

DESIGN OF THERMALLY STABLE 2D PHOTONIC CRYSTALS FOR THERMOPHOTOVOLTAIC SYSTEMS

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ABSTRACT

For maximized energy conversion efficiency on thermophotovoltaic (TPV) systems, 2D photonic crystal (PhC) selective emitters have to be operated at elevated temperature of over 1100 °C. Since 2D photonic crystal selective emitters have periodic micro/nano-scale structures at the surface, they easily lose their structural integrity at such a high temperature in much shorter time than the required system's operation life. In this work, thermal failure modes of 2D photonic crystal selective emitters are characterized and top level functional requirements to prevent thermal degradation are defined and decomposed. By uncoupling the coupled nature of the surface diffusion, we found a system thermally stable over a long operation of TPV systems.

Keywords: 2D Photonic Crystals, selective Emitters, Thermal Stability, Thermo Photovoltaic

1 INTRODUCTION

Photovoltaics (PVs) are energy conversion systems that can directly convert solar radiation into electricity. Most of the solar photovoltaics are using p-n junction solar cell, which has a theoretical limit, known as Shockley-Queisser (SQ) limit. This limit, or loss, results from the mismatch of wavelength on emitter side and PV cell side. To overcome this SQ limit, there were several tries known as the third generation solar cells, such as multi-layer ("tandem") or multi-junction photovoltaic cells. However, as of this year, the cost of multi-layers or multi-junction solar cells is still too high to use except for specialized applications.

Solar Thermo Photovoltaic (S-TPV) cells are also one of the third generation solar cells [Swanson, 1979 & Davies, 1994]. However, S-TPVs pursue a very different strategy to increase the solar-to-electricity energy conversion efficiency based on the same photovoltaic principle. Rather than focusing on the PV cell, the emphasis is shifted to controlling the spectra of the photons entering the PV cell. Figure 1 shows the strategy to achieve this effect [Andreev, 2007 & Baxter, 2009]. Broadband solar insolation is first absorbed by the surface, which heats the absorber to 1000 - 2000 °C. On the other side of the absorber is the emitter, which re-radiates photons that are optimized to match the photovoltaic cell.

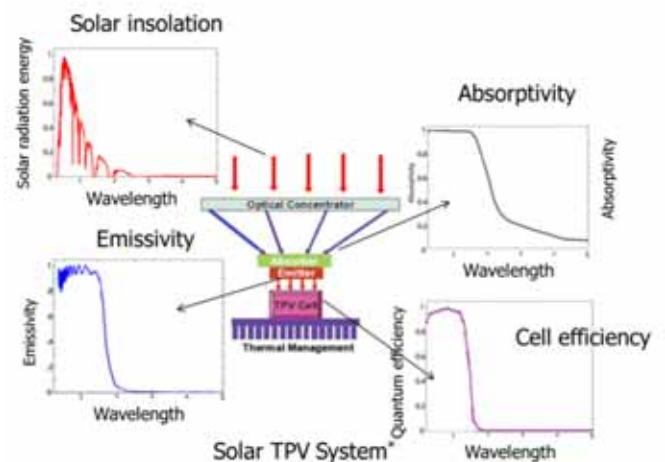


Figure 1. Illustration of a solar-TPV converting system.

The theoretical maximum efficiency of such solar TPV converters is known as 85.4 % at 2300 °C for full concentration and 54% at same temperature with no-concentration [Nils-Peter, 2003 & Martí, 2003]. These numbers came from the simple calculation of assuming black absorber, no heat losses, adiabatic and reversible. However, still, to achieve maximum energy conversion efficiency, the system has to be operated at over 1100 °C.

In detail, solar TPV's efficiency gains come from the spectral control of photons. The spectral control for solar TPV includes two parts. One part of the spectral control is absorption of solar radiation. The other part is the delivery of photons emitted from the solar absorber to the photovoltaic cell. The later part has been studied more due to the broader application of TPV, other than solar TPVs. Two strategies have been pursued for this photon emission control. One is the control of emission directly by using selective emitters based on new materials [Nelson, 1995 & Bitnar, 2002], novel surface structures [Heinzel, 2000], interference filters [Martin, 2002 & Hofler 1983], and photonic crystals. The major difficulty with this approach lies in the high temperature operation of the emitters, at which materials can lose their stability. The other strategy is spectral control on the PV cell side, by reflecting back unwanted photons, which are mostly below the band-gap. This approach has the advantage that spectral reflectors on the cell side are operated near room temperature.

So far, many problems associated with selective absorber, selective emitter, and interference filters have been solved. However, no one yet has reported intensive study on thermal stability of selective emitters. In this study, to solve thermal stability issues on selective emitters, we applied axiomatic approaches.

2 SECTIVE EMITTER DESIGN

For high efficiency of S-TPVs, or even for TPV systems, achieving good spectral control at high temperatures is the most challenging part. Because, in general, the feature size of the spectral control device (in the case of 2-D photonic crystal) is of the order of 100 nm to sub-microns. This nano/micro-scale device cannot maintain its geometrical features and optical performance at very high temperatures, 800 – 1300 °C, the general operation temperatures of S-TPV and TPV. Very little research has been reported on the thermal stability of selective emitters. To verify thermal degradation modes of selective emitters, we performed firing test with focused ion beam (FIB) milled micron-size hole at 1,200 °C.

2.1 THERMAL DEGRADATION MODES

By having 1,200 °C firing test with single-crystal and polycrystalline tungsten samples, we found four major degradation modes: grain growth, oxidation, surface diffusion and evaporation. At first, we could observe surface diffusion (figure 2) and recrystallization (figure 3). Figure 2 is thermal stability test results of micro-sized holes on poly-crystalline tungsten surface: (a) polished surface with focused ion-milled 5 μm diameter and 2 μm deep trenches; (b), (c) and (d) 100-hour annealing at 1,200 °C.

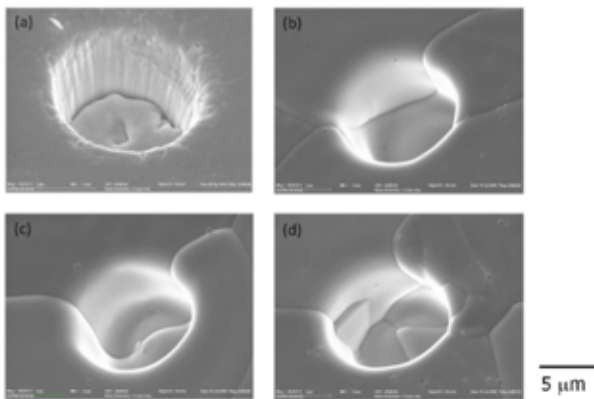


Figure 2. Thermal degradation on micro-holes

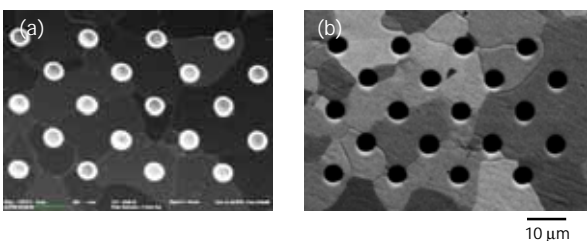


Figure 3. Grain growth and recrystallization

Figure 3 is the more zoomed out view to see the grain boundaries and their growing. Polished poly-crystalline tungsten, twenty holes were drilled using focused ion beam milling and fired for 100 hours. (a) is the SEM image of 100 hours annealed at 1,200 °C and (b) is that of additional 40 hours more annealing at 1,200 °C. Fast grain growth was observed in the beginning, but once fired at 1,200 °C for 100 hours, additional firing did not show much increase in grain size.

It was not clear whether smoothing out of the curved surface came from surface diffusion or evaporation/re-condensation. However, reviews on analytical studies revealed that both phenomena are closely related to curvature of the sub-micro meter structures. Based on Mullin's analysis, a theoretical model for the micro/nano-scale structure thermal degradation caused by surface diffusion is proposed. In the full form of Mullin's equation, the second derivative of the curvature along the surface $\partial^2 K / \partial s^2$, pressure, and temperature are the key parameters that affect the spatial distribution of surface diffusion [Mullins, 1957]. Since the operational conditions can be assumed as isothermal and isobaric, surface diffusion is fully determined by the second derivative of curvature, equation (1). The velocity of the surface in the normal direction $v_{n,d}$ is then given by [Mullins, 1957]:

$$v_{n,d} = \gamma \Omega^2 n \frac{D_s}{kT} \frac{\partial^2 K}{\partial s^2} \quad (1)$$

where n is the number of atoms per unit area and D_s is the coefficient of surface diffusion.

At high temperatures, the amount of material that is vaporized from a solid surface can be significant and creates a locally high vapor pressure promoting re-deposition on nearby surfaces. In this case, the normal surface velocity $v_{n,e}$ by which evaporation and re-condensation occurs is also derived [Balluffi, 2005]:

$$v_{n,e} = - \frac{\gamma \Omega^2 P_{eq}}{kT} K \quad (2)$$

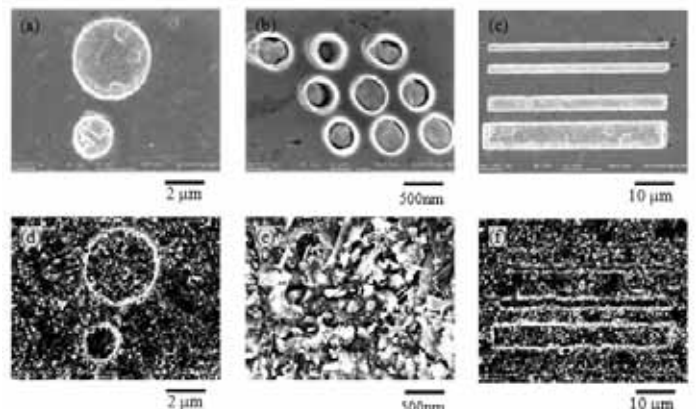


Figure 4. Thermal oxidation on sub-micron structures

where, A is a vapor transport rate constant, P_{eq} is the vapor pressure in equilibrium with a local region of the surface with zero curvature, k : Boltzmann constant, T : absolute temperature, and K : curvature.

Thermal oxidation also deformed the geometry of micro/nano-scale structures on the surfaces, figure 4, and in the case of selective emitters, any chemical change can significantly alter the emitted spectrum as well. For example, in air, tungsten begins to oxidize at room temperature with significant oxidation occurring around 400-500 °C. Tungsten trioxide (WO_3) is permeable to oxygen, which allows the oxide layer to grow quickly. If tungsten is heated, further sublimation will begin around 750 °C. It is, therefore, critical to provide the solution for preventing or minimizing thermal oxidation.

2.2 FUNCTIONAL REQUIREMENTS

From the firing tests with tungsten micro-sized samples, we could verify four independent thermal degradation modes: grain growth, surface diffusion, evaporation/recondensation, and oxidation. To obtain thermally stable 2D photonic crystals, we could define the functional requirements:

- FR1: Minimize/prevent grain boundary movement
- FR2: Minimize/prevent surface diffusion
- FR3: Minimize/prevent evaporation/recondensation
- FR4: Minimize/prevent contacting with oxygen

2.3 DESIGN PARAMETERS

Since grain boundary movement is a phenomenon for only polycrystalline materials, we could avoid grain growth or recrystallization by using single crystal materials or performed pre-annealing process in advance, DP1. It's been proved with pre-annealed samples, figure 5. The samples were pre-annealed for 100 hours at 1200 °C before drilling the holes, (b) non-treated polished tungsten with drilled holes, (c) and (d) 100-hour firing at 1200 °C in almost oxygen free condition. (e) and (f) were treated by the same method as (a) and (d) but with nano-scale holes, diameter of 300 nm, (g) and (h) are images after 100 hours firing at 1200 °C. As it can be seen from figure 5, pre-annealing could minimize the deformation of sub-micron structures.

For surface diffusion and evaporation/recondensation,

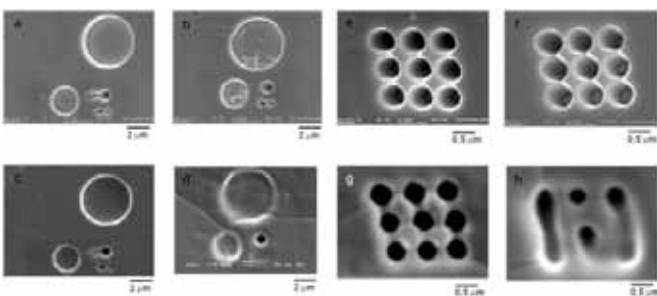


Figure 5. Firing tests with pre-annealed samples

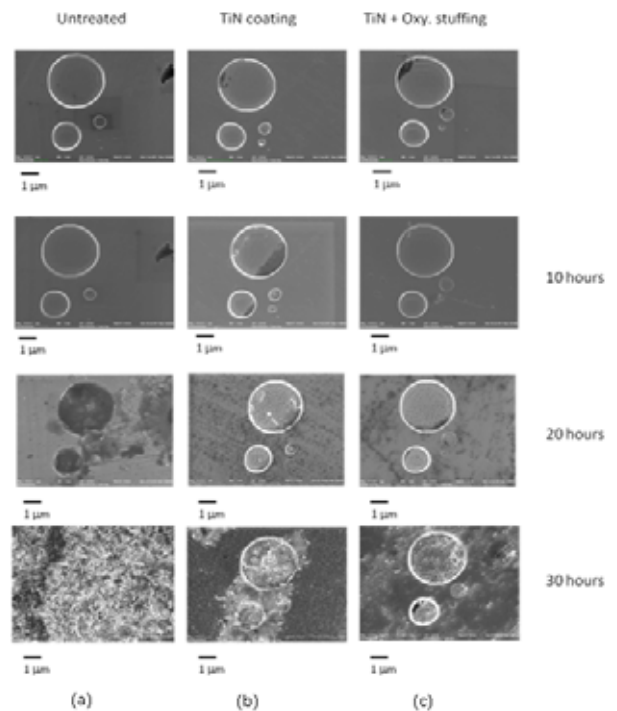


Figure 6. Oxidation barrier coating: TiN

we proposed flat surface 2D photonic crystals. Generally, 2D photonic crystals are arrays of periodic cylindrical holes. However, if we fill the holes with optically transparent materials and make the surfaces flat, there will be no driving force for surface diffusion or evaporation/recondensation. In this case, the design parameter will be “flat surface photonic crystals”, but the one parameter will be cover both functional requirements of FR2 and FR3, which is known as physical coupling.

For FR4, Minimize/prevent contacting with oxygen, we proposed a method of oxygen barrier coating. By having dense diffusion barrier coating, such as TiN, we could still maintain the transmittance and prevent the contacting of oxygen to tungsten substrates. Furthermore, oxygen stuffing on TiN film makes the barrier denser by filling the grain boundary with oxygen molecules; we could achieve high resistance on thermal oxidation, figure 6.

In figure 6, Oxidation of tungsten surface and the role of oxidation barrier can be observed. (a) pristine sample, (b) TiN coated sample and (c) TiN and oxygen stuffed samples were observed every 10 hours after firing at 1200 °C with oxygen present condition. As you can see, TiN with oxygen stuffed samples showed thermal resistance on oxidation, DP4.

By summary, we could find each independent. Some of them were physically coupled (DP2 and DP3) design parameters. For each functional parameter, design parameters for thermally stable sub-micron structures are having pre-annealing, flat surface, and oxidation barrier coating.

- DP1: Pre-annealing
- DP2: Flat Surface
- DP3: Flat Surface (physically coupled with FR2)
- DP4: Oxidation (diffusion) barrier coating

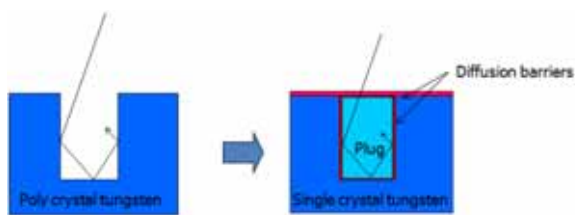


Figure 7. New design: Flat Surface Photonic Crystal

2.4 NEW DESIGN

From these design parameters, proposed new design, figure 7, of photonic crystal structure is the flat surface photonic crystal (FSPC), which is the physical realization of a flat surface that behaves like a 2-D PhC, which is achieved through plugging of the micro- and nano-structure of the PhC with an IR-transparent ceramic. The most critical components of the design are IR optical transparency of the plugging material, inter-diffusion barrier, and compatible thermal expansion between substrate and plugging material to prevent cracking and dislodging of the ceramic plugs. When ramping to the high operation temperature, establishing compressive stress while the plugging material and tungsten expand will mechanically secure the plug inside the micro-/nano-structure. For this compressive stress to be maintained, the thermal expansion coefficient (TEC) of plugging ceramic should be slightly higher than that of the substrate. For a tungsten photonic crystal (WPhC), hafnium oxide (HfO_2) is selected based on its IR transparency, TEC, and thin film manufacturability via a sol-gel deposition process. Based on the previously discussed results, the inter-diffusion barrier is 5 nm of oxygen-stuffed TiN. The flat surface photonic crystals are fabricated with hafnium oxide plug in silicon substrates, figure 8.

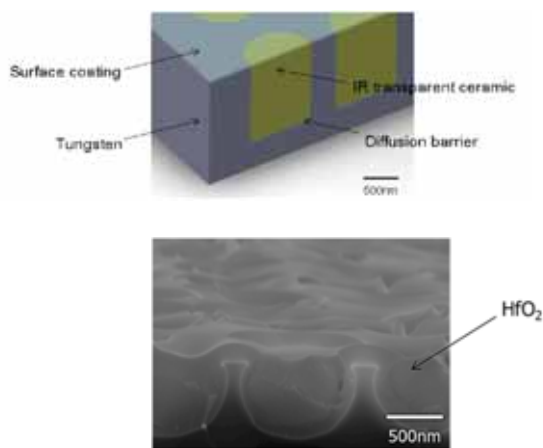


Figure 8. Flat Surface Photonic Crystal (fabricated sample)

Silicon is used for quick verification of the concept of FSPC, since its relatively easy process of fabrication and firing test at lower temperature. At first, we could confirm that the optical property is not changing much with plugs and oxidation barrier, figure 9.

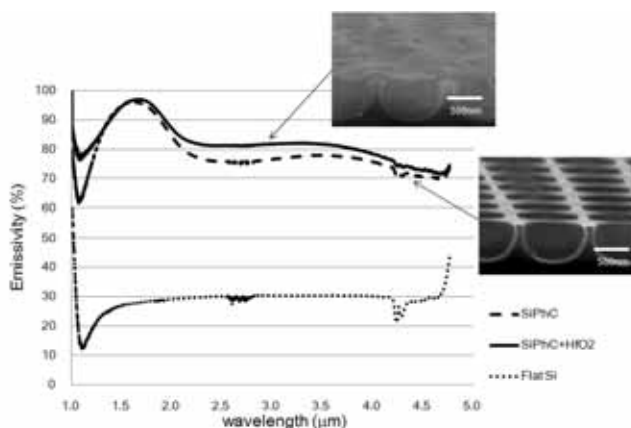


Figure 9. Optical property of flat surface photonic crystal

3 RESULTS

Thermal degradation tests of flat surface photonic crystals were performed with hafnium oxide plugged silicon photonic crystals. The samples were fired for 100 hours at 400 °C, which is equivalent temperature for tungsten at 1,200 °C in homologous temperature of 0.4. Cross sectional SEM images of each sample were taken every 25 hours and their optical properties are also measured, figure 10 & 11.

Figure 10 shows significant thermal degradation of silicon photonic crystal structure and minimal change in the flat surface HfO_2 plugged samples over 100 hours of firing. From figure 10, the effects of surface diffusion and evaporation and re-condensation on the untreated samples are clearly shown, while the flat surface photonic crystals' structure remained same and don't lose its structural integrity.



Figure 10. Firing test with flat surface photonic crystals

Finally, figure 11 shows the influence of thermal degradation on optical performance. The emissivity spectra for each sample from figure 10, after 0, 50, and 100 hours fired at 400 °C. The silicon photonic crystal emissivity is considerably reduced as the surface thermally degrades at the sample without the plugged fills, and the emission curve approaches that of a flat silicon surface. In contrast, the HfO_2 plugged silicon photonic crystal, sample (b), retains its structure when heating and does not lose its optical performance even after 100 hours of firing at 400 °C.

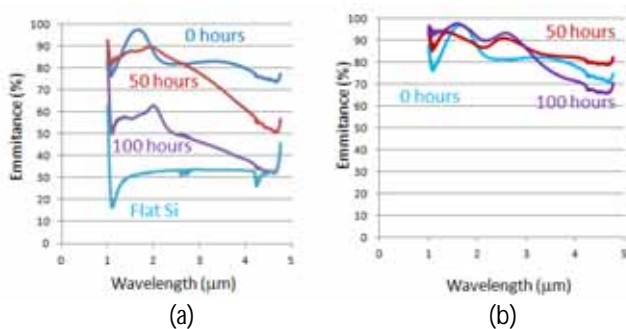


Figure 11. Optical properties of FSPC with firing tests

4 CONCLUSION

A novel idea of flat surface photonic crystal (FSPC) was proposed by axiomatic approaches and the design was validated by experiments. Pre-annealing polycrystalline tungsten prevented the grain growth. A thin layer of diffusion barrier will prevent oxidation while maintaining the optical performance. By filling in the micro/nano-scale cavities with a damascened IR transparent ceramic, the surface of the emitter will have negligible second derivative of the curvature, and thus eliminates the surface diffusion even at high temperatures.

5 REFERENCES

[1] Andreev, V., Khvostikov, V., and Vlasov, A., "Solar thermophotovoltaics," *Springer Series in Optical Sciences*, Vol. 130, pp.175-197, 2007.
 [2] Balluffi, Robert W. and Allen, Samuel M. and Carter, W. Craig., *Kinetics of Materials*, Cambridge, MA: John Wiley & Sons, 2005.

[3] Baxter, J., et al, "Nanoscale design to enable the revolution in renewable energy," *Energy Environ. Sci.*, Vol. 2, pp.559-588, 2009.
 [4] Bitnar, B., et al, "Characterisation of Rare Earth Selective Emitters for Thermophotovoltaic Applications," *Solar Energy Materials and Solar Cells*, Vol. 73, pp. 221-234, 2002.
 [5] Davies, P. A., and Luque, A., "Solar Thermophotovoltaics - Brief Review and a New Look," *Solar Energy Materials and Solar Cells*, Vol. 33, pp. 11-22, 1994.
 [6] Heinzl, A., et al, "Radiation Filters and Emitters for the Nir Based on Periodically Structured Metal Surfaces," *Journal of Modern Optics*, Vol. 47, pp. 2399-2419, 2000.
 [7] Hofler, H., Paul, H. J., Ruppel, W., and Wurfel, P., "Interference Filters for Thermophotovoltaic Solar-Energy Conversion," *Solar Cells*, Vol. 10, pp. 273-286, 1983.
 [8] Martí, A., and Luque, A., eds., "Next Generation Photovoltaics: High Efficiency through Full Spectrum Utilization, UK: Institute of Physics Publishing, 2003.
 [9] Martin, P. M., et al, "Sputtered Si: H Alloys for Edge Filters: Application to Thermophotovoltaics," *Applied Optics*, Vol. 41, pp. 6702-6707, 2002.
 [10] Mullins, W. W., "Theory of Thermal Grooving," *Journal of Applied Physics*, Vol. 28, No. 3, p.333, 1957.
 [11] Nelson, R. E., "Thermophotovoltaic Emitter Development," The First NREL Conference on the Thermophotovoltaic Generation of Energy, *AIP Conference Proceedings*, 321, pp. 80-88, 1995.
 [12] Nils-Peter, H. and Peter, W., "Theoretical limits of thermophotovoltaic solar energy conversion," *Semicond. Sci. Technol.*, Vol.18, pp. 151-157, 2003.
 [13] Swanson, R. M., "Proposed Thermophotovoltaic Solar-Energy Conversion System," *Proceedings of the IEEE*, Vol. 67, pp. 446-447, 1979.