Heterogeneous Metasurface for High Temperature Selective Emission

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We demonstrate selective emission from a heterogeneous metasurface that can survive repeated temperature cycling at 1300 K. Simulations, fabrication and characterization were performed for a cross-over-a-backplane metasurface consisting of platinum and alumina layers on a sapphire substrate. The structure was stabilized for high temperature operation by an encapsulating alumina layer. The geometry was optimized for integration into a thermophotovoltaic (TPV) system and was designed to have its emissivity matched to the external quantum efficiency spectrum of 0.6 eV InGaAs TPV material. We present spectral measurements of the metasurface that result in a predicted 22\% optical-to-electrical power conversion efficiency in a simplified model. Furthermore, this broadly adaptable selective emitter design can be easily integrated into full-scale TPV systems.

Thermophotovoltaic (TPV) energy conversion was first identified as a promising technology for converting waste heat into electricity in the 1960s\textsuperscript{1}. Since then, work has demonstrated the potential of combustion-TPV systems to act as compact, portable power sources with energy densities nearly 10 times that of rechargeable batteries\textsuperscript{2,3} that are critical for a broad range of military and commercial applications. TPV systems convert thermal radiation emitted from a high temperature source (the emitter) into electricity by means of a photovoltaic (PV) diode. If we treat a TPV system as a heat engine with hot (\(T_{BB}\)) and cold side (\(T_{PV}\)), we can calculate the theoretical thermodynamic (Carnot) efficiency limit: \(\eta_{\text{Carnot}} = \frac{T_{BB} - T_{PV}}{T_{BB}}\). For \(T_{BB} = 1300\) K and \(T_{PV} = 300\) K, \(\eta_{\text{Carnot}} = 0.77\). In practice, the efficiencies of TPV systems have been fundamentally limited to \(\sim 15\%\) by the mismatch between the blackbody spectrum of the heated emitter and the external quantum efficiency (EQE) of the TPV material. (Other system considerations have reduced demonstrated efficiencies of combustion-TPV systems to \(\sim 2.5\%\).\textsuperscript{3}) Thus, a significant amount of work over the past 30 years has focused on improving the optical-to-electrical conversion efficiency by recycling out of band photons\textsuperscript{4}, using multiple bandgap cells\textsuperscript{5}, modifying the emissivity of an object away from the typical blackbody\textsuperscript{6-8}, or a combination of these techniques\textsuperscript{9}.

Numerous geometries for modifying the emission spectrum have been studied, including metal (such as tungsten) photonic crystals\textsuperscript{7,10}, inverse opals\textsuperscript{11}, and metal-dielectric-metal (MDM) metasurfaces\textsuperscript{8,12-14}. While the first

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two groups have shown promise regarding emissivity and survivability at operating temperatures, questions remain about the ability to scale these geometries beyond laboratory demonstrations. MDM metasurfaces, on the other hand, can easily be fabricated by standard foundry lithography techniques while exhibiting extremely tailorable emission spectra that can be made angle-independent when the layer thicknesses are significantly sub-wavelength. The main limitation of the MDM metasurface geometry has been the presence of interfacial stress in the multilayer stack that can lead to delamination at high temperature. However, this issue can be mitigated by properly choosing non-reactive metals and dielectrics that have matching coefficients of thermal expansion (CTEs) from room temperature to > 1300 K. In this letter, we report on the modeling, fabrication, and characterization of a MDM metasurface with a dielectrically symmetric geometry comprised of a platinum (Pt) cross above a Pt backplane, an alumina (Al₂O₃) spacer layer and Al₂O₃ encapsulation on a sapphire substrate that survived repeated temperature cycling to 1300 K. With this geometry, our model predicts at least 23% photonic-to-electronic energy conversion efficiency, 43% spectral efficiency, and 1.2 W/cm² of output power when coupled with a 0.6 eV strain-relaxed InGaAs PV cell.

Our emitter design is shown in Figure 1(a). The design has five degrees of freedom: p (unit cell period), h (thickness of the spacer layer), t (thickness of the cross), w (long dimension of the cross), and l (short dimension of the cross). We use Pt as our metal because it has good optical properties and should not oxidize at temperatures below 1500 K in an air environment. Additionally, it has well matched CTE to Al₂O₃ from room temperature to 1500 K, decreasing the likelihood of delamination of a Pt/Al₂O₃ stack. The geometry is similar to that used in previous demonstrations, though our final design uses an encapsulation layer and operates in a different design parameter regime. The mechanism for the resonance has been previously described.

The fabrication procedure is outlined in Figure 1(b). To begin, an optically thick (200 nm) layer of Pt (with a 20 nm chrome adhesion layer) and h = 90 nm thick layer of Al₂O₃ were e-beam evaporated onto a crystalline sapphire (Al₂O₃) wafer (MTI Corp). Next a layer of ZEP-520 e-beam resist (EBR) was spun onto the wafer, exposed by an e-beam writer, and then developed to expose the Al₂O₃ underneath. A second layer of Pt (thickness t = 45 nm) was then deposited on the whole chip, followed by lift-off of the EBR. An SEM image of a device array at this stage in the fabrication process can be seen in the inset of Figure 2(a). Finally, an additional 150 nm-thick layer of Al₂O₃ was deposited via Atomic Layer Deposition (ALD) to encapsulate the crosses (Figure 2(b), inset). We fabricated twenty five 500 µm × 500 µm arrays of crosses, with 400 nm < p < 600 nm, 150 nm < l < 250 nm, 250 nm < w < 300 nm in
We chose these numbers based on reflectance simulations of the unencapsulated structure performed using the FDTD (finite difference time domain) Solutions package from Lumerical Solutions, Inc. A search of parameter space led to a set of optimized parameters that resulted in a broad and deep reflection dip that is independent of the incident angle of radiation. A representative reflectivity spectrum can be seen in Figure 2(a) (green line), for \( w = 275 \text{ nm}, \ l = 150 \text{ nm}, \ p = 400 \text{ nm}, \ h = 90 \text{ nm}, \) and \( t = 45 \text{ nm} \).

We measured the unencapsulated (blue line, Figure 2(a)) and encapsulated (Figure 2(b)) structures in a microscope-coupled Fourier-transform infra-red (FTIR) spectrometer fitted with a HgCdTe detector. By comparing the curves in Figure 2(a), we can see good agreement between simulation and experiment. FTIR measurements of the encapsulated sample’s infra-red absorption features (Figure 2(b)) reveal a broadening of the resonances compared to the unencapsulated structure.

To test the multilayer structure’s robustness to high-temperature thermal cycling, we annealed the encapsulated samples in an argon atmosphere at 1300 K, in two, five and five minute increments. After each annealing cycle, we characterized the emitter arrays with the FTIR spectrometer through an optical microscope. Two measurements with were taken with the FTIR to measure the reflectivity between 0.9 and 3.2 μm and between 3.2 and 10 μm, respectively. Figure 3(a) shows the FTIR spectrum for a particular pattern  \( (w = 275 \text{ nm}, \ l = 250 \text{ nm}, \ p = 550 \text{ nm}) \) before thermal cycling (red), after the first two-minute cycle (green) and after three cycles and twelve total minutes at 1300 K (blue). The slight shift from the pre-baked spectrum after the first bake is likely due to a measured 5 nm change in the thickness of the ALD-deposited \( \text{Al}_2\text{O}_3 \) that occurred because of densification during the initial anneal. Figure 3(b) and (c) show an optical image for 10 of the 25 pre-anneal encapsulated metamaterial arrays and a
representative SEM image of four unit cells of one of the arrays, respectively. Figure 3(d) and (e) are the same as (b) and (c) but after the three thermal cycles. By comparing the pre- and post-cycle images we notice no discernable macroscopic change in the visible-frequency spectral properties or microscopic change in the shape of the encapsulated crosses after all three thermal cycles. Additionally, there is no evidence of delamination anywhere on the chip, as the post-anneal sample resembles the pre-anneal sample. Combined with the FTIR measurements, these results indicate that the encapsulated structure is highly stable to thermal cycling.

FIG. 2. (a): Comparison of simulated and experimental reflectance spectra for the unencapsulated structure. (b) Variation in reflectance spectra five different encapsulated structures with $w = 275$ nm. SEM images of the unencapsulated (a) and encapsulated (b) structures are shown in the insets. The SEM image of the encapsulated structure appears blurry because the imaging electrons do not penetrate the encapsulating layer.

For comparison, we plot the same data for the unencapsulated structure (Fig. 3(f)–(j)). Upon heating, the Pt crosses undergo a morphological change (Fig. 3(j) inset compared to Fig. 3(h)) to lower their energy by reducing their surface area, forming globules, which results in a dramatic shift in the infrared reflection spectra (Fig. 3(d), red to green line) as well as the optical appearance (Fig. 3(g) to (i)). The morphological change occurs within the first two minutes at 1300 K and the new surface configuration is stable to additional heating and temperature cycling, as indicated by the similarity between the blue and green curves. Recent work\textsuperscript{14} demonstrated robust operation up to 900 K of a Pt/Al$_2$O$_3$ metasurface but without the encapsulation layer. Our results indicate that the encapsulation layer is necessary to reach temperatures $> 1300$ K for integration into efficient TPV systems.
FIG. 3. (a) Reflectivity of the encapsulated emitter before (red), after a two minute thermal anneal cycle at 1300 K (green) and after three cycles and 12 total minutes at 1300 K (blue). (b) Pre-anneal optical image of ten of the 500μm x 500μm arrays. (c) SEM image of one part of one of the arrays. (d,e): Post-anneal optical and SEM images revealing no microscopic or macroscopic morphological change in the metasurface. (f-j): Same as (a-e) but for the unencapsulated structure. The change in the reflectivity after annealing is reflected in the visible frequency spectrum optical image (i) and the SEM image (j) showing a morphological change. All curves in (a) and (f) correspond to the emitter array in the second row and fourth column of the optical images, with \( w = 275 \text{ nm}, l = 250 \text{ nm}, p = 550 \text{ nm} \).

We used the measured, room temperature absorption spectra to represent the emissivity \((\varepsilon_{\text{emit}}(\omega) = 1 - R(\omega))\) of the metasurface at high temperature. While other metals, such as tungsten\(^{19}\), have shown their emissivity above 2μm increase >30% at 1300 K compared to room temperature (as predicted by a temperature-dependent Drude model\(^{20}\)), two recent publications\(^{14,21}\) indicated no quantifiable change in the emissivity of platinum, though further studies are needed to properly quantify the emissivity of Pt as a function of temperature. We thus use the room-temperature emissivity to model how well our emitter will behave in a TPV system (Figure 4) and calculate the TPV cell efficiency \(\eta_{\text{TPV}}\) and the generated power \(P_{\text{out}}\). We can understand \(\eta_{\text{TPV}}\) as the product of the power-spectral efficiency \((\eta_{\text{ps}}: \text{power absorbed by the PV diode divided by the power emitted by the selective emitter}, P_{\text{rad}})\) and the diode’s efficiency \((\eta_{\text{diode}}: \text{power conversion efficiency of absorbed photons})\). Consequently, we can write

\[
\eta_{\text{TPV}} = \eta_{\text{ps}} \eta_{\text{diode}} = \frac{P_{\text{abs}}}{P_{\text{rad}}} \frac{P_{\text{out}}}{P_{\text{abs}}} = \frac{V_{\text{OC}} I_{\text{SC}} FF}{P_{\text{rad}}}
\]

(1)

where \(V_{\text{OC}}\) is the diode’s open circuit voltage, \(I_{\text{SC}}\) is the diode’s short circuit current, and \(FF\) is the fill factor, which will be defined below. Since the emitter is at \(T_{\text{emit}}=1300 \text{ K}\) and the PV diode is at \(T_{\text{PV}} = 300 \text{ K}\), the amount of power radiated to the TPV cell from the emitter can be expressed as:
\[ P_{\text{rad}} = \int_0^\infty \frac{\omega^2}{(2\pi)^2 c^2} \frac{h\omega}{kT_{\text{emit}}} \exp\left(\frac{h\omega}{kT_{\text{emit}}}\right) - 1 \varepsilon(\omega) d\omega \] 

where \( c \) is the speed of light, \( k \) is the Boltzmann constant, \( \omega \) is the angular frequency, and we are ignoring the negligible radiation path from the PV cell to the emitter because \( T_{\text{emit}} \gg T_{\text{PV}} \) and we are assuming angle and polarization-independent emission and an anti-reflection (AR) coated PV cell. The integrand of Eq. 2 with \( \varepsilon = 1 \), assuming a perfect blackbody, is drawn as the green dashed line in Fig. 4 and plotted on the right vertical axis, while the emissivity \( \varepsilon_{\text{emit}} \) (blue line) is plotted along the left vertical axis. The full integrand of Eq. 2 (the product of the blackbody power spectrum and \( \varepsilon_{\text{emit}} \)) represents the actual radiated power spectrum at 1300 K and is plotted as the cyan line along the right vertical axis.

The amount of power generated by the PV cell \( (P_{\text{out}}) \) is proportional to the number of electron-hole pairs generated and thus is also proportional to the number of emitted, above-bandgap photons, \( n_{\text{emit}} \) (as opposed to the emitted power density) which we can write as

\[ n_{\text{emit}} = \int_0^\infty \frac{\omega^2}{(2\pi)^2 c^2} \frac{1}{\exp\left(\frac{h\omega}{kT_{\text{emit}}}\right) - 1} \varepsilon(\omega) d\omega \]
The EQE of the TPV material is defined as the percentage of incident photons converted to electron-hole pairs and is plotted as the black line against the left vertical axis of Fig. 4. The integrand of Eq. 3 with $\varepsilon = 1$ represents a blackbody photon density ($\bar{n}_{BB}$) at 1300 K and is plotted as the red dashed line. The integrand with $\varepsilon = \varepsilon_{emit}$ represents the emitted photon density of our metamaterial emitter, $\bar{n}_{emit}$, and is plotted as the magenta line. Both curves are normalized by $qV_{OC}FF$ to place them in units of power so that they can be plotted along the right vertical axis. To obtain this normalization, we use the standard model of a PV diode with the dark current set to the thermodynamic limit ($T/k \ln(2 \pi \hbar c^2 E_c/4kT)$) to find $I_{SC}$ and $V_{OC}$ and then find the maximum extractable power by finding $V_{max}$ and $I_{max}$, which allows us to calculate the maximum fill factor $FF = I_{max}V_{max}/I_{SC}V_{OC} = 0.745$, which agrees well with reported data for our material. Using this normalization, we can visually observe in Figure 4 the relevant figures of merit for our selective emitter. The shaded cyan and magenta areas correspond to $P_{rad}$ and $P_{out}$, respectively, and thus $\eta_{TPV}$ is visually approximated by the ratio of the magenta area to the cyan area. Additionally, the spectral efficiency ($\eta_{spec}$) – the percentage of emitted photons converted to electron-hole pairs – is the ratio of the shaded magenta area to the full area under the magenta curve.

We characterized the post-thermal cycling emissivity of all twenty five arrays and found that the highest efficiency-power product $\eta_{TPV}P_{out}$ corresponded to $w = 288$ nm, $l = 250$ nm, $p = 600$ nm when paired with the 0.6 eV InGaAs TPV material, generating 1.2 W/cm$^2$ with $\eta_{TPV} = 0.22$ and $\eta_{spec} = 0.43$. For comparison, replacing our selective emitter with a perfect black body emitter results in 1.3 W/cm$^2$ with $\eta_{TPV} = 0.08$ and $\eta_{spec} = 0.10$. Our selective emitter succeeds by significantly suppressing the emission of below-bandgap photons and having the peak of the emissivity align with the peak of the TPV EQE. The poor performance of a TPV system without a selective emitter can be seen in Fig. 4 by looking at the areas under the dashed green and red curves. The vast majority of emitted photons (90%) are below-bandgap, corresponding to energy that will not be converted to electricity and that could be absorbed elsewhere in the PV structure, which could raise the temperature of the TPV material and decrease its EQE. The selective emitter improves the efficiency of an overall combustion-TPV system by increasing $\eta_{TPV}$, thus decreasing wasted emission and also the amount of fuel needed to keep the emitter at 1300 K.

Additional gains in efficiency and output power could be achieved by using a TPV material – such as other strain-relaxed InGaAs as well as InGaAsSb – with lower band gap than the 0.6 eV material used in the analysis thus far. The metrics of the emitter-TPV cell system using these four different TPV materials can be seen in Table 1. We also evaluated the system at 1500 K to illustrate the potential benefits of higher temperature operation. For each emitter
at both temperatures, the measured emission spectra for each of the 25 arrays was input into our model to maximize the efficiency-power product. The quaternary, 0.52 eV InGaAsSb material outperforms the other three materials at both temperatures due to its low band gap and high EQE peak (>95%). Because we did not design our emitter to overlap with the EQEs of these materials, it is possible that the optimal efficiencies and output powers are higher than what is reported in this table.

TABLE I. Comparison of TPV system metrics with different PV materials. Values were found by maximizing $\eta_{spec} P_{out}$.

<table>
<thead>
<tr>
<th>TPV Material</th>
<th>Band Gap (eV)</th>
<th>$\eta_{TPV}$</th>
<th>1300 K</th>
<th>$\eta_{spec}$</th>
<th>$P_{out}$ (W/cm$^2$)</th>
<th>1500 K</th>
<th>$\eta_{spec}$</th>
<th>$P_{out}$ (W/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>InGaAs</td>
<td>0.60$^{24}$</td>
<td>0.22</td>
<td>0.43</td>
<td>1.2</td>
<td>0.26</td>
<td>0.52</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.55$^{25}$</td>
<td>0.21</td>
<td>0.53</td>
<td>1.2</td>
<td>0.25</td>
<td>0.62</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.50$^{26}$</td>
<td>0.17</td>
<td>0.67</td>
<td>1.0</td>
<td>0.20</td>
<td>0.74</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>InGaAsSb</td>
<td>0.52$^{27}$</td>
<td>0.24</td>
<td>0.61</td>
<td>1.5</td>
<td>0.27</td>
<td>0.66</td>
<td>3.7</td>
<td></td>
</tr>
</tbody>
</table>

In conclusion, we have demonstrated a spectrally-selective emitter based on a CTE-matched cross-over-a-backplane metasurface which can survive temperature cycling at 1300 K due to the inclusion of an encapsulation layer. Fabricated emitters are predicted to demonstrate $\eta_{TPV} = 0.22$, $\eta_{spec} = 0.43$, and $P_{out} = 1.2$ W/cm$^2$ when coupled to an ideal 0.6 eV InGaAs TPV cell at 1300 K. Further experiments are underway to test longevity as a function of number of thermal cycles, time at elevated temperature, and ambient environmental conditions. Our results indicate that Al$_2$O$_3$ encapsulation layer is critical to stabilizing the cross-on-a-backplane geometry when raised to 1300 K. Our design, because of its geometry and heterogeneous structure, can easily be scaled using nanoimprint or stepper lithography in order to cover large surfaces in a cost-effective manner, making it a viable candidate for future commercial TPV systems.

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