Porous silicon and graphene-based nanostructures for novel solar energy systems

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Abstract. The investigation of composite porous silicon (PS) and graphene nanostructured materials for low work function PETE (photon-enhanced thermionic emission for solar concentrator systems) and thermionic plasma energy systems synthesis is reported in this article. These two types of materials are suggested for further development and study due to remarkable physical effects taking place in the aforementioned structures. The nature of low-work function phenomenon is discussed and interpreted as due to the influence of functionalization and synthesis parameters on the structure properties of composite materials. The Raman spectroscopy technique is utilized in order to characterize porous silicon based nanostructured composite layers (PS/Ag). The interpretation of PS/Ag Raman spectra is suggested. The significant decrease in the effective electron work function to an exceptionally low value of 1 eV is achieved with a perforated nickel collector functionalized with nanosized graphene layers. SEM X-ray microanalysis of the thermionic energy converter (TEC) collector surface is performed, the interpretation of the anode work function lowering effect is proposed.

1. Introduction
The process of solar energy conversion can be implemented by one of the two distinct approaches. The first one is the so-called "quantum" approach commonly realized in photovoltaic cells that allow the use of solar energy to excite electrons. The second one is the "thermal" approach, that requires concentrated sunlight as a source of thermal energy in order to generate electricity using the heat engine. In practice the direct combination of the two methods rapidly loses effectiveness with a significant increase in operating temperatures resulting in the degradation of photovoltaic cells as well as with a decrease in operating temperatures that leads to the loss of heat engine’s effectiveness.

The simultaneous implementation of the photovoltaic and thermionic effects in the systems based on the photon-enhanced thermionic emission (PETE) phenomenon allows us to negate these drawbacks by using the quantum and thermal mechanisms at the same time in one physical process [1]. This type of energy conversion devices is based on the effect of thermionic emission of photoexcited electrons from a semiconductor cathode at high temperature. Such solar concentrators are able to operate at elevated temperatures higher than 200° C, which in turn, allows the utilization of thermal energy to implement the thermionic emission process, thus leading to an overall increase in the theoretical efficiency of the combined conversion to values of approximately 50% [1].

The possibility of synthesizing systems based on PETE with semiconductor (GaN) electrodes was established in [1], however, the number of incident photons characterized with energies exceeding the band gap of GaN ($E_g = 3.3$ eV) is less than 1% of their total quantity. This drawback results in a
severe limitation of the overall energy conversion efficiency. That is why, the studies of porous silicon (PS) as well as PS-based composite structures for subsequent electrode synthesis are promising, since the band gap of such materials can be modified in a wide range from 1 to 3 eV due to the quantum confinement effect [2] and significant opportunities for surface functionalization [3,4,5].

Synthesis of anodes (collectors) for plasma energy systems based on thermionic emission process requires the creation of materials with a low electron work function (ϕe) from the surface. The problem of ϕe reducing is traditionally solved by using alkaline and alkaline-earth metals, in particular, caesium (Cs) [6]. Collectors based on caesium-coated tungsten are traditionally used due to their high thermal stability and a relatively low achievable electron work function (ϕe = 1.7 eV). The use of a nickel anode coated with graphene layers intercalated with caesium atoms allowed for a drastic decrease in the work function of electrons from the surface of the material (ϕe < 1 eV) and, as a consequence, a threefold increase in the energy conversion efficiency (up to 25%) [6].

The implementation of energy systems characterized with the unique combination of relatively low emitter temperature (Tₑ), exceptionally high efficiency and an emission surface of several square metres will reveal the perspective for utilizing these devices in ground autonomous small-scale nuclear power generation with direct conversion and co-generation in conventional thermal power plants.

It is well known that the electromotive force developed by thermionic energy converter (TEC) is generally determined by the work function of electrons from the emitter material surface (ϕₑ), while the output voltage losses depend on the electron work function of the collector material (ϕc) and plasma voltage losses in the inter-electrode gap. The efficiency of TEC can be increased mainly by decreasing the ϕₑ. Since a significant increase in the emitter electron work function achieved by selecting a suitable material is ineffective due to the considerable reduction in the generated electric current density (in accordance with Richardson's law) at the technologically specified emitter temperature (at which the evaporation rate of the cathode material remains acceptable), the only viable option to improve the TEC energy efficiency is to reduce the anode electron work function ϕc. High efficiency of laboratory TEC was demonstrated in [7,8] experimentally by implementing continuous circulation of caesium vapour through a nickel anode with a number of holes (0.1 mm in diameter). This effect was observed only if the collector surface was coated with graphite layer acquired by using an aquadag suspension, while being inexistent on a pristine metal surface.

The implementation of alkali and alkaline earth metal coatings is not the only method of the material work function modification in existence. In particular, we propose high electron affinity PS and PS-based nanocomposites functionalized with silver nanoparticles as low work function anodes for PETE – systems.

2. Experimental details

PS layers were obtained with anodization of monocrystalline (111) n-type silicon wafers with resistivity of 4.5 Ω·cm. Pre-treatment of the wafers was performed with volatile liquids (acetone) and ultrasonication for 15 minutes. The anodization process was conducted in an electrochemical cell filled with HF-Isopropyl alcohol-Distilled water solution. Anodization time varied in the range of 0.5 to 40 min. The deposition of silver was carried out from an aqueous solution of silver nitrate in a three-electrode electrochemical cell. The silver chloride electrode was used as the reference electrode. Porous silicon acted as a working electrode. The deposition of silver on the surface of porous silicon samples was performed by applying a potential of 700 mV for one minute.

The investigation of thermionic energy converter (TEC) properties dedicated to the search of methods for drastically raising the efficiency (several-fold) and operating life (by approximately an order of magnitude) relative to the existing TEC systems [7] showed that it is possible to achieve high efficiency of energy conversion with composite nanostructured electrodes [9]. An efficiency of approximately 20% was obtained using an experimental TEC under laboratory conditions in an electric energy generation mode with dynamic feeding of caesium vapour into the inter-electrode gap (IEG) at an emitter temperature of Tₑ ~ 1600 K and collector temperature of Tᶜ ~ 700 K.
The experiments performed in [7, 8] were repeated independently using a laboratory TEC with a laser-perforated collector coated with nanosized graphite flakes. The study was performed with planar electrodes featuring a variable IEG (0.2 – 3 mm). The setup allowed the use of either equilibrium or dynamic feeding of caesium vapours without the necessity to introduce significant changes into the equipment [9]. Vacuum-melted polycrystalline Mo coated with the Pt layer (~3 μm in thickness) was used as an emitter while a laser-perforated (121 holes with a diameter of 0.1 mm on a square of 4 × 4 mm) [10] nickel foil with a thickness of 0.2 mm, 8 mm in diameter was used as a TEC collector. The emitter was heated by electron bombardment ($T_E = 1350 \, K$, $T_C = 750 \, K$, $T_{Cs} = 570 \, K$).

3. Results and discussion

The current-voltage characteristics (CVCs) of TEC were measured by the pulse method using electric current scanning from a static working point on the CVC corresponding to the diffusion mode of operation [6]. The CVCs were measured and optimized both under the circumstances of equilibrium feeding of caesium vapours and after repeated activation of TEC electrodes using the conditions suggested in [4, 5]. The measurement time was at least 1000 h [6]. It appears to be possible to explain the experimental CVCs under the assumption that the anode material electron work function does not exceed 1 eV.

Figure 1 represents the results of the SEM analysis of the collector surface (beam energy 20 keV, secondary electrons mode). One can see from the figure that there are two distinct areas on the surface of the material: within and outside the concentric rings around each hole in the collector. The existence of these areas implies the fact that diffusion occurs on the collector surface starting from the boundary area of the hole. The experiments reported in [7] showed that the effect of electron work function lowering does not appear in an unmodified nickel collector even in the case of dynamic feeding mode of caesium vapours into the IEG.

The distribution of elements between the adjacent holes was measured based on the X-ray spectra excited with fast electrons from the microscope beam and recorded with an Oxford Instruments detector. Figure 2 shows the X-ray spectrum of the region designated as “Spectre 12” on Figure 1. One might notice the appearance of a considerable amount of Cs atoms within the area of darker concentric rings whereas the area outside those rings does not contain any Cs as one could clearly see from Figure 3 (X-ray spectrum of the “Spectre 7” region). This can be attributed to the fact that Cs atoms, being only physically adsorbed on the surface of the original graphite coating, were removed after the cooling process of Cs reservoir. On the other hand, the region of Figure 2 represented by the areas within the concentric circles in Figure 1 is characterized with Cs atoms intercalated between the structured graphite grains constituting the graphene layers. The considerable increase in the number of O atoms, (see the X-ray spectrum in Figure 2) is due to the fact that the oxygen atoms practically “followed” Cs atoms while simultaneously oxidizing them thus creating a chemical bond. These bonds between the O atom and the two Cs atoms one of which intercalated between graphene layers and the other one arrived from the Cs vapour resulted in the overall dipole moment increase thus diminishing the electron work function value [6]. The content of elements within the anode surface layer is summarised in Table 1.

| Chemical element | Content within the concentric rings | Content outside the region of concentric rings |
|------------------|-------------------------------------|-----------------------------------------------|
| C                | 22                                  | 37                                            |
| O                | 46                                  | 4                                             |
| Ni               | 14                                  | 41                                            |
| Mo               | 9                                   | 18                                            |
| Cs               | 9                                   | 0                                             |
Raman spectroscopy technique has been widely used to characterize crystalline and amorphous silicon as well as silicon based composite materials [11]. Raman shift equals to 521 cm\(^{-1}\) and 480 cm\(^{-1}\) (transverse optical TO – mode) for crystalline (c-Si) and amorphous (a-Si) samples respectively [3]. Thus, if the structure of a particular sample resembles c-Si and a-Si then the corresponding Raman spectra should be close to those of crystalline and amorphous silicon. A significant offset of the Raman peak initially located at the frequency anticipated for monocrystalline silicon towards lower energy caused by the increase in PS matrix anodization time from 0.5 to 40 minutes is observed, its nature is related to the formation of silicon nanocrystals within the material’s surface. The sizes of these nanocrystals calculated using the quantum confinement theory [12] turned out to be 62.7, 62.7, 44.4, 44.4 and 34.6 Å with respect to 0.5, 1, 10, 20, 40 min anodization times. A number of Raman bands characterized with low frequency were observed in the spectra of PS-based material. The existence of these bands was attributed to the mechanical oscillations of metal (Ag) nanoparticles on the surface of the material under the influence of optical radiation. The size of Ag particles was calculated using Lamb theory [13, 14] for spheroidal and torsional vibration modes. This approach lead to the value of Ag nanoparticles size of 0.7 nm in diameter. These effects are interpreted as due to the influence of functionalizing silver nanoparticles and synthesis parameters on the structure and properties of composite PS/Ag material.
4. Conclusion

The substantial anode work function lowering was achieved in a perforated nickel collector coated with nanosized graphite layer, as a result of a structural modification of the graphite surface layer due to intercalation of Cs atoms between the graphite/graphene surface layers as a result of the dynamic Cs vapour feeding technique realization. This effect led to a significant increase in the overall energy conversion efficiency of the TEC. The PS/Ag nanostructured material was investigated by means of Raman spectroscopy. The porous silicon matrix structure prior to deposition of functionalizing silver particles is similar to that of monocrystalline silicon. The deposition of silver nanoparticles in the pores on the surface of the material resulted in the deformation of silicon lattice, accompanied by the appearance of uncharacteristic for monocrystalline silicon bands in the Raman spectra of investigated samples. The calculation of the Si nanocrystals’ characteristic dimensions was conducted in accordance with the confinement model as a function of PS matrix anodization time. The existence of low-energy Raman bands has been attributed to the mechanical oscillations of silver nanoparticles under the influence of incident optical signal.

5. Acknowledgments

The technological part of this study was carried out at the Department of Micro- and Nanoelectronics, Saint Petersburg Electrotechnical University “LETI”. The authors are grateful to V.S. Levitsky for the PS/Ag Raman spectra measurement.

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