turns out that, the yield, formation rate and radiation-chemical yield of products obtained from radiation - heterogeneous decomposition of water become several times higher than pure water in more active nano-size [1-11] materials than other size materials in these systems by γ-quanta influence.

In the given work, it has been studied the dependence of amount, formation rate and radiation-chemical yield of molecular hydrogen obtained from radiation-heterogeneous decomposition of water on its particle sizes (d=50, 100, 300÷500 nm) and filling rate of d=50 nm particle size nano-silica surface (θ=0.5; 1; 2; 4; 10) of water in the system of silica + water absorbed on its surface (Si+H_2O) by γ-quanta (^{60}Co, P=18,17 rad/sec, T=300K) influence.

2. Experimental part

High purity (99,9%) silica with d=50, 100, 300÷500 nm particle sizes ("Skyspring Nanomaterials, Inc.", made in USA) has been taken as a research object. After thermal processing of silica (τ=72 hour) in an open air at T= 473K, required mass has been scaled and added to ampoule (V = 19 ml) which is purified in special mode and thermally processed (T=773K). After thermal processing (T=673K) of silica in a vacuum (P=10^{-3}mm c.st.) condition in the ampoule (4 hours), it has been cooled and required amount of air-purified bidistillated water adsorbed on it, then it has been closed [9, 10, 12] and irradiated at ^{60}Co source with P=18.17 rad/sec dose rate.

Absorption dose rate has been determined by Ferrosulfat and methane methods. Absorption dose rate at a specific research object has been calculated by using electronic density comparison methods [12].

It has been analyzed by chromatographic method that, the composition of last molecular products obtained from radiation-heterogeneous processes is H_2, O_2 and H_2O_2. As a part of O_2 captured on surface and H_2O_2 was in the solution, errors were more in the determination of their amount. Therefore, more accurate information of kinetic regularity of the radiation-heterogeneous decomposition process of water has been given according to the amount of molecular hydrogen.

The reaction products have been analyzed by chromatography "Agilent-7890". In order to clarify the results, the modernized "Tsvet-102" chromatography (8-10% accuracy) has been used in parallel. It has been used the column with 1m length and 3mm internal diameter in chromatography, activated charcoal with d=0.25÷0.6 mm size - in the column and high purity (99,9%) argon as a gas carrier - in both chromatography.

3. Results and Discussion

First of all, the obtain kinetics of molecular hydrogen which is the product of radiation heterogeneous decomposition of water absorbed on the surface of silica with d=50, 100, 300÷500 nm particle sizes by γ–quanta (^{60}Co, P=18.17 rad/sec, T=300K) influence has been established (figure 1).

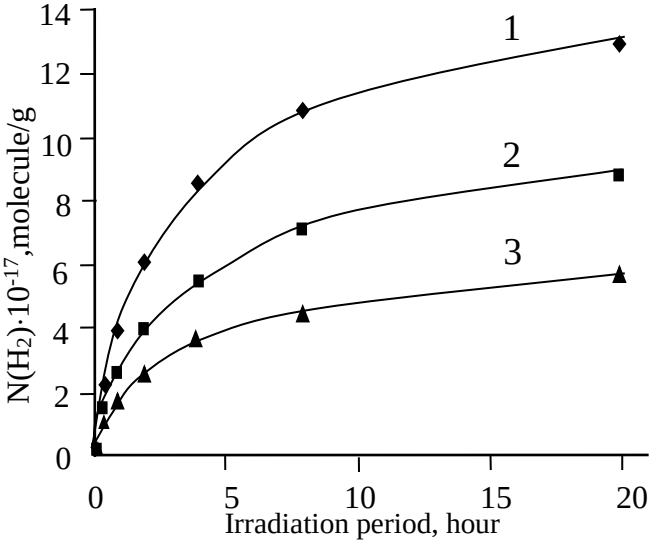

Fig. 1. Obtain kinetics of molecular hydrogen which is the product of radiation heterogeneous decomposition of water (filling rate of surface, θ=4) absorbed on the surface of silica with d=50, 100, 300÷500 nm particle sizes by γ–quanta (^{60}Co, P=18.17 rad/sec, T=300K) influence

Formation rate - $w(H_2)$ and radiation-chemical yield - $G(H_2)$ of molecular hydrogen which is the product of radiation-heterogeneous decomposition of water, have been defined for the given particle sizes in kinetic part of Figure 1. Defined values for the formation rate and radiation-chemical yield of molecular hydrogen have been given in table 1. It turns out from obtained results (table 1) that, formation rate and radiation-chemical yield of molecular hydrogen change depending on particle size of silica. With the participation of silica, the size effect is more apparent in radiolytic decomposition of water up to certain values (d≤100 nm) of the particle size of silica. If radiation-chemical yield of molecular hydrogen obtained from radiolysis of water absorbed in the surface levels is $G_{ads}(H_2)$ in the particle size where size effect is observed and $G_{\text{hom}}(H_2) = 0{,}45$ molecule/100·eV – in homogenous phase (pure water), then the relation of $G_{ads}(H_2) > G_{\text{hom}}(H_2)$ shows that, the energy absorbed by silica is transferred to the water adsorbed on the surface through energy carriers (electron-hole pair, excitons, various radiation defects, etc.).

Table 1. Formation rate - $w(H_2)$ and radiation-chemical yield - $G(H_2)$ of molecular hydrogen obtained from radiation-heterogeneous decomposition of water absorbed on the surface of silica with d=50, 100, 300÷500 nm particle size by γ–quanta (^{60}Co, P=18,17 rad/sec, T=300K) influence

	Si + H_2O			
	pure water [17]	50 nm	100 nm	*300÷500 nm*
$w(H_2)\cdot10^{-14}$, molecule/(g·sec)	0.0564	1.23	0.79	0.52
$G(H_2)$, molecule/(100 eV)	0.446	10.85	6.97	4.6

The obtain kinetics of molecular hydrogen in $Si + H_2O$ system has been investigated at different filling rates (T = 300K) of particle surface in order to define the distance, to which the energy was transferred from the contact environment (Figure 2).

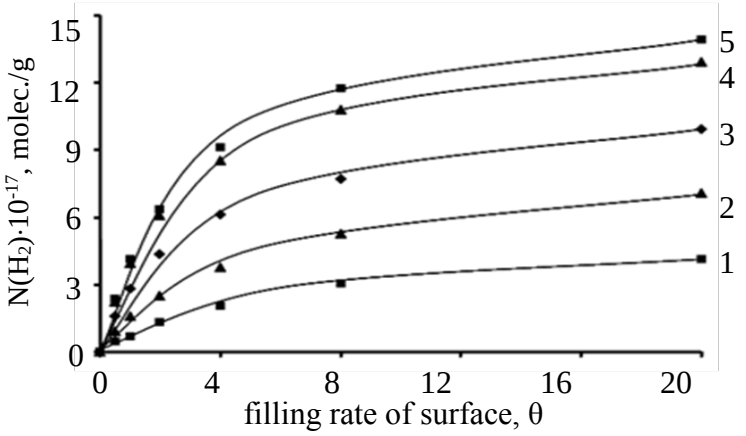

Fig. 2. Dependence of particle surface of radiation-chemical yield of molecular hydrogen obtained from radiation-heterogeneous decomposition of water in nano-Si with d=50 nm particle size + H_2O system by γ –quanta (^{60}Co, P=18.17 rad/sec, T=300K) influence on the filling rate of water (1 - θ=0.5; 2 - θ=1; 3 - θ=2; 4 - θ=4; 5 - θ=10).

Formation rate – $w(H_2)$ and radiation-chemical yield – $G(H_2)$ of molecular hydrogen obtained from radiation-heterogeneous decomposition of water have been defined from kinetic part of figure 2. Obtained results (table 2) show that, formation rates and radiation-chemical yields of molecular hydrogen increase directly proportional in the lower values (θ<4) of filling rate of silica surface of water, but stationary area begins in its higher values (θ≥4).

Table 2. Dependence of formation rate –($w(H_2)$) and radiation-chemical yield –($G(H_2)$) of molecular hydrogen obtained from radiation-heterogeneous decomposition of water on its filling rate (θ) in the system of silica with d=50 nm particle size + water adsorbed at different filling rates of particle surface by γ–quanta influence (^{60}Co, P=18.17 rad/sec, T=300K).

	Filling rate of surface, θ				
	0.5	1	2	4	10
$w(H_2)\cdot10^{-14}$, molecule/(g·sec)	0.25	0.49	0.87	1.23	1.3
$G(H_2)$, molecule/(100·eV)	2.21	4.32	7.68	10.85	11.48

Obtained results show that, effective transmission distance corresponds to quadruple filling rate of surface in the process of radiation-heterogeneous decomposition of water with the presence of silica. If we take diameter of water d = 0.276 nm, this distance corresponds to approx. l ≈ 1.0-1.2 nm. As free running distance ($\lambda\approx10^2$nm) of the non-equilibrium energy carriers (electron-hole pair, excitons, different type radiation defects and so on.) generated inside the silica particles can be compared with the size of investigated particles, they are transfered directly to the adsorption levels. The way - electrons go until they completely lose their kinetic energy (free running distance- λ) changes depending on their kinetic energy [24]. It is evident from both experiments and theoretical calculations that, this distance is $\lambda = 10 \div 10^2$ nm in the electrons with $E_i \approx 10^2 – 10^5$ eV energy and $\lambda \geq 10^2$ nm - in the electrons with E_i = 10-15 eV energy [28-29].

Compared to other processes (Thomson scattering, photoeffect, formation of electron), mainly Compton scattering [13-24] occurs from the interaction of γ–quanta (^{60}Co, E_γ*=1.17, 1.33 MeV*) with atoms or molecules, which form system, while passing from *Si*, H_2O and *Si+*H_2O systems. Kinetic energies of Compton electrons vary in the range of 0÷1.02 MeV depending on

scattering angle. Compton electrons with high kinetic energy (δ-electrons) gradually lose their kinetic energy as a result of elastic and non-elastic collision with atom or molecules that form it in the medium and become heat electrons [24-25]. These processes can be symbolically expressed as follows:

$$Si(H_2O) \xrightarrow{\gamma, e^-} \begin{cases} Si_i^+\left(H_2O_i^+\right) + e^- \\ Si_j^*\left(H_2O_j^*\right) \end{cases} \quad (1)$$

here, $Si_i^+\left(H_2O_i^+\right)$ is the ionization and $Si_j^*\left(H_2O_j^*\right)$ - electron-excitation states of jth and ith orbital of silica (water), respectively.

Water molecules are absorbed by $\equiv$Si centers on silica particle surface and form the complex

$$\equiv \mathrm{Si} + \mathrm{H_2}O \rightarrow \equiv Si - \mathrm{H_2}O_s \quad (2)$$

Si^+ (cation and Frenkel pair type radiation defects) defects, formed in silica particle by γ-quanta influence, migrate to surface and as a result positively charged complex:

$$\equiv \mathrm{Si}^{+} + \mathrm{H_2}O \rightarrow \equiv Si - \mathrm{H_2}O_s^+ \quad (3)$$

is formed on silica-water boundary from ion-dipole interaction and as a result of migration of holes (h^+) formed in volume to surface, the complex:

$$\equiv \mathrm{Si} - \mathrm{H_2}O_s + h^+ \rightarrow \left[\equiv Si - \mathrm{H_2}O_s\right]^+ \quad (4)$$

is formed. Positively charged $\left[\equiv Si - \mathrm{H_2}O_s\right]^+$ complex is charged with heat and tunnel electrons and forms electron-excitation complex:

$$\left[\equiv \mathrm{Si} - \mathrm{H_2}O_s\right]^+ + e^- \rightarrow \left[\equiv Si - H_2O_s\right]^* \quad (5)$$

And also excitons formed in particle volume transmit their energy to absorption centers and form the excitation complexes:

$$\equiv \mathrm{Si} - \mathrm{H_2}O_s + ex \rightarrow \left[\equiv Si - H_2O_s\right]^* \quad (6)$$

In the complex, excitation energy is transferred to water and participates in direct decomposition of water.

$$\left[\equiv \mathrm{Si} - \mathrm{H_2}O_s\right]^* \rightarrow \equiv Si - OH + H \quad (7)$$

Then, oxidation of the particle surface occurs as a result of reaction (8).

$$2 \equiv \mathrm{Si} - O\mathrm{H} \rightarrow \equiv Si - O - Si \equiv + \mathrm{H_2}O \quad (8)$$

The holes (h^+) formed in silica particle by ionizing rays, are localized by $Si-SiO_2$ ($O_3{\equiv}Si-Si{\equiv}Si_3$) on the border of neutral oxygen vacancy ($O_3{\equiv}Si-Si{\equiv}O_3$) and semiconductor-

dielectric in oxide layer formed on surface as a result of drift and in both case tense Si-Si bonds are broken and they can form positive E´ ($O_3{\equiv}Si^+$) center with paramagnetic properties and P_b - center with the appropriate amphotericity ($-Si{\equiv}O_3$, $-Si{\equiv}Si_3$):

$$O_3 \equiv Si - Si \equiv O_3 + h^+ \rightarrow O_3 \equiv Si^+ + -Si \equiv O_3 \quad (9)$$

$$O_3 \equiv Si - Si \equiv Si_3 + h^+ \rightarrow O_3 \equiv Si^+ + -Si \equiv Si_3 \quad (10)$$

E´ center, which is in the contact with water molecules, can participate in direct decomposition of water [26-28]:

$$O_3 \equiv Si^+ - e^- + H_2O \rightarrow O_3 \equiv Si - OH + H \quad (11)$$

and the restoration of Si-Si bonds

$$O_3 \equiv Si^+ + -Si \equiv O_3 + e^- \rightarrow O_3 \equiv Si - Si \equiv O_3^* \quad (12)$$

$$O_3 \equiv Si^+ + -Si \equiv Si_3 + e^- \rightarrow O_3 \equiv Si - Si \equiv Si_3^* \quad (13)$$

by recharging with thermal or tunnel-electrons (e^-) from semiconductor. In this case (12-13), matrix passes to electron-excitation state ($O_3 \equiv Si - Si \equiv O_3^*, O_3 \equiv Si - Si \equiv Si_3^*$). If this electron-excitation energy (7.6 eV) is transferred to water molecule, it can decompose the water.

Molecular hydrogen is formed by (14) reaction.

$$H + H \rightarrow H_2 \quad (14)$$

For above mentioned (3)-(13) processes of non-equilibrium charge carriers and energy carriers as excitons formed in the volume of particle by gamma-quanta influence on $Si+H_2O$ system, with water, they must migrate to surface absorption levels. The migration of particles to surface level can take place by diffusion and drift mechanism and their migration distance is limited.

The process of radiation-heterogeneous decomposition of water occurs in the contact of nano-silica with water under the influence of ionizing rays. Obtained results show that, size effect is observed when particle size is d≤100 nm in the processes of water radiation-heterogeneous decomposition at T=300K and the yield of hydrogen, from water radiation-heterogeneous decomposition with the participation of the smallest nano-silica particles, becomes $G(H_2)$ =10÷11 molecule/100eV, and the value observed in stationary area θ≥4 of the dependence of molecular hydrogen yield on surface filling rate of water in radiation-heterogeneous decomposition of water with the participation of d=50 nm nano-silica, becomes $G(H_2)$=10÷11 molecule/100eV.

The results obtained from calculations and experiments show that, most of energy carriers (electron-hole pairs, excitons, various radiation defects, etc.) formed in silica with d=50 nm particle size by γ-quanta influence go to surface levels and participate in radiolytic decomposition processes of water.

References

1. G. Merga, B.H. Milosavijevic, D. Meisel. J.Phys. Chem. B 2006, 110, p.5403-5408.
2. N.G. Petrik, A.B. Alexandrov, A.I. Vall. J.Phys. Chem. B 2001, 105, p.5935-5944.
3. T. Schatz, A.R. Cook, D. Meisel. J.Phys. Chem. B 1999, 103, p.10209-10213.
4. J.A. LaVerne. J. Phys. Chem. B 2005, 109, p.5395-5397.
5. J.A. LaVerne, L. Tandon. J.Phys. Chem. B 2003, 107, p.13623-13628.
6. J.A. LaVerne, S.E. Tunnies. J.Phys. Chem. B 2003, 107, p.7277-7280.
7. J.A. LaVerne, L. Tandon. J.Phys. Chem. B 2002, 106, p.380-386.
8. T. Schatz, A.R. Cook, D. Meisel. J.Phys. Chem. B 1998, 102, p.7225-7230.
9. A.A. Garibov, T.N. Aghayev, G.T. Imanova, K.T. Eyyubov. PAST, 2015, №5(99), p.48-51.
10. A.A. Garibov, T.N. Aghayev, G.T. Imanova, S.Z. Malikova, N.N. Hajiyeva. HECh, 2014, p. 48-51.
11. T.A. Yamamoto, S. Seino, M. Katsura et al. Nanostructured Materials. 1999, v.12, N 5, p.1045-1048.
12. A.K. Pikayev. Dosimetry and radiation chemistry, M., Nauka, 1975.
13. Y.D. Jafarov, A.A. Garibov, S.A. Aliyev and others. Calculation of the absorbed dose of gamma irradiation in oxide dielectrics // Atomic energy, 1987, v.63, ed. 4, p.269-270.
14. V. Santos, M. Zeni, C.P. Bergmam // Rev. Adv. Mater. Sci. 2008, №17, 62.
15. J.E. Turner, R.N. Hamm, H.A. Wrighr, R.H. Rachie, J.L. Magee, A. Chatterjee, W.E. Bolch // Radiat. Phys. Chem. 1988, 32, p.503-510.
16. H.G. Paretzke, J.E. Turner, R.N. Hamm, H.A. Wrighr, R.H. Rachie. Calculated yilds and flucuations for electron degradation in liquid water and water vaper. J. Chem. Phys., 84: p.3182-3188, 1986.
17. A.K. Pikayev. Modern radiation chemistry. Radiolysis of gases and liquids. M.: Nauka, 1986, p.440.
18. V.L. Bugaenko, V.M. Byakov, V.L, Grishkin // *Secon* All-Union Conference on Theoretical and Applied Radiation Chemistry, Obninsk, 1990. Proc. rep. M.: SRI tech. research, 1990. p.29.
19. I.G. Kaplan and V.Y. Sukhonosov. Simulation of the passage of fast electrons and the ealy stage water radiolysis by the Monte Carlo method. Radiat.Res., 127: p.1-10, 1991.
20. A.A. Garibov, Y.D. Jafarov, E.A. Shirshov. 4th International Conference "Nuclear and Radiation Physics", Alma-Ata, 2003, p.335-337.
21. Y.D. Jafarov, A.A. Garibov. International Conference "Physico-chemical Processes in Inorganic Materials (FHP-9)" Kemerovo, 2004, v.1, p.32-34.
22. S. Uehara, H. Nikjoo // J.Radiat.Res.2006, 47, p.69-81.
23. Y.D. Jafarov, M.R. Hasanova, F.N. Nurmammadova. The fifth Eurasian conference Nuclear science and its application Ankara, 2008, p.95-96.
24. Y.D. Jafarov. Mathematical modeling of radiolysis process of water under the impact of low-energy electrons, Problems of atomic science and technology, 2011, N5, Series: Nuclear Physics Investigations (56), p.42-47.
25. N.G. Petrik, A.B. Alexandrov, T.M. Orlando, A.İ. Vall Trans. ANS 1999, 81, p.101-102.
26. J. Kontsky, J. Kosik. Radiation damage of structural materials // Materials science monograph 3, 4.9. Elsexier 1994.
27. M.A. Elango Elementary inelastic radiative processes M.: Nauka, 1988, p.152
28. V.P. Kovalev. Secondary electrons. M: Energoatomizdat, 1987, p.329.

ЗАВИСИМОСТЬ ВЫХОДА МОЛЕКУЛЯРНОГО ВОДОРОДА, ПОЛУЧЕННОГО ПРИ РАДИАЦИОННО-ГЕТЕРОГЕННЫХ ПРЕВРАЩЕНИЯХ ВОДЫ В СИСТЕМЕ Si+H_2O ПРИ ВОЗДЕЙСТВИИ ГАММА-КВАНТОВ, ОТ РАЗМЕРОВ ЧАСТИЦ КРЕМНИЯ И СТЕПЕНИ ЗАПОЛНЕНИЯ ПОВЕРХНОСТИ ВОДОЙ

Я.Д. Джафаров, С.М.Баширова, С.М.Алиев

Резюме: Выявлена зависимость количества, скорости образования и радиационно-химического выхода молекулярного водорода, полученного при радиационно-гетерогенных превращениях воды в системе Si(d_{Si} =50, 100, 300÷500 нм)+адсорбированная H_2O при воздействии гамма-квантов (^{60}Co, P=18,17 рад/с, T=300K), от размеров частиц кремния и степени заполнения поверхности водой (θ). Для частиц данных размеров (d_{Si} =50, 100, 300÷500 нм) получены максимальные значения радиационно-химического выхода молекулярного водорода, равные $G(H_2)$=10,85; 6,97 и 4,6 молекул/(100 эВ) соответственно. Проведенные в системе Si(d_{Si} =50нм)+H_2O исследования при разных значениях степени заполнения поверхности(θ=0,5; 1,0; 2,0; 4,0 и 10,0) показывают, что радиационно-химический выход молекулярного водорода при θ<4 прямо пропорционален степени заполнения поверхности, а при значениях $\theta \geq 4$ наблюдается состояние насыщения. Приведены механизмы процессов, достаточно хорошо объясняющие экспериментальные данные.

Ключевые слова: наночастица, радиолиз, радиационно-химический выход

QAMMA–KVANTLARIN TƏSİRİLƏ Si+H_2O SİSTEMİNDƏ SUYUN RADİASİYA-HETEROGEN ÇEVRİLMƏSİNDƏN ALINAN MOLEKULYAR HİDROGENİN ÇIXIMININ SİLİSİUMUN HİSSƏCİK ÖLÇÜLƏRİ VƏ HİSSƏCİK SƏTHİNİN SUYUN DOLMA DƏRƏCƏSİNDƏN ASILILIĞI

Y.D.Cəfərov, S.M.Bəşirova, S.M.Əliyev

Xülasə: Qamma-kvantların (^{60}Co, P=18,17 rad/san, T=300K) təsirilə d=50, 100, 300÷500 nm hissəcik ölçülü silisium + onun səthin müxtəlif dolma dərəcəsində adsorbsiya olunmuş su sistemində suyun radiasiya-heterogen çevrilmədən alınan molekulyar hidrogenin miqdarı, əmələgəlmə sürəti və radiasiya-kimyəvi çıxımının silisumun hissəcik ölçüsü və suyun silisium səthinin dolma dərəcəsindən (θ) asılılığı öyrənilmişdir. Həmin (d=50, 100, 300÷500 nm) hissəcik ölçülərinə uyğun molekulyar hidrogenin maksimum radiasiya-kimyəvi çıxımları uyğun olaraq $G(H_2)$=10,85; 6,97 və 4,6 molekul/(100·eV) qiymətləri alınmışdır. d=50 nm hissəsik ölçülü nano-silisium + H_2O sistemində hissəcik səthinin suyun dolma dərəcənin müxtəlif qiymətlərində (θ=0,5; 1; 2; 4; 10) aparılan tədqiqatlar göstərir ki, molekulyar hidrogenin radiasiya-kimyəvi çıxımı, θ<4 qiymətlərində səthin dolma dərəcəsilə düz, $\theta \geq 4$ qiymətlərində isə doyma halı müşahidə olunur. Alınmış təcrübi nəticələri kifayət dərəcədə izah edən mexanizm və izahatlar verilib.

Açar sözlər: nanohissəcik, radioliz, radiasiya-kimyəvi çıxım.