The application of composite porous silicon (PS) and graphene-based nanostructures for PETE (photon-enhanced thermionic emission for solar concentrators) and thermionic plasma energy conversion systems is discussed in this paper. Raman spectroscopy technique is utilized to investigate the surface structure properties of PS based composite layers (PS/Ag). The interpretation of PS/Ag Raman spectra is suggested; the nature of a significant monocrystalline silicon TO-phonon mode Raman peak shift towards lower energies is related to PS silicon surface functionalization followed by subsequent PS structure alteration.

The process of solar energy conversion can be implemented by one of the two distinct approaches. The first one is the “quantum” approach currently utilized in photovoltaic cells that provide a possibility to use solar energy “per quanta” to excite electrons. The second one is the so-called “thermal” approach, which requires concentrated sunlight to act as a source of thermal energy for electricity generation using various types of heat engines.

Thermionic energy converters (TECs) represent a promising type of heat engines allowing the direct conversion of thermal energy into electricity. A typical thermionic converter consists of a cathode (emitter) operating at high temperatures and an anode (collector) kept at a relatively low temperature while also being separated from the cathode with an inter-electrode vacuum gap (IEG). A fraction of the electrons possess enough thermal energy to overcome the TEC cathode work function and escape into vacuum, thus generating current between the two electrodes [1]. Thermionic energy converters were initially developed and implemented in the 1950s, their conversion efficiencies approaching 10–15% [2]. Both the US NASA and the Soviet space programs stimulated further development of TEC satellite energy sources and other TEC related applications requiring high-power independent energy generators capable of resisting high temperatures and significant current densities in order to function properly.

In practice the devices utilizing both quantum and thermal energy conversion approaches rapidly lose their effectiveness due to the degradation of photocells caused by a significant increase in operating temperatures required to retain heat engine’s performance at a sufficient level. Concentrators based on the photon-enhanced thermionic emission (PETE)
effect provide a promising opportunity to overcome this drawback by simultaneously realizing the photovoltaic and thermionic phenomena allowing the implementation of both quantum and thermal mechanisms in a single physical process. The prototype proposed by Schwede et al. [1] is based on the effect of thermionic emission of photo-excited electrons from a semiconductor cathode at elevated temperatures. The convertor operated at temperatures higher than 200° C, which facilitated thermal energy utilization to sustain the thermionic emission process, leading to an increase in the efficiency of the combined conversion to the values of 50% [1].

The possibility of PETE-based systems synthesis with semiconductor (GaN) electrodes was also demonstrated by Schwede et al. [1]. Unfortunately, the efficiency of these prototypes is reduced significantly due to a critical drawback: the number of incident photons with energies exceeding the band gap of GaN (E_g = 3.3 eV) is less than 1% of their total number. This fact, in turn, provides a solid foundation for the studies of alternative structures, including porous silicon (PS) and PS-based nanocomposites for PETE electrode synthesis, since the band gap of such materials can be altered in a wide range from 1 to 3 eV due to the presence of quantum confinement effect [3] and significant possibilities for surface functionalization [4,5,6].

Since a considerable increase in the cathode electron work function (φ_e) achieved by choosing a suitable material is ineffective due to the significant reduction in the generated electric current density (according to Richardson's law) at the emitter temperature characterized with an acceptable evaporation rate of the cathode material, the only viable option to improve the TEC energy conversion efficiency is to decrease the anode electron work function (φ_a) value. The problem of φ_a reducing is usually solved by using alkaline or alkaline-earth metal coatings, in particular, cesium (Cs). Anodes based on tungsten covered with Cs are traditionally implemented due to their high thermal stability and a relatively low achievable electron work function (φ_a = 1.7 eV). The use of a nickel anode coated with graphene layers intercalated with cesium atoms resulted in an unprecedented decrease in the work function of electrons from the surface of the material (φ_a < 1 eV) thus leading to a threefold increase in the energy conversion efficiency (up to 25%) [7].

PS layers were obtained with anodization of monocrystalline (111) n-type silicon wafers with resistivity of 4.5 Ω·cm. 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. 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 [5].

![Raman Spectra](image)

Fig. 1. PS/Ag Raman spectra 505-550 cm\(^{-1}\) - (a), 60-170 cm\(^{-1}\) - (b)

Raman spectroscopy technique has been used to study both crystalline and amorphous silicon and silicon-based nanostructures. Raman shift equals to 521 cm\(^{-1}\) and 480 cm\(^{-1}\) (transverse optical TO – mode) for monocrystalline (c-Si) and amorphous (a-Si) samples respectively [8]. Representative Raman spectra of composite PS/Ag layers depending on anodization time are shown in Figure 1a. Initial porous silicon Raman spectrum is shown as a reference. The Raman shift of the original sample is 521 cm\(^{-1}\) which is indicative of its monocrystalline structure. It should be noted than an increase in anodization time (from 0.5 to 40 min) leads to a shift in location of a Raman peak initially positioned at 521 cm\(^{-1}\) towards lower energies. Thus, according to the confinement model [9] it is proposed that this phenomenon is caused by the vibrational confinement related to the formation of silicon nanocrystallites in the composite material structure due to the deposition of silver nanoparticles inside the pores on PS surface. Such modification of porous silicon crystalline structure characterized with a shift of the 521 cm\(^{-1}\) TO-mode Raman peak is presumably related to the effect of stretching and structure alteration as a result of the deposition of silver nanoparticles inside the pores in the silicon matrix surface. The diameters of Si nanocrystallites calculated according to the confinement model [9] turned out to be
62.7 Å, 62.7 Å, 44.4 Å, 44.4 Å and 34.6 Å for silicon matrix anodization times of 0.5 min, 1 min, 10 min, 20 min and 40 min respectively.

Figure 1b shows Raman spectra of PS/Ag layers in the range of 60 to 170 cm\(^{-1}\). According to [10] the emergence of Raman bands located at 85 cm\(^{-1}\) and 146 cm\(^{-1}\) is caused by silver lattice vibrations. Duval et al. [11] states that Raman spectra of both metal nanoparticles and composite nanostructures based on those contain a low-frequency peak the nature of which is related to the mechanical oscillations of nanoparticles under the influence of optical radiation. In order to perform an evaluation of the dimensions intrinsic to the silver nanoparticles deposited on the PS surface, Lamb theory [11] for the vibration modes of spherical particles was used. Herein, the diameter of Ag nanoparticles deposited on PS surface equalled to approximately 0.7 nm. Thus, it could be stated that the increase in anodization time of PS leads to a rise in the thickness of the porous layer as well as in the pore diameter.

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References