Photonic Crystal Emitters for Thermophotovoltaic Energy Conversion

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Abstract. This paper reports the design, fabrication, and characterization of 2D photonic crystal (PhC) thermal emitters for a millimeter-scale hydrocarbon TPV microgenerator as a possible replacement for batteries in portable microelectronics, robotics, etc. In our TPV system, combustion heats a PhC emitter to incandescence and the resulting radiation is converted by a low-bandgap TPV cell. The PhC tailors the photonic density of states to produce spectrally confined thermal emission that matches the bandgap of the TPV cell, enabling high heat-to-electricity conversion efficiency. The work builds on a previously developed fabrication process to produce a square array of cylindrical cavities in a metal substrate. We will present ongoing incremental improvements in the optical and thermo-mechanical properties, the fabrication process, and the system integration, as recently combined with fabrication using novel materials, such as sputtered coatings, to enable a monolithic system.

1. Introduction

The increasing power demands of communication equipment, sensors, micro robotics platforms, and portable electronics has driven recent interest in micro- and millimeter-scale thermophotovoltaic (TPV) generators. Thermophotovoltaic energy conversion is a solid-state high-temperature heat-to-electricity conversion scheme with no moving parts that allows for scalable energy production with high specific energy from a variety of heat sources. In TPV systems, thermal radiation from a heat source at high temperature drives a suitable low-bandgap photovoltaic cell (PV). The heat can be produced by hydrocarbon combustion, ideal for lightweight, high specific energy portable power sources [1–3]; by radioisotope decay, ideal for space missions and remote missions requiring power sources with long lifetimes and low maintenance [4]; or by concentrated solar radiation [5]. A selective emitter between the source and the cell enables high heat-to-electricity conversion efficiency by enhancing in-band (convertible) radiation and suppressing out-of-band (nonconvertible) radiation that would otherwise be wasted.
The high temperature requirements of TPV applications constrain the choice for the selective emitter. Multilayer stacks [6], cermets [7], and other heterogeneous platforms are subject to thermo-mechanical stresses and chemical reactions at material interfaces that are initiated at elevated temperatures. Even homogeneous material platforms can degrade at high temperature: radius of curvature driven surface diffusion shortens the lifetime of complex structures such as 3D PhCs [8,9]. Our unique approach, the refractory metal 2D PhC consists of a square periodic array of holes etched into the low-emissivity polished metallic substrate. The PhC is fabricated in a single material, with a simple geometry that minimizes degradation by diffusion [10] and meets the requirements of TPV systems offering high spectral selectivity and high-temperature stability.

This 2D PhC emitter has been fabricated on single-crystal tungsten (W) substrates [11,12], on polycrystalline Ta and Ta-W alloy substrates [13,14], as well as sputtered Ta coatings [15]. The emissivity of the substrate material is selectively enhanced to near that of a blackbody emitter by the resonant cavity modes resulting from the etched holes. The spectral range of enhancement can therefore be easily tailored to the specific system needs by tuning cavity geometry to match the PhC to different low-bandgap TPV cells. In this paper, we present an overview of the advances that have been made over the past decade specifically in the design, materials, and fabrication of these 2D metallic PhCs that enable the high heat-to-electricity system efficiency of TPV systems.

2. Advances in Design, Optimization, and Simulation

Our chosen PhC design consists of a 2D square array of cylindrical holes etched in a large area metallic surface. This relatively simple design allowed us to simultaneously achieve near-blackbody emittance at short wavelengths as well as emittance almost as low as a polished metal at long wavelengths, with a sharp cutoff separating the two regimes [12]. The high emittance at short wavelengths is achieved by matching for each resonance the radiative rate to the absorptive rate. This is assisted by the fact that both the radiative and absorptive rates increases with mode number and hence frequency. At long wavelengths the emittance can be shown to be due to a surface area weighted effective impedance created by the holes [16].

The spectral emissivity of the PhC at normal incidence was initially determined by MEEP via finite-difference time-domain (FDTD) numerical methods [17]. However its high computational requirements limited its application in determining the optimized hemispherical emissivity. Thus, for quicker estimation, a mode matching formalism was developed matching the radiation fields at the boundary of free space and the cylindrical cavities via expansion in the basis of a small number of cavity modes for shorter wavelengths and utilizing a surface area weighted impedance for longer wavelengths [16]. Recently, rigorous coupled wave analysis methods (RCWA) [18] were also made available to simulate the full hemispherical performance relatively quickly. In all simulation methods, the material properties of the substrates were taken into account using a Lorentz-Drude model fitted to the elevated temperature emissivity to capture the optical dispersion of the substrate at high temperature. Nonlinear optimization determined the period, cavity radius, and height with bounds based on fabrication constraints [19]. The figure of merit used in the optimization was spectral selectivity defined as the ratio of power emitted in the desirable wavelength range to the total power at a given temperature. It has been verified that the most significant influence on the spectral properties in the range of interest is given by the cavity radius, whereas the period mainly influences the spectral position of the diffraction limit.

3. Advances in Substrate Materials

The emitter of a TPV system must withstand high temperatures for long operational lifetimes, be simple and relatively low-cost to fabricate, and have spectrally selective emission over a large
uniform area. Refractory metals, such as Ta and W, are most suitable for TPV applications due to their high melting point, low vapor pressure, low infrared emissivity, and ability to be etched. Single-crystal tungsten (W) was initially chosen for its optical and thermo-mechanical properties and relative availability [11, 12]. Tungsten was difficult to integrate into a system because it was difficult to machine and weld and because high quality, low cost, large area W was not available. Polycrystalline tantalum (Ta) is machinable, weldable and is available as high-purity, large area, cold rolled sheets, and allowed a direct system integration path [13]. Polycrystalline Ta5%W combined better thermo-mechanical properties of W with the more compliant material properties of Ta [14]. Substrates were cut, lapped, and polished to an optical finish. Some were pre-annealed to stabilize grain structure growth.

Metallic coatings were investigated in parallel as an alternative route to system integration. In initial studies, evaporated Ta coatings on Si were found to have low film density and high surface roughness, resulting in low reflectance in the near-infrared wavelength range [20] and thick sputtered W coatings on Si delaminated at high temperatures [21]. On the other hand, thick sputtered Ta coatings on polished Inconel 625, a readily available low-cost nickel-chromium-based superalloy used in many high-temperature applications, were found to be suitable substrates for high-temperature energy conversion applications [15]. The PhC fabricated in the Ta coating showed little deterioration of either the optical or thermo-mechanical properties after annealing for 1h at temperatures up to 1100°C and 24h at 900°C with the HfO2 thermal barrier coating.

4. Advances in Fabrication Methods
As shown in Fig. 2, the fabrication process begins with by defining a periodic pattern in photoresist (PR). The requirement for large area photonic crystal excluded methods such as electron beam lithography. The requirement for low cost metallic substrates excluded contact lithography where surface defects and roughness can result in large inaccuracies in the pattern. Thus interference lithography was used, which provides excellent pattern coherence across large areas of exposure and resolution comparable to stepper and electron-beam lithography. Two orthogonal exposures in a Mach-Zehnder setup generated the pattern. In order to prevent standing-wave induced vertically sinusoidal walls in the PR resulting from reflections from the hard-mask layer, a numerically optimized anti-reflection coating (ARC)/SiO2/PR stack was used.
A general process flow for the fabrication of our 2D PhC involves (1) pattern generation, (2) pattern transfer into a hard mask by etching, (3) pattern transfer into the metallic substrate by etching, and (4) surface passivation for thermal stability.

where the SiO\(_2\) served as a protection layer for the ARC while etching the PR.

Using reactive ion etching (RIE), the pattern was transferred through the tri-layer stack into the hard mask. Originally a chromium (Cr) hard-mask was used, patterned by wet chemical etching [11]. Initial results were acceptable however it was found that improvements to the optical properties (emittance) of the PhC could be achieved by fabricating a more precise structure, using dry etching. Reactive ion etching of the Cr hard-mask improved uniformity and accuracy of the cavities, facilitating large-area photonic crystal fabrication [22]. Switching from a Cr hard-mask to a plasma-enhanced chemical vapor deposition (PECVD) dense SiO\(_2\) mask improved the performance of the PhC in the long wavelength. Indeed, residual Cr on the surface of the Ta decreased the reflectance whereas SiO\(_2\) was completely removed by hydrofluoric acid.

Deep reactive ion etch (DRIE) process for Ta using a Bosch process was developed, which enabled ~8 µm deep cavities with an aspect ratio of 1:8, with very steep and smooth sidewalls. The thermal emitters fabricated by this method showed unprecedented spectral selectivity, enhancement of the emissivity below cut-off approaching unity, and a sharp cut-off between the high emissivity region and the low emissivity region, while maintaining the low intrinsic emissivity of bare Ta above the cut-off wavelength.

One of the greatest challenges of TPV is operating at such high temperatures, which impose strict requirements on the materials used. To address the problems of surface diffusion and surface reactions at high temperatures, a thin surface protective coating of HfO\(_2\) was deposited by atomic layer deposition (ALD), which acts as a thermal barrier coating and diffusion inhibitor due to its lower surface diffusion [23, 24]. In a number of studies, we observed the degradation of Ta samples without such a coating even after 3h at 900°C due to the formation of tantalum carbide on the surface, resulting in an increased emissivity at long wavelengths. In contrast, those with the coating have consistently showed no degradation of either the optical or structural properties for up to 144h at 900°C.

5. Conclusion
Selective emitters are an enabling component of a TPV system. Even a simple multilayer stack PhC has been shown to double the fuel-to-electricity conversion efficiency versus a greybody emitter for a millimeter-scale TPV system [3]. A similarly large increase in efficiency is predicted for a 2D PhC. Using our 2D PhC, a TPV microgenerator can thus greatly exceed the performance of batteries. This paper presented an overview of the advances made over the past decade specifically in the design, materials, and fabrication of 2D metallic PhCs that enable high heat-to-electricity system efficiency of TPV systems, in particular our hydrocarbon TPV microburner.
Acknowledgments
The authors would like to thank: J. Daley and T. Savas at NSL (MIT), and R. Geil at the University of North Carolina at Chapel Hill for assistance with fabrication of the PhC. H.C. Starck for Ta and Ta3%W substrates; and Southwest Research Institute for Ta sputtering. Fabrication was done in part at NSL at MIT and at CNS at Harvard University, a member of the National Nanotechnology Infrastructure Network (NNIN), supported by the National Science Foundation (NSF) under NSF Award No. ECS-0335765. Fabrication was supported as part of the Solid-State Solar-Thermal Energy Conversion Center (S3TEC), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under Award # DE-SC0001299 / DE-FG02-09ER46577 and by the U.S. Army Research Laboratory and the U.S. Army Research Office through the Institute for Soldier Nanotechnologies, under Contract # W911NF-13-D-0001.

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