CHEMO-EMF IN THE SILICON SOLAR CELL EXPOSED TO LOW-ENERGY HYDROGEN ATOMS

Vladislav V. Styrov[1,2*], Sergey V. Simchenko[1], Valentin N. Golotyuk[3]

1 Azov State Technical University, Universitetskaya 7, 87555, Mariupol, Ukraine
2 Berdyansky State Pedagogical University, Schmidta 4, 87430, Berdyansk, Ukraine
3 Public Joint–Stock Company "Kvazar", Severo-Syretskaya 3, 04136, Kiev, Ukraine

ABSTRACT

A new reactive gas-semiconductor system is experimentally found and examined for the electron-hole pairs (e-h pairs) generation in the semiconductor due to exoergicty of a surface chemical reaction. This system is "atomic hydrogen-crystalline silicon". The p-n silicon homojunction was used to produce chemo-emf and chemicurrent in the semiconductor system due to e-h pairs creation. The ideal geometry of the semiconductor system would require the top semiconductor layer be of a nanosized thickness since only the upper layer of the semiconductor is involved in chemical excitation. To make the beginning of a research we howere harnessed the commercial silicon solar cell fabricated with the certain technological changes to have a bare semiconductor surface. A special procedure was worked out to prepare the silicon surface free of the blocking layer of silicon oxide.

The chemo-emf in the open circuit up to a few mV and the short circuit chemicurrent up to the record 700 nA were achieved that are the promising magnitudes to pave a way for direct chemical energy to electrical energy conversion by semiconductor systems.

Key words: nanostructures, energy conversion, p-n junction, silicon, atomic hydrogen, solar cells.

INTRODUCTION

The problem of renewable and ecological ("green") sources of energy requires searching for the new approaches to overcome a number of challenges on this way. For instance the fuel cells energy production still encounters the high cost of the up to date devices [1, 2].

Recently a new direction has been started based on direct chemical-to-electrical energy conversion on metal-semiconductor Schottky nanostructures (see e.g. [3-7] and references therein). In Schottky nanodiodes the exoergic chemical events on the ultrathin (nanosized) metal film, forming the top part of the Schottky diode, give rize to kinetically hot electrons in the metal layer. The hot electrons cross ballistically the metal film, then surmounting the Schottky barrier and (after entering semiconductor) producing electric current in the

---

* e-mail: v2styrov@gmail.com, tel: (+38)0629523377

external circuit. This direction was pioneered by the authors of [3,4]. However the nonadiabatic nature of the energy transfer from the "heavy" systems (nuclei of the reagents on the surface) to the "light" system (electrons in the solid) requires breaking of the adiabatic approximation of Bohr-Oppenheimer and leads to relatively low efficiency of the energy conversion process [3, 7].

We are developing an alternative concept of direct chemical energy-to-electricity conversion using the semiconductor p-n junctions [8]. Here the exo-thermic chemical reaction produces by its exoergic steps the electron-hole (e-h) pairs in the uppermost semiconductor layer, contacting with the chemically active ambience. The nonequilibrium carriers move to the junction region and produce chemo-emf when the components of e-h pairs are separated by the electric field of the junction. The working near-surface semiconductor layer operating in this fashion has a nanometer thickness due to intrinsic mechanisms of the chemical energy transfer. The semiconductor region between this working near-surface layer and the junction itself plays a role of a certain "buffer", where the e-h pairs could be lost because of the recombination process. Thus the thinner top layer of the semiconductor structure the better performance expected.

The principle of the operation of the device in question needs that a semiconductor-reagents system be possible to transform the chemical energy into e-h pairs energy on the first stage of the energy conversion process. The urgent task to advance the problem is to find the suitable semiconductor-reactants systems with high e-h pairs yield. Unfortunately at present only a few systems are known satisfying the requirements described (see [9] and references therein).

Here we addressed the promising and widely used semiconductor - silicon. The previous attempts to use Si for the above purpose failed because of the existing of the blocking silicon oxide layer on the Si-surface. We managed to solve this problem by an appropriate surface preparation procedure. As a testing reaction in searching for the system needed we traditionally have applied the reaction of recombination of hydrogen atoms. Besides we examined here the reaction of recombination of H+O atoms.

The standard silicon solar cell was here utilized since the technology of such devices is well developed for the sunlight-to-electricity conversion. It is worth notice that both the chemical energy and the light energy conversion into electric current on semiconductors are similar in its operation principles.

EXPERIMENTAL

Though only of nanosized-thickness top layer will be optimal as a semiconductor for our purpose to minimize the recombination of carriers, we confined themselves here for the initial stage of research to examinations of the standard silicon solar cell. The latter was produced by the Public Joint-Stock Company

"Kvazar" (Ukraine). The upper n – layer of the p-n junction is formed by diffusion of phosphorus into the silicon wafer, and the base p –layer is doped by boron. The Ohmic contacts were made by an Ag – technology. However the changes in the technology of the solar cell fabrication were brought so as to remain bare the top layer of the semiconductor. The silicon (111) surface morphology characterized using the scanning electron microscope is shown in the *Fig.1*.
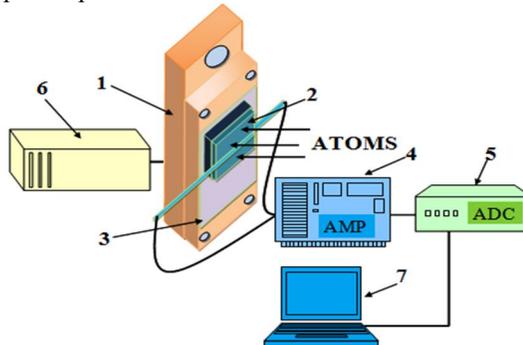
The schematic sketch of the measurements is displayed in the *Fig. 2*.
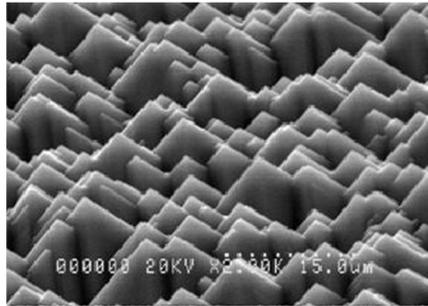
Fig. 1 – Morphology of the silicon top layer surface of the solar cell

The hydrogen atoms of thermal energies were produced by H_2 -dissociation in HF- discharge (40 MHz) and the fluxes j ($m^{-2} s^{-1}$) incident on the sample were measured by an isothermal wire platinum microcalorimeter.

The chemo-emf signal produced from the sample $2 \times 2 cm^2$ was registered by the measurement circuit composed of the laboratory-made instrumental electrometric direct current amplifier, and an analogue-digital converter (ADC) supplied with the pre-amplifier.

Fig. 2 – A schematic sketch of the chemo-emf measurements in the silicon solar cell exposed to low-energy hydrogen atoms: 1- microheater, 2- sample, 3- mica plate, 4- instrumental amplifier, 5- analog-digital converter, 6- power supply unit, 7- personal computer

The signal from the ADC was displayed on the monitor of a PC to be then processed and analyzed. Both the current and the voltage regimes were applied.

The sample was subjected to HF- chemical etching before placing in a vacuum chamber. After mounting on the microheater and pumping the sample was treated in a special procedure composed of a sequence of bombardment by low-energy Ar+ ions (produced by an ion-gun) and atomic hydrogen exposure at varying temperatures.

EXPERIMENTAL RESULTS AND DISCUSSION

The as-fabricated oxidized sample of a solar cell with the durable SiO_2 layer did not show any effect under exposure to hydrogen atoms.

After the proper preparation of the Si-surface, as indicated above, the admission of the atomic flux to the sample (by switching on the HF-discharge) revealed the chemo-emf (ε_{ch}) generation. The kinetics of ε_{ch} is illustrated in the fig.3. The ε_{ch} value quickly reached almost steady state magnitude (within 1-1.5 s) and this state was stable during at least 25 min (the time of observation).

The "switching off" the atomic flux turned its value to the initial zero level. Appearance of ε_{ch} unambiguously implies that e-h pairs are generated in chemical H-atoms – semiconductor interaction, since only an ambipolar process can be responsible for chemo-emf production. The quick jump up in the ε_{ch} value at the beginning of the H-atoms – surface interaction, when the surface is pure after Ar^+ ions bombardment (free of adsorbed H-atoms), clearly indicates that the process of H-atoms adsorption (the most intensive at the unoccupied surface) is active in the e-h pairs production. This is in a qualitative agreement with the heat of adsorption q_1 of H-atoms on the (111) surface of silicon: $q_1 \approx 3$ eV$>E_g=1,17$ eV [10] (E_g is the silicon bandgap). The event of the atomic recombination (abstraction) itself is probably insufficiently energized to ionize the silicon lattice.
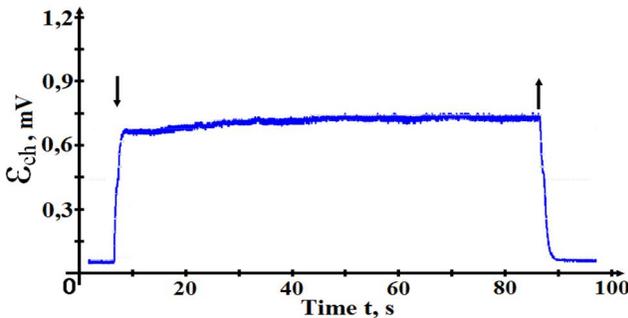
Fig. 3 – The typical kinetics of chemo-emf ε_{ch} produced in the Si solar cell under exposure to hydrogen atomic flux (T=300K, $j \approx 10^{20} m^{-2} s^{-1}$). The moments of the flux "switching on" (↓) and "switching off" (↑) are indicated

The total cycle of the reaction may be represented as follows:

$$H + H + Si \xrightarrow{\quad q_1 \quad} \quad H + His \quad H_2 + Si$$
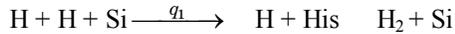
(the quantities above arrows show the exoergic effect of the corresponding reaction event, $q_1 + q_2 + Q = D_g$, where $D_g = 4,48 eV$ is the heat of dissociation of the H_2 – molecule in the gas phase, Q – is the energy carrying away if any from the surface by desorbing vibrationally excited H_2-molecule). Hence a deficit of energy ($q_2 < E_g$) may occur for the e-h pair excitation in the recombination event.

The stationary state existing does not contradict to inactive character of the $H + HSi \rightarrow H_2 + Si$ abstraction stage for electronic excitation, since the stationary process of atomic recombination includes the continuously repeated adsorption stage.

The dependence of the ε_{ch} on the atomic flux is shown in the *Fig. 4* (the absciss is represented in logarithm scale).

The ε_{ch} increases with the temperature increase, *Fig. 5*. The activation energy cannot be determined since this dependence is strongly deviated from the exponential one. The most probable explanation of this dependence is the coverage-dependent activated interaction of atoms with the silicon surface.

The short-circuit current in our system achieved the magnitude of 700nA. To our knowledge this is a record value for n-p junction systems up to now. The open circuit voltage was about 1,1mV.

The results represented is promising for the further advancing the semiconductor system in question for transformation of chemical energy into electric current through e-h pairs generation.
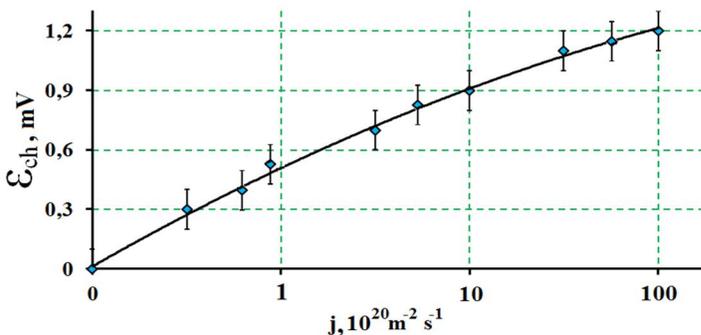
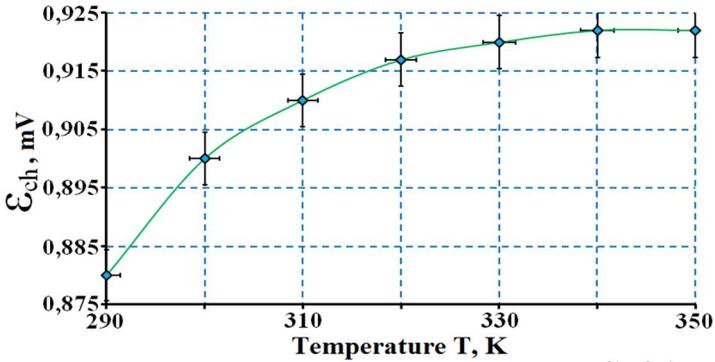**Fig. 4** – Dependence of ε_{ch} in the solar cell on the atomic flux (T=300K)

Fig. 5 – Dependence of ε_{ch} on the sample temperature ($j \approx 10^{21} m^{-2} s^{-1}$)

Even more pronounced effect of chemo-emf generation was found for a mixed flux of H+O atoms, produced by passing the (H_2+O_2) mixture through HF-discharge (P $\approx$1Pa). The respective ε_{ch} kinetics is demonstrated by *fig.6*. Here the entire flux is only approximately estimated by Pt calorimeter because of different heat of recombination of H and O atoms (for the latter $D_g=5,12eV$ in gas phase) and different catalytic properties of Pt with respect to H and O atoms.

On the whole this kinetics is similar to that observed for H-atoms alone, though a new feature appears at the initial part of the kinetics in the form of a initial peak.
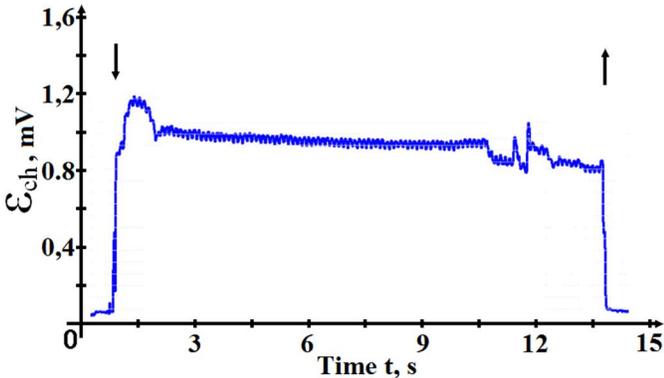

Fig. 6 – The typical kinetics of chemo-emf ε_{ch} produced in the Si-solar cell under exposure to H+O atom flux (T=300K, $j \approx 2 \cdot 10^{20} m^{-2} s^{-1}$). The moments of the flux "switching on" ($\downarrow$) and "switching off" ($\uparrow$) are indicated

This feature may help to kinetically separate an involvement of the recombination stage in e-h pairs production in this case. The latter would be possible due to higher exoergicity of the reaction O+O (5,12 eV).

These studies to be advanced in more detail fashion targeted to harness all the achievements of the third-generation photovoltaic solar cell nanotechnologies.

CONCLUSIONS

The paper addressed the problem of direct chemical energy conversion into electricity. An approach based on the concept of hot electrons in metal – semiconductor Schottky nanodiodes developed in last decade in Germany and the USA has met a serious challenges because of low efficiency of hot electrons production on metal surface in the surface chemical reactions. The common fuel cell is yet expensive enough as current sources. We used a new approach to the problem in question harnessing the convenient semiconductor p-n junctions using them in a manner similar to that utilized in photovoltaic solar cell devices. The nonequilibrium electron-hole pairs on the top part of the p-n system was produced in the chemical interaction of hydrogen atoms and separated by the junction electric field, producing chemo-emf. We found for the first time that silicon can serve as an active material of the converter. The standard solar cells are promising devices for the chemical energy-to-electricity conversion.

REFERENCES

[1] Chuan-Jian Zhong, Jin Luo, Bin Fang et al., Nanotechnology, 2010, Vol. 21, No6, P. 2001-2013.
[2] R.W. Lashway, MRS Bulletin, 2005, Vol. 30, No8, P. 581-583.
[3] H. Nienhaus, Surface Science Reports, 2002, Vol. 45, P. 1-78.
[4] Eric W. McFarland, Jing Tang, Nature, 2003, Vol. 421, P. 616-618.
[5] J.I. Park, G.A. Somorjai,Vacuum Science and Technology, 2006, Vol. B 24, No4, P. 1967-1971.
A. Zuppero et al.,United States Patent 6,268,561, issued July 31, 2001.
[6] J.R. Creighton, M.E. Coltrin, J.J. Figiel et al., Sandia Report – SAND 2010-7734, P. 1-20.
[7] A.Y. Kabansky, V.V. Styrov, in the book "Advanced Materials for Energy Conversion II" (Eds. D. Chandra, R.G. Bautista, L. Shlapbach), Publication of TMS, Charlotte, USA, 2004, P. 43-52.
[8] V.V. Styrov, Physics of low-dimensional structures, 2001, No9/10, P. 1-19.
[9] H. Lim, K. Cho, I. Park, and J.D. Joannopoulos, Physical Review B, 1995, Vol. 52, No24, P. 17231-17237.