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# Solar Cells on the Base of Semiconductor- Insulator-Semiconductor Structures

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## 1. Introduction

The conventional energy production is not based on sustainable methods, hence exhausting the existing natural resources of oil, gas, coal, nuclear fuel. The conventional energy systems also cause the majority of environmental problems. Only renewable energy systems can meet, in a sustainable way, the growing energy demands without detriment to the environment.

The photovoltaic conversion of solar energy, which is a direct conversion of radiation energy into electricity, is one of the main ways to solve the above-mentioned problem. The first PV cells were fabricated in 1954 at Bell Telephone Laboratories (Chapin et al., 1954); the first applications for space exploration were made in the USA and the former USSR in 1956. The first commercial applications for terrestrial use of PV cells were ten years later. The oil crisis of 1972 stimulated the research programs on PV all over the world and in 1975 the terrestrial market exceeds the spatial one 10 times. Besides classical solar cells (SC) based on p-n junctions new types of SC were elaborated and investigated: photoelectrochemical cells, SC based on Schottky diodes or MIS structures and semiconductor-insulator-semiconductor (SIS) structures, SC for concentrated radiation, bifacial SC. Currently, researchers are focusing their attention on lowering the cost of electrical energy produced by PV modules. In this regard, SC on the base of SIS structures are very promising, and recently the SIS structures have been recommended as low cost photovoltaic solar energy converters. For their fabrication, it is not necessary to obtain a p-n junction because the separation of the charge carriers generated by solar radiation is realized by an electric field at the insulator-semiconductor interface. Such SIS structures are obtained by the deposition of thin films of transparent conductor oxides (TCO) on the oxidized silicon surface. A overview on this subject was presented in (Malik et al., 2009).

Basic investigations of the ITO/Si SIS structures have been carried out and published in the USA (DuBow et al., 1976; Mizrah et al., 1976; Shewchun et al., 1978; Shewchun et al., 1979). Theoretical and experimental aspects of the processes that take place in these structures are examined in those papers. Later on the investigations of SC based on SIS structures using, as an absorber component, Si, InP and other semiconductor materials have been continued in Japan (Nagatomo et al., 1982; Kobayashi, et al., 1991), India (Vasu & Subrahmanyam, 1992; Vasu et al., 1993), France (Manificier & Szepessy, 1977; Calderer et al., 1979), Ukraine

(Malik et al., 1979; Malik et al., 1980), Russia (Untila et al., 1998), the USA (Shewchun et al., 1980; Gessert et al., 1990; Gessert et al., 1991), Brasil (Marques & Chambouleyron, 1986) and the Republic of Moldova (Adeeb et al., 1987; Botnariuc et al., 1990; Gagara et al., 1996; Simashkevich et al., 1999). The results of SIS structures fabrication by different methods, especially by pyrolytic pulverization and radiofrequency sputtering, are discussed in those papers. The investigation of electrical and photoelectrical properties of the Si based SIS structures shows that their efficiency is of the order of 10% for laboratory-produced samples with an active area that does not exceed a few square centimeters. The spray deposition method of ITO layer onto the silicon crystal surface results in an efficient junction only in the case of n-type Si crystals, whereas in the case of p-type silicon crystals radiofrequency sputtering must be used to obtain good results.

Bifacial solar cells (BSC) are promising devices because they are able to convert solar energy coming from both sides of the cell, thus increasing its efficiency. Different constructions of BSC have been proposed and investigated. In the framework of the classification suggested in (Cuevas, 2005) the BSC structures could be divided into groups according to the number of junctions: a) two p-n junctions, b) one p-n junction and one high-low junction, and c) just one p-n junction. In all those types of BSC are based on a heteropolar p-n junction. In this case, it is necessary to obtain two junctions: a heteropolar p-n junction at the frontal side of the silicon wafer and a homopolar n/n<sup>+</sup> or p/p<sup>+</sup> junction at its rear side. Usually these junctions are fabricated by impurity diffusion in the silicon wafer. The diffusion takes place at temperatures higher than 800°C and requires special conditions and strict control. In the case of the back surface field (BSF) fabrication, these difficulties increase since it is necessary to carry out the simultaneous diffusion of impurities that have an opposite influence on the silicon properties. Therefore the problem arises concerning the protection of silicon surface from undesirable impurities.

The main purpose of this overview is to demonstrate the possibility to manufacture, on the base of nSi, monofacial as well as a novel type of bifacial solar cells with efficiencies over 10%, containing only homopolar junctions with an enlarged active area, using spray pyrolysis technique, the simplest method of obtaining SIS structures with a shallow junction. The utilization of such structures removes a considerable part of the above-mentioned problems in BSC fabrication. The results of the investigations of ITO/pInP SC obtained by spray pyrolysis are also discussed.

## 2. The history of semiconductor-insulator-semiconductor solar cells

First, it must be noted that SC obtained on the base of MIS and SIS structures are practically the same type of SC, even though they are sometimes considered as being different devices. The similarity of these structures was demonstrated experimentally and theoretically for two of the most common systems, Al/SiO<sub>x</sub>/pSi and ITO/SiO<sub>x</sub>/pSi (Shewchun et al, 1980). The tunnel current through the insulator layer at the interface is the transport mechanism between the metal or oxide semiconductor and the radiation-absorbing semiconductor, silicon in this case.

One of the main advantages of SIS based SC is the elimination of high temperature diffusion process from the technological chain, the maximum temperature at the SIS structure fabrication not being higher than 450°C. The films can be deposited by a variety of techniques among which the spray deposition method is particularly attractive since it is simple, relatively fast, and vacuumless (Chopra et al., 1983). Besides, the superficial layer of

the silicon wafer where the electrical field is localized is not affected by the impurity diffusion. The TCO films with the band gap of the order of 3.3-3.7 eV are transparent in the whole region of solar spectrum, especially in the blue and ultraviolet regions, which increase the photoresponse comparative to the traditional SC. The TCO layer assists with the collection of separated charge carriers and at the same time is an antireflection coating. In SC fabrication the most utilized TCO materials are tin oxide, indium oxide and their mixture known as indium tin oxide (ITO). Thin ITO layers have been deposited onto different semiconductors to obtain SIS structures: Si (Malik et al., 1979), InP (Botnariuc et al., 1990), CdTe (Adeeb et al., 1987), GaAs (Simashkevich et al., 1992). Therefore, solar cells fabricated on the base of SIS structures have been recommended as low cost photovoltaic solar energy converters. The reduction in cost of such solar cells is due to the simple technology used for the junction fabrication. The separation of light generated carriers is achieved by a space charge region that in the basic semiconductor is near the insulator layer.

The number of publications concerning the fabrication and investigation of SIS structures is very big, therefore we will limit our consideration of the given structures only to those on the base of the most widespread solar materials – silicon and indium phosphide. To be exact, main attention will be focused on SC on the base of ITO/nSi and ITO/pInP.

## 2.1 SIS structures on the base of silicon crystals

As shown above, one of the ways to solve the problem of the cost reduction of the electrical energy provided by SC is to use SIS structures. First publications regarding the obtaining and investigation of ITO/nSi structures appeared in 1976. (Mizrah & Adler, 1976). Power conversion efficiencies of 1% were reported for an ITO/nSi cell, obtained by the magnetron dispersion of ITO layers on the surface of nSi crystals with an active area of 0.13 cm<sup>2</sup>. The data obtained from the investigated I-V dark characteristics and known band gaps and the work functions of ITO and Si allows to make the band diagram of these structures (Fig. 1). The efficiency of 10% was observed for ITO/nSi cells, obtained by the spray deposition of ITO layers onto nSi crystals with the area of 0.1 cm<sup>2</sup> (Manifacier & Szepessy 1977; Calderer et al., 1979). ITO/nSi SC with the power conversion efficiencies of 10% were fabricated by deposition onto n-type Si crystals by the electron-beam evaporation of a mixture of 90:10 molar % In<sub>2</sub>O<sub>3</sub>: SnO<sub>2</sub> powder (Feng et al., 1979).

The results of those works have been analyzed in detail (Shewchun et al., 1978; Shewchun et al., 1979) from both experimental and theoretical points of view. Given the general theory of heterojunctions is incomprehensible, how they can work as effective SC formed by materials with different crystalline types and lattice constants, when an intermediate layer with many defects appears at the interface. It is intriguing to note here that various authors have received quite contradictory results. Examining these data, authors in (Shewchun et al., 1979) concluded that the performance of those SC depended on the intermediate thin insulator layer. Its main function is the compensation of the defects due to the mismatches of the crystalline lattices. Its thickness is not greater than 30 Å, which ensures the tunnel transport of the carriers through the barrier. The theoretical analysis of ITO/nSi solar cell has shown that they are similar to MIS structures: their parameters depend on the thickness of the insulating layer at the interface, the substrate doping level, concentration of surface states, oxide electric charge and temperature. The optimization of these parameters can provide 20% efficiency.

In (Shewchun et al., 1979) this issue was examined in terms of energy losses during conversion of sunlight into electricity. Different mechanisms of energy loss that limit

ITO/nSi solar cell efficiency are probably valid for other SIS structures too. Dark current-voltage characteristics were used as experimental material and it was shown that after a certain threshold of direct voltage these characteristics do not differ from similar characteristics of p-n junctions in silicon, and the current is controlled by diffusion processes in silicon volume. Different mechanisms of energy loss that limit ITO/nSi solar cell efficiency are presented in Table 1 (Shewchun et al., 1979).

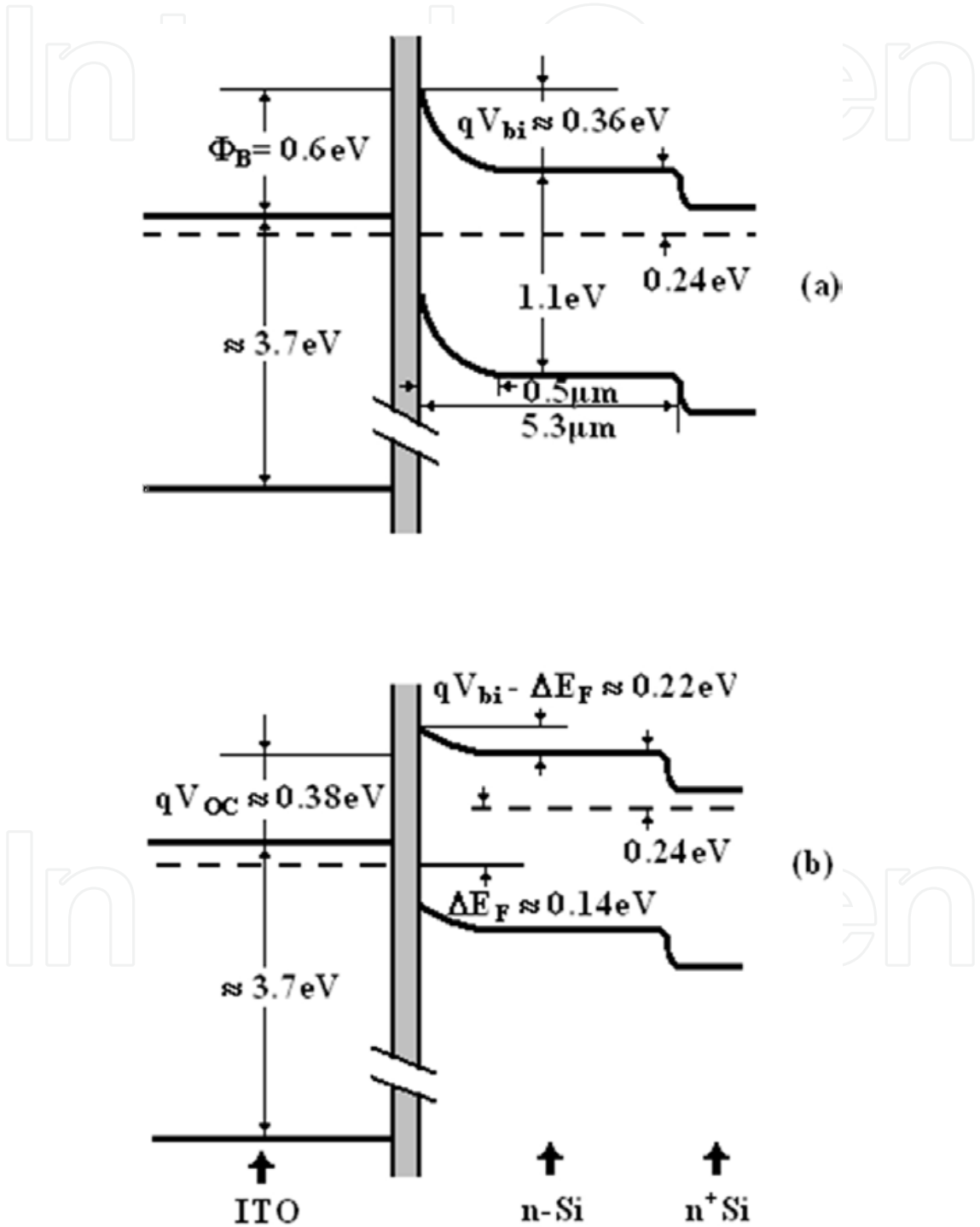


Fig. 1. Energy band diagram of the ITO/nSi/n+Si structure (a) - in the dark, (b) - at solar illumination under open circuit conditions. The shaded area - the insulating SiOx layer.

Mechanism	Loss rate
1. Absorption and reflection in the ITO layer	up to 8%
2. Recombination in space charge region	0.1 1%
3. $V_{CD}$ height reduction	0 – 12%
too high work function	0-3%
inhomogeneous $SiO_x$ layer	0-3%
low doped ITO layer	0-3%
too large saturation current	0-3%
4. Low fill factor	0-10%
series resistance of the intermediate layer	
series resistance of the contacts	
shunt	

Table 1. The energy loss mechanisms, which do not provide the maximum possible efficiency of 20%

An increase of the conversion efficiency of SC based on ITO/nSi structures can be achieved by the optimization of the thickness of the frontal ITO layer and of the insulator  $SiO_2$  layer; the optimization of the concentration of electrons in absorbing Si wafers; the texturing of the Si wafers surface.

The thickness of the frontal ITO layer is a very important factor because it affects the quantity of the absorbed solar radiation depending on both absorption and reflection. It is necessary to select such ITO layer thickness that determines a large minimum of the reflection in the region of maximum sensitivity of the  $n^+ITO/SiO_2/nSi$  SC. At the same time, the thickness of the frontal ITO layer determines their electrical resistance and, therefore, the value of the photocurrent, but for all that, the growing of the ITO layer thickness has an contrary effect on the solar cells efficiency, diminishing the absorption and increasing the photocurrent. At the same time, the thickness of the frontal ITO layer determines the efficiency of this layer as an anti reflection coating.

The properties of the SIS structures, largely, also depend on the thickness of the  $SiO_2$  insulator layer at ITO/Si interface. This  $SiO_2$  layer increases the height of the junction potential barrier and diminishes the saturation current. Besides, the insulator  $SiO_2$  layer must be tunnel transparent for charge carrier transport. The optimal  $SiO_2$  insulator layer thickness must be not more than some tens of Å.

All silicon wafers must be oriented in the (100) plane because only such crystallographic orientation could be used to get a potential barrier by ITO spray deposition. Single crystalline Si wafers with different carrier concentration from  $10^{15}cm^{-3}$  up to  $10^{18}cm^{-3}$  have been used to fabricate ITO/nSi SIS structures by spray deposition.

The influence of the structural state of the Si single crystalline wafers on the conversion efficiency will be discussed in the next section of this overview.

The paper (Feng et al., 1979) studied the current transport mechanism of ITO/Si structures, the TCO layer beings obtained by evaporation under the action of an electron beam. Pre-treatment of Si crystals with  $Cl_2$  has led to the increased yield from 2.3% to 5.5%. In this case the current transport mechanism was dominated by recombination in the space charge



layer, while there is the thermo emission over the potential barrier in the absence of  $\text{Cl}_2$ . Systematical studies of the properties of the ITO/nSi structures, obtained by spray pyrolysis, were carried out in 1980 (Ashok et al., 1980). The optical and electrical characteristics of the ITO layer as well as the thickness of the insulator layer have been optimized to yield the following photovoltaic parameters on  $0.5\Omega\cdot\text{cm}$  nSi:  $V_{oc}=0.52\text{V}$ ,  $J_{sc}=31.5\text{mA}/\text{cm}^2$ ,  $\text{FF}=0.70$ , conversion efficiency is 11.5%. The dark I-V and C-V characteristics have also been evaluated to identify the mechanisms of barrier formation and current flow. C-V data indicate an abrupt heterojunction, while dark I-V characteristics are suggestive of a tunneling process to determine current flow in these devices in conformity with the Riben and Feucht model (Riben & Feucht, 1966). A comparison of spray deposited ITO/nSi and  $\text{SnO}_2/\text{nSi}$  was presented by Japanese researchers (Nagatomo et al. 1982). The diode and photovoltaic properties of these structures are very similar, but the conversion efficiency of ITO/nSi is higher, up to 11-13%, whereas for  $\text{SnO}_2/\text{nSi}$  these values do not exceed 7.2% (Nagatomo et al., 1979). As is reported in the paper (Malik et al., 2008; Malik et al., 2009), the authors fabricated ITO/nSi solar cells using n-type single crystalline silicon wafers with a  $10\Omega\cdot\text{cm}$  resistivity and an 80nm thick ITO film with a sheet resistance of  $30\Omega/\square$  that was deposited by spray pyrolysis on the silicon substrate treated in the  $\text{H}_2\text{O}_2$  solution. This ITO thickness was chosen in order to obtain an effective antireflection action of the film. The cells obtained in such a way can be considered as structures presenting an inverted p-n junction (Fig. 2).

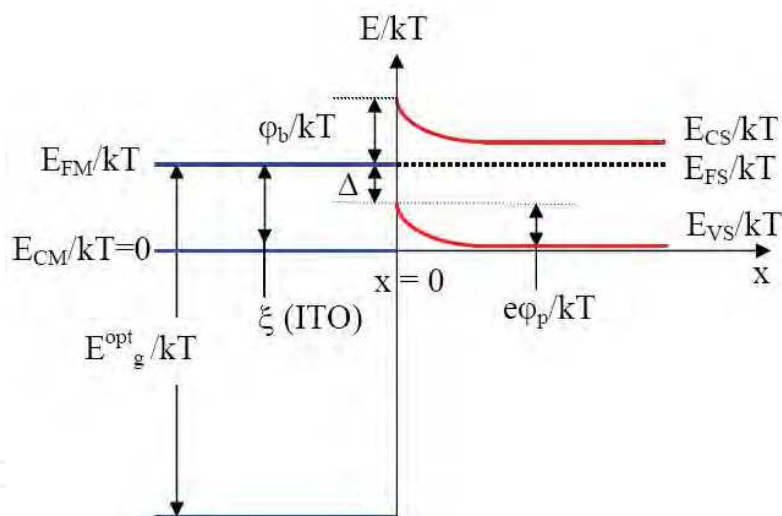


Fig. 2. Energy diagram (in  $kT$  units) of the heavy doped ITO/n-Si heterojunction

Under the AM0 and AM1.5 solar illumination conditions, the efficiency is 10.8% and 12.2%, respectively. The theoretical modeling based on p-n solar cells shows an excellent agreement between the theoretical and the experimental results. It is also shown that using  $1\Omega\cdot\text{cm}$  silicon substrates is a promising alternative for obtaining solar cells with 14% efficiency under AM1.5 illumination conditions.

Various models for energetic band diagrams and the carrier transport mechanism in SIS ITO/nSi cells have been proposed so far. Among them are the thermo ionic emission as the dominant charge transport mechanism in the SC obtained by spray deposition of  $\text{SnO}_2$  onto nSi crystals (Kato et al., 1975), and the recombination current in the depletion layer for the CVD deposited ITO/nSi junction (Varma et al., 1984). Majority of authors suggested that

trap -assisted multi step tunneling through the depletion layer is the determinant current flow mechanism (Ashok et al., 1980; Saim & Campbell, 1987; Kobayashi et al., 1990; Simashkevich et al., 2009).

The mechanism of the current transport through the potential barrier is determined by the energetic band diagram and the height of the barrier. When the later is very high, a physical p-n junction is formed in Si crystals near the surface (Fig. 2). Otherwise, the ITO/nSi SC operate as MIS structures or Schottky diodes (Fig. 1). Some data about the efficiencies of ITO/nSi SC are presented in Table 2.

References	ITO deposition method	Area (cm <sup>2</sup> )	Eff. (%)	Note
Mizrah et al., 1976	R.F. Sputtering	0.13	1	
Manifacier et al., 1977	Spray	1.5	10	
Feng et al., 1979	Electron beam	1 - 4	10	
Calderer et al., 1979	Spray	1.5	10	
Ashok et al., 1980	Spray	0.3	11.5	BSF
Nagatomo et al., 1982	Spray		11-13	
Gagara et al., 1996	Spray		10.1	
Vasu et al., 2005	Electron beam	1.0	5.5	
Malik et al., 2008	Spray	1 - 4	11.2	

Table 2. Efficiencies of ITO/nSi solar cells fabricated by various deposition techniques of ITO films on smooth (non textured) Si crystal surfaces

The analysis of the works referred to shows that the conversion efficiency of ITO/nSi solar cells obtained by various methods is about 10% and in some cases reaches 12%. Their active area is not more than a few square centimeters, which is not enough for practical application.

2.2 ITO/nSi solar cells with textured surface of Si crystalls

As can be seen from Table 1, the optical losses of ITO/nSi solar cells are up to 8%, other estimates show that they can exceed 10% (Garcia et al., 1982). Those losses depend on the surface state of silicon wafers and can be minimized by creating a textured surface of the light absorbing semiconductor material, thus reducing the reflection and increasing the absorption. The texturization leads to the enlargement of the junction area of a photovoltaic cell and to the increase of the conversion efficiency. The enlargement of the junction area in the case of silicon crystals is usually achieved by means of selective chemical etching in KOH (Bobeico et al., 2001; Dikusar et al., 2008; Simashkevich et al., 2011). As a result, pyramids or truncated cones with the base dimensions of 5µmx5µm or with a diameter of 10µm on the Si surface are formed.

The efficiency of 12.6% under AM1 simulated irradiation was obtained for SnO<sub>2</sub>: P/SiO<sub>2</sub>/nSi SC with the active area of 2cm<sup>2</sup>(Wishwakarma et al., 1993) Those cells were fabricated by deposition of SnO<sub>2</sub> layers doped with P by CVD method on the textured surface of the Si crystals with resistivity of 0.1 Ohm.cm. SiO<sub>2</sub> insulating layer was obtained by chemical



methods. The textured surface of the Si crystals reduces the frontal reflectivity, and consequently increases the short circuit current by around 10%.

ITO/nSi obtained by spray deposition of ITO layers on nSi wafers oriented in (100) plane, were obtained in Japan (Kobayashi et al, 1990). The final size of the active area of the cell was 0.9cm x 0.9cm. Mat-textured Si surfaces were produced by the immersion of the Si wafers in NaOH solution at 85°C. For so treated specimens the solar energy conversion efficiency of 13% was attained under AM1 illumination.

The paper (Simashkevich et al., 2011) studied the properties of ITO/nSi SC with improved parameters. The performed optimization consists in the following: the optimization of the thickness of the frontal ITO layer and of the thickness of the insulator SiO<sub>2</sub> layer; the optimization of the concentration of the electrons in absorbing Si wafers; the texturing of the Si wafers surface.

The performed investigations make it possible to come to the following conclusions. The optimum thickness of the frontal ITO layer was determined experimentally from the photoelectric investigations and is equal to 0.5µm. The SiO<sub>2</sub> layer can be obtained by different methods. In the case of fabrication n<sup>+</sup>ITO/SiO<sub>2</sub>/nSi solar cells by spray pyrolysis, the optimal SiO<sub>2</sub> layer thickness was obtained by a combined thermo chemical method selecting the temperature regime and the speed of the gas flow during ITO layer deposition. The optimal SiO<sub>2</sub> insulator layer thickness, measured by means of ellipsometric method, is about 30-40Å.

To determine the optimal electron concentration ITO/nSi SIS structures were investigated obtained by ITO spray deposition on the surface of phosphor and antimony doped single crystalline Si wafers with different carrier concentrations: 10<sup>15</sup>cm<sup>-3</sup>, 5·10<sup>15</sup>cm<sup>-3</sup>, 6·10<sup>16</sup>cm<sup>-3</sup>, and 2·10<sup>18</sup>cm<sup>-3</sup>, produced in Russia (STB Telecom) and Germany (Siltronix, Semirep). The investigation of the electrical properties of n<sup>+</sup>ITO/SiO<sub>2</sub>/nSi SC shows that the optimum values of the barrier height, equal to 0.53eV and the space charge region thickness equal to W=0.36µm, have been obtained in the case of Si crystals with the electron concentration 5·10<sup>15</sup>cm<sup>-3</sup>. Carrier diffusion length (L) is one of the main parameters for bifacial solar cells. For this silicon crystal L is about 200µm. The BSF region at the rear side of the cell was obtained by phosphor diffusion.

To enlarge the active area and reduce optical losses due to radiation reflection, the active area of Si wafer, oriented in a plane (100), was exposed to the anisotropic etching.

The etching was spent by two expedients for reception of the irregular and regular landform. In both cases, the boiling 50% aqueous solution of KOH was used as the etching agent. The processing time was 60 - 80s. In the first case, the etching process was yielded without initially making a landform on the silicon wafer surface for the subsequent orientation of the etching process.

Fig. 3a shows that the landform of the silicon surface is irregular and unequal in depth. The depth of poles of etching is within the limits of 2-3µm.

In the second case, the method of making the ranked landform in the form of an inverse pyramid was applied. The chemical micro structuring of the silicon wafer surface was carried out in the following order: the deposition of a SiO<sub>2</sub> thin film with 0.1µm thickness by electron beam method; the deposition on the SiO<sub>2</sub> thin film of a photo resists layer and its exposure to an ultraviolet radiation through a special mask; removal of the irradiated photo resist and etching SiO<sub>2</sub> with HF through the formed windows; removal of the remaining photo resist thin film. The anisotropic etching of the silicon surface through the windows in SiO<sub>2</sub> thin film was carried out. The result of this type of etching is shown in Fig. 3b.

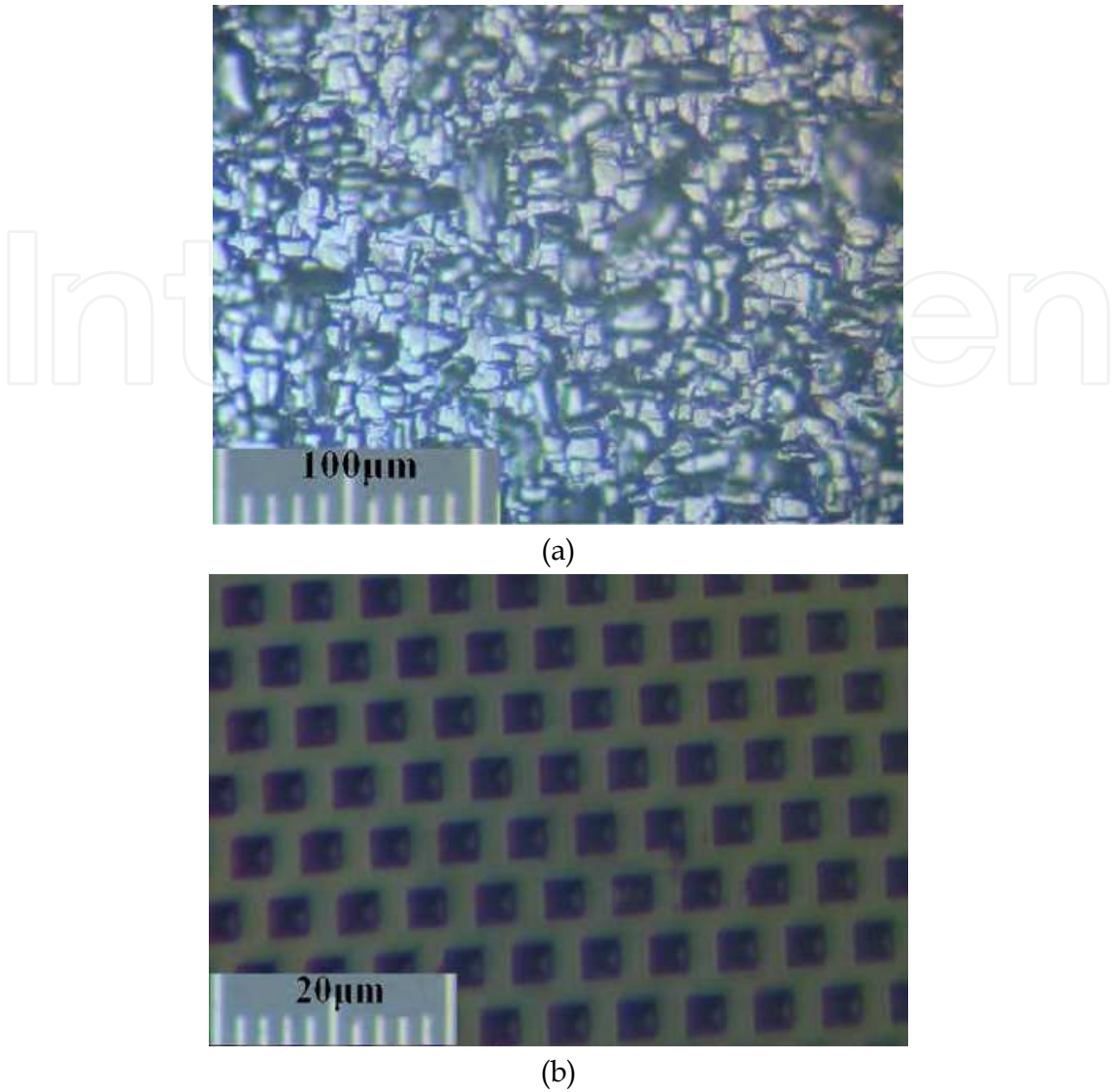


Fig. 3. Images of the silicon wafers surface landform a) irregular etching; b) regular etching

It is evident that the micro structured surface represents a plane with a hexagonal ornament formed by inverse quadrangular pyramids with 4μm base and 2-3μm depth. After the deposition of ITO layers on the both types of the textured surfaces of the silicon wafers (Fig. 3) and Cu evaporated grid on the frontal side and continuous Cu layer on the rear side, two types of the optimized structures have been fabricated (Fig. 4).

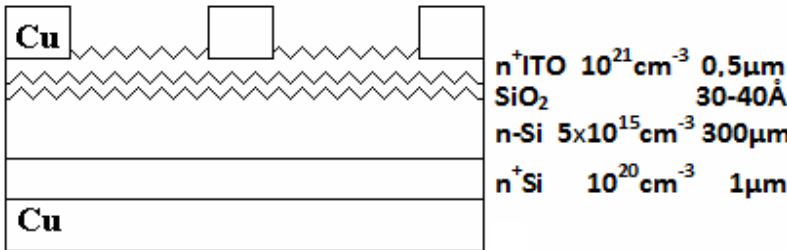


Fig. 4. The schematic image of ITO/SiO<sub>2</sub>/nSi/n<sup>+</sup>Si solar cell with optimized parameters and textured Si surface

The measurements of these characteristics and of solar energy conversion efficiency have been carried out under standard conditions (AM1.5, 1000W/m<sup>2</sup>, 25°C) with the solar simulator ST 1000. The load I-V characteristics of the n<sup>+</sup>ITO/SiO<sub>2</sub>/n/n<sup>+</sup>Si SC are presented in Fig. 5 and Fig. 6.

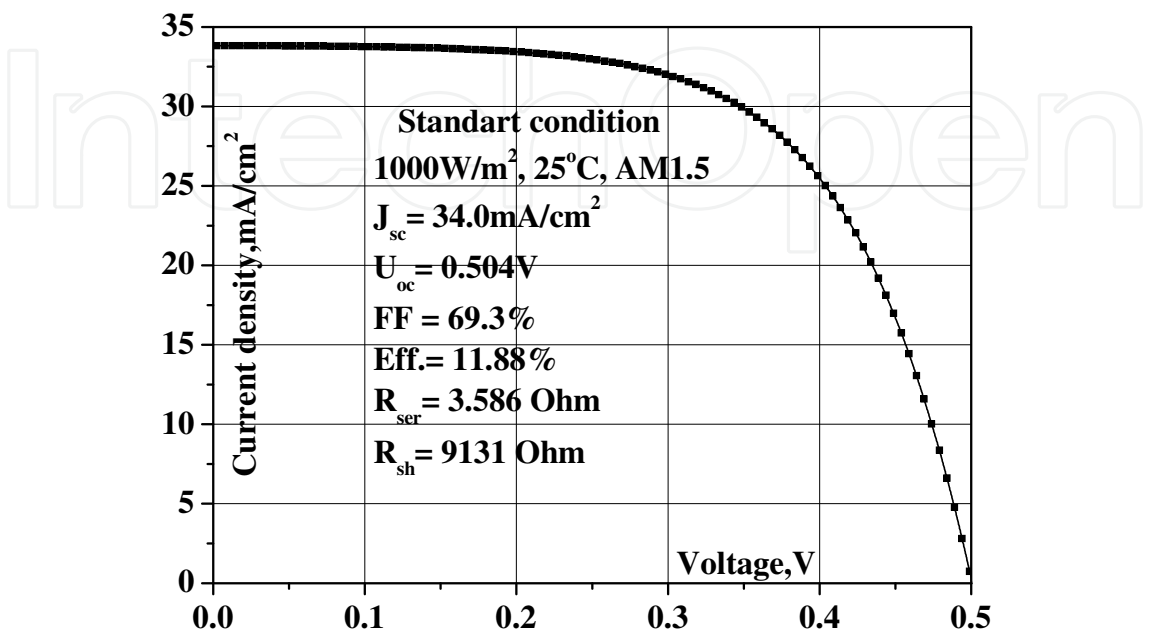


Fig. 5. Load I-V characteristic of ITO/SiO<sub>2</sub>/nSi solar cells with irregular landform Si surface

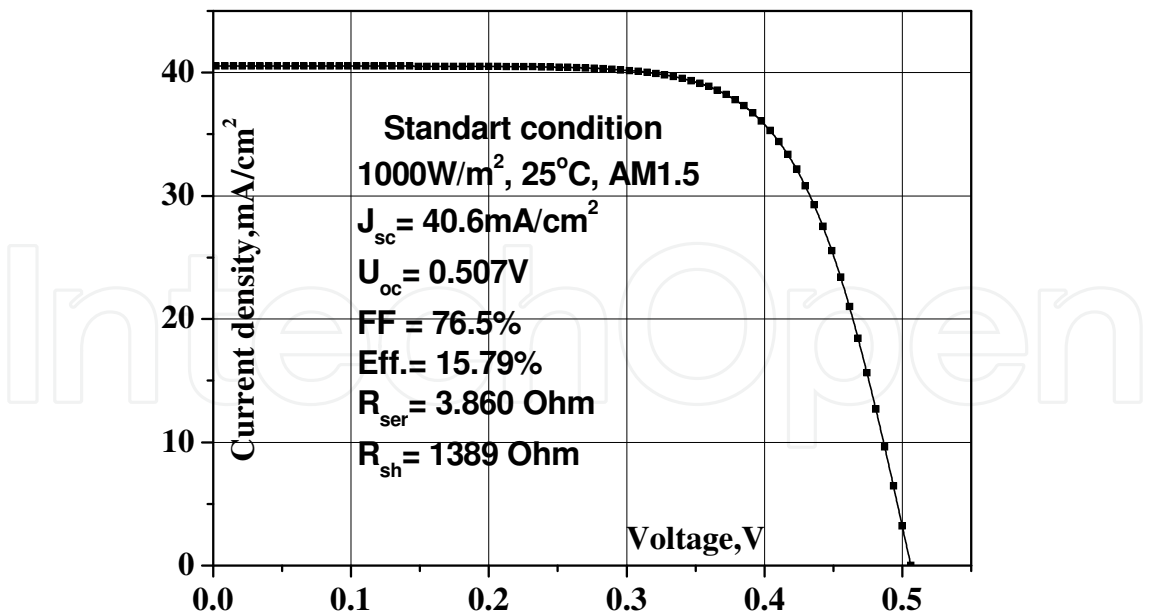


Fig. 6. Load I-V characteristic of ITO/SiO<sub>2</sub>/nSi solar cells with regular landform Si surface

For samples obtained on textured Si wafers with irregular landform (Fig. 5), the efficiency and other photoelectric parameters increased in comparison with the SC described earlier (Gagara et al, 1996, Simashkevich et al, 1999). Besides, the results improved when Si wafers

with regular landform (Fig.3b) were used for ITO/SiO<sub>2</sub>/nSi solar cell fabrication. The respective load I-V characteristic is presented in Fig. 6.

The summary data regarding the methods of ITO layer deposition onto the textured silicon wafers and the obtained efficiencies are presented in Table 3.

References	ITO deposition method	Area (cm <sup>2</sup> )	Eff. (%)	Note
Kobayashi et al., 1991	Spray	2.25	13	Textured Si surface
Vishvakarma et al., 1993	CVD	2.0	12.6	Textured Si surface
Simashkevich et al., 2011	Spray	4.0	11.88	Irregular texture Si surface
Simashkevich et al., 2011	Spray	4.0	15.79	Regular texture Si surface

Table 3. Efficiencies of ITO/SiO<sub>2</sub>/nSi solar cells fabricated by various deposition techniques of ITO layers onto the textured silicon wafers

2.3 SIS structures on the base of InP and other crystals

Indium phosphide is known to be one of the most preferable materials for the fabrication of solar cells due to its optimum band gap; therefore, it is possible to obtain solar energy conversion into electric power with high efficiency. On the base of InP, SC have been fabricated with the efficiency of more than 20 % (Gessert, et al, 1990). In addition, InP based SC are stable under harsh radiation conditions. It was shown (Botnaryuk, Gorchiak et al., 1990, Yamamoto et al, 1984, Horvath et al, 1998) that the efficiency of these SC after proton and electron irradiation decreases less than in the case of Si or GaAs based SC. However, due to the high price of InP wafers, in terrestrial applications, indium phosphide based SC could not be competitive with SC fabricated on other existing semiconductor solar materials such as silicon.

2.3.1 Fabrication of ITO/InP photovoltaic devices

Let us consider the fabrication process of ITO/InP photovoltaic devices. Two main methods of the ITO layer deposition onto InP crystals are used. The first method consists in the utilization of an ion beam sputtering system (Aharoni et al., 1986). The fabrication process of InP photovoltaic devices using this method and the obtained results are described in detail elsewhere (Gessert et al., 1990; Aharoni et al., 1999).

A schematic diagram of the ITO/InP solar cell fabricated by the above-mentioned method is presented in Fig. 7. The operation of solar cells shown in Fig. 7 can be attributed to two possible mechanisms. One is that the conductive ITO and the substrate form an nITO/pInP Schottky type barrier junction. The second is the formation of a homojunction due to the formation of a “dead” layer (thickness – d) at the top of the InP substrate. This “dead” layer is caused by the crystal damage, which results from the impingement of the particles sputtered from the target on the InP top surface. The “dead” layer volume is characterized by extremely short free carrier’s life times, i.e. high carrier recombination rates, with respect to the underlying InP crystal.

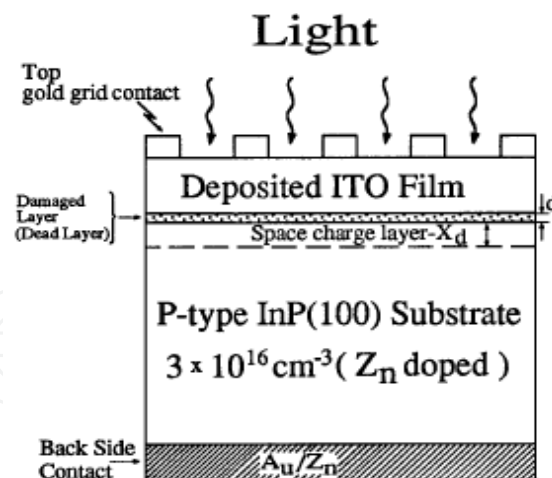


Fig. 7. Schematic diagram of the ITO/InP photovoltaic device obtained by ion beam sputtering.

Accordingly, it forms the “n” side of a homojunction with the “p” type underlying InP. The formation of an n-p junction in InP may be due to tin diffusion from the ITO into the InP, where tin acts as a substitution donor on In sites. The record efficiency of 18.9% was obtained in (Li et al., 1989) for ITO/InP structures, when the ITO layer was deposited by magnetron dispersion on p<sup>+</sup>p/InP treated preliminary in Ar/O<sub>2</sub> plasma.

Using the above-described sputtering process, a small-scale production of 4cm<sup>2</sup> ITO/InP photovoltaic solar cells has been organized at Solar Energy Research Institute (now National Renewable Energy Laboratory), Golden, Colorado, the USA (Gessert et al., 1991). Although only a small number of the 4cm<sup>2</sup> ITO/InP cells (approximately 10 cells total) were fabricated, the average cell efficiency is determined to be 15.5%, the highest cell performance being 16.1% AM0. Dark I-V data analysis indicates that the cells demonstrate near-ideal characteristics, with a diode ideality factor and reverse saturation current density of 1.02 and 1.1 · 10<sup>-12</sup>mA/cm<sup>2</sup>, respectively (Gessert et al, 1990).

The second, a simpler, method of ITO/InP photovoltaic devices fabrication consists in spray-pyrolitic deposition of ITO layers onto InP substrates (Andronic et al., 1998; Simashkevich et al., 1999; Gagara et al., 1986; Vasu et al, 1993). ITO layers were deposited on the surface of InP wafers by spraying an alcoholic solution of InCl<sub>3</sub> and SnCl<sub>4</sub> in different proportions. The following chemical reactions took place on the heated up substrate:



ITO thin films with the thickness of 150-250nm were deposited by the above-mentioned spray method in various gaseous environments: O<sub>2</sub>, Ar, or air atmosphere. When the inert gas was carrier gas, the installation could be completely isolated from the environment that allowed obtaining the structures in the atmosphere without oxygen. A thin insulator layer with the thickness up to 10nm is formed on InP surface due to the oxidation of the substrate during spraying. The oxidation of InP wafers in HNO<sub>3</sub> for 20-30s was realized in the case of inert gas atmosphere. In the case of InP crystals, a thin insulator P<sub>2</sub>O<sub>5</sub> layer with the thickness 3-4 nm was formed on InP wafer surface during the ITO layers deposition. Ohmic contacts to pInP were obtained by thermal vacuum evaporation of 95 % Ag and 5 % Zn alloy on the previously polished rear surface of the wafer.



Structures with different crystallographic orientation and holes concentration in the InP substrates were obtained. The optimum concentration of the charge carriers in plnP substrates was  $10^{16}\text{cm}^{-3}$ , but the InP wafers with these carrier concentrations and the thickness of 400 nm had a high resistance. For this reason, p/p<sup>+</sup>InP substrates were used in order to obtain efficient solar cells with a low series resistance. In some cases a plnP layer with the thickness up to 4 μm and concentration  $p = (3...30) \cdot 10^{16} \text{ cm}^{-3}$  was deposited by the gas epitaxy method from the InPCl<sub>3</sub> H<sub>2</sub> system on the (100) oriented surface of InP heavily doped substrate with the concentrations  $p^+ = (1...3) \cdot 10^{18} \text{ cm}^{-3}$  for the fabrication of ITO/plnP/p<sup>+</sup>InP structures. Ag and 5 % Zn alloy evaporated in a vacuum through a special mask were used as an ohmic contact to the ITO and to InP crystal. A schematic diagram of ITO/p/p<sup>+</sup>InP structure obtained by spray pyrolytic method is presented in Fig. 8.

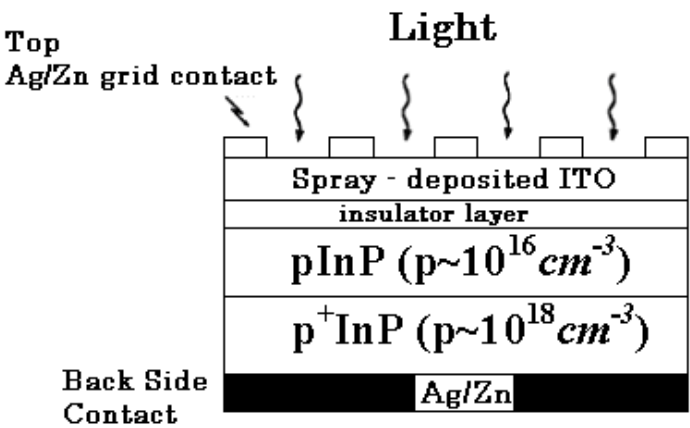


Fig. 8. Schematic diagram of the ITO/InP structure obtained by spray pyrolytic method.

2.3.2 Electrical properties of ITO/InP solar cells

The energy band diagram of the ITO/pInP structure proposed in (Botnariuc et al., 1990) is presented in Fig. 9. The current flow mechanism of the ITO/InP structures, obtained in different fabrication conditions, was clarified in (Andronic et al., 1998) on the base of the energy band diagram below.

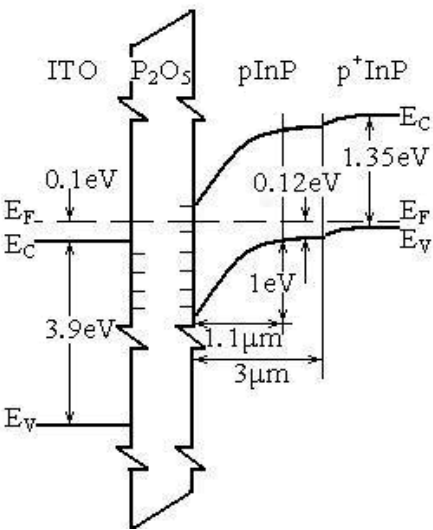


Fig. 9. Energy band diagram of ITO/InP structure obtained in oxygen atmosphere

The I-V characteristics of ITO/pInP structures at different temperatures, obtained in the non-oxide environment are given in Fig. 10a.

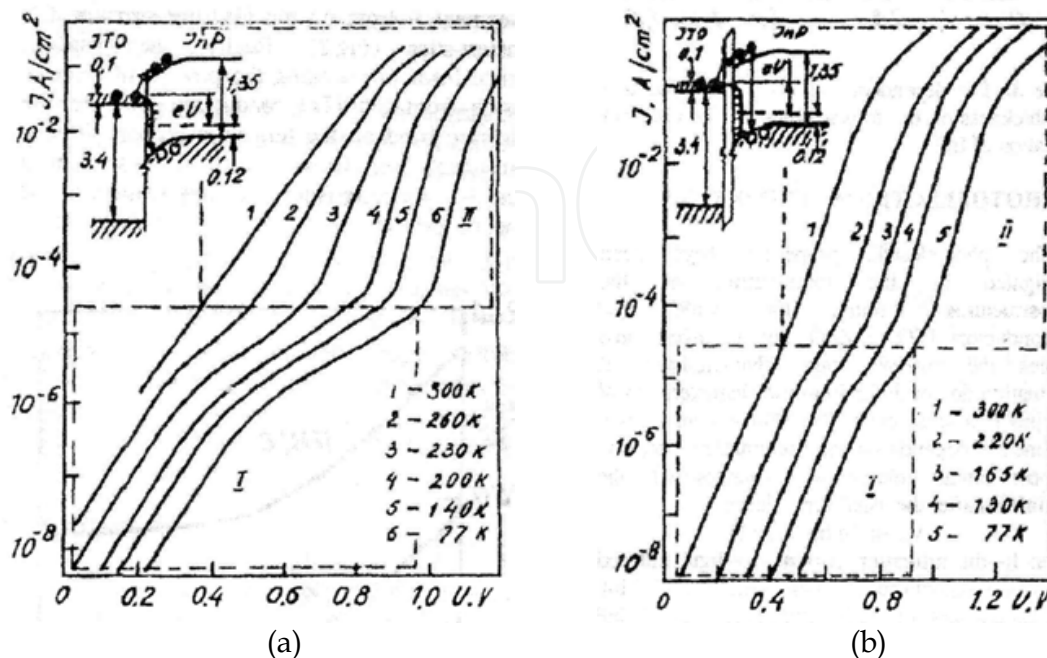


Fig. 10. Dark current-voltage characteristics at direct bias a) obtained in nitrogen atmosphere: b) obtained in oxygen atmosphere

One can suppose the existence of two channels of carriers transport through the structure interface (insertion in Fig. 10a). The first channel is the following: the majority carriers from InP are tunneling through the barrier at the interface and then recombining step by step with electrons from ITO conduction band (Ribben & Feucht, 1966). According to this model, the I-V characteristic slope should not depend on temperature. The second channel appears at the direct bias of more than 0.6V and is determined by the emission of electrons from the ITO conduction band to the InP conduction band. This emission should occur by changing the I-V curves slope at different temperatures. As one can see from the experimental data, these two channels are displayed by two segments on I-V characteristics.

Fig. 10b shows the I-V characteristics of the ITO/InP structures achieved in an oxygen environment or under substrate oxidation. In this case, the presence of the insulator layer on the interface could be expected. The ITO/InP structures capacity-voltage measurements confirm this supposition. During the fabrication of the ITO/InP structure in oxygen atmosphere, a thin insulator layer on the interface is obtained. Changing the segment II from the ITO/InP structure I-V characteristics shows the presence of a thin insulator layer. The insulator presence leads to changing the process of electron emission from the ITO conduction band to the InP conduction band on the tunneling process through this insulator layer. Thus, the form of segment II on the I-V characteristics becomes similar to the segment I form.

### 2.3.3 Photoelectric properties of ITO/InP solar cells

Photoelectric properties of these SC have been investigated at the illumination of the heterostructures through the wide gap oxide layer. For all investigated samples, the current-voltage characteristics at illumination do not differ from the characteristics of respective

homojunction solar cells. The current short circuit  $I_{sc}$  linearly depends on the illumination intensity; the open circuit voltage  $U_{oc}$  changes with the illumination after the usual logarithmic dependence:

$$U_{oc} = \frac{kT}{q} \ln \left( \frac{I_{sc}}{I_o} + 1 \right)$$

(3)

where  $I_L$  - light induced current,  $I_s$ - the saturation current,  $T$ - temperature.  
The dependence of ITO/InP cells parameters in AM 0 conditions versus InP substrate orientation and hole concentration was studied. InP wafers with the orientation in (100) and (111) B directions were used to obtain solar cells by the deposition of ITO layers (Table 4).

Substrate	$p, 10^{16}cm^{-3}$	$V_{oc}, (mV)$	$I_{sc}, (mA/cm^2)$	$\eta, (\%)$
pInP (111)B	2.6	674	28.3	10.4
	6.5	699	23.8	9.6
	15	689	25.3	9.5
p <sup>+</sup> /pInP (100)	10	707	25.9	11.1
	30	695	28.6	11.0
	2.0	707	30.8	11.6
pInP (111)A	3.7	568	22.0	5.0
	5.7	722	17.7	5.3
	37	545	14.3	3.7

Table 4. The dependence of ITO/InP cells parameters in AM0 conditions versus InP substrate crystallographic orientation

The photo sensibility spectral distribution of the p<sup>+</sup>/pInP(100) structure is presented in Fig. 11.

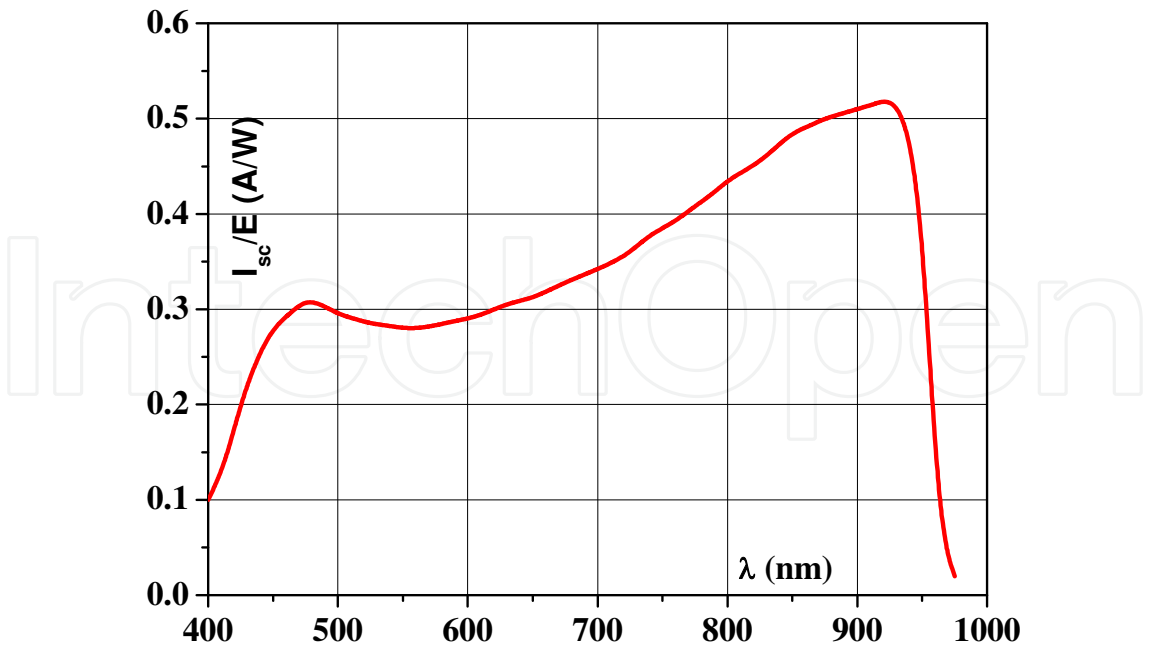


Fig. 11. The photo sensibility spectral characteristic of the p<sup>+</sup>/pInP (100) SC

The region of the spectral sensibility of Cu/nITO/pInP/Ag:Zn structure is situated between 400 - 50 nm.

The minimum efficiency was observed when solar cells were obtained by deposition of ITO layers onto InP wafers oriented in (111) A direction. To increase the efficiency, those solar cells were thermally treated in  $H_2$  atmosphere at the temperature of  $350^\circ C$  during 10 minutes to reduce the series resistance (Bruk et al, 2007).

It was shown that before the thermal treatment the following parameters had been obtained under AM 1.5 illumination conditions:  $U_{oc} = 0.651$  V,  $I_{sc} = 18.12$  mA/cm<sup>2</sup>, FF = 58 %, Eff. = 6.84 % (Fig. 12, curve 1).

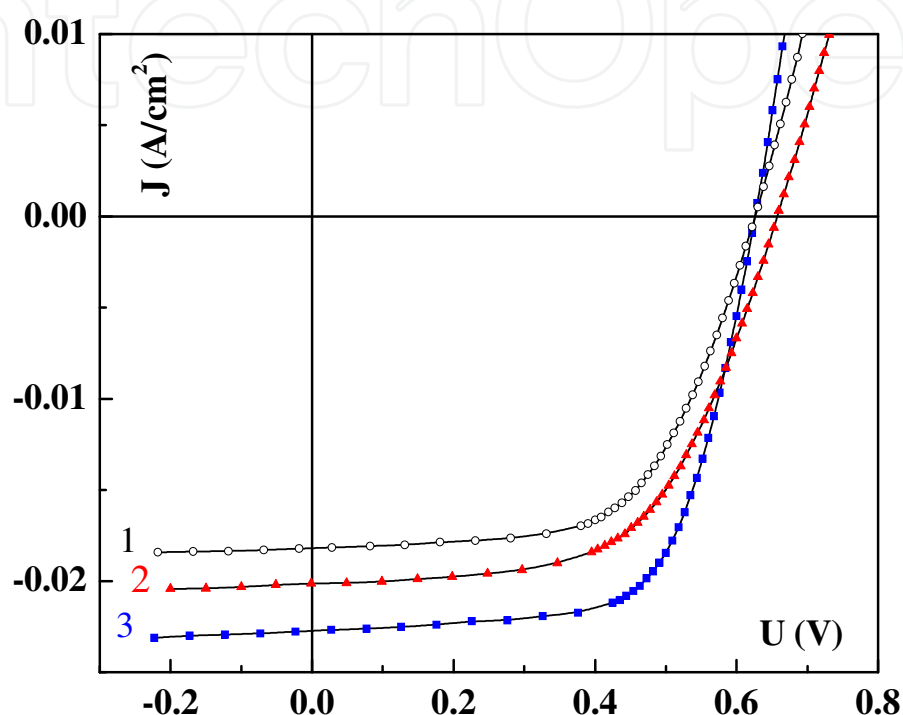


Fig. 12. Load I-V characteristics of Cu/nITO/pInP/Ag:Zn solar cells: 1-before thermal treatment; 2-after thermal treatment in  $H_2$ ; 3-best parameters after thermal treatment in  $H_2$

After the thermal treatment the parameters were:  $U_{oc} = 0.658$  V,  $I_{sc} = 20.13$  mA/cm<sup>2</sup>, FF = 58 %, Eff. = 7.68 % (Fig.12, curve 2). The photoelectric parameters of the SC received on InP wafers with the concentration  $p = 3.10^{17} \text{ cm}^{-3}$  after the thermal treatment were  $U_{oc} = 0.626$  V,  $I_{sc} = 22.72$  mA/cm<sup>2</sup>, FF = 71 %, Eff. = 10.1 % (Fig. 12, curve 3), that is better than for analogous SC without treatment in  $H_2$ .

The thermal treatment in  $H_2$  leads to the undesirable decrease of the photo sensibility in the short wave region of the spectrum (Fig.13).

The highest sensibility is observed at 870nm, which indicates that the maximum contribution in the photo sensibility is due to the absorption in InP.

ITO/InP structures grown by spray pyrolysis were also investigated in Semiconductor Laboratory of the Indian Institute of Technology, Madras (Vasu & Subrahmanyam, 1992; Vasu, et al., 1993). The maximum efficiency of 10.7% was achieved under 100mW/cm<sup>2</sup> illumination for junctions having 5% by weight of tin in the ITO films. The texturing of the InP crystal surface in ITO/InP SC (Jenkins et al., 1992) reduces the surface reflection. These cells showed improvement in both short circuit current and fill factor, the efficiency can be increased by 6.74%. The texturing reduces the need for an optimum antireflection coating.

SIS structures for SC fabrication were also obtained on the base of other semiconductor materials besides Si and InP. ITO/CdTe (Adeeb et al., 1987) and ITO/GaAs (Simashkevich et al., 1992) structures were obtained by spray pyrolysis of ITO layers on pCdTe and pGaAs crystals. For ITO/CdTe the efficiency was 6%, for ITO/GaAs SC it did not exceed 2.5%.

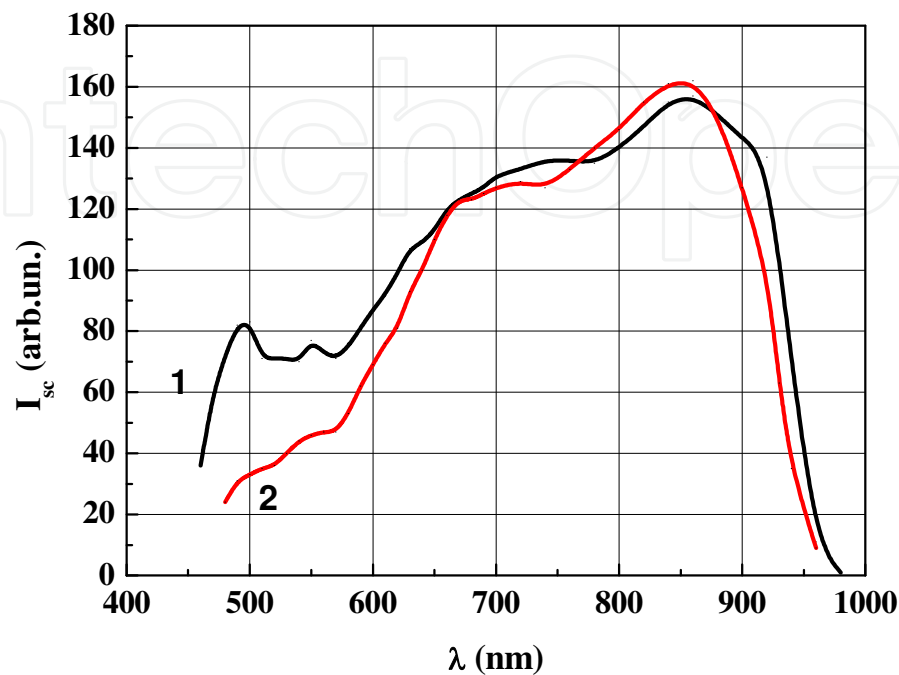


Fig. 13. The spectral photo sensibility of Cu/n+ITO/pInP/Ag:Zn structure: 1- before H<sub>2</sub> annealing, 2- after H<sub>2</sub> annealing

2.3.4 Degradation of photoelectric parameters of ITO/InP solar cells exposed to ionizing radiation

The degradation of photoelectric parameters of ITO/InP solar cells after their irradiation by protons with energies  $E_p=20.6\text{MeV}$  and flux density up to  $F_p=10^{13}\text{cm}^{-2}$  and by electrons with  $E_e=1\text{MeV}$  and  $F_e\leq 10^{15}\text{cm}^{-2}$  was investigated (Andronic et al., 1998). The results of the photoelectrical parameter measurements at AM0 conditions after the irradiation are presented in Fig. 14. Higher efficiency of 11.6% is obtained if the InP substrate is oriented in [100] plane.

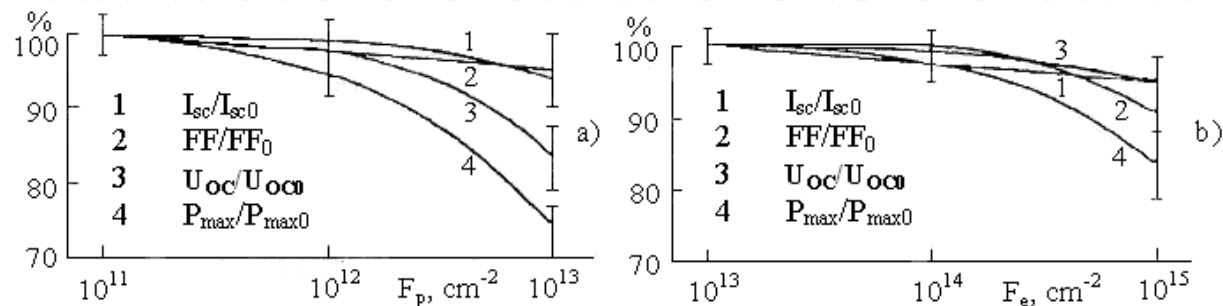


Fig. 14. The degradation of ITO/InP heterostructures photoelectric parameters under protons (a) and (b) electrons irradiation



We notice that after the irradiation of ITO/InP solar cells with an integral proton flux of  $10^{13}\text{cm}^{-2}$ , their efficiency decreases by 26%, that is less than in the case of Si and GaAs based solar cells. In the spectral characteristics of ITO/pInP solar cells after proton irradiation a small decrease of the photosensitivity in the long wavelength region of the spectrum was observed due to the decrease of the diffusion length.

Comparing the results of the radiation stability study of ITO/InP SC, fabricated by spray pyrolysis, with the results of similar investigations of other InP based structures, it is possible to conclude that in this case the radiation stability is also determined by the low efficiency of radiation defects generation and, hence, by the low concentration of deep recombination centers, reducing the efficiency of solar energy conversion in electric power.

### 3. Fabrication of ITO/nSi solar cells with enlarged area by spray pyrolysis

From the brief discussion above it can be concluded that the deposition of ITO layers by spray pyrolysis on the surface of different semiconductor materials allows manufacturing SC through a simple and less expensive technology. The most effective are ITO/InP SC but because of a very high cost of the InP crystals they cannot be widely used in terrestrial applications. To this effect ITO/nSi SC with the efficiency higher than 10% may be used, but it is necessary to develop the technology for SC fabrication with the active area enlarged up to 70-80  $\text{cm}^2$  as is the case of traditional silicon SC with p-n junction.

#### 3.1 Deposition of ITO layers on enlarged silicon wafers

ITO layers are deposited on the nSi crystals surface using the specially designed installation (Simashkevich et al., 2004; Simashkevich et al., 2005) (Fig. 15) that has four main units: the spraying system (7), the system of displacement and rotation of the support on which the substrate is fixed (4, 5), the system of heating the substrate, and the system of the evacuation of the residual products of the pyrolysis (8). The heating system consists of an electric furnace (2) and a device for automatic regulation of the substrate temperature with the thermocouple (3). The rest of the installation parts are: the power unit (1), the cover (10), and the shielding plate (12). Silicon wafers (11) are located on the support (9) and with the displacement mechanism are moved into the deposition zone of the electric furnace (6). The construction of this mechanism provides the rotation of the support with the velocity of 60 rotations per minute, the speed necessary for the obtaining of thin films with uniform thickness on the all wafer surface. The alcoholic solution of the mixture  $\text{SnCl}_4 + \text{InCl}_3$  is sprayed with compressed oxygen into the stove on the silicon wafer substrate, where the ITO thin film is formed due to thermal decomposition of the solution and the oxidation reaction. On the heated up substrate there are the chemical reactions describe above in formulas (1) and (2).

The BSF  $n/n^+$  junction was fabricated on the rear side of the wafer by a diffusion process starting from  $\text{POCl}_3$  gas mixture. The junction formation ended with a wet chemical etching of  $\text{POCl}_3$  residual in a 10% HF bath. A junction depth of  $1\mu\text{m}$  was chosen in order to minimize recombination. To reduce the surface recombination velocity the wafers were thermally oxidized at the temperature of  $850^\circ\text{C}$ . The main steps of the fabrication of BSC are schematized in Fig. 16.

#### 3.2 Properties of ITO layers

The properties of the thus obtained ITO films depend on the concentration of indium chloride and tin chloride in the solution, the temperature of the substrate, the time of

spraying and the deposition speed. ITO films had a microcrystalline structure that was influenced by the crystal lattice of the support as the X-ray analysis showed. They had cubic structure with the lattice constant 10.14Å (Brak et al., 2009)). The SEM image of such an ITO film is presented in Fig. 17.

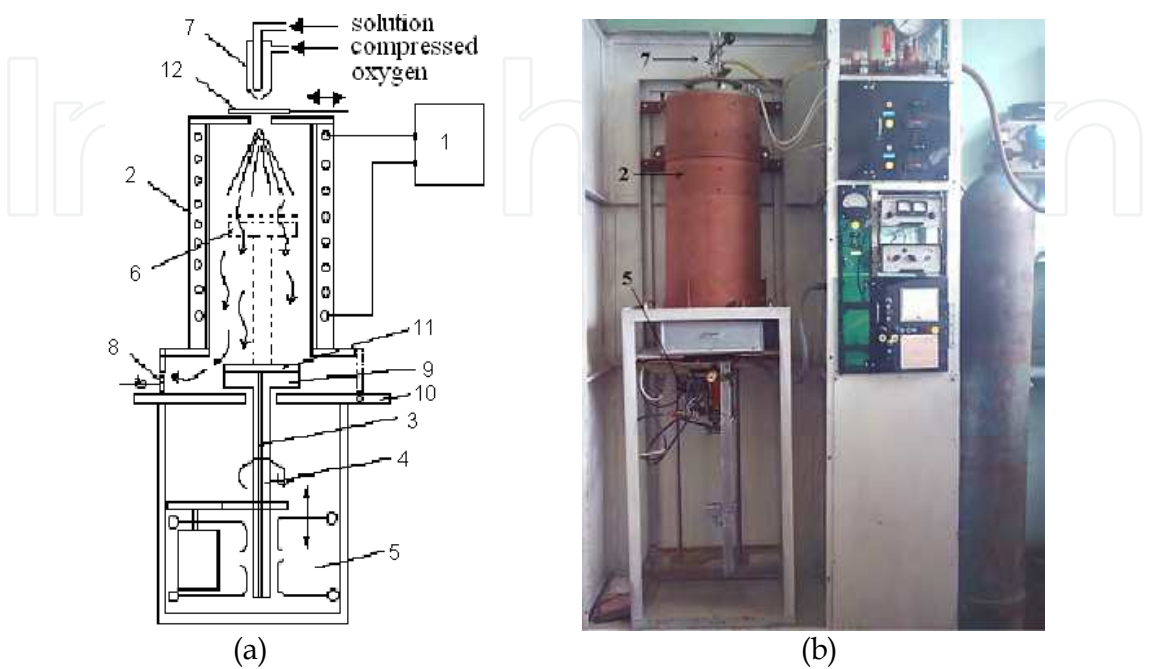


Fig. 15. Schematic a) and real b) view of the installation for ITO thin films deposition

ITO/SiO<sub>2</sub>/nSi solar cells with the active area of 8.1cm<sup>2</sup> and 48.6cm<sup>2</sup> were fabricated. In some cases a BSF region was obtained at the rear contact by phosphor diffusion.

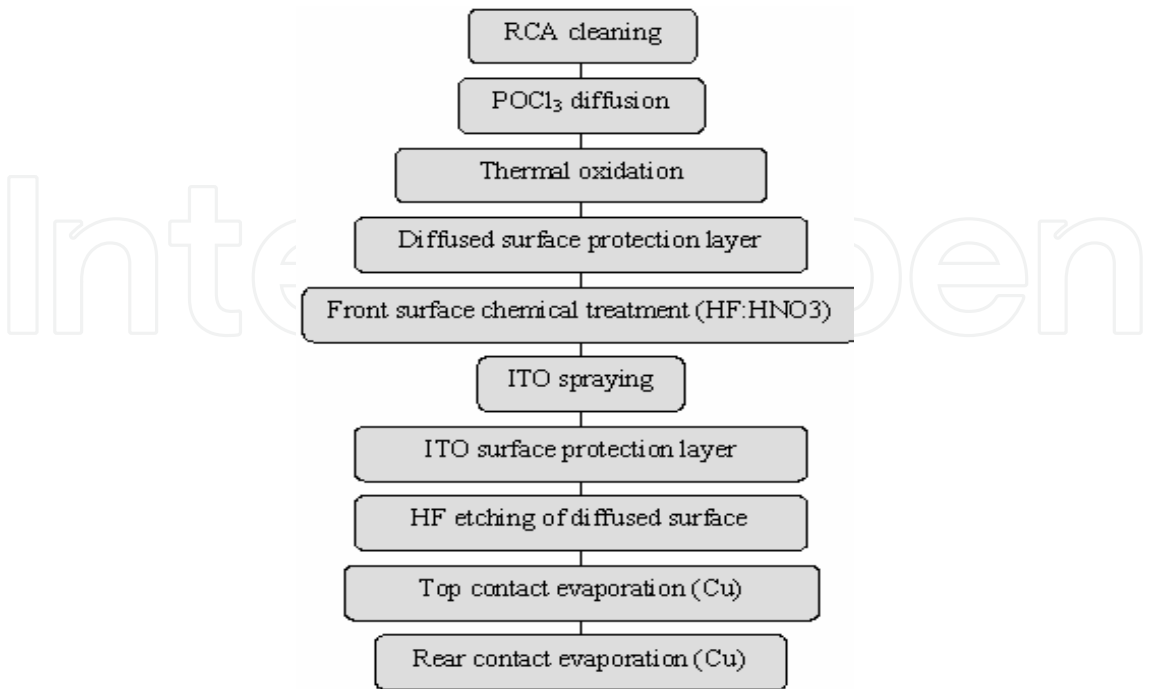


Fig. 16. SC process sequence.

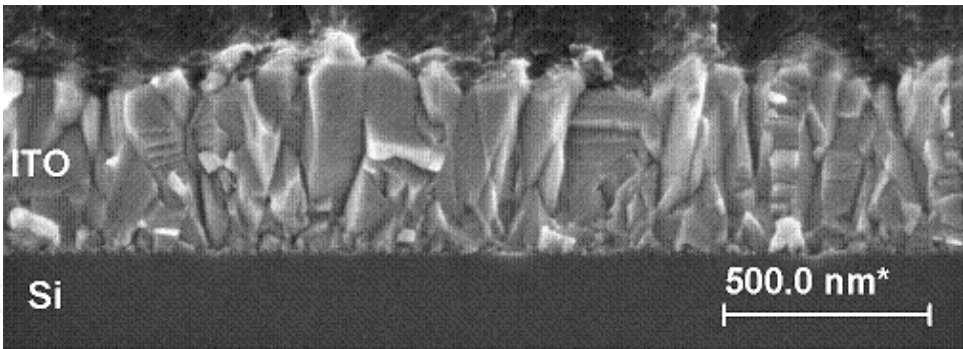


Fig. 17. SEM image of ITO film

From Fig. 17 it is clear that the ITO film with the thickness of 400nm has a columnar structure, the column height being about 300nm and the width 50-100nm. ITO films with the maximum conductivity  $4.7 \cdot 10^3 \text{ } \Omega\text{-}^1\text{cm}^{-1}$ , the electron concentration  $(3.5\div 15) \cdot 10^{21}\text{cm}^{-3}$ , the mobility  $(15\div 30)\text{cm}^2/(\text{V s})$ . and maximum transmission coefficient in the visible range of the spectrum (87 %) were obtained from solutions containing 90 %  $\text{InCl}_3$  and 10 %  $\text{SnCl}_4$  at the substrate temperature  $450^\circ\text{C}$ , deposition rate  $100 \text{ } \text{\AA}/\text{min}$ , spraying time 45 s. ITO layers with the thickness 0.2mm to 0.7mm and uniform properties on the surface up to  $75\text{cm}^2$  were obtained. The dependence of the electrical parameters of ITO layers as a function of their composition is given in Table 5.

Parameters	Ratio of $\text{InCl}_3\text{:SnCl}_4\text{:C}_2\text{H}_5\text{OH}$ component in the solution					
	10:0:10	9.5:0.5:10	9:1:10	8.5:1.5:10	8:2:10	0:10:10
$\sigma, \text{S cm}^{-1}$	$2.6 \cdot 10^2$	$2.6 \cdot 10^3$	$4.7 \cdot 10^3$	$2.6 \cdot 10^3$	$1.3 \cdot 10^3$	42.4
$n, \text{cm}^{-3}$	$1.1 \cdot 10^{20}$	$5.5 \cdot 10^{20}$	$1.1 \cdot 10^{21}$	$6.5 \cdot 10^{20}$	$5.8 \cdot 10^{20}$	$5.3 \cdot 10^{19}$
$\mu, \text{cm}^2/(\text{V s})$	15	29	27	25	14	5

Table 5. The dependence of the electrical parameters of ITO layers as a function of their composition

The band gap width determined from the spectral dependence of the transmission coefficient is equal to 3.90eV and changes only for the content of 90-100% of  $\text{InCl}_3$  in the spraying solution. If the content of  $\text{InCl}_3$  is less than 90% the band gap remains constant and equal to 3.44eV. The optical transmission and reflectance spectra of the deposited on the glass substrate ITO thin films (Simashkevich et al., 2004) shows that the transparence in the visible range of spectrum is about 80%, 20% of the incident radiation is reflected. The ITO thin film thickness was varied by changing the quantity of the sprayed solution and it was evaluated from the reflectance spectrum (Simashkevich et al., 2004). The thickness of the layer was determined using the relationship (Moss et al., 1973):

$$d=\lambda_1 \cdot \lambda_2/ \{(\lambda_2-\lambda_1) \cdot 2n\} \tag{4}$$

where: n-refraction index equal to 1.8 for ITO (Chopra et al., 1983);  $\lambda$ -the wavelengths for two neighboring maximum and minimum; d-the thickness of the ITO layer. Using this relation the thickness of ITO layers deposited on the nSi wafer surface in dependence on the quantity of the pulverized solution has been determined. This relation is linear and the layer thickness varies from  $0.35\mu\text{m}$  up to  $0.5\mu\text{m}$ .

### 3.3 Obtaining of ITO/nSi structures

The nSi wafers oriented in the (100) plane with resistivity 1.0 Ohm.cm and 4.5 Ohm.cm (concentrations  $5 \cdot 10^{15} \text{ cm}^{-3}$  and  $1 \cdot 10^{15} \text{ cm}^{-3}$ ) were used for the fabrication of SIS structures. Insulator layers were obtained on the wafers surface by different methods: anodic, thermal or chemical oxidation. The best results have been obtained at the utilization of the two last methods. The chemical oxidation of the silicon surface was realized by immersing the silicon wafer into the concentrated nitric acid for 15 seconds. A tunnel transparent for minority carriers insulator layers at the ITO/Si interface have been obtained thermally, if the deposition occurs in an oxygen containing atmosphere. Ellipsometrical measurement showed that the thickness of the  $\text{SiO}_2$  insulator layer varies from 30 Å to 60 Å. The frontal grid was obtained by Cu vacuum evaporation. The investigation of the electrical properties of the obtained SIS structures demonstrates that these insulator layers are tunnel transparent for the current carriers. Thereby the obtained ITO/nSi SIS structures represent asymmetrical doped barrier structures in which a wide band gap oxide semiconductor plays the role of the transparent metal.

## 4. Physical properties of $\text{n}^+\text{ITO}/\text{SiO}_2/\text{nSi}$ structures

### 4.1 Electric properties

Current-voltage characteristics in the temperature range 293K–413K were studied. The general behavior of the I-V curves of directly biased devices in Fig. 18 is characterized by the presence of two straight-line regions with different slopes (Simashkevich et al., 2009). Two regions with different behavior could be observed from this figure. In the first region, at external voltages lower than 0.3 V, the I-V curves are parallel, i.e., the angle of their inclination is constant.

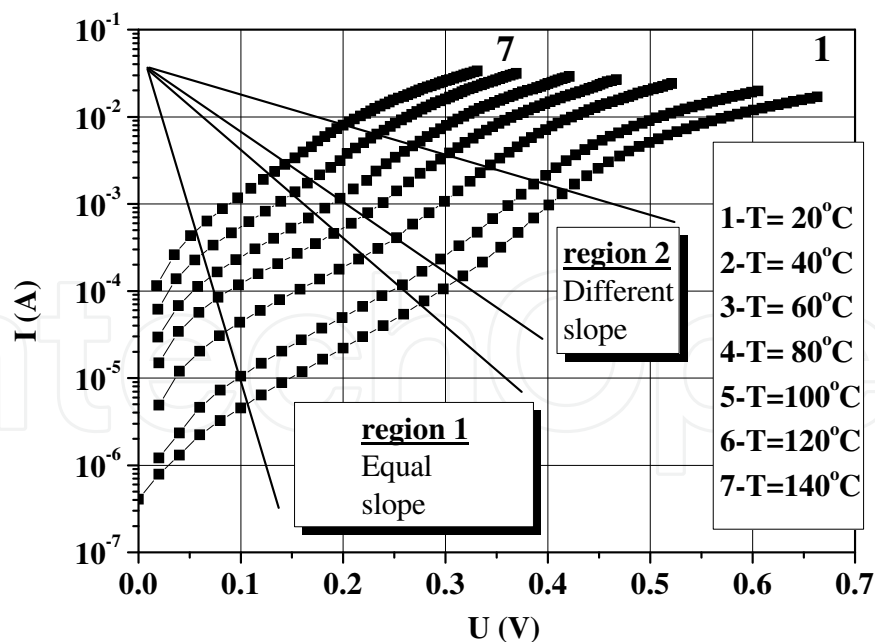


Fig. 18. Temperature dependent direct I-V characteristics in the dark of the  $\text{n}^+\text{ITO}/\text{SiO}_2/\text{nSi}$  solar cells

In this case, according to (Ribben & Feucht, 1966), the charge carrier transport through the potential barrier is implemented through the tunnel recombination processes in the

space charge region, and the current-voltage dependence could be described by the relation:

$$I = I_0 \exp(AV) \exp(BT) \quad (5)$$

where  $A$  and  $B$  are constant and do not depend on voltage and temperature, respectively. The numerical value of the constant  $A$ , determined from dependences presented in Fig. 18 is equal to  $15 \text{ V}^{-1}$ . The value of the constant  $B$ , which is equal to  $0.045 \text{ K}^{-1}$ , was calculated from the same dependences that have been re-plotted as  $\ln I = f(T)$ . In (Ribben & Feucht, 1966) the constant  $A$  is expressed by the relation:

$$A = 8\pi/3h \cdot (m_e^* \epsilon_s S/N_d)^{1/2} \quad (6)$$

where  $m_e^*$  – is the electron effective mass (in Si in the case considered);  $\epsilon_s$  – the dielectric permeability of the silicon, and  $S$  represents the relative change of the electron energy after each step of the tunneling process. Note that  $1/S$  represents the number of tunneling steps.

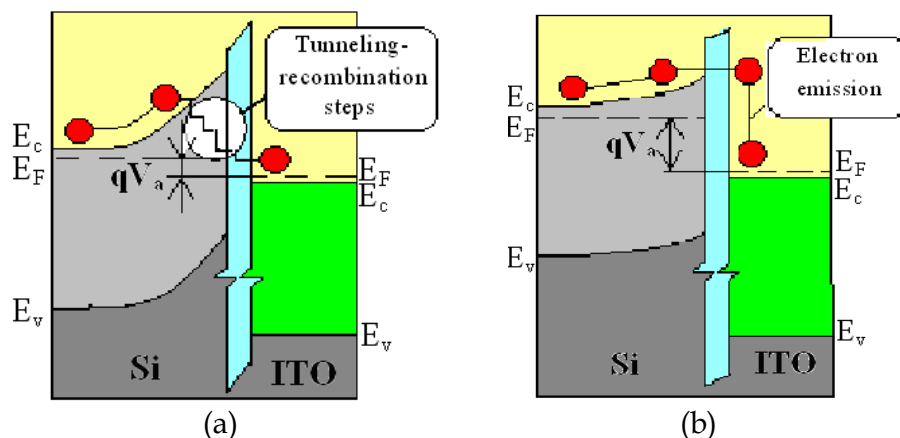


Fig. 19. The energy band diagram for: a) biases lower than 0.3 V (the region 1 in Fig. 18), b) biases higher than 0.3 V (region 2 in Fig. 18)

The numerical value of  $A$  is easily calculated, since the other parameters in the respective expression represent fundamental constants or Si physical parameters. Hence, the mechanism of the charge carrier transport at direct biases of less than 0.3 V could be interpreted as multi-step tunnel recombination transitions of electrons from the silicon conduction band into the ITO conduction band (see the energy band diagram in Fig.19a), the number of steps being about 100.

At voltages higher than 0.3 V (see different slope region in Fig. 18) the current flow mechanism through the ITO/nSi structure changes. The slopes of the I-V curves become temperature dependent that is confirmed by the constant value  $n$  about 1.6 of the parameter  $n$  in the relation:

$$I = I_0 \exp(qV_a/nkT) \quad (7)$$

where

$$I_0 = C \exp(-\phi_B/kT) \quad (8)$$

$C$  is a constant depending on the flux current model (emission or diffusion) (Milnes & Feucht, 1972).



Such an I-V dependence expressed by relations (7) and (8) is typical for transport mechanisms involving emission of electrons over potential barriers (Fig. 19b). Thus, at temperatures higher than 20°C, an initial voltage that stimulates the electron emission from Si into ITO over the potential barrier at the Si/ITO interface in  $n^+ITO/SiO_2/nSi$  structures is of about 0.3 V. From  $\ln I = f(1/kT)$  it is possible to determine the height of the potential barrier  $\phi_B$  in ITO/nSi structures because the slope of the above-mentioned dependence is equal to  $\phi_B - qV_a$ . The calculated value of  $\phi_B$  is 0.65 eV, which is in correlation with the experimental data. A close value of the height of the potential barrier  $\phi_B$  equal to 0.68 eV was determined also from relation (8) (Simashkevich et al., 2009).

To sum up, in  $n^+ITO/SiO_2/nSi$  structures two mechanisms of the direct current flow are observed: (i) tunneling recombination at direct voltages of less than 0.3 V and (ii) over barrier emission at voltages higher than 0.3 V. In the former case, the direct current flow could be interpreted as multi-step tunnel recombination transitions of electrons from the silicon conduction band into the ITO conduction band, the number of steps being of about 100. The reduction of the influence of the former as well as a fine adjustment of the  $SiO_2$  thickness in investigated structures will lead to an increased efficiency of converting solar energy into electric energy.

#### 4.2 Photoelectric properties

The spectral distribution of the quantum efficiency as well as the photosensitivity of the obtained PV cells have been studied (Simashkevich et al., 2004). The monochromatic light from the spectrograph is falling on a semitransparent mirror and is divided into two equal fluxes. One flux fall on the surface of a calibrated solar cell for the determination of the incident flux energy and the number (N) of incident photons. The second flux falls on the surface of the analyzed sample and the short circuit current  $J_{sc}$  is measured, thus permitting the calculation of the number of charge carriers, generated by the light and separated by the junction, and then the quantum efficiency for each wavelength (Fig. 20).

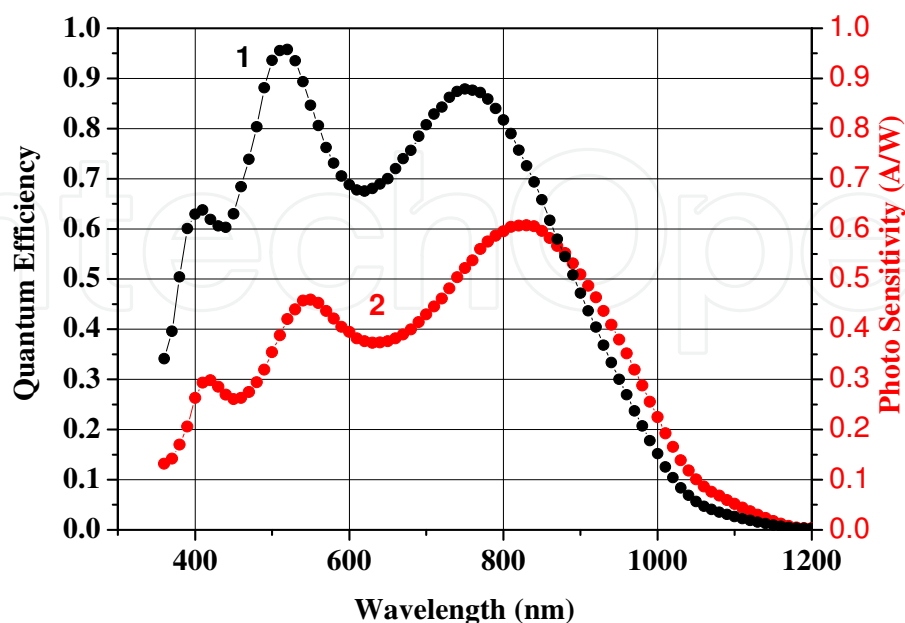


Fig. 20. Spectral distribution of the quantum efficiency (1) and photo sensitivity (2) of the  $n^+ITO/SiO_2/nSi$  solar cells

The reproducibility of the process and the performances of the devices during samples realization were checked in each batch of samples as well as batch-to-batch. The enlargement of the area of the solar cells up to  $48.6\text{cm}^2$  leads to the increasing of the series resistance and to the diminishing of the efficiency down to 7%. Thus, the method of obtaining  $\text{n}^+\text{ITO}/\text{SiO}_2/\text{nSi}$  structures based on the thin  $\text{In}_2\text{O}_3:\text{Sn}$  layers, which are formed on the surface of Si wafers, traditionally chemically treated, passivated and heated to the temperature of  $450^\circ\text{C}$ , by spraying chemical solutions of indium tin chloride was elaborated. Solar cells based on  $\text{n}^+\text{ITO}/\text{SiO}_2/\text{nSi}$  structures with an active surface up to  $48.6\text{cm}^2$  have been fabricated.

Maximum efficiency of 10.52% is obtained in the case of (100) crystallographic orientation of Si wafer with BSF region at the rear surface and active area of  $8.1\text{cm}^2$ , ITO thickness  $0.3\mu\text{m}$ ,  $\text{SiO}_2$  thickness -  $30\text{\AA}$  and the concentration of charge carriers (electrons) in silicon  $(1-5)\times 10^{15}\text{cm}^{-3}$  (Fig. 21).

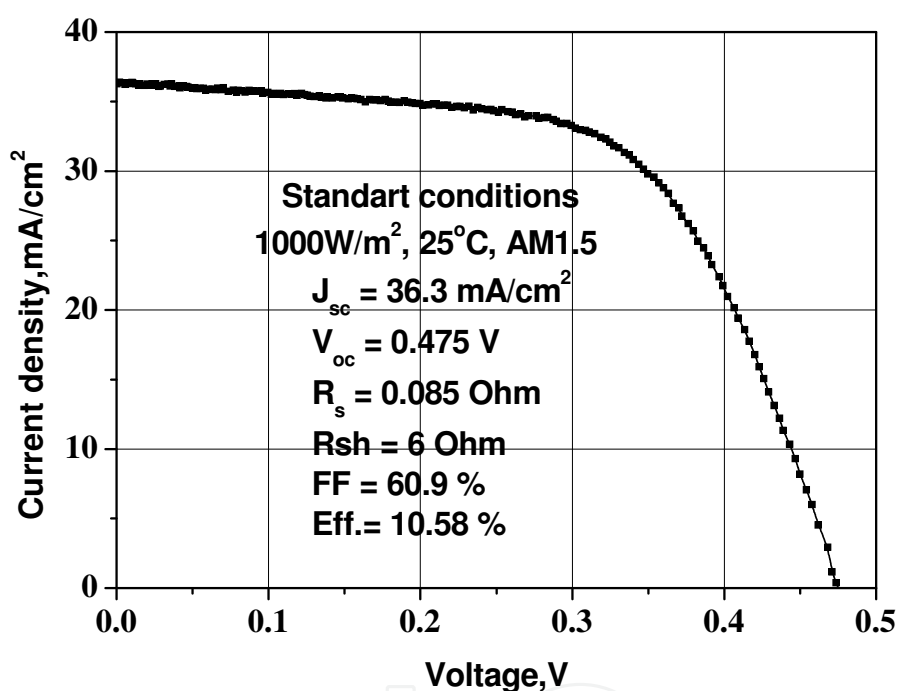


Fig. 21. Load I-V characteristic of the  $\text{n}^+\text{ITO-SiO}_2\text{-nSi}$  cells with active area  $8.1\text{cm}^2$  and BSF region at rear surface.

The developed technology demonstrates the viability of manufacturing solar cells based on  $\text{n}^+\text{ITO}/\text{SiO}_2/\text{nSi}$  junctions by assembling two 15W and two 30W power solar panels (Fig. 22) (Usatii, 2011).

## 5. Bifacial $\text{n}^+\text{Si}/\text{nSi}/\text{SiO}_2/\text{n}^+\text{ITO}$ solar cells

For the first time BSC that are able to convert the solar radiation incident of both sides of the cell into electric power have been produced and investigated fifty years ago (Mori, 1960). This type of SC has potential advantages over traditional monofacial SC. First, there is the possibility of producing more electric power due to the absorption of solar energy by the frontal and rear sides of the device, next, they do not have a continuous metallic rear contact, therefore they are transparent to the infrared radiation, which warms

the monofacial SC and reduces their efficiency. As was presented in (Cuevas, 2005), different types of BSC have been fabricated since then, but all those BSC are based on p-n junctions fabricated by impurity diffusion in the silicon wafer. In case of BSF fabrication, these difficulties increase since it is necessary to realize the simultaneous diffusion of different impurities, which have an adverse influence on the silicon properties. Therefore, the problem of protecting the silicon surface from the undesirable impurities appears.



Fig. 22. General view of ITO/nSi photovoltaic converters a) SC with active area 48.6 cm<sup>2</sup>, b) solar modules with different power

A novel type of BSC formed only by isotype junctions was proposed in (Simashkevich et al., 2007), where the possibility was demonstrated to build BSC on the base of nSi crystals and indium tin oxide mixture (ITO) layers obtained by spraying that contain only homopolar junctions with a n<sup>+</sup>/n/n<sup>+</sup> structure. The utilization of such structures removes a considerable part of the above-mentioned problems of BSC fabrication because a single diffusion process is carried out.

### 5.1 Fabrication and characterization of n<sup>+</sup>ITO/SiO<sub>2</sub>/n/n<sup>+</sup>Si bifacial solar cells

In the work (Simashkevich et al., 2007) the results are presented of producing and investigating the silicon based BSC only on majority carriers. The first frontal junction is a SIS structure formed by an ITO layer deposited on the surface of n-type silicon crystal. The starting material is an n-type doped (0.7–4.5 Ohm·cm) single crystalline (100) oriented Cz-Silicon 375 μm thick nSi wafer with the diameter of 4 inches. The electron concentrations were 10<sup>15</sup> cm<sup>-3</sup> - 10<sup>17</sup> cm<sup>-3</sup>.

An usual BSF structure consisting of a highly doped nSi layer obtained by phosphorus diffusion was fabricated on the topside of the wafer by a diffusion process starting from POCl<sub>3</sub> gas mixture. The rear n/n<sup>+</sup> junction formation ends with a wet chemical etching of POCl<sub>3</sub> residual in a 10 % HF bath. A junction depth of 1 μm has been chosen in order to minimize recombination.

To reduce the surface recombination velocity the wafers have been thermally oxidized at a temperature of 850°C. Grids obtained by Cu evaporation in vacuum were deposited on the

frontal and back surfaces for BSC fabrication. The schematic view of the bifacial ITO/nSi solar cell is presented in Fig. 23.

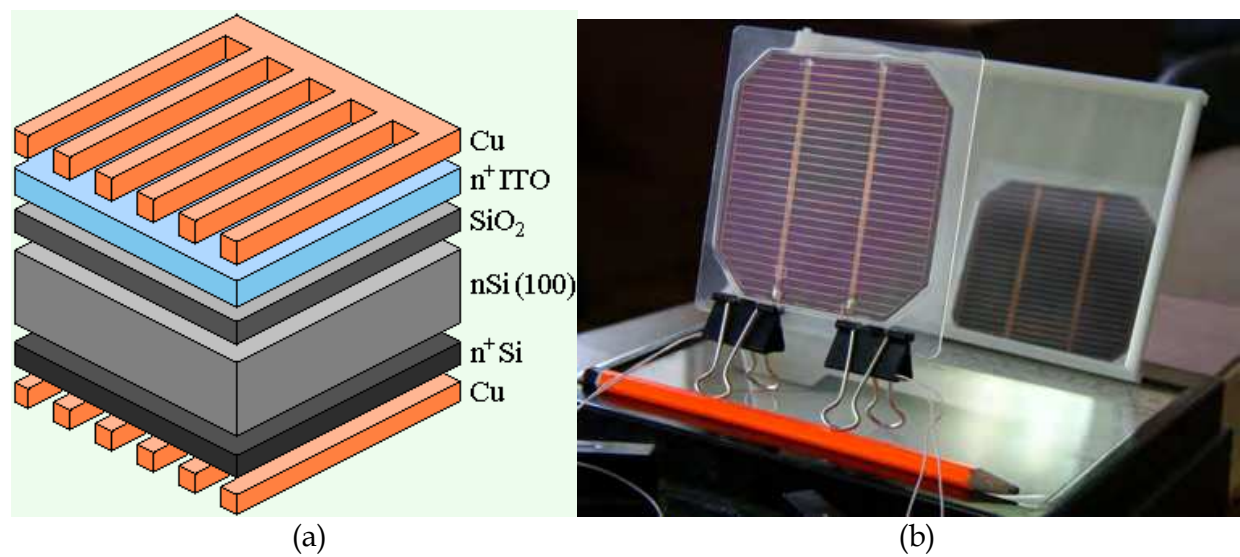


Fig. 23. The schematic a) and real b) view of the ITO/nSi BSC

The spectral distribution of the quantum efficiency of BSC, obtained on silicon wafers with different electron concentration, has been studied at frontal and back illumination (Fig.24). With the frontal illumination, in the region of the wavelengths from 400nm to 870nm the value of QY changes in the limits 0.65–0.95. With the back illumination, QY is equal to 0.6–0.8 in the same region of the spectrum (Bruk et al., 2009).

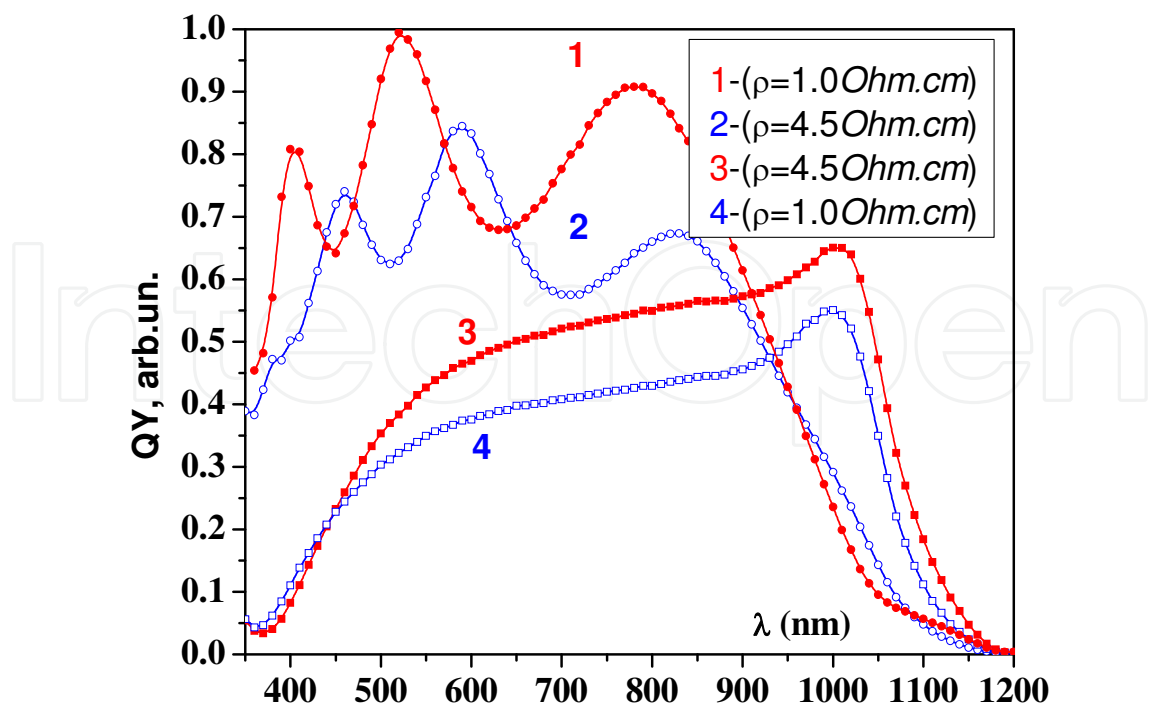


Fig. 24. Spectral distribution of the quantum efficiency 1, 2-frontal illumination; 3, 4-rear illumination

The I-V load characteristics at AM1.5 spectral distribution and 1000W/m<sup>2</sup> illumination are presented in Fig.25.

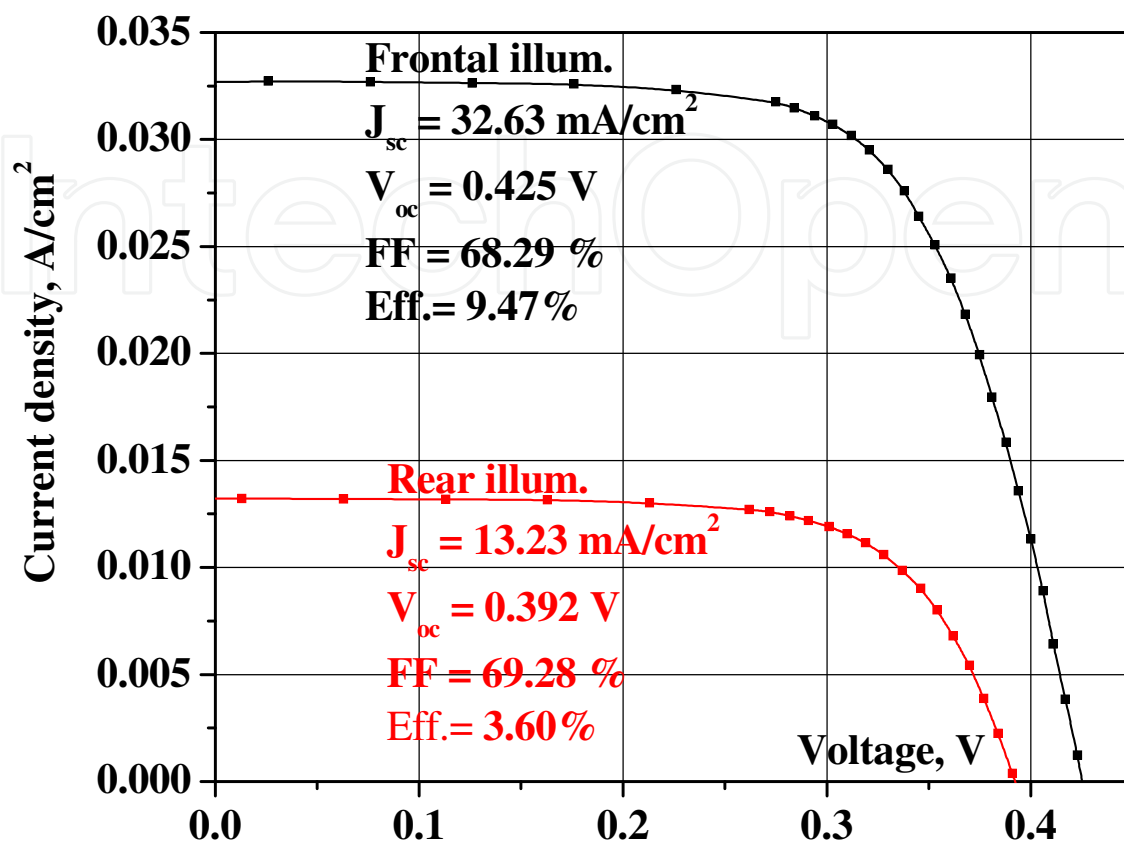


Fig. 25. The I-V load characteristics and the photoelectric parameters of the elaborated BSC at AM1.5 spectral distribution and 1000W/m<sup>2</sup> illumination

The photoelectric parameters of the elaborated BSC have been determined in standard AM1,5 conditions: for the frontal side  $V_{oc}=0.425V$ ,  $J_{sc}=32.63mA/cm^2$ ,  $FF=68.29\%$ ,  $Eff.=9.47\%$ ,  $R_{ser}=2.08\Omega$ ,  $R_{sh}=6.7 \cdot 10^3\Omega$ ; for the back side  $V_{oc}=0.392V$ ,  $J_{sc}=13.23mA/cm^2$ ,  $FF=69.28\%$ ,  $Eff.=3.6\%$ ,  $R_{ser}=3.40\Omega$ ,  $R_{sh}=1.26 \cdot 10^4\Omega$ .

The summary efficiency of the BSC is equal to 13.07%.

## 5.2 n<sup>+</sup>ITO/SiO<sub>2</sub>/n/n<sup>+</sup>Si bifacial solar cells with textured surface of Si crystals

Using the method of n<sup>+</sup>ITO/SiO<sub>2</sub>/n/n<sup>+</sup>Si bifacial solar cells fabrication described in (Simashkevich et al., 2007) with improved parameters in conformity with p.2 of this communication, in (Simashkevich et al., 2011) two types of bifacial solar cells have been obtained which have different profiles of silicon wafer surface (Fig. 26 and Fig. 27).

It is seen from these data that the effected technology optimization allows to increase of the summary efficiency from 13.07% to 15.73% in the case of irregular etching of the silicon surface and to 20.89% in the case of regular etching. The bifaciality ratio also increases from 0.38 up to 0.75.

On the basis of physical parameters of the silicon wafer, ITO layers and of the results of our experiments, the energy band diagram of the n<sup>+</sup>Si/nSi/SiO<sub>2</sub>/n<sup>+</sup>ITO structure was proposed (Simashkevich et al., 2007).



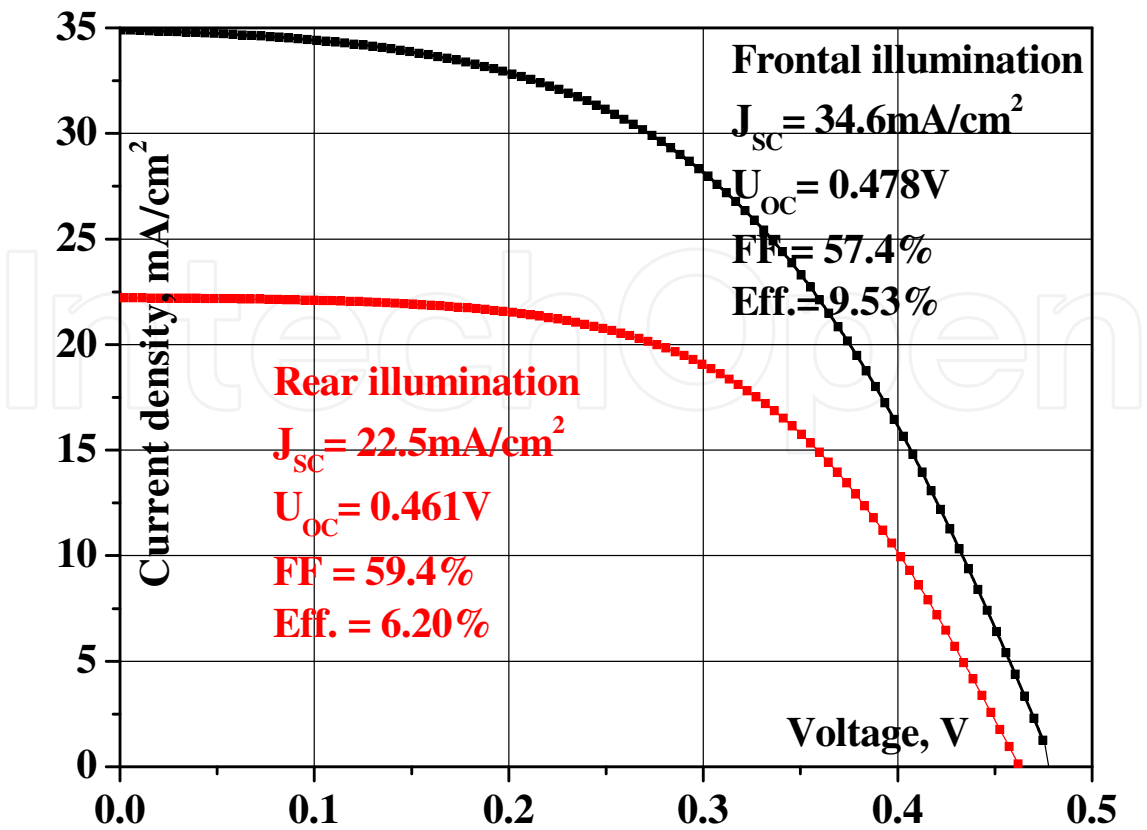


Fig. 26. Load I-V characteristic of n<sup>+</sup>ITO/SiO<sub>2</sub>/n/n<sup>+</sup>Si BSC with irregular Si surface

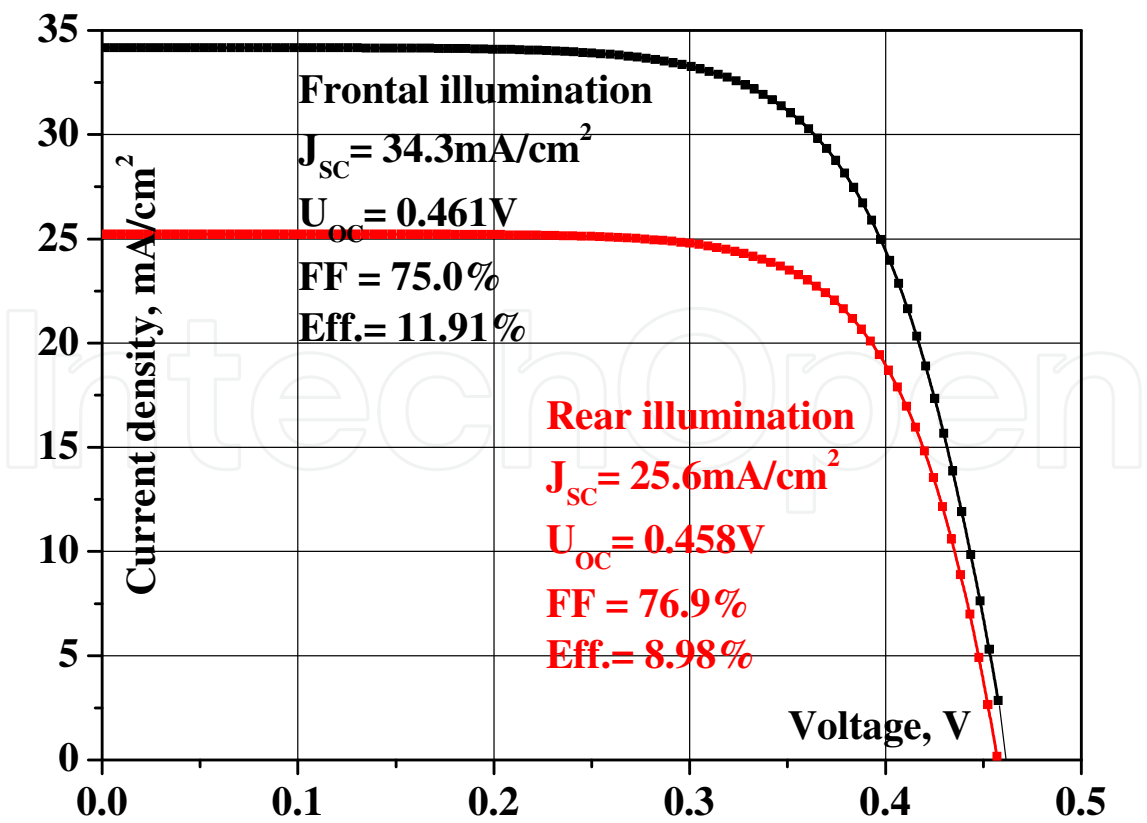


Fig. 27. Load I-V characteristic of n<sup>+</sup>ITO/SiO<sub>2</sub>/n/n<sup>+</sup>Si BSC with regular Si surface

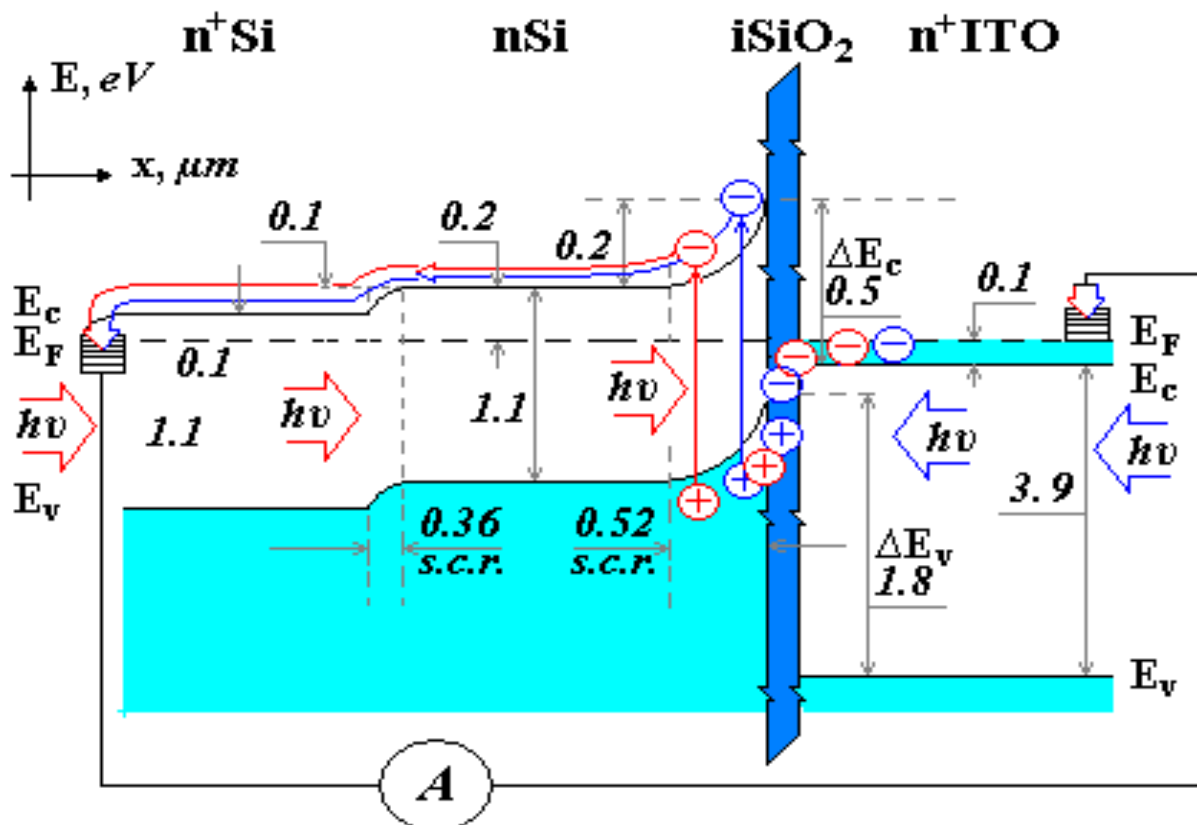


Fig. 28. Energy band diagram of the bifacial Cu/n+ITO/SiO<sub>2</sub>/nSi/n+Si/Cu structure

Fig. 28 shows this energy band diagram at illumination in the short-circuit regime. At the illumination through the frontal contact, the solar radiation is absorbed in the silicon wafer. The light generated carriers are separated by the nSi/SiO<sub>2</sub>/ITO junction. The BSF of the n+Si/nSi junction facilitate the transport of the carriers to the back contact. The same processes take place at the illumination through the rear contact.

## 6. Conclusion

SC fabricated on the basis of semiconductor-insulator-semiconductor structures, obtained by deposition of TCO films on the surface of different semiconductor solar materials (Si, InP, CdTe etc) are promising devices for solar energy conversion due to the simplicity of their fabrication and relatively low cost. One of the main advantages of SIS based SC is the elimination of the high temperature diffusion process from the technological chain, which is necessary for obtaining p-n junctions, the maximum temperature at the SIS structure fabrication being not higher than 450°C. The TCO films can be deposited by a variety of techniques among which the spray deposition method is particularly attractive since it is simple, relatively fast and vacuum less. Between different TCO materials, the ITO layers are the most suitable for the fabrication of SIS structures based solar cells.

Silicon remains the most utilized absorbing semiconductor material for fabrication by spray pyrolysis of such type of SC. The maximum efficiency of ITO/nSi SC is 10-12%, but in the case of textured surface of Si crystals the efficiency reaches more than 15%. ITO/nSi SC with enlarged area up to 48 cm<sup>2</sup> have been obtained by the spray method, the efficiency is 10.58% for cells with area of 8.1cm<sup>2</sup>.

InP based SIS structures fabricated by deposition of ITO layers onto pInP crystal surfaces have high efficiencies, at the same time they are more simple to fabricate in comparison with diffusion junction cells. The efficiency of ITO/InP solar cells obtained by spray pyrolysis depends on the crystallographic orientation of the InP wafers, The maximum efficiency of 11.6% was obtained in the case of fabrication of ITO/pInP/p<sup>+</sup>InP structures using InP wafers oriented in the (110) plane. ITO/InP SC, obtained by spray pyrolysis demonstrates radiation stability. After the irradiation of ITO/InP solar cells with an integral proton flux of  $10^{13}\text{cm}^{-2}$ , their efficiency decreases by 26%, that is less than in the case of Si and GaAs based solar cells.

A new type of bifacial solar cells n<sup>+</sup>Si/nSi/SiO<sub>2</sub>/n<sup>+</sup>ITO based only on isotype junctions was elaborated and fabricated. It was demonstrated that the simultaneous illumination of both frontal and rear surfaces of the structures allow to obtain a summary current. The technological process of manufacturing such solar cells does not require sophisticated equipment. Bifacial solar cells with summary efficiency of 21% and 65% bifaciality coefficient have been obtained using as an absorbent material of single crystalline silicon with a textured surface.

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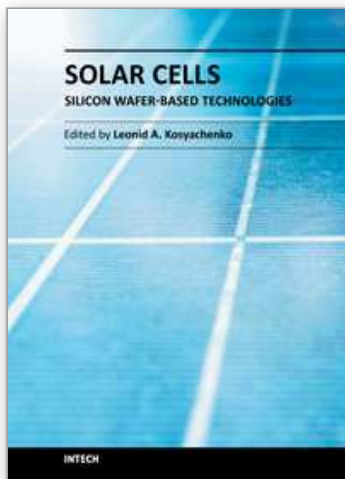
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The third book of four-volume edition of 'Solar Cells' is devoted to solar cells based on silicon wafers, i.e., the main material used in today's photovoltaics. The volume includes the chapters that present new results of research aimed to improve efficiency, to reduce consumption of materials and to lower cost of wafer-based silicon solar cells as well as new methods of research and testing of the devices. Light trapping design in c-Si and mc-Si solar cells, solar-energy conversion as a function of the geometric-concentration factor, design criteria for spacecraft solar arrays are considered in several chapters. A system for the micrometric characterization of solar cells, for identifying the electrical parameters of PV solar generators, a new model for extracting the physical parameters of solar cells, LBIC method for characterization of solar cells, non-idealities in the I-V characteristic of the PV generators are discussed in other chapters of the volume.

### **How to reference**

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