Nanostructures based on functionalized porous silicon for promising solar energy systems

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Abstract. The promising application of functionalized composite materials based on porous silicon (PS) for perspective solar energy conversion systems is considered in this paper. PS-based nanostructures are suggested for further realization of photon-enhanced thermionic emission for solar concentrators and thermionic electrodes due to the remarkable properties displayed by these materials. Nanostructured layers functionalized with silver (PS/Ag) are obtained via electrochemical etching and deposition processes. The investigation of acquired materials functionalized with fractal-like silver agglomerates is performed. Electronic absorption spectroscopy is utilized in order to characterize the surface structure of PS/Ag layers. Localized surface plasmon resonance phenomenon taking place within the array of silver nanoparticles is observed. Two distinct absorption bands located in the visible spectrum are detected; their emergence is related to the resonance effect taking place in the two nanoparticle arrays appearing during the synthesis process. The intensity of these bands can be manipulated with synthesis parameters of porous silicon matrix.

1. Introduction

1.1. The current state and perspectives of solar energy systems

Currently, solar energy systems are of great importance to both the scientific communities and manufacturers due to the increasing demand for compact, autonomous, reliable and efficient power sources for various applications including spacecraft, and remote ground-based installations.

Conventionally, solar energy conversion process is performed via one of the two distinct principles: the first is "quantum" mechanism, utilized in photovoltaic cells and the second one is the "thermal" mechanism that requires the presence of concentrated solar radiation to generate electricity using an assortment of heat engines for example, thermionic energy converters or TECs. A standard thermionic converter consists of an emitter (cathode) performing at high temperatures, a collector (anode) operating at significantly lower temperatures and an inter-electrode vacuum gap separating the two electrodes. Electrons that possess sufficient thermal energy values overcome the cathode potential barrier (the emitter work function) thus creating the thermionic current defined with the Richardson’s law \cite{1}. Thermionic energy converters, being initially created in 1950s \cite{1} allow performing a direct transformation of thermal energy into electricity, while also providing reasonably high efficiency values. Further increase in efficiency of such devices requires the creation of anode materials possessing low anode electron work function (\(\phi_c\)) values. This fact thwarted the thermionic energy converters’ development for several decades due to the high degree of complexity in terms of both the
physical principles and technologies required to design and manufacture collector coatings characterized with sufficiently low $\phi_c$ values. The solution to this problem was suggested by Mustafaev et al. [2] who introduced nanostructured collector consisting of nickel matrix covered with graphene layers intercalated by Cs atoms. Such surface configuration leads to a drop in the electron work function from the collector to the values lower than 1 eV [2].

A number of experimental prototypes that attempt to combine the thermal and quantum mechanisms already exist but most of them rapidly lose their effectiveness due to the degradation of photovoltaic cells, normally operating at much lower temperatures than those required to sustain thermionic current density at a reasonable level.

1.2. Photon-enhanced thermionic emission process for solar energy converters

Photon-enhanced thermionic energy converters (PETE concentrators) proposed by Stanford scientists [1] are a perspective type of devices that provide an opportunity to realize quantum and thermal approach in a single physical process thus negating the drawbacks of earlier mentioned direct combinations. The principle of operation of these devices is based on the thermionic emission of photoexcited electrons from a semiconductor cathode. The cathode electron work function has to meet the requirement of maintaining the complicated balance between maximizing thermionic current density and operating voltage. The incident solar radiation excites electrons to the spherical cathode’s conduction band, while the excess heat that would account for thermalization losses in case of a contemporary solar cell, contributes to the emergence of the thermionic emission process. Conventional solar cells also lose efficiency due to the existence of absorption losses. While the latter can be mitigated with the utilization of appropriate materials including GaAs, possessing the band gap value of 1,519 eV, the thermalization losses are much more sophisticated to deal with.

The prototype with a gallium nitride cathode created by Nicholas Melosh et al. [1] however possesses one critical drawback: the number of incident photons characterized with energies larger than the band gap value of GaN ($E_g = 3.3$ eV) comprises approximately 1% of their total quantity, thus significantly decreasing the theoretical efficiency of this prototype. Nevertheless, this device operated reliably at the temperatures lower than those in a classical thermionic energy converter, but higher than in a regular photovoltaic cell.

Despite the aforementioned drawback, the prototype with GaN as a semiconductor emitter demonstrated high efficiency value of about 25% at a temperature of 200 °C. Under these circumstances a modern photoelectric element would stop operating, whereas the novel converter demonstrated a further growth in its efficiency with increment in temperature. It was also suggested to couple these devices with a TEC in order to utilize excess thermal energy generated by the device thus raising the total theoretical efficiency up to 50%. According to [1] Cs/p+-GaAs system is also suitable for realizing a PETE converter, due to the fact that GaAs band gap value is close to the optimum in terms of emission current/operating voltage balance while by modifying the cesium coating characteristics (layer thickness etc.), the preferable value of the electron work function can be engineered. In this case the electrons created by interband light and initially possessing energies lower than $E_{vac}$ are scatter by specific lattice phonons and participate in the thermalization process thus supplementing the emission of “hot” electrons ($E > E_{vac}$) directly from the tail of Maxwell distribution [1].

GaAs, while being a good candidate for PETE electrode realization, possesses a number of significant drawbacks including the high production cost of a single-crystal GaAs substrate as well as the technological problems in GaAs wafers’ manufacturing.

We suggest porous silicon (PS) and PS-based nanostructures for perspective PETE electrode synthesis as controllable in terms of the band gap modification that could be varied in a wide range between 1 and 3 eV thanks to the presence of the so-called quantum confinement effect [3] whereas their developed surface structure and morphology renders possible further functionalization [4, 5].
1.3. Theoretical justification of plasmon resonance in nanoparticles

Metallic (gold and silver) nanoparticles as well as structured and orientated arrays based on those show resonant behavior at specific incident electromagnetic (EM) radiation frequencies, in case of the fulfillment of the following conditions: 1) the value of the dielectric permittivity (its real part) of the nanoparticle is negative for these particular frequencies, 2) the wavelength of the propagating in free space EM radiation is by at least an order of magnitude larger than the size of the nanoparticle. A plasmon is a quasi-particle that corresponds to the result of plasma oscillations' quantization, which in turn represent the collective oscillations of free electron gas within the borders of a certain metal nanoparticle (metal NP) or an array. Each type of surface plasmons (including localized surface plasmons) emerge at the interface between media with a positive real part of dielectric permittivity (e.g. glass, air, etc.) and the surface of a metal nanoparticle. It should be also noted that plasmon resonance is a physical phenomenon, due to the fact that the two resonance conditions can be simultaneously met at nanoscale. The second condition indicates that the plasmon resonance in the metal NPs or arrays is basically an electrostatic resonance. It is implied by this statement, that the harmonic electromagnetic fields within a certain nanoparticle and in the vicinity of it oscillate almost in-phase which means that at any given moment of time, such fields can be considered electrostatic. Thus, the electrostatic nature of plasmon resonance in nanoparticles and their negative dielectric permittivity values lead to the enhancement of local electric fields within and around nanoparticles. Figure 1 shows a model of a spherical nanoparticle characterized with a negative dielectric permittivity value $\varepsilon$ under the influence of a uniform external electromagnetic field $E_0$. Since the value of $\varepsilon < 0$, the polarization vector $P$ is directed opposite to $E_0$, resulting in the formation of a particular configuration of surface electric charges, creating a “depolarizing” field $E'$, codirected to $E_0$. Hence the total electric field $E = E_0 + E'$ within the spherical nanoparticle increases. It should be also noted that if the particle size is considerably smaller than the wavelength of incident radiation the frequency of plasmon resonance in metal nanoparticles does not change with their size directly. In order to consider the position of plasmon resonance one has to take into account their shape and geometric dimensions. Such size invariance indicates that in the case of a particular array of similar in terms of shape, but different in size metallic nanoparticles, it can exhibit resonant properties at almost identical frequencies. Consequently, localized surface plasmon resonance (LSPR) will be simultaneously excited on all NPs at once. Both the thickness and the period of the metal nanoparticle arrays affect LSPR frequency mainly by altering the effective photon flux.

![Figure 1. The 2D model of a metal spherical nanoparticle under the influence of external electric field.](image)

In order to further analyze the plasmon resonance phenomenon we provided the results of a simplified analysis of the dispersion relation (the dependence of dielectric permittivity $\varepsilon$ on the
frequency $\omega$ of incident EM radiation). For the sake of simplicity, we considered the case of free electron gas (see [6] for example). Here we have

$$\varepsilon(\omega) = \varepsilon_0 \left(1 - \frac{\varepsilon^2 N}{\varepsilon_0 m \omega^2}\right) = \varepsilon_0 \left(1 - \frac{\omega_p^2}{\omega^2}\right),$$

(1)

where $e$ is the elementary charge, $\varepsilon_0$ vacuum permittivity, $m$ is the mass of the electron and $N$ is the total number of electrons per unit volume. In equation (2) $\omega_p$ is the so-called plasma frequency defined by the formula

$$\omega_p^2 = \frac{e^2 N}{\varepsilon_0 m},$$

(2)

It is evident from (1) that

$$\varepsilon(\omega) < 0 \text{ if } \omega < \omega_p,$$

(3)

Taking into account equation (1) one can conclude that at a certain frequency each metal exhibits resonance properties although the exact parameters of surface plasmon resonance are conditioned by a number of factors including electron density and dimensions of a specific nanoparticle array.

The phenomenon of localized surface plasmon resonance has a number of potential applications in the field of surface enhanced Raman scattering (SERS) [7, 8], scanning near-field optical microscopy, nano-lithography. It should be also noted that energy conversion devices can benefit greatly from semiconductor structures functionalized with resonant arrays of metal nanoparticles due to their ability to amplify electromagnetic radiation of particular frequencies thus providing a promising method for band gap and surface modification of various materials.

2. Experimental details

The PS/Ag structure comprises an array of fractal-like aggregates of silver nanoparticles with a size of about 500 nm and single isolated silver nanoparticles ($D = 20$ nm) located on the surface of a porous silicon matrix (monocrystalline (111) n-type porous silicon wafers with resistivity of 4.5 $\Omega \cdot$cm). Pretreatment of the wafers was performed with volatile liquids (acetone) and ultrasonication for 15 minutes. An anodic etching technique was utilized in order to obtain the initial porous silicon matrix layer [7]. In conventional anodizing setups, metallic layers are deposited on the back side of a silicon wafer, and then are utilized as electrodes for anodic etching. The metal layer has to be subjected to an etching procedure before the process of metal NPs’ deposition on the surface of porous silicon can take place. Anodization time varied in the range of 0.5 to 40 min [8].

The newly realized anodizing system does not require the formation of an auxiliary metal layer. The cell consists of two symmetrical containers filled with hydrogen fluoride (HF) Isopropyl alcohol-Distilled water solution throughout the anodizing reaction process. The silicon wafer is installed so that it separates the two parts of the cell. The anode current enters the silicon wafer through HF, which is in direct contact with the silicon wafer. Anode current is provided by platinum electrodes located in the left and right parts of the cell. When setting the voltage so that the left electrode is the cathode and the right electrode is the anode, porous silicon is formed on the left surface of the silicon substrate.

The second stage of the synthesis process utilized the method of cathode electrochemical deposition from an aqueous solution of AgNO$_3$ in order to manufacture an array of silver nanoparticles on the of PS matrix surface. A silver chloride electrode was utilized as a reference electrode, which retains its potential in solutions with a hydrogen index from 0 to 15. To maintain the point of reference for the potential, the Elins P-40X potentiostat was used. The deposition of silver on the surface of porous silicon samples was performed by applying a potential of 700 mV for one minute.
3. Results and discussion
The method of electron absorption spectroscopy with a Perkin-Elmer Lambda 900 spectrophotometer was utilized to measure the UV/Vis absorption spectra of nanostructured PS/Ag layers. According to [4] it is suggested that during the stage of the silver deposition on PS matrix the distribution of surface energy facilitates the formation of fractal-like Ag aggregates. Depending on the anodizing time and the anodizing current density, the pore depth and branching of the resulting porous silicon structure changes [7, 8]. Figure 2 shows the UV/Vis spectra of PS/Ag layers, with anodizing current density used as a parameter. The absorption band is clearly visible at a wavelength of $\lambda_0 = 360$ nm.

The existence of this band is in good agreement with the theoretical results obtained by Mayergoyz [6]; its nature is attributed to the emergence of a surface plasmon resonance peak within the array of spherical silver nanoparticles. The absorption intensity at this wavelength increases with an increment in the anodizing current density from 2 to 30 mA/cm$^2$ on the PS synthesis step.

Figure 3 shows the UV/Vis spectra of PS/Ag composite layers with the anodizing time $t = 10$ min and anodizing current density as a parameter. One can see from the figure that a wide band ($\sim 60$ nm) is located in the spectrum within the ultraviolet spectral region ($\lambda_0 = 265$ nm). Its nature is associated with the existence of dendrite fractal-like aggregates of silver on the PS matrix surface. The absorption intensity in this band decreases with an increment in the anodizing current density from 2 to 30 mA/cm$^2$ on the PS synthesis step.

This fact indicates that the distribution of surface energy changes to more favorable to the formation of spherical silver nanoparticles instead of the fractal ones inside the pores on the silicon matrix surface.

These results show the possibility to realize a mechanism allowing the modification of the absorption values within the two bands (360 and 265 nm). In order to achieve this goal one has to synthesize an array of plasmon metal nanoparticles with a variable dispersion in size and fractality. In order to suppress the absorption value in the 265 nm band it is necessary to fabricate a regular structure of Ag agglomerates characterized with almost identical sizes and shapes. This can be achieved by using higher anodizing current densities (see figure 3) thus facilitating the formation of a more regular array of Ag NPs during the process of electrochemical silver deposition as a result of second synthesis step.
4. Conclusion
Composite nanostructured PS/Ag layers were investigated by means of UV/Vis spectroscopy. Two distinct absorption bands located at 360 and 265 nm wavelengths were detected. The nature of these bands was attributed to the excitation of localized surface plasmon resonance within two sub arrays of silver nanoparticles existing on the PS surface. LSPR wavelengths equaled 360 nm and 265 nm for the spherical and the fractal-like sub arrays of nanoparticles respectively.

The utilization of PS and PS-based nanostructures for PETE electrode synthesis proved to be quite promising due to a number of unique properties (including LSPR) demonstrated by them. Although, contemporary devices show reasonable levels of performance being able to achieve relatively high energy conversion efficiencies, further research in this field is required in order to improve the existing characteristics and create more reliable, facile and reproducible synthesis technics.

The perspective energy conversion devices such as PETE solar concentrators using an entirely new tandem process provide an opportunity to achieve significantly higher efficiencies of a combined power generation mechanism.

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