Proceedings of the ASME 2016 5th International Conference on Micro/Nanoscale Heat and Mass Transfer
MNHMT2016
January 4-6, 2016, Biopolis, Singapore

MNHMT2016-6698

IMPROVED THERMAL EMITTERS FOR THERMOPHOTOVOLTAIC ENERGY CONVERSION

Veronika Stelmakh[*], **Walker R. Chan,**
John D. Joannopoulos, Marin Soljacic, Ivan Celanovic
Massachusetts Institute of Technology
Cambridge, Massachusetts, 02139
Email: stelmakh@mit.edu

Kimberly Sablon
Sensors and Electron Devices Directorate
U.S. Army Research Laboratory
Adelphi, Maryland, 20783

ABSTRACT

Thermophotovoltaic (TPV) energy conversion enables millimeter scale power generation required for portable microelectronics, robotics, etc. In a TPV system, a heat source heats a selective emitter to incandescence, the radiation from which is incident on a low bandgap TPV cell. The selective emitter tailors the photonic density of states to produce spectrally confined selective emission of light matching the bandgap of the photovoltaic cell, enabling high heat-to-electricity conversion efficiency. The selective emitter requires: thermal stability at high-temperatures for long operational lifetimes, simple and relatively low-cost fabrication, as well as spectrally selective emission over a large uniform area. Generally, the selective emission can either originate from the natural material properties, such as in ytterbia or erbia emitters, or can be engineered through microstructuring. Our approach, the 2D photonic crystal fabricated in refractory metals, offers high spectral selectivity and high-temperature stability while being fabricated by standard semiconductor processes. In this work, we present a brief comparison of TPV system efficiencies using these different emitter technologies. We then focus on the design, fabrication, and characterization of our current 2D photonic crystal, which is a square lattice of cylindrical holes fabricated in a refractory metal substrate. The spectral performance and thermal stability of the fabricated photonic crystal thermal emitters are demonstrated and the efficiency gain of our model TPV system is characterized.

[*]Address all correspondence to this author

INTRODUCTION

The increasing power demands of communication equipment, sensors, micro robotics platforms, and portable electronics has driven recent interest in micro- and millimeter-scale generators. Thermophotovoltaic (TPV) energy conversion is one approach to harness the high specific energy of hydrocarbon fuels [1–3]. In a TPV system, combustion heats an emitter to incandescence and the resulting thermal radiation is converted to electricity by a low-bandgap TPV cell. The difference between a solar photovoltaic system and a TPV system is that a TPV system produces its own light—the spectrum does not need to be the solar spectrum or even blackbody and the cells do not need to be silicon. The selective emitter however is the crucial component of any practical TPV system.

One of the key challenges of TPV is making efficient use of the thermal radiation by matching the thermal radiation spectrum to the quantum efficiency of the TPV cell. The TPV cell can convert in-band radiation (photon energies above its bandgap) reasonably efficiently to electricity but out-of-band (photon energies below its bandgap) radiation is wasted. This spectral matching can be accomplished using a selective emitter (either natural or engineered) that strongly emits at some wavelengths and weakly emits at others, using a cold side filter that transmits some wavelengths to the cell and reflects others back to the selective emitter, or using both. However cold side filters require a low loss emitter-filter-cell optical cavity, which is difficult to achieve in a practical system. Natural emitters tend to have low overall emissivity, allowing parasitic heat loss mechanisms to dominate the

heat balance. Early research in TPV has relied on natural materials such as ytterbia or erbia. While TPV mantles made from such rare earth oxides are low-cost, their spectral performance can be greatly improved. Engineered emitters are a promising approach: recent advances in photonic crystals allow near-perfect control of the thermal emission spectrum.

Photonic crystals are classified as 1D, 2D, or 3D according to the number of periodic dimensions and their emission spectrum is primarily determined by the geometry rather than by specific material properties, allowing the cutoff wavelength to be tuned. Moreover, they typically offer near blackbody emission resulting from resonant phenomenon at the desired wavelengths and near zero emission elsewhere resulting from the low loss materials from which they are fabricated. Photonic crystals have been fabricated in different refractory metals: single-crystal tungsten (W) bulk substrates [4–8], polycrystalline tantalum (Ta) and Ta-W alloy bulk substrates [9, 10], and even sputtered Ta coatings [11]. Refractory metals are preferred in high-temperature (∼900–1200°C) TPV applications due to their high melting point, low vapor pressure, advantageous low emissivity in the infrared, and ability to be etched.

In this work, we examine selective emitters, natural and engineered, in the context of a combustion driven TPV system. We then present our 2D photonic crystal selective emitter design that enables high system efficiency while being relatively simple to fabricate in a refractory metal substrate.

SELECTIVE EMITTER PERFORMANCE

Selective emitters are characterized by their high-temperature emittance, as shown in Fig. 1(a). Here, we compared a 1D silicon/silicon dioxide multilayer stack [12], our 2D photonic crystal design (current design [10] and improved design [13]), a natural erbia emitter [14], and a blackbody emitter, with an ideal emitter. A step function with unity in-band emissivity and zero out-of-band emissivity was used as the ideal selective emitter.

There are typically two common figures of merit for a selective emitter: spectral selectivity (η_{sp}) and effective in-band emissivity (ε_{in}):

$$\eta_{sp} = \frac{\int_0^{\lambda_{PV}} \varepsilon(\lambda)\, e_b(\lambda)\, d\lambda}{\int_0^{\infty} \varepsilon(\lambda)\, e_b(\lambda)\, d\lambda} \tag{1}$$

$$\varepsilon_{in} = \frac{\int_0^{\lambda_{PV}} \varepsilon(\lambda)\, e_b(\lambda)\, d\lambda}{\int_0^{\lambda_{PV}} e_b(\lambda)\, d\lambda} \tag{2}$$

where $e_b = 2hc^2/[\lambda^5(e^{hc/\lambda k_B T} - 1)]$ is the Planck blackbody, $\varepsilon(\lambda)$ is the hemispherically-averaged wavelength-dependent emissivity of the selective emitter, λ is the wavelength, λ_{PV} corresponds to the bandgap of the PV cell, h is Planck's constant, c

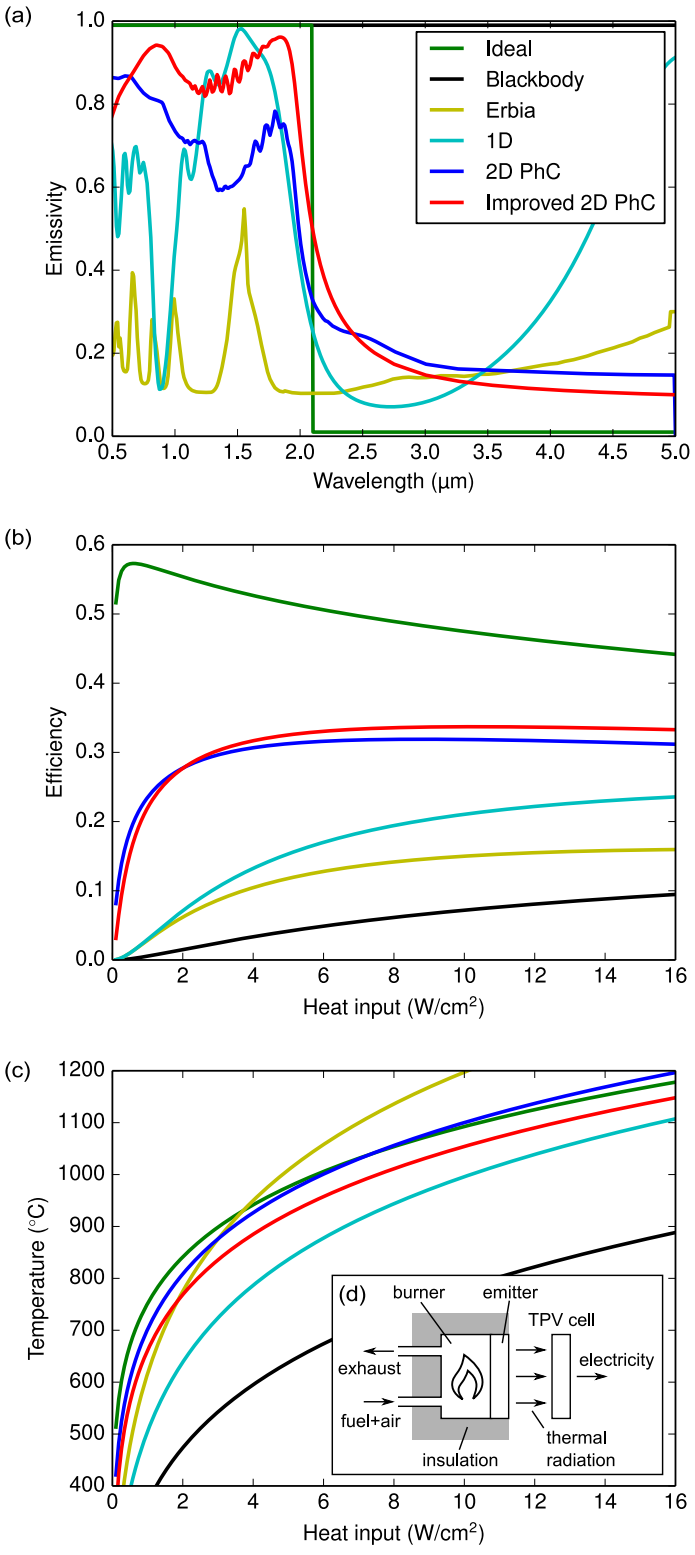

FIGURE 1. PERFORMANCE OF DIFFERENT SELECTIVE EMITTERS IN A SIMPLE TPV SYSTEM.

TABLE 1. Hot side efficiency (η_{hs}) and temperature (T) of different emitters in a TPV system with a 10 W fuel input.

Emitter	η_{hs} (%)		T (°C)
	Absolute	Relative	
Ideal	47.5	100	1092
Blackbody	7.1	15.0	779
Erbia	15.0	31.6	1197
1D	21.1	44.3	995
2D PhC	31.9	67.1	1100
Improved 2D PhC	33.7	71.0	1054

is the speed of light, k_B is the Boltzmann constant, and T is the temperature.

These figures of merit do not directly reflect the selective emitter's performance in a real TPV system: they do not predict, for example, whether the 1D emitter (high ε_{in} and moderate η_{sp}) or the erbia emitter (moderate η_{sp} and low ε_{in}) will give a more efficient system. Thus, in this work, a new figure of merit is used: the efficiency with which the emitter and and ideal burner turn fuel into in-band radiation. This hot-side efficiency is defined as

$$\eta_{hs} = \frac{Q_{in}}{Q_{fuel}} \tag{3}$$

where Q_{fuel} is the caloric content of the fuel, and Q_{in} is the in-band radiation. This figure of merit requires a simple system model of the hot side (burner and emitter) of a combustion driven TPV system, as shown in Fig. 1(d). We assumed that the hot side was perfectly thermally insulated from the environment with the exception of thermal radiation from the selective emitter and the fuel, air, and exhaust flows necessary to sustain combustion. In the present model, we did not account for the efficiency of the cell. The hot side efficiency of the system using different selective emitters and the temperature the emitters reach was compared in Fig. 1(b) and (c), respectively. Using this model, we can now determine which emitter gives a more efficient system. In the case of our previous example, we see that the 1D emitter is better than the erbia emitter for this application: despite the moderate η_{sp}, the 1D emitter has a higher η_{hs} because its temperature is lower due to its higher emissivity resulting in reduced exhaust loss.

At a fuel flow of 10 W/cm^2, η_{hs} for a system with a blackbody emitter was found to be only 7%; the 2D photonic crystal achieved an efficiency of 32%; and the ideal selective emitter reached 47%, as listed in Table 1. Our 2D photonic crystal reached 67% of the ideal selective emitter limit of a combustion driven TPV system. Furthermore, by filling the cavities of the photonic crystal, we could improve the in-band emissivity which alters the heat balance of the model system (a larger percentage of the fuel's energy is radiated rather than lost out the exhaust) resulting in a slightly improved efficiency. Additionally, all the efficiencies, including the ideal, can be increased by recuperating heat from the exhaust to preheat the incoming air.

2D PHOTONIC CRYSTAL EMITTER

Design and Fabrication

Our chosen photonic crystal design consists of a 2D square periodic array of cylindrical cavities etched in a large area polished metallic surface, as shown in Fig. 2(a). The emissivity in the desired wavelength range is enhanced by the introduction of resonant cavity modes. 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 [8]. 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 [15].

The geometric parameters of the cavity array define the cutoff wavelength, which is tuned by selecting the appropriate radius r, period a, and depth d. Rigorous coupled wave analysis methods (RCWA) [16] were used to obtain the reflectance of the optimized parameters found by nonlinear optimization. The figure of merit used in the optimization was spectral selectivity previously defined. 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.

Our 2D photonic crystal is fabricated on polished metallic substrates, such as Ta, using interference lithography and reactive ion etching (RIE) of a hard mask and a subsequent deep RIE (DRIE). A layer of SiO_2 is deposited by plasma-enhanced chemical vapor deposition (PECVD) onto the cleaned substrates to be used as a hard mask for the Ta etching. An anti-reflection coating (ARC) is then spin-coated and another layer of SiO_2 is e-beam evaporated onto the sample to serve as a protection layer when etching and ashing the ARC. Finally, a layer of negative photoresist is spin-coated onto the sample for the lithography process. Interference lithography is performed using a Mach-Zehnder setup with a 325 nm helium cadmium laser to obtain a large periodic pattern with high uniformity. The square array of cylindrical holes is created by double exposure of the photoresist and the cavity diameter is enlarged to the optimized value by isotropic plasma ashing. The pattern is subsequently transferred into the SiO_2 mask by reactive ion etching (RIE). The final etching of the Ta substrate is done by a Bosch etch process using SF_6 and C_4F_8 as the etching and passivating gaseous species. The residual passivation layer is removed by oxygen ashing and

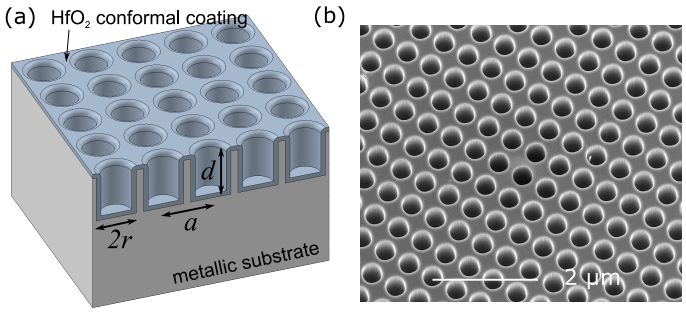

FIGURE 2. (A) GEOMETRIC PARAMETERS OF OUR 2D PHOTONIC CRYSTAL DESIGN. (B) SEM OF THE FABRICATED 2D TA PHOTONIC CRYSTAL.

the residual SiO_2 layer is removed by hydrofluoric acid. A conformal layer of HfO_2 is deposited via atomic layer deposition (ALD) at 250°C to prevent degradation of the coatings at high temperatures. The resulting fabricated photonic crystal is shown in Fig. 2(b).

High temperature performance

The intended use of the photonic crystals at target operating temperatures >900°C and expected lifetimes of years impose strict requirements on both the thermal stability of the fabricated microstructures and their optical properties as well as the thermal and thermo-mechanical stability of the emitter substrates in the context of system integration. The conformal HfO_2 ALD layer has been shown to limit the formation of carbides and enhance the thermal stability of the photonic crystal such that it can sustain annealing at 900°C for 144 hours without structural degradation or decrease in optical performance (characterized by visual inspection of micrographs and from the measured spectral reflectance). Without the coating, thermal degradation of the reflectance spectra was observed, possibly due to a rounding of structure profiles from surface diffusion or surface reactions [17].

Improvements discussion

The current 2D photonic crystal design offers significant improvements over other emitter designs. However additional improvements can be made to further better the angular optical performance and the system integration.

In regards to the angular improvement, previous work has shown that a dielectric filled 2D photonic crystal overcomes the narrow angular emission of the current photonic crystal, thus increasing the overall energy conversion efficiency and power density of TPV systems [13, 18]. Because of the higher index of refraction, the optical diameter of the dielectric filled cavities can be maintained while reducing the physical diameter. A smaller physical diameter shifts the short wavelength diffraction cutoff at all angles. On the other hand, keeping the optical diameter the same maintains the desired long wavelength cutoff. Hafnium oxide is the dielectric material of choice because of its transparency in the visible and infrared region, its compatible thermal expansion coefficient, and, as previously mentioned, its stability at high temperatures. A filled cavity photonic crystal can be fabricated following the same procedure but depositing the conformal ALD HfO_2 coating until the cavities are filled. The surface of the photonic crystal is then finished by chemical mechanical polishing. An experimental demonstration of such a photonic crystal is underway.

In regards to the integration improvement, a 2D photonic crystal was recently fabricated in a sputtered Ta coating on Inconel for use as a selective emitter in a monolithic TPV system [19]. The spectral efficiency and in-band irradiance of the fabricated selective emitter was found to be approximately double that of the non-structured surface. The high temperature stability of the fabricated photonic crystal was tested by annealing for one hour at 700, 900, and 1100°C, and for 24 hours at 900°C. No delamination, surface deterioration, or microstructural damage was observed from visual inspection of micrographs. Minimal degradation of the optical spectrum was observed, paving the way for a new integration path of the selective emitter in thermophotovoltaic energy conversion applications.

CONCLUSION

In this work, a brief comparison of TPV system efficiencies using different emitter technologies was presented using a simple model we developed to quantify the performance of emitters in a combustion driven TPV system. We have shown that 2D photonic crystals offer the best performance while being stable at high temperatures and relatively easy to fabricate. The design and fabrication of the 2D photonic crystal was also presented. Indeed, our 2D photonic crystal realizes 67% of the ideal emitter limit and could be improved to 71%.

ACKNOWLEDGMENT

The authors would like to thank: Jim Daley and Tim Savas at NSL (MIT), and Robert Geil at the University of North Carolina at Chapel Hill for assistance with fabrication of the photonic crystal. Fabrication was done in part at the Nanostructures Laboratory (NSL) at MIT and at the Center for Nanoscale Systems (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 by 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. Research was

also supported 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.

REFERENCES

[1] Chan, W. R., Wilhite, B. A., Senkevich, J. J., Soljacic, M., Joannopoulos, J. D., and Celanovic, I., 2013. "An all-metallic microburner for a millimeter-scale thermophotovoltaic generator". In Journal of Physics: Conference Series, Vol. 476, p. 012017.

[2] Fraas, L., Ballantyne, R., Samaras, J., and Seal, M., 1994. "A thermophotovoltaic electric generator using GaSb cells with a hydrocarbon burner". *Proceedings of 1994 IEEE 1st World Conference on Photovoltaic Energy Conversion - WCPEC (A Joint Conference of PVSC, PVSEC and PSEC),* ***2***.

[3] Wenming, Y., Siawkiang, C., Chang, S., Hong, X., and Zhiwang, L., 2005. "Research on micro-thermophotovoltaic power generators with different emitting materials". *Journal of Micromechanics and Microengineering,* ***15***(9), p. S239.

[4] Heinzel, A., Boerner, V., Gombert, A., Blasi, B., Wittwer, V., and Luther, J., 2000. "Radiation filters and emitters for the NIR based on periodically structured metal surfaces". *J. Mod. Opt.,* ***47***.

[5] Sai, H., Kanamori, Y., and Yugami, H., 2003. "High-temperature resistive surface grating for spectral control of thermal radiation". *Appl. Phys. Lett.,* ***82***, pp. 1685–1687.

[6] Rephaeli, E., and Fan, S., 2008. "Tungsten black absorber for solar light with wide angular operation range". *Applied Physics Letters,* ***92***(21), p. 211107.

[7] Celanovic, I., Jovanovic, N., and Kassakian, J., 2008. "Two-dimensional tungsten photonic crystals as selective thermal emitters". *Applied Physics Letters,* ***92***(19), p. 193101.

[8] Yeng, Y. X., Ghebrebrhan, M., Bermel, P., Chan, W. R., Joannopoulos, J. D., Soljacic, M., Celanovic, I., Soljacic, M., and Celanovic, I., 2012. "Enabling high-temperature nanophotonics for energy applications". *Proceedings of the National Academy of Sciences,* ***109***(7), pp. 2280–2285.

[9] Rinnerbauer, V., Ndao, S., Yeng, Y. X., Chan, W. R., Senkevich, J. J., Joannopoulos, J. D., Soljačić, M., and Celanovic, I., 2012. "Recent developments in high-temperature photonic crystals for energy conversion". *Energy & Environmental Science,* ***5***(10), p. 8815.

[10] Stelmakh, V., Rinnerbauer, V., Geil, R. D., Aimone, P. R., Senkevich, J. J., Joannopoulos, J. D., Soljacic, M., Celanovic, I., Soljačić, M., and Celanovic, I., 2013. "High-temperature tantalum tungsten alloy photonic crystals: Stability, optical properties, and fabrication". *Applied Physics Letters,* ***103***(12), pp. 0–4.

[11] Stelmakh, V., Peykov, D., Chan, W. R., Senkevich, J. J., Castillo, R., Coulter, K., Wei, R., Joannopoulos, J. D., Soljačić, M., and Celanovic, I., 2015. "Thick Sputtered Tantalum Coatings for High-Temperature Energy Conversion Applications". *Journal of Vacuum Science & Technology A*.

[12] Chan, W. R., Bermel, P., Pilawa-Podgurski, R. C. N., Marton, C. H., Jensen, K. F., Senkevich, J. J., Joannopoulos, J. D., Soljacic, M., and Celanovic, I., 2013. "Toward high-energy-density, high-efficiency, and moderate-temperature chip-scale thermophotovoltaics". *Proceedings of the National Academy of Sciences,* ***110***(14), pp. 5309–5314.

[13] Yeng, Y. X., Chou, J. B., Rinnerbauer, V., Shen, Y., Kim, S.-G., Joannopoulos, J. D., Soljacic, M., and Čelanović, I., 2014. "Global optimization of omnidirectional wavelength selective emitters/absorbers based on dielectric-filled anti-reflection coated two-dimensional metallic photonic crystals". *Optics Express,* ***22***(18), p. 21711.

[14] Guazzoni, G. E., 1972. "High- temperature spectral emittance of oxides of erbium, samarium, neodymium and ytterbium". *Applied Spectroscopy,* ***26***(1), Jan., pp. 60–65.

[15] Ghebrebrhan, M., Bermel, P., Yeng, Y. X., Celanovic, I., Soljacic, M., and Joannopoulos, J. D., 2011. "Tailoring thermal emission via Q matching of photonic crystal resonances". *Physical Review A - Atomic, Molecular, and Optical Physics,* ***83***(3), pp. 1–6.

[16] Liu, V., and Fan, S., 2012. "S 4: A free electromagnetic solver for layered periodic structures". *Computer Physics Communications,* ***183***(10), pp. 2233–2244.

[17] Rinnerbauer, V., Yeng, Y. X., Chan, W. R., Senkevich, J. J., Joannopoulos, J. D., Soljačić, M., and Celanovic, I., 2013. "High-temperature stability and selective thermal emission of polycrystalline tantalum photonic crystals.". *Optics express,* ***21***(9), May, pp. 11482–91.

[18] Chou, J. B., Yeng, Y. X., Lenert, A., Rinnerbauer, V., Celanovic, I., Soljačić, M., Wang, E. N., and Kim, S.-G., 2014. "Design of wide-angle selective absorbers/emitters with dielectric filled metallic photonic crystals for energy applications.". *Optics express,* ***22 Suppl 1***(January), pp. A144–54.

[19] Stelmakh, V., Chan, W. R., Senkevich, J. J., Joannopoulos, J. D., Soljačić, M., and Celanovic, I., 2015. "Sputtered Tantalum Photonic Crystal Coatings for High-Temperature Energy Conversion Applications". *IEEE Transactions on Nanotechnology*.