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Plasmonic photo-thermoelectric energy converter with black-Si absorber

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ABSTRACT

Thermal to electrical energy conversation by Seebeck element was enhanced by up to ~ 50% by dispersing 50 nm diameter Au nanoparticles over the black-Si light harvesting surface at an optimized concentration. Size of Au nanoparticles is the defining factor for the spectral position of the extinction maximum at which the cumulative absorption of black-Si (without nanoparticles) can be augmented resulting in an increase of voltage produced by a Seebeck element. Black-Si with reflectivity of 1–2% over the entire visible spectral range is a promising material for extending the operational range of solar and thermal energy converters into longer wavelength regions. Numerical simulations reveal efficient localization of light energy absorption inside black-Si.

1. Introduction

Harvesting of thermal energy and its conversion into electrical power holds great potential to increase the overall efficiency of energy usage and reduce greenhouse gas emissions. However more promising are smaller scale applications for thermoelectrical converters [1] for sensors and monitoring devices [2–4]. The current state-of-the-art of ~ 25% efficiency Si solar cells [5] still waste up to 75% of radiative energy that reaches the Earth surface. Only 80% of sunlight can be absorbed in Si due to photon energy exceeding the bandgap of 1.12 eV (1100 nm wavelength) with 20% of light reaching the Earth surface at wavelengths where Si is transparent. With the emergence of efficient engineered thermoelectrical materials with a high Seebeck coefficient (thermopower), a rival/complimentary technology for sustainable electrical power generation can emerge. The waste thermal energy generated from any industrial sources (around ~ 50% in most cases) as well as due to heating of solar cells can be recovered using such thermal-to-electrical energy converters.

One of the most prominent applications of thermal-to-electrical converters is power supply on long space missions, such as Viking and Pioneer [6], where robustness and reliability are of critical importance. Some are still operational after 30 years of service – far beyond the planned lifetime. Both, high temperature and its gradient are required which pose obvious challenges for practical and miniaturized realization of thermoelectrical converters. The figure of merit for a thermoelectrical material is

$$ZT \equiv \frac{\alpha^2 T}{\rho\kappa} > 1, \tag{1}$$

where α is the Seebeck coefficient, T is the absolute temperature, ρ is the electrical resistivity, κ is the thermal conductivity. Balance between heat dissipation and electrical current generation should be engineered to reach $ZT > 1$ at the lowest possible temperatures; e.g., for Bi_2Te_3 $ZT \le 1$ at 400 K and for $Si_{1-x}Ge_x$ at 1200 K. Alloys such as BiSbTe, Bi–Te, as well as quaternary systems such as Ag–Pb–Sb–Te, with nano-engineered electrical and thermal transport modifications due to electron band split via quantum confinement in nanocrystallites and a complimentary reduction of heat transport due to larger surfaces and grain boundaries were shown to have increased ZT [7,8]. The thermoelectric efficiency of a device at the Carnot limit requires the $ZT \to \infty$ which limits the large scale applications of thermoelectric converters [1].

Heat management at nanoscale is a related active field of research. A thermal diode based on two polymorphs of SiC with

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different absorption resonances which are radiatively coupled via a small nano-gap with photons as thermal energy carriers has been proposed [9]. Search of efficient heat absorbers which can reemit thermal energy into a narrow spectral range window that matches the absorption band of a solar cell is well underway. Such a solar thermo-photovoltaic converter, in principle, could reach extraordinary efficiency; the thermodynamic limit for a $T_S = 6000$ K emitter (Sun) with an intermediate absorber and reemiter at $T_i = 2544$ K (tungsten) with a $T_c = 300$ K absorber (solar cell) would have the thermodynamic Carnot's efficiency limit of $\eta = (1 - T_i^4/T_s^4)(1 - T_c/T_i) \simeq 85.4\%$ and could surpass the $\sim 34\%$ Shockley–Queisser limit for direct absorption of Solar radiation by a single junction solar cell [10]. Therefore, there is strong incentive to investigate how light absorption tailored for photo-thermal devices, including thermoelectrical converters, can find efficient uses in certain niche applications.

Here we present a plasmonic photo-thermal converter which exhibits up to twice larger photo-thermo-electrical conversion efficiency using a commercially available 6% efficient Seebeck element and black-Si (b-Si) as a hot contact – all under typical atmospheric conditions – a result that previously had only been achieved in a vacuum [11]. Additionally, Au colloidal nanoparticles were used to further enhance the photo-thermoelectrical conversion efficiency by 50%.

2. Material and methods

B-Si absorber was fabricated from single side polished p-type ⟨100⟩ orientation and a 500- μm-thick Si wafer. A RIE-101iPH (SAMCO Inc.) tool capable of performing reactive ion etching and inductively coupled plasma assisted RIE was used for fabrication. A sub-micrometer height nano-needles were formed randomly on the surface by etching Si for 15 min in SF_6/O_2 plasma, at a process pressure of 35 mTorr, and 100 W RIE power [12]. The aspect ratio of needles and the air-Si volume fraction is controlled by plasma etching parameters. The formed nanorough surface causes reflectance to become as low as 1–2% across the entire 300–1000 nm spectral range.

We use a commercial Seebeck element (TEP1-1264-1.5, Nihon Techno Ltd.) for thermal-to-electrical power conversion by placing b-Si in vacuum grease (X-23-7877, Shinetsu silicone) mediated thermal contact with p- and n-type contacts of the element as shown in Fig. 1(a). In this setup we investigate the effect of b-Si and its additional plasmonic nanoparticles modification on photo-thermoelectric conversion efficiency. The maximum efficiency of a thermoelectric generator can be estimated from the power balance between temperature gradient (ΔT) driven current I, and the power consumed in the electrical circuitry composed of an internal resistance of the thermoelectric generator (r) and an external load (R) acting in series: $\alpha \Delta T I = I^2(R + r)$, here α [V/K] is the Seebeck coefficient. Following algebra steps, the power can be expressed as

$$I^2R = -r(I^2 - \alpha\Delta T I/r) = -r(I - \alpha\Delta T/(2r))^2 + \alpha^2\Delta T^2/(4r). \quad (2)$$

The maximum power is generated when the term in brackets is zero, i.e., $I = \alpha\Delta T/(2r)$, which is equivalent to the requirement of matching resistances in the internal and external circuits ($R = r$). The maximum power is given as the last term in Eq. (2) $P_{max} \equiv \alpha^2\Delta T^2/(4r)$ and can be estimated numerically. The Bi–Te Seebeck element (TEP1-1264-1.5, Nihon Techno Ltd.) with $\alpha \simeq 570\ \mu$V/K, $r = 2.8\ \Omega$, and working temperature of the hot electrode up to 300 °C. The maximum efficiency of heat-to-electrical power conversion reaches 6% and is achieved when temperature gradients between hot and cold contacts are $T_h - T_c = (150 - 30)$ °C.

Experimentally, temperature gradient, established in the Seebeck element, was measured by sandwiching the thermoelectric converter between two Peltier devices, which were then used to set the temperatures T_h and T_c of the hot and cold contacts respectively. T_c was set to values in the range from 20 to 60 °C, while T_c was varied from 30 to 70 °C. In this temperature range, the output voltage was observed to be linearly dependent on the difference $T_h - T_c$. Thereby the thermoelectric conversion slope of 28 mV/°C was obtained. Using this relationship, the temperature of the b-Si substrate was estimated.

Output voltage was measured under both, 532 nm laser, and metal halide lamp illumination (MS-L160, Cerma Precision Co. Ltd.) which has spectrum close to that of the Sun in the 400–1000 nm range (Fig. 1(b)). Calibration of temperature to the output voltage of the Seebeck element was carried out using a temperature controlled heater (VPE20-30S, VICS Co. Ltd.).

Additional photo-thermoelectric enhancement due to plasmonic effects was investigated by decorating b-Si with colloidal Au nanoparticles of varying dimensions. Commercially available solutions with colloidal Au particles with diameters in the range 15–100 nm (Tanaka Co. Ltd.) were used.

3. Numerical modeling

Numerical simulations of light absorption were carried out using a commercially available finite difference time domain (FDTD) solver Lumerical. The b-Si surface texture was digitally reproduced from a SEM image of the collector material. In the case of Au nanoparticle decoration, representative particle distributions were obtained by steps of initial random particle placement followed by subsequent position corrections via an adaptive overlap

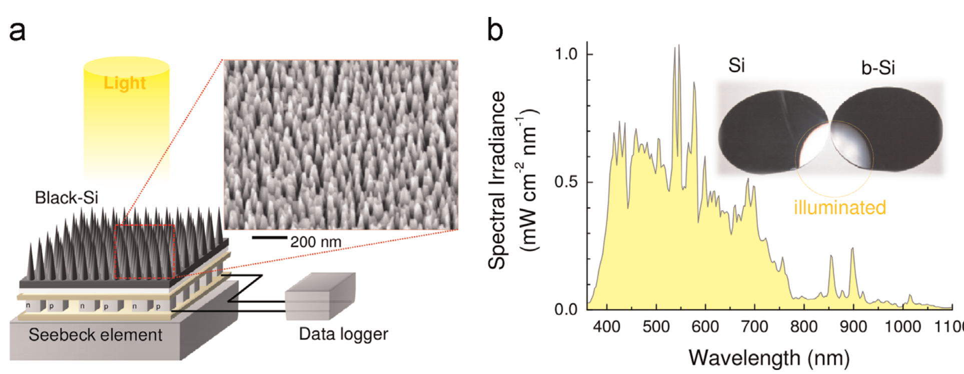

Fig. 1. (a) A schematic representation of the experimental setup used for measurement of Seebeck effect driven photo-thermal voltage generation using b-Si absorbers. Inset shows a SEM image of a typical b-Si surface; scale bar is 200 nm. (b) Spectrum of metal-halide lamp used in experiments at 72.8 mW/cm^2 flux. Inset contrasts the appearance of Si and b-Si surface under the metal halide lamp illumination.