Application of Embedded Metal Nanostructures for Solar Cells

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Abstract: - Thin island metal films embedded in the p-n semiconductor junction of a photovoltaic structure enable significantly change their efficiency. A type of metal defines this change. In this work we present our results of experimental trials of creation photovoltaic heterostructures ITO/C-Si with thin metal films embedded into the semiconductor junction. We applied such metals as gold and silver which can appear the localized surface plasmon resonance effects, when the islet dimensions are several nanometers. We found that the gold nanoparticle significantly improves the photovoltaic conversion efficiency when the silver nanoparticles prevent the photocurrent generation. Generated photo-power in the samples with embedded gold island films was more to approximately 10 times than without this interlayer. All metal island films and ITO emitter films were prepared using low-pressure triode dc sputtering system.

Key-Words: Metal island films, Localized surface plasmon-polariton, Diode Schottky, Solar cells

1 Introduction

The efficiency of photovoltaic (PV) converters is limited due too high electrical and optical losses [1]. One of the most determining factors of optical losses is the luminescence or radiative recombination which further restricts the possible efficiency [2]. The fact is, each absorbed photon can excite only one pair of charged particles, an electron and a hole. Thus, in order to significantly increase the efficiency of solar cells, it is necessary to increase the number of charged particles that are generated by absorption of a photon. A way to increase a number of electrons excited by light is application of metal nanoparticles capable to form a localized surface plasmon resonance [3] or SPR. It is known that the photon absorbed by a gold particle excites an ensemble of charged carriers, electrons and holes, due to polarization of the particle [4]. Thus, the SPR can be considered as a source of additional electrons obtained by absorption of "hot" or high-energy photons.

Inside a p-n junction of the diode photovoltaic structure there is a high-strength built-in electric field. The gold nano-particles imbedded into the silicon p-n junction will be under influence of this electric field. Such as the gold has a work function greater than the work function of the silicon, each of gold nano-particles forms a Schottky contact with the n-type silicon and an Ohmic contact with the ptype silicon. Thus, all gold particles embedded into the p-n junction form a set of forward-biased nanodiodes Schottky which are in the injection mode. Under solar irradiation these nano-diodes should inject additional electrons, excited in the gold nanoparticles, in the conductive band of the silicon and additional free holes in the valence band of the silicon [5].

One of approaches to build cheaper and more efficient PV structures is to use the heterostructures instead of p-n junctions built from the same material. By this way, one can eliminate from the technological chain such processes as ion implantation or diffusion. Thus, in the PV structures based on application of p-type silicon wafers, an ntype silicon emitter, prepared by ion implantation, diffusion or atomic layer epitaxy, may be changed on the another semiconductor layer with defined electron concentration. Typical examples for such structures are n-ZnS/p-Si and n-ZnS:Al/p-Si heterojunction [6]. ITO/A-SI:H/SI or heterostructure [7]. Here, the ITO (In2O3-SnO2) layer was used as an emitter on the PV heterostructure.

The goal of this work is to investigate possibility to improve an efficiency of the PV structure using thin island metal film. Here, we present the results of our experimental trials.

2 Experimental Details

Metal island thin films and ITO emitter coatings were deposited by a triode sputtering method in the low-pressure plasma discharge [8]. The ITO sputtering target was made of indium oxide and tin oxide in the ratio In_2O_3 :SnO₂ = 90:10. Aluminum electrodes were prepared by vacuum evaporation method. The photovoltaic structures were prepared on the (100) surface of the single-crystalline p-type silicon substrates with resistivity of ~5-9 Ω ·cm. The glass slides were applied as witness substrates to measure and study the optical properties of grown thin films. Each deposition of metal and ITO thin films was provided on both silicon and glass substrates. Figure 1 represents a side view of the grown thin film structure. We used gold and silver island thin films to produce the plasmon resonance under light irradiation.



Fig. 1 Experimental PV structure.

External view of the prepared samples is shown in figure 2. The sample represents a multilayer system grown on the single-crystalline substrate of p-type. The front surface of the substrate is coated in series by gold island interlayer with approximate thickness of 2 nm and transparent conductive In_2O_3 -SnO₂ (ITO) thin film with rough thickness of 200 nm. A sheet resistance of Au, Ag, and ITO films was measured using a standard 4-point method. Optical characterization of all films was done at wavelength of 200-1100 nm using the UV-2800 UV/VIS spectrophotometer of UNICO. The surface structure was studied using the SPM DI300 in AFM contact mode the computerized metallurgical and microscope "Nicon-Optiphot 100" with optical magnification of up to $\times 1600$.



Fig. 2 External view of the PV sample.

In order to compare the influence of metal islands imbedded into the semiconductor junction of solar cell on their parameters, we prepared a series of the same pairs of samples. In the pair, one of the samples was prepared with gold or silver island film, and the second one was built without a metal film. All the rest of parameters of the samples remained the same. To obtain the I-V and P-V characteristics of our PV-structures, they were measured at the same conditions at constant temperature of 20° C under illumination of an incandescent lamp (its radiation spectrum significantly biased in the IR range) on the distance of 10 cm providing maximum light intensity of ~1800 Lx that relates to approximately 15 W/m^2 .

3 Results and Discussion

Figure 3 represents the transmittance spectra measured on thin gold and silver island films. Also, the spectrum of pure glass substrate presented here.



Fig. 3 Transmittance spectra of island metal thin films.

As shown, both gold and silver films deposited during short time represent the large absorption peaks situated through visible part of spectrum. These peaks characterize arising the plasmon behaviour of electrons in the thin metal islands. The thicker films deposited by this method not show such absorption peak since the localized plasmonpolaritons disappear in the coalescing films [9]. Deepness, largeness and location of absorption peaks fully defined by the material of metal, and shape and dimensions of islands. Our thin metal films were non-continuous and they were consisted of disks with diameter of 12-14 nm and height of 2-3 nm. Their sheet resistance is sufficient high. These films were embedded into the p-n junction formed by ITO thin film deposited on the silicon surface. Figure 4 represents the AFM 3D topography of thin island gold film with thickness of 2-3 nm. This film consists of islands regularly distributed on the substrate surface and contains approximately 30 islands on the area of 100×100 nm². Silver island films look the same.



Fig. 4 AFM image of the gold film of 2 nm thick on the glass substrate.

Figure 5 represents the transmittance characteristics of ITO thin films of different thickness on glass.



Fig. 5 Transmittance characteristics of ITO thin films of different thickness.

All these films present interferential behaviour. We applied the films with the sheet resistance of 36 $k\Omega/sq$ for preparation the emitters in the photovoltaic structures. All these films have good transmittance in the visual spectrum.

The I-V characteristics were measured using a variable load resistor. The load resistance was

varied in the interval from 1 Ω up to 900 Ω . Figure 6 and 7 present I-V characteristics measured for samples with two different structures: (a) Al/ITO/Si/Al and (b) Al/ITO/Au/Si/Al. The P-V characteristics were calculated on the base of measured I-V characteristics.

As shown in figures 6 and 7, the generated power in the structure with embedded gold interlayer is in 10 times more than in the structure without it. In the samples with gold interlayer, the metal islands form different types of contact with emitter and base of the P/N structure.



Fig. 6 I-V and PV characteristics of the Al/ITO/Si/Al photovoltaic structure.



Fig. 7 I-V and PV characteristics of the Al/ITO/Au/Si/Al photovoltaic structure.

As known, the type of contact depends on the type of semiconductor, P or N, and the difference between the work functions between contacting materials [10]. The work function of the gold is higher than the work function of the ITO. Therefore, the gold islands create Schottky contacts with the emitter and Ohmic contacts with the base of the diode P/N structure. At the same time, a natural high-strength electrical field is built-in in this P/N junction and our Schottky nano-diodes are undergo high electrical field. On the other hand, a light irradiation of the grown thin-film gold islands generates localized SPR inside the gold particles in the visible range of light. Under the built-in electrical field, the directly biased nano-diodes Schottky emit their excited additional electrons in the conducting band and the holes in the valence band of the P/N structure. This way, we obtain a significant increase in the short-circuit current and open circuit voltage of the device.

We tried illustrate this increasing by using the schematic energy band diagram. To create this diagram, we parameters of applied materials shown in the table 1. Here are the reference data and our measured and calculated results.

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Parameter	C-Si	Au	ITO	Source
Work function, φ, eV		5.47		[11]
			4.7	[12]
Mobility, μ, cm ² /V·s	410			[1]
			50	[13]
Bandgap, Eg, eV	1.12			[1]
			3.75	[14]
Relative permittivity, ε_r	11.9			[1]
			3.95	[14]
Electron affinity, χ, eV	4.05			[15]
Film thickness, d, nm		~2	~200	*
Sheet resistance, Ω/sq		1.25M	36k	*
Charge carrier concentration,	$2.5 \cdot 10^{15}$	$5.9 \cdot 10^{22}$	$1.7 \cdot 10^{17}$	**
$n/p, cm^{-3}$				
Depletion width, w, nm	41		570	***

* Our measurements;

** Calculation,
$$n = \frac{1}{q\mu\rho}$$
, cm^{-3} ;
*** Calculation, $w = \sqrt{\frac{2\varepsilon_0\varepsilon_r V_0}{qN_A}}$, cm.

Figure 8 represents the schematic energy diagram built using electrical and optical properties of deposited gold and ITO thin films. Calculation of a built-in potential, V_{0Si} , on the junction Si-Au and V_{0ITO} on the junction Au-In₂O₃ were provided by the same way as it was done by E.M. Nasir [6].



Fig. 8 A schematic energy diagram for the experimental PV cell.

This diagram illustrates the behaviour of p-n heterojunction with embedded gold island film under illumination. As it was mentioned above, the metal (gold) particle with a work function greater than the work function of the emitter ITO layer of ntype and greater than that of p-type base crystalline Si is embedded inside the depletion region with width w. This width is a sum of depletion regions in the ITO-Au contact and in the Au-Si contact: w =w_{Si} + w_{ITO}. Therefore, it forms a Schottky contact with the emitter ITO layer and an Ohmic contact with the base (p-type silicon). This particle is subjected to a strong electric field $E = V_b/w$ produced by the built-in potential, V_b , in the depletion region. Thus, all the gold particles form a set of forward-biased nano-diodes Schottky.

Under solar light irradiation, hv, we seeing two mechanisms of absorption: first one is a usual absorption of the photon in the active part of the solar cell producing one pair electron-hole, second mechanism is an absorption by the gold particle producing localized SPR in gold particles. Excited electrons from the metal particles-islets are injected into the conducting band of the semiconductor due to the resonance energy exceeding the Schottky barrier. These additional electrons will be collected by emitter electrode of the PV cell, thus increase the load current. So, each photon absorbed by the gold particle produces a group of charged carriers due to polarization of the gold and injects them into the conductive (electrons) and valence (holes) bands of the ITO and silicon. Therefore, we obtain the amplification effect or the photon amplifier generating additional charged carriers utilized in the grown structure. Parallel connection of a plurality of nano-diodes Schottky to the silicon p-n junction leads to increase in the voltage generated by the system Using the additional charged carriers generated within the gold particles and injected into the semiconductor environment, we can increase the useful electricity.

It is of interest to compare influence of different metals on the PV cell efficiency.



Fig. 9 Comparison of the short-circuit current in different PV structures.

Figure 9 presents measured short-circuit currents for different PV structures. Here, we compare three different structures: the system with embedded silver island film, the system without an interlayer, and the system with the gold interlayer. Insert in figure 3 illustrates a principal measuring scheme. Firstly, we measured a short-circuit current and an open-circuit voltage generated by grown PVsystems under the same illumination. After that, we measured I-V characteristics by change of loading resistance. As shown in figure 9, the silver layer prevents to the spread of the generated charged carriers and promotes their rapid recombination. We explain this effect by the formation of Ohmic contact between the silver particles and ITO emitter.

4 Conclusion

In this paper, we experimentally investigated the effect of type of interlayer island metal films embedded into the P/N junction on the properties of PV structures. It was shown that non-continuous thin films deposited using sputtering in the triode system realizing the plane plasma discharge of low pressure appear the surface plasmon resonance behavior under illumination at light of visible spectrum. The type of metal films defines a photovoltaic structure behavior. The gold island film prepared by the triode sputtering and embedded

into the P/N junction of the photovoltaic structure has appeared significant increase in the PV cell efficiency.

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