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Three-dimensional metallo-dielectric selective thermal emitters with high-temperature stability for thermophotovoltaic applications

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ABSTRACT

Selective thermal emitters concentrate most of their spontaneous emission in a spectral band much narrower than a blackbody. When used in a thermophovoltaic energy conversion system, they become key elements defining both its overall system efficiency and output power. Selective emitters' radiation spectra must be designed to match their accompanying photocell's band gap and simultaneously, withstand high temperatures (above 1000 K) for long operation times. The advent of nanophotonics has allowed the engineering of very selective emitters and absorbers; however, thermal stability remains a challenge since nanostructures become unstable at temperatures much below the melting point of the used materials. In this paper we explore a hybrid 3D dielectric–metallic structure that combines the higher thermal stability of a monocrystalline 3D silicon scaffold with the optical properties of a thin platinum film conformally deposited on top. We show experimentally that these structures exhibit a selective emission spectrum suitable for TPV applications and that they are thermally stable at temperatures up to 1100 K. These structures are ideal in combination with III–V semiconductors in the range $E_g = 0.4$–0.55 eV such as InGaAsSb ($E_g = 0.5$–0.6 eV) and InAsSbP ($E_g = 0.3$–0.55 eV).

1. Introduction

Thermophotovoltaic (TPV) systems [1] generate electricity from heat without any moving part. In such systems, photons thermally emitted by a high-temperature emitter are converted into electricity through a standard photovoltaic (PV) cell at near room temperature. Only those photons with energy above the PV cell's band gap (E_g) can be converted into electricity; furthermore, only those with energy slightly above E_g can be converted efficiently, as high energy photons rapidly lose their excess energy by thermalization of the generated electron–hole pairs. As a result, high-efficiency TPV systems rely on photon filtering and recycling strategies; *i.e.*, ways of returning useless or inefficient photons back to the emitter where they are reabsorbed helping to keep its temperature. An appealing alternative for rising efficiency is to directly avoid the radiation of inefficient photons using the so-called selective thermal emitters [2–6], which are able to radiate in a much narrower spectrum than a blackbody and that can be matched to the TPV cell band gap for maximum conversion efficiency.

During the last years, photonic structures with feature sizes in the order of the wavelength have been demonstrated to be an excellent platform for the engineering of highly selective and customizable emitters and absorbers, owing to the unprecedented control over light they offer. For instance Yablonovitch already proposed in his pioneering work on photonic crystals [7] that spontaneous emission could be inhibited within the photonic band gap regions. Since then, several structures have been proposed for selective thermal emission in the TPV context such as 1D metal–dielectric stacks [8], 2D arrays of metallic microcavities [4,9,10], and metallic 3D photonic crystals [3,6]. Metallic structures are typically preferred as they naturally keep the emission low at long wavelengths, while the emissivity can be enhanced at shorter wavelengths through micro-structuring.

In addition to efficiency, selective emitters must be designed to endure long operation times at high temperatures (> 1000 K). Therefore, in order to attain the desired emission selectivity and high-temperature stability, photonic selective emitters rely on refractory metals, such as tungsten [5] and tantalum [10,11]. Unfortunately, it turns out that the micro- and nano-structures are unstable at temperatures much below the melting point of these materials due to, mainly, recrystallization and surface diffusion effects [12,13]. Surface diffusion can rapidly wreck 2D or 3D microstructures [4] and lead to capillary instabilities in the case of

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thin films [14]. These effects can be partially alleviated by using high quality monocrystalline materials [4] and by depositing certain layers on top of the structure [6] thus reducing surface diffusion, although the claimed operation temperatures are still much below the melting point of the used materials.

In this paper we explore a different approach based on a 3D dielectric–metallic structure that combines the higher thermal stability of a monocrystalline 3D dielectric scaffold with the optical properties of a thin metallic film conformally deposited on top. In particular, we explore Si/SiO_2/Pt structures. We show experimentally that these structures exhibit a selective emission spectrum suitable for TPV applications, comparable with state-of-the-art full metallic structures, and that they are thermally stable at temperatures up to 1100 K. These structures are well suited for TPV systems in combination with III–V semiconductors in the range $E_g = 0.4$–0.55 eV such as InAsSbP [15,16] ($E_g = 0.3$–0.55 eV) and InGaAsSb [17,18,19] ($E_g = 0.5$–0.6 eV).

2. Sample fabrication

The 3D Si scaffold microstructures were obtained by electrochemical etching of *n*-type crystalline silicon in hydrofluoric (HF) acid solution [20]. Samples were prepared with an active area of 2.6 cm^2. In contrast to colloidal crystal techniques, perfectly ordered 3D macroporous silicon structures can be fabricated in very large areas, even at full wafer scale. The fabrication process is depicted in Fig. 1. The starting material was *n*-type CZ $\langle 100 \rangle$ c-Si wafers with a resistivity $\rho = 0.5$–$0.8\ \Omega$ cm. An n^+ layer was implanted on the wafer back surface in order to work as a transparent back contact during the electrochemical etching. First of all, the pores' nucleation sites were defined through a square array (pitch of 2 μm) of inverted pyramids created using standard photo-lithography and anisotropic etching techniques (Fig. 1a). Then, a square-array of perfectly ordered pores were electrochemically etched in 5% HF aqueous solution, with a small amount of ethanol for wetting purposes, at a controlled solution temperature of 10 °C. During the etching, an in-depth modulation of the pores' diameter was introduced by modulating in time the etching photocurrent [21] (Fig. 1b). Finally, the pore walls were widened isotropically through consecutive dry-oxidation/oxide-removal steps (Fig. 1c, d) until the points of maximum diameter connected laterally (Fig. 1e), creating the 3D cubic symmetry [22] (Fig. 1f). On each step, a SiO_2 layer of 100 nm was grown in a tube furnace with a 70 min dry oxidation at 1040 °C in pure oxygen atmosphere. We have produced 3D cubic microstructures with a periodicity, *a*, of 2 μm and a total porosity, *p*, around 70%.

The fabricated 3D Si scaffolds (see Fig. 1) resemble a 3D cubic lattice of overlapped air spheroids embedded in Si. The produced Si scaffold obtained in this way retains the monocrystalline nature of the original substrate, which has deep implications on its thermal stability. The monocrystalline core will remain stable up to the melting temperature of silicon due to the lack of grain boundaries; however, microstructures are still sensitive to oxygen and surface diffusion effects [23,24], which soften them in solid phase. Hopefully, both effects can be effectively suppressed under the appropriate non-oxidizing atmospheres. For instance, silicon micro- and nanostructures can withstand very high temperatures in N_2 ambient for long times without any degradation, as a very thin nitride film forms over the structures which suppresses surface diffusion [25]. We appreciated no changes on the structures after 8 h annealing in a standard horizontal tube furnace at 1400 K in nitrogen ambient. We tested both, bare 3D samples and samples with 50 nm of grown thermal dry oxide. In fact, a thin thermal SiO_2 layer is also known to suppress surface diffusion [25], completely freezing the microstructures at high temperatures. In addition to the excellent thermal stability, crystalline silicon has a very high thermal conductivity and is a very elastic material, which might help to relieve the thermal gradients and stresses through the 3D network without cracking.

Three-dimensional macroporous structures behave as photonic crystals [21,22], and exhibit interesting thermal emission characteristics [26–28]; however, they are not good candidates for TPV applications since it is very difficult to efficiently reduce thermal emission at large wavelength bands [28]. In order to take advantage of the good thermal stability of crystalline silicon 3D structures we decided to deposit a conformal thin metal layer over the structure. In such metallo-dielectric structure the silicon scaffold would provide good thermal stability while the metallic film would define the optical properties, behaving much like a full-metallic photonic structure. In particular, 5 nm $Al_2O_3 + 50$ nm Pt layers were deposited over the samples by atomic layer deposition (ALD) (see Fig. 2). The thin alumina layer was not intended but required by the process, which was performed by the finish company Beneq Oy, in order to ensure a proper deposition of platinum. The ALD technique allows for a conformal deposition, while platinum was chosen for two main reasons namely it can be deposited by ALD and the considerably high Pt–Si eutectic temperature of 1103 K. In order to avoid the eutectic formation and reach higher operation temperatures we investigated both depositing the Pt directly over Si and over a 30 nm of high-quality SiO_2 layer previously grown by dry oxidation.

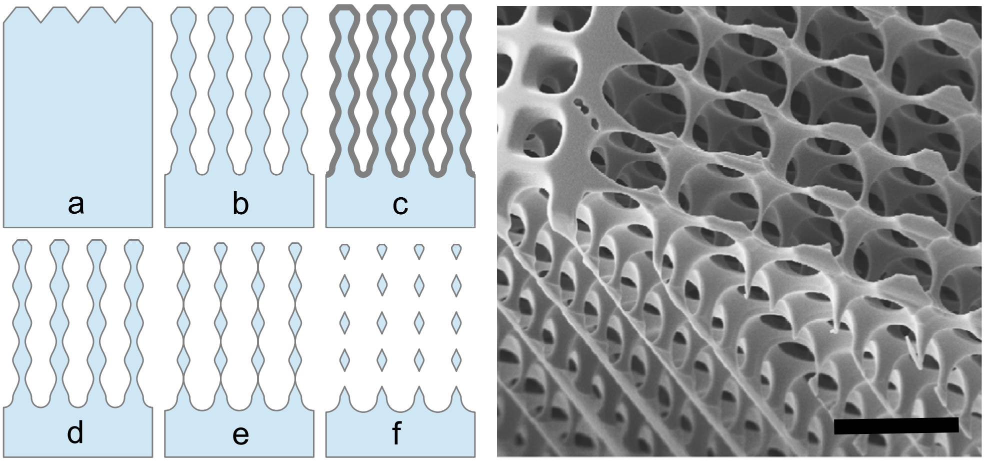

Fig. 1. Schematic of the scaffold fabrication. (a) Pore nucleation. (b) Electrochemical etching. (c, d) Oxidation/oxide-strip widening cycle. (d–f) Increased porosity after several cycles. The SEM image shows a highly-porous final structure. Scale bar is 4 μm.