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Research Article

Solar Cells Efficiency Increase Using Thin Metal Island Films

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Metal nanodimension structures have multiple applications in modern technology. Noncontinuous thin island metal films of several types of metals deposited on dielectric or semiconductor surface introduce a unique behavior. In response to light exposure in certain range, the metal islands present a resonant absorption of light accompanied with a collective behavior of free electrons in these islands. In this paper, we present one of the possible ways to increase the efficiency of solar cells with metal islands imbedded in a semiconductor junction. Rough calculation was performed for a silicon solar cell and showed an increase of 17.5% in the overall efficiency of the cell.

1. Introduction

Solar cells, as alternative energy sources, attract much attention in recent decades due to enormous energy obtained by earth from the sun, about 1.2×10^{17} W. Solar cells have the potential to replace fossil fuels as the main means of electric power generation. However, solar cells of all types suffer from two main deficiencies: relatively low conversion efficiency and high cost in comparison with conventional fossil fuel electric sources. The search of ways to reduce fabrication costs and increase efficiency of photovoltaic devices is the main goal of researchers and developers.

Unfortunately, efficiency of solar cells based on semiconductor materials is limited due to high electrical and optical losses [1]. Moreover, the luminescence (radiative) recombination further restricts the possible efficiency; thus, the efficiency of silicon solar cells cannot theoretically exceed 31% [2].

There are several ways to increase efficiency of solar cells. The first one consists in combining semiconductor photovoltaic converters with suitable heat absorbing bodies that is, water or oil for heat them and use this thermal energy. This specific method is already applied in industry. However, this method requires additional capital investments and significant complication of used equipment.

The second method to improve efficiency is based on utilizing various semiconductor materials in order to enlarge the spectral efficiency. Multijunction devices, or heterojunction devices, can reach larger spectral efficiency by capturing different parts of the solar spectrum. A multi-junction device is a stack of individual single-junction cells in descending order of bandgaps. The top cell captures the high-energy photons and passes the rest of the photons on to be absorbed by lower-bandgap cells. Sze has shown [3] that consecutive combination of 36 junctions may attain an ideal efficiency of 72%. The main problems in establishing such PV cells are high technological complexity and high cost, respectively.

The third method we have in mind to increase efficiency is using hot electrons that generate charged carriers with energy that is higher than the semiconductor bandgap. It is known that each photon excites only one electron-hole pair, and the exceeding energy dissipates as heat due to thermalization processes. These processes occur since photons cannot split to two or more particles. However, a "hot" particle may transfer the exceeding energy to other free particles by impact and thus to create another electron-hole pairs. Such chain ionization impact reaction exists in all semiconductors with very low efficiency. However, by this way, efficiency may be increased only using low-dimensional structures such as quantum wells [4], quantum dots [5], or nanocrystals of

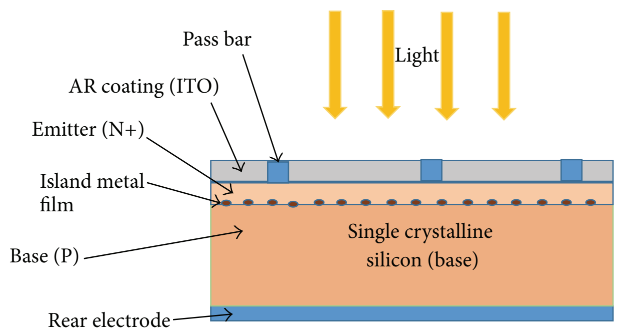


Figure 1: A side view of the proposed PV system.

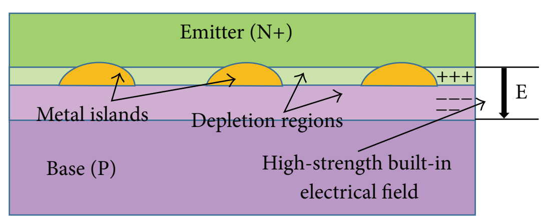


Figure 2: An improved photovoltaic structure.

above 5 nm sizes [6]. Detailed analysis of low dimensional structures that are applicable for the solar light converting was done by Green [7]. It is necessary to take into account that the complication of the semiconductor structure also leads to the SRH (Shockley-Reed-Hall) recombination increase.

Thin metal island films represent another type of low dimensional structures. As known, such thin films built from several types of metals have an interesting property: in response to light exposure in a certain spectral range, in the islands of the metal occurs resonant absorption of light. This phenomenon can be explained by the appearance of localized plasmons-polaritons with intensity and frequency that are relative to the size of islands in the film. The localized surface plasmons represent collective behavior of free electrons confined to the small metal particles. In other words, surface plasmons are coherent fluctuations in electron density, occurring at a "free-electron" metal-dielectric or metal-air interface. Mie theory and Maxwell-Garnet theory explained the surface plasmon resonance (SPR) in terms of higher moment oscillation and particle size [8, 9]. It was found that the width and peak position of the SPR are depending on the particle size, shape, and environment [10, 11]. Thus, the effect of the SPR can be considered as a source of electrons obtained by absorption of fast or high-energy photons. Obviously, this source of electrons should be used in solar cell technology.

The metal nanoparticles are utilized to provide extra scattering in order to increase the efficiency of the photovoltaic cells [12] or for the enhancement of photovoltaic devices [13] by using the surface plasmon resonance within the visible and near-visible spectral range. In this paper, we describe the novel idea of SPR application for increasing solar cells efficiency. When a photon with suitable energy is absorbed by a metal particle, a plasmon polariton arises; that is, conducting electrons in the metal particles are excited and log in resonance. Energy of these excited electrons increases and becomes sufficient for transition to the conducting band of the semiconductor. Thus, each metal island becomes a generator of free electrons confined within the island. Our goal is to create conditions for transition of these additional electrons to the conducting band of the semiconductor.

2. Mechanism of Efficiency Increasing: Qualitative Analysis

Figure 1 presents a side view of our novel photovoltaic (PV) cell. As shown, the PV system looks like a conventional diode structure; a single crystalline base of the device was chosen for simplicity of arguments and calculations. There is only one distinction between usual PV cell and our novel device: an island metal film is imbedded in the interface between base and emitter. The area of the semiconductor in the vicinity of this interface is depleted. Therefore, this area is the most active part of the diode photovoltaic system. The charged carriers generated in the depletion regions are separated by the built-in electrical field and may be used for electric generation. Thus, the electrons injected into this area will be used with maximum efficiency.

A metal island thin film imbedded into the semiconductor P/N structure is shown in Figure 2. The built-in high-strength electrical field inside the depletion zone is shown also. The main criterion for selection of the metal is its ability to generate plasmon-polaritons under light absorption and its energy compatibility with the semiconductor surrounding the metal islets. This criterion limits the range of metals which can be used. It could not be transition metals as the absorption of light in them leads to intraband transition of excited electrons and does not form plasmons [11]. Metals which can be applied are alkali metals, alkaline earth metals, noble metals, and semimetals.

The second criterion for selection of metal is the opportunity to create a Schottky diode in contact with the semiconductor. The second requirement enables us to form a lot of nanodimension Schottky diodes, each of which is served as an additional source of electrons. For this purpose, the work functions of metal and semiconductor must satisfy the following relation:

$$\emptyset_M - \emptyset_{s/c} > 0, \tag{1}$$

where $\emptyset_M$ is the electron work function of the metal and $\emptyset_{s/c}$ is the electron work function of the semiconductor. As known, this inequality generates a space-charge region in the semiconductor and a potential barrier with the height $q\varphi_s$ written for the n-type semiconductor as follows [3]:

$$q\varphi_s = \emptyset_M - q\chi - (E_C - E_F), \tag{2}$$

where $q\chi$ is the electron affinity or the width of the conducting band in the semiconductor, E_C is the bottom of the conducting band, and E_F is the Fermi level for the given temperature. Here, the difference $(E_C - E_F)$ is determined

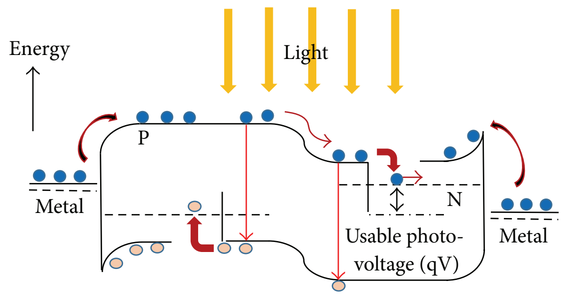


FIGURE 3: A schematic energy diagram for the novel PV cell.

by the concentration of dopant atoms in the semiconductor. This way, each metal island forms a Schottky barrier with the emitter and an Ohmic contact with the base.

As known, the Schottky diode built on the n-type semiconductor transfers electrons from its emitter (metal part) to the base, under external positive bias. In our case, the built-in voltage created on the p-n junction of the photovoltaic system plays a role in this bias. In order to begin emission of electrons in the conductive band of the semiconductor from metal islands, the electrons in the metal island should be excited. These electrons obtain exciting energy from the sunlight. Figure 3 represents a schematic view of the energy diagram for our construction under irradiation.

Under solar light irradiation, the high-energetic photons absorbed by the semiconductor generate electron-hole pairs with very-high energy which mainly lost on thermalization processes, thus decreasing the PV cell efficiency. In our system, these high-energetic photons are absorbed by the metal nanoparticles to produce plasmon-polaritons. Excited electrons from these metal 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 increasing the current in the load.

3. Mechanism of Efficiency Increasing: Quantitative Analysis

To approximate calculation, we used the parameters of the solar cell based on the single-crystalline silicon. The built-in voltage in the depletion region of the photovoltaic cell, shown in Figures 1 and 2, is described by the well-known relation [3]

$$V_b = V_t \ln \frac{N_A N_D}{n_i^2}, \tag{3}$$

where $V_t = kT/q$ is the thermal voltage, k is the Boltzmann's constant, T is the absolute temperature of the environment in K, q is the electron's charge, N_A and N_D are the impurity concentrations in the base and the emitter, respectively, and n_i is the equilibrium intrinsic concentration of charge carriers. This voltage produces a sufficient electrical field to provide separation of all charge carriers within the depletion region.

Due to sunlight irradiation, additional charge carriers are generated in this structure and produce electricity. Efficiency of such conventional PV cell is defined by the incident power P_{in}, semiconductor properties, and the quality of electric contacts [14]:

$$\eta = \frac{P_{\text{m}}}{P_{\text{in}}} = \frac{I_{\text{m}} V_{\text{m}}}{P_{\text{in}}} = \frac{\text{FF} \cdot I_{\text{sc}} V_{\text{oc}}}{P_{\text{in}}}, \tag{4}$$

where P_{m} is the maximum produced power, I_{m} and V_{m} are the maximum produced current and voltage, respectively, I_{sc} and V_{oc} are the short circuit current and the open circuit voltage respectively, and the FF is a Fill-Factor of the PV cell. Maximum efficiency of such one-junction solar cell cannot exceed the Shockley-Queisser limit depended by the bandgap width and the semiconductor quality [15].

Maximum produced current may be calculated from the basic Shockley equation. This current is described as a function of the generated current, I_L [16]:

$$I_{\text{m}} = I_L \left(\frac{V_t}{V_{\text{m}}} - 1 \right). \tag{5}$$

This current is proportional to the generated current. Therefore, efficiency of the cell may be increased by increasing the generation current or at the expense of increasing the electron flux generated by PV cell.

As known, only photons with energy higher than the bandgap may be absorbed by semiconductor with generation of electron-hole pairs. However, most of the photons which have energy enough to excite charged carriers produce too energetic electron-hole pairs. These charged particles decay to states near the edges of their respective bands. The excess energy is lost as heat and cannot be converted into useful electric power. Moreover, this heat decreases the PV cell efficiency due to thermal generation of intrinsic charge carriers [14].

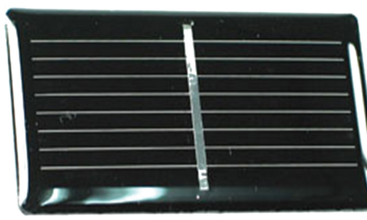
Each metal island embedded within the depletion zone forms a Schottky diode with the emitter part of the solar cell, if the metal was selected in accordance with the relation (1). A current across this diode is defined by three distinctly different mechanisms: diffusion of carriers from the semiconductor into the metal, thermionic emission of carriers across the Schottky barrier, and quantum-mechanical tunneling through the barrier [17]. Such as our diodes are positioned in the external electrical field, generated by the built-in potential of the photovoltaic diode, the thermionic emission mechanism only defines current in these diodes. As known, the thermionic theory assumes that electrons with energy larger than the top of a Schottky barrier will cross it. The thermionic emission current is proportional to the square of the junction temperature, and the current density can be expressed in the following form:

$$J_n = A^* T^2 \exp\left(-\frac{\varphi_s}{V_t}\right) \left(\exp\left(\frac{V_a}{V_t}\right) - 1\right), \tag{6}$$

where V_a is the direct voltage applied to the diode, in our case $V_a = V_b$, A^* is the Richardson's constant

$$A^* = \frac{4\pi q m^* k^2}{h^3}, \tag{7}$$

Table 1: Parameters of the standard PV cell of SZGD6030 type [19].

	Monocrystalline black solar cell Efficiency: 15% Peak voltage (V_{mp}): 0.48 V Open circuit voltage (V_{oc}): 0.55 V Peak current (I_{mp}): 280 mA Short circuit current (I_{sc}): 302 mA Dimensions: 60 × 30 × 2.8 mm

and m^* is the effective mass of the electron in the semiconductor.

Full addition current which should be obtained due to inserting the metal island film into the PV junction may be estimated as a sum of currents introduced by each island in the following way:

$$I_{\mathrm{ad}} = A \sum_{j}^{N} S_j J_{nj}, \tag{8}$$

where J_{nj} is the current from the metal island, j is an index, N is an average number of metal islands per unit area, S_j is an average contact surface area between the metal's island and emitter, and A is the active surface area of the PV cell. Therefore, the maximum generated current (see relation (5)) will take the following form:

$$I_{\mathrm{m}} = (I_L + I_{\mathrm{ad}}) \left(\frac{V_t}{V_{\mathrm{m}}} - 1 \right). \tag{9}$$

4. Discussion

For a quality assessment of the influence of the metal island interlayer, imbedded within the PV junction, on the cell's efficiency, we take a standard PV cell. The cell's parameters are shown in Table 1. Evidently, the exact parameters of the cell are not opened; however, it is known that the used silicon was grown by the Czochralski method, and the missing parameters may be taken from [18].

Parameters of the gold island film were taken from the experimental work [11], in which the number and size of gold particles were evaluated using AFM microscopy. To be specific, we chose for our evaluation a gold film with an average thickness of $h = 1.5$ nm. An average diameter of the island equals approximately to $\emptyset = 20$ nm. An average number of islands is ~30 on an area of 100 × 100 nm. Now, we can estimate a number of free electrons existing in the island using assumption that each gold atom contributes one electron to the conductive band. The number of gold atoms in the unit of volume is equal to

$$N_a = \frac{\gamma}{m_A} N_A = \frac{19.3}{197} \cdot 6.02 \cdot 10^{23} = 5.9 \cdot 10^{22}\ \mathrm{cm}^{-3}, \tag{10}$$

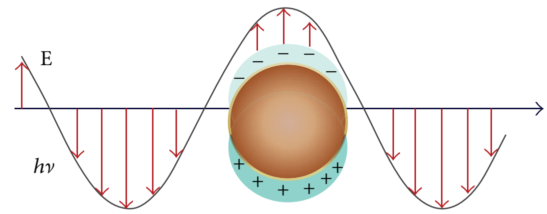


Figure 4: Excitation of the SPR in the gold island [18].

where $\gamma = 19.3\ \mathrm{g/cm}^3$ is the density of the gold, $m_A = 197$ g/mole is the atomic weight of the gold, and $N_A = 6.02 \cdot 10^{23}$ 1/mole is the Avogadro's number. An average volume of one island is

$$V_i = h \cdot \pi \frac{\emptyset^2}{4} = \frac{1.5 \cdot \pi \cdot 20^2 \cdot 10^{-21}}{4} = 4.7 \cdot 10^{-19}\ \mathrm{cm}^3. \tag{11}$$

Therefore, an average number of free electrons in the island will be

$$n_{\mathrm{e}} = N_a \cdot V_i = 2.8 \cdot 10^4 \text{ electrons}. \tag{12}$$

An average number of islands per surface unit area in defined conditions [11] is

$$N_i = \frac{30}{10^4 \cdot 10^{-14}} = 3 \cdot 10^{11}\ \mathrm{cm}^{-2}. \tag{13}$$

Thus, if we assume that all free electrons from all islands will participate in the conductance process, we obtain the additional electron current density, which will be equal to

$$\begin{aligned} J_{\mathrm{ad}} &= q n_{\mathrm{e}} N_i = 3 \cdot 10^{11} \cdot 2.8 \cdot 10^4 \cdot 1.6 \cdot 10^{-19} \\ &= 1.4 \cdot 10^{-3}\ \mathrm{A/cm}^{-2}. \end{aligned} \tag{14}$$

Due to excitation of SPR in the gold islands under light irradiation, also holes come into resonance and create the corresponding current, as shown in Figure 4 [18]. So, getting additional current must be doubled.

Therefore, the total resulting current obtained from a conventional PV cell [19] with imbedded thin gold island film between base and emitter will be equal to

$$I_{\mathrm{ad}} = 2 J_{\mathrm{ad}} A = 2 \cdot 1.4 \cdot 10^{-3} \cdot 6 \cdot 3 = 50.4\ \mathrm{mA}. \tag{15}$$

Calculation of efficiency of the novel PV cell with (5) and (4) shows an increase in efficiency of 17% and gives 17.5% instead 15% without the gold film. This result agrees well with the experimental data [20] where efficiency of organic solar cells, based on the bulk heterojunction system with silver nanoparticles, was increased by 17% as well.

5. Conclusion

In this paper, we investigated the possibility to increase the solar cell efficiency through introduction of gold island film between the emitter and base of a silicon semiconductor diode structure. We showed that the gold islands create a set of elementary Schottky diodes. These diodes are in forward bias condition due to its built-in electrical field within the emitter-base diode structure. These Schottky diodes can inject the free electrons, excited by sunlight irradiation, in the conduction band of the semiconductor, and by this way increase the maximum current generated by the solar cell.

Tentative calculation done on a standard solar cell showed an increase in the efficiency of 17.5%. This result is in good agreement with experiments.

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