EFFICIENT LOW-COST SOLAR CELLS BASED ON ITO–*n*Si

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Abstract

A vapor phase pyrolysis deposition (VPPD) method has been described in [1] and applied to prepare indium tin oxide (ITO) thin films with thicknesses about 400 nm, with a conductivity of $8.3 \cdot 10^3\ \Omega^{-1}\ cm^{-1}$, and a transparency of 80% in the visible spectral range. The layers have been deposited on the (100) surface of the *n*-type Si wafers with a concentration of $10^{15}\ cm^{-3}$, and their morphology has been examined. The as-deposited ITO thin films consist of crystallites with a height of 300–400 nm and a width of 100–200 nm. Properties of low-cost Cu/ITO/SiO_2/*n*-Si/n^+Si/Cu solar cells fabricated by depositing ITO layers on *n*-Si wafers have been studied. The maximum efficiency has been found to be 13.8%.

1. Introduction

Today, an optimum way of a direct conversion of solar energy into electricity is to resort to solar cell (SC) devices. This approach is an ecologically friendly method of using renewable energy sources. However, a widespread application of photovoltaic converters is hampered by their relatively high cost. To solve this problem, it is necessary to develop methods based on easier-preparation processes at lower temperatures compared to those in the manufacturing conventional photovoltaic devices based on *p-n* junctions. One of these methods is the utilization of SC based on semiconductor–insulator–semiconductor (SIS) structures, which can be easily implemented by the deposition of a transparent conductive oxide (TCO) layer on the surface of "solar" semiconductors. A thin insulator layer at the oxide–semiconductor interface is mostly formed during the TCO deposition for which a variety of techniques are applied. Among them, the spray pyrolysis deposition method is of a particular interest due to its simplicity, moderate preparation temperatures, high deposition rates, and vacuum-less conditions [2]. The TCO films with a band gap on the order of 3.3–4.5 eV are transparent in the entire region of the solar spectrum, including the blue and ultraviolet regions. In SC the TCO layer contributes also to the collection of separated charge carriers and, at the same time, it acts as an antireflection coating. In the SC fabrication, the most frequently used TCO materials are tin dioxide (SnO_2), indium oxide (In_2O_3), and their mixture known as indium tin oxide (ITO). Namely, ITO thin films have been applied for the first time for the preparation of Si-based SIS structures [3]. A detailed review of the development of the SC based on ITO/*n*-Si structures is presented in [4]. The theoretical analysis of energy losses in ITO/*n*-Si based SC has shown that their conversion efficiency depends on the thickness and structure of the insulating layer at the TCO–semiconductor interface as well as on the substrate doping level, concentration of surface states, oxide electric charge, and temperature. The optimization of these parameters could result in a device efficiency of about 20% [5]. However, the reported efficiencies do not exceed 13% [4].

The aim of the present work is to study the structure of the ITO–Si interface, increase the conversion efficiency of Si-based SIS solar cells with the ITO thin film transparent emitter, and simplify the fabrication process for obtaining low-cost Cu/ITO/SiO_2/*n*-Si/n^+Si/Cu solar cells with an efficiency close to 14%.

2. Experimental

2.1. Preparation of ITO thin films and ITO/n-Si structures

ITO thin films were deposited at 450°C on the *n*-Si (100) wafer surface by spraying an ethanol solution of $InCl_3$ and $SnCl_4$ in a ratio of 10:1 using compressed oxygen. The following chemical reactions take place on the heated substrate:

- $4InCl_3 + 3O_2 = 2In_2O_3 + 6Cl_2$
- $SnCl_4 + O_2 = SnO_2 + 2Cl_2$ (1)

In our earlier studies, ITO thin films were deposited in a setup using direct spray pyrolysis [6]. In the present work, the ITO layers were prepared by a specially developed Vapor Phase Pyrolysis Deposition (VPPD) method for a conformal coverage of the Si wafer surface. The VPPD technique was implemented by upgrading the spray pyrolysis setup presented in [7]. A special emphasis was made on a further development of the spray pyrolysis deposition method in order to obtain a more refined aerosol with the properties of a vapor flux. In the proposed VPPD setup (Fig. 1), the solution is sprayed first into a glass tube with a labyrinth of obstacles for a better dispersion and purification from large size droplets. Hence, a flux of solution vapors, rather than a flux of dispersed droplets, comes on the substrate surface. In addition, the vapor flow is in a wider range and can be better controlled. Polycrystalline ITO films with a columnar structure of the ITO crystallites were obtained. The crystallites show a width of 100–200 nm and a height of up to 400 nm, being thus comparable with the film thickness.

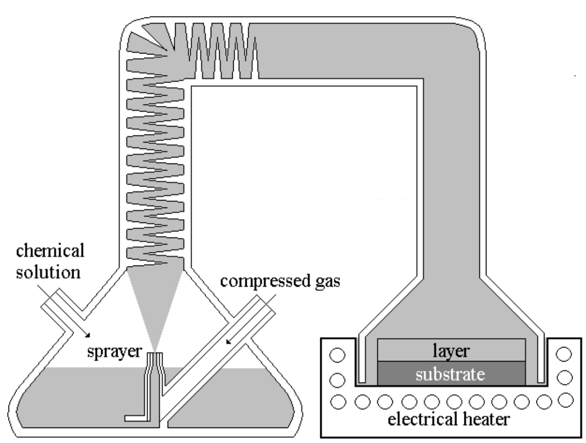
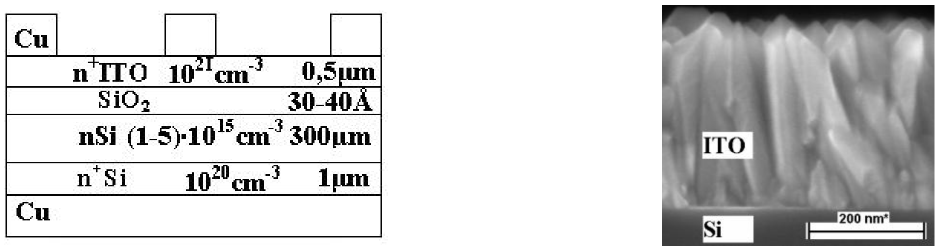


Fig. 1. Schematic drawing of the VPPD setup.



(a) (b)

Fig. 2. (a) Schematic image of the fabricated ITO/SiO_x /nSi and **(b)** its cross section

For ITO layers deposition and ITO/*n*-Si structure obtaining, *n*-Si (100) oriented wafers with a resistivity of 4.5 Ω cm were used as substrates. The surface treatment of silicon wafers (in all cases, it was the polished side of the plate) was carried out, without the traditional RCA treatment, in the following sequence: degreasing with a NH_3 solution heated to 70–80°C: H_2O_2:H_2O (1 : 1 : 8) for 15–20 min; processing in hydrofluoric acid for 2 min; rinsing in distilled water and holding at a temperature of 450°C for 10 min immediately prior to the ITO deposition. The as-obtained ITO/*n*-Si structure was the base for the SC fabrication, which ends by the deposition of a Cu grid contact on the front side of the SC and a Cu continuous contact on their rear side. The schematic image of the fabricated Cu/ITO/SiO_2/*n*-Si/n^+Si/Cu solar cell and the cross section of this structure are presented in Figs. 2a and 2b, respectively. The thicknesses of their component layers and the values of the substrate electrical parameters are also presented there.

It should be noted that the spray pyrolysis is a non-vacuum low temperature method for ITO layers deposition, which can be considered as a promising approach for the low-cost effective processing of SC based on ITO/*n*-type Si structures. To achieve this goal, it is necessary to determine and adjust the optimum preparation parameters of the ITO layer, the thickness of the insulator SiO_2 layer and, especially, the Si wafer surface state.

The thickness of the front ITO layer can be adjusted for an antireflection condition coating. At the same time, it should be taken into account that the thickness of this layer determines its electrical resistance and therefore affects the magnitude of the photocurrent. High values of open circuit voltage and conversion efficiency may be achieved by the formation of a SiO_2 insulator layer with the thickness allowing obtaining a maximum potential barrier height and a minimum saturation current at the ITO/Si interface. At the same time, the SiO_2 insulator layer must be tunnel transparent for the charge carrier transport; therefore, the optimal SiO_2 layer thickness must not exceed a few tens of Angstrom. In addition, it is also necessary to select the optimal Si wafer thickness for a better match to the carrier collection length.

2.2. Characterization methods

The crystallographic structure of the ITO thin-films was studied by X-ray diffraction using an X‘PERT-MPD (Philips) diffractometer using CuK_α radiation (1.5405 Å). The K_β component was eliminated by using a Ni filter. The morphology of the ITO layers was investigated by scanning electron microscopy (SEM) using a TESCAN VEGA microscope. The chemical composition of the films was studied in the same SEM microscope by an integrated

INCA energy dispersive X-ray EDX analysis system. Measurements of the thickness and surface morphology of SiO_2 films were performed using a scanning probe microscope (SPM) and an atomic force microscope (NTEGRA Aura, NT-MDT).

Photovoltaic parameters of the SC devices, i.e., short-circuit current density (J_{sc}), open-circuit voltage (U_{oc}), fill factor (FF), and efficiency (Eff.) were determined from the illuminated current–voltage characteristics under standard test conditions. The simulated sunlight was obtained using a Telecom STV sun tester with a Philips 1000W Xe arc-lamp and an AM1.5 filter. The light source was calibrated to 100 mW/cm^2 using a calibration cell.

3. Properties of ITO–*n*Si heterostructures

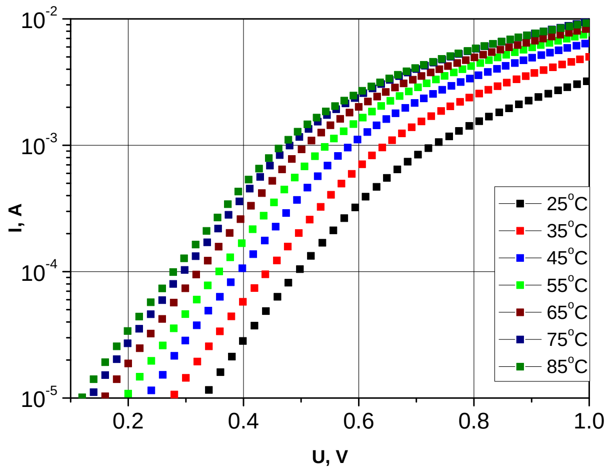
3.1. Electrical properties

In all types of heterostructures, the mechanism of charge carrier transport through a barrier strongly depends on the interface status, which, in its turn, is determined by the chemical and thermal treatment of contacting surfaces of semiconductor materials. In particular, in the case of structures of the type oxide semiconductor/semiconductor, for example, ITO/*n*-Si, the quality of the interface is heavily dependent on the surface state of the silicon wafer. Before the ITO layer deposition, the Si surface could be degreased and etched, as described in [8], or without etching, as in the present paper. Dark current–voltage characteristics in a temperature range of 293–413 K have been studied in both cases. The general behavior of the *I–U* curves of directly biased devices investigated in [8] is characterized by the presence of two straight-line regions with different slopes. In the first region, at external voltages lower than 0.3 V, the *I–U* curves are parallel; that is, their slope is constant. In this way, 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 multistep tunnel recombination transitions of electrons from the silicon conduction band into the ITO conduction band. For structures without etching Si surface, which are studied in the present paper, Fig. 3a shows that, for the samples of the same type at the applied voltages corresponding to the straightening of the band and the disappearance of the potential barrier, the slopes of the *I–U* dependences do not differ. The mechanism of the charge carrier transport through the barrier corresponds to the model [9], according to which the transfer of charge carriers is the tunneling through the potential barrier and recombination transitions in the space charge region. Thus, the current–voltage characteristic can be described by the following equation:

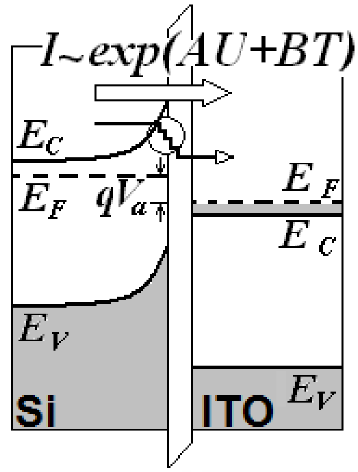
$$I = I_o \exp(AU) \exp(BT) \tag{2}$$

where *A* and *B* are constants independent of voltage and temperature, respectively.
The values of factors *A* and *B* calculated for the curves presented in Fig. 3a in the case of voltages less than 0. 6 V are 14 V^{-1} and 0.05 K^{-1}, respectively.

In this case, the feature of the mechanism does not correspond to the charge carrier transport over the barrier. The observed fact can be explained by the presence of a thin oxide layer at the ITO/Si interface obtained on the silicon surface during the manufacture of the structures (Fig. 3b).



(a)



(b)

Fig. 3. (a) Dark *I–U* characteristics (low-temperature anneals) and **(b)** band diagram of ITO/*n*-Si heterostructures.

The mechanism of the charge carrier transport through the barrier for the ITO/Si heterostructures obtained by ITO layers deposition on non-etched Si wafers surface corresponds to the mechanism from the first region of ITO/*n*-Si structures obtained in [8].

At voltages higher than the diffusion potential of 0.6 V, the current flow for all types of samples is determined by the Ohm law.

3.2. Photoelectrical properties

The photoresponse of these structures (see Fig. 4) was observed in the energy range corresponding to the energy values of the widths of the silicon and ITO bands gap.

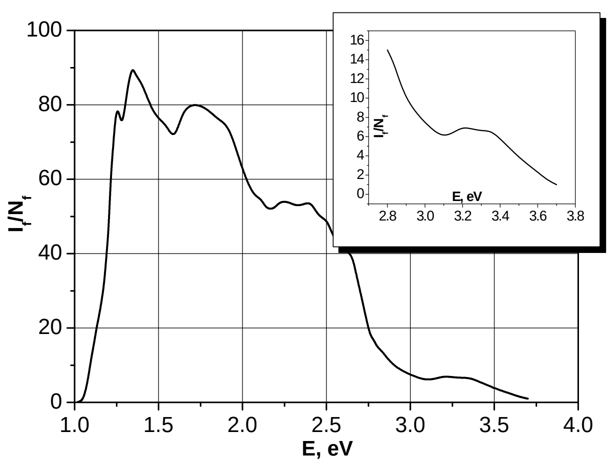


Fig. 4. Spectral distribution of photosensitivity of Cu/ITO/SiO_2/*n*-Si/n^+Si/Cu structures.

In fact, the energy of the incident light flux higher than 1 eV leads to the beginning of light absorption in silicon and the generation of electron–hole pairs. The pairs are separated by the junction electric field; as a result, the appearance of an electrical signal is observed. At the luminous flux of energy of 3.7 eV, when the light is already absorbed in a very narrow layer near the frontal surface in ITO, the photoresponse disappears due to an intense recombination of nonequilibrium charge carriers. The insert in Fig. 4 shows an enhanced photosensitivity of Cu/ITO/SiO_2/*n*-Si/n^+Si/Cu photovoltaic cells in the ultraviolet region of the spectrum.

The load *I–U* characteristics of the obtained Cu/ITO/SiO_2/*n*-Si/n^+Si/Cu solar cells measured in different radiation power (*W*) conditions in a range of 100–1000 W/m^2 are presented in Fig. 5. From these data, the dependences of short-circuit current I_{sc} and open-circuit voltage U_{oc} on the radiation power values has been calculated. A linear $I_{sc} = f(W)$ dependence and a logarithmic $U_{oc}= f(W)$ dependence were found, which is typical for all *p–n* junctions.

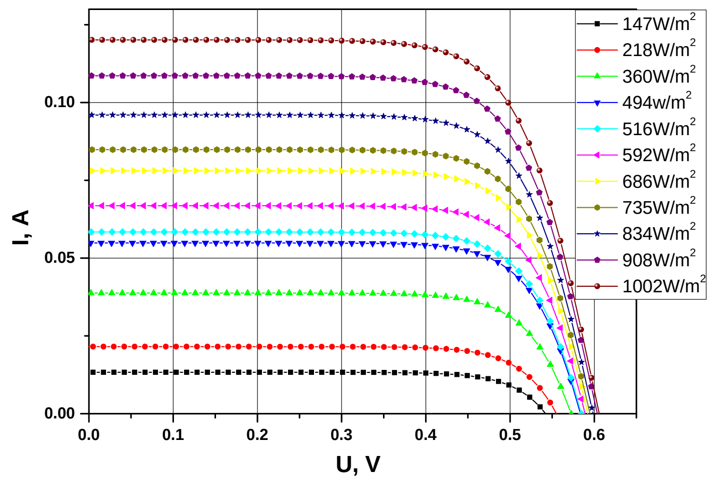


Fig. 5. Load *I–U* characteristics of Cu/ITO/SiO_2/*n*-Si/n^+Si/Cu SC under different radiation power conditions.

It is clear from Fig. 5 that, at 147 W/m^2, the following photoelectrical parameters values were obtained: short-circuit current density of 3.59 mA/cm^2, open-circuit voltage of 541 mV, fill factor of 0.76, and efficiency of 10.06%. An increase in *W* to 1000 W/m^2 leads to the following values: short-circuit current density of 32.46 mA/cm^2, open-circuit voltage of 606 mV, fill factor of 0.70, and efficiency of 13.80%. These data have been obtained for a cell with an active area of 6 cm^2.

4. Conclusions

(1) Technological conditions for non-vacuum manufacturing of MIS type efficient low-cost Cu/ITO/SiO_2/*n*-Si/n^+Si/Cu solar cells have been elaborated. Photovoltaic devices with efficiencies of up to 14% have been fabricated using the VPPD method.
(2) It has been found that the most effective Cu/ITO/SiO_2/*n*-Si/n^+Si/Cu solar cells are obtained without etching the silicon substrates oriented in the (100) plane in HNO_3 : HF.
(3) The spectral distribution of the photosensitivity of ITO/SiO_2/*n*-Si structures covers a wide range of energies (1.1–3.7 eV), particularly the ultraviolet range of the spectrum of solar radiation.

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