

High Temperature Nanostructures for Thermophotovoltaics

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ABSTRACT

A fundamental challenge in solar-thermal-electrical energy conversion is the thermal stability of nano-engineered materials and devices at high operational temperatures. Selective tungsten emitters based on 2-D photonic crystals have been found effective in controlling the motion of photons at certain wavelengths for thermophotovoltaic (TPV) systems. The nano-structured patterns, however, easily lose their structural integrity at high temperatures, which would disrupt the tight tolerances required for spectral control of the selective emitters. A novel idea of flat surface photonic crystal (FSPC) is developed to circumvent the surface diffusion at high temperatures. The key idea of FSPC is to make optically micro/nano structured but geometrically flat surface, which is fabricated by plugging the nanostructure with the IR-transparent ceramic. A silicon FSPC is tested at an equivalent homologous temperature to tungsten at 1200°C for 100 hours and is observed to exhibit minimal physical and spectral degradation in contrast to the severe performance deterioration observed with a conventionally prepared 2D PhC. Combining this result with an Arrhenius accelerated lifetime model, an equivalent tungsten device is anticipated to survive over 40 years at 800°C, demonstrating a significant step toward feasible FSPC selective emitter design for commercial implementation of solar TPV.

Keywords: selective emitter, photonic crystal

1 INTRODUCTION

Because of their potential for high-efficiency energy conversion, selective absorption/emission-based thermophotovoltaics (TPVs) are attractive for solar energy harvesting [1]. Past work on solar TPVs (STPVs) has primarily focused on the design of micro-/nano-patterned selective emitters to control the emission spectrum [2–4] and thus obtain highly efficient devices [5]. With the recent progress in nanofabrication, and photonic crystal structure (PhC) design, the most advanced, highly-selective surfaces have achieved near-blackbody emission in the near infrared region with a sharp cut-off—with 4:1 emissivity contrast over a 10 percent wavelength separation [2]. Optimization of similar physically realizable designs is expected to bring PhCs closer to commercial viability.

Although significant progress has been made in tailoring the emission spectrum of selective emitters, their

long-term, high-temperature stability still remains an impediment to commercial implementation of the TPV technology. For maximum efficiency, a TPV emitter is required to operate at temperatures between 1,100 and 2,000K [6], which poses a significant thermal-stability challenge to the nanostructured selective emitters [6]. Even so, most reported tests on TPV devices have been only for short times at elevated temperatures, clearly inconsistent with the operational requirements of the STPVs [3,7].

Because of its intrinsic thermal stability and inherent infrared radiation selectivity, based on interband structure, tungsten (W) is commonly chosen as the material for selective emitters [11]. However, the micro-/nano-structures on W surface significantly degrade during prolonged high-temperature operation due to thermally activated processes [13]. Recent experimental data have shown that a W PhC could withstand repeated thermal cycling between room temperature and 1,200K for an hour or so with limited degradation [6], but continuous operation for at least 10 years, perhaps even 30 years, is the requirement for economical viability of the TPVs [7].

2 THERMAL TESTING

2.1 Degradation Modes

To identify the thermal degradation modes of W PhCs, we have conducted high-temperature firing tests on patterned single-crystal and polycrystalline W samples at 1,500K [8]. Not surprisingly, the following major modes of degradation were observed: oxidation, recrystallization and grain growth, surface diffusion, and evaporation and re-condensation—all thermally activated processes. Of these the most severe is surface oxidation. Modeling suggests that even at an extremely low O₂ partial pressure of 10–12 Torr, at 1,400K, W surface oxidizes at a rate of about 8 nm/day [8]. This highlights the challenge for preventing oxidation, even by vacuum packaging. A stable diffusion barrier coating must therefore be considered to avoid oxidation. We have found that a 5 nm thick oxygen-stuffed titanium nitride (TiN) diffusion barrier with vacuum packaging could effectively minimize oxidation and not affect the emission spectrum [8].

In polycrystalline W, re-crystallization and grain growth degrade the nanostructured surfaces (Fig.1a&b). Firing tests confirm that pre-annealing leads to greater thermal structural stability compared with an unannealed sample (Fig.1c). Thus pre-annealing may be considered as a low-cost, large-scale fabrication alternative to the more

expensive single-crystal W in which recrystallization and grain growth would obviously be absent.

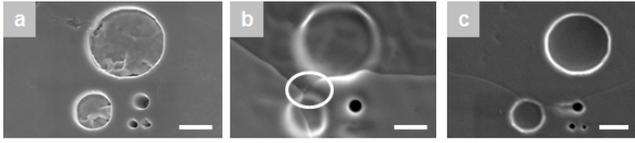


Figure 1: Scanning electron microscope (SEM) images of 5 μm , 2 μm , 500 nm, and 100 nm diameter holes focused-ion-beam milled in polycrystalline W. (a), Post-drilling. (b), After firing at 1,500 K for 40 hrs, with noticeable grain growth (circled). (c), Pre-annealed samples. The pre-annealed sample was less affected by thermal exposure. The scale bar is 2 μm .

Even if oxidation and recrystallization and grain growth could be avoided, surface diffusion, evaporation and re-condensation still remain the primary concerns for the stability of nanostructured surfaces operating at high temperatures. Flat W can survive operation at 2,000K for long periods for that temperature is well below the melting temperature of W, 3,680K, but, micro- and nano-scale cavities and corrugations even on single-crystal W cannot survive more than 100 hours at 1,500K. In this case, structural degradation is due to surface diffusion, evaporation and re-condensation (Fig. 2).

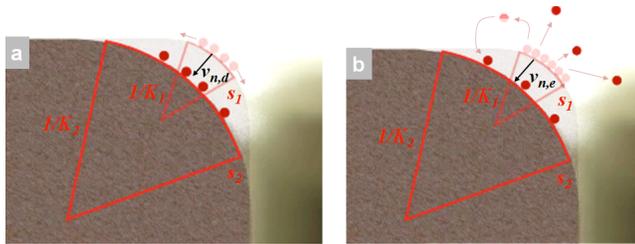


Figure 2: Schematics of thermal degradation inside hole cross-section. (a), Caused by diffusion. (b), Caused by evaporation/re-condensation. Atoms are represented by maroon circles, and subscripts and drawings labeled 1 and 2 represent the surface at times t_1 and t_2 , respectively. Because the operational conditions are isothermal and isobaric, surface diffusion is fully determined by the second derivative of the curvature.

Based on Mullin's analysis [9], a theoretical model for thermal degradation of the micro- and nano-scale structures shows that diffusion rate is proportional to the second derivative of the feature curvature K along the surface. Similarly, the amount of material that vaporizes from a convex solid surface can be significant, and it creates locally high vapor pressure promoting re-deposition in nearby areas. The flux is also proportional to the curvature [10]. Not surprisingly, temperature plays a dominant role in all these processes, and at high temperatures the degradation is particularly severe.

The challenge, then, is to design and fabricate micro/nano-structured surfaces that can survive high temperatures for more than 30 years of continuous operation. Accordingly, we have proposed a novel planar photonic crystal (PPhC) design to circumvent surface diffusion, evaporation, re-condensation, and oxidation at high temperatures [11].

2.2 Modeling

For experimental validation of the PPhC design, Si was employed as the PhC material because of its ubiquity in micro-, nano-fabrication. Moreover, since the developed fabrication process would be compatible with a W PhC, and other refractory metals, the future fabrication process can easily be adapted for large-scale production of the W PPhCs.

To select thermal conditions for accelerated lifetime tests, and to compare thermal degradation rates of Si and W, models are employed. Previous work has demonstrated that vacancy-driven atomic diffusion in metals is universal in that it scales with the homologous temperature, T_h , defined as:

$$T_h = \frac{T}{T_m} \quad (1)$$

where T is the temperature and T_m the melting temperature. If the W selective emitters are required to operate, say, at $T=1,500\text{K}$ and since the melting temperature, T_m , of W is 3,680K, $T_h = 0.4$. Thus the Si PPhCs tested at $T_h = 0.4$, i.e., at $T=673\text{K}$, are expected to exhibit comparable degradation due to surface diffusion. Hence 673K was chosen as the test temperature for the Si PPhCs.

Moreover, to describe thermal degradation due to diffusion, evaporation and re-condensation, the Arrhenius relationship is commonly employed [12]. Assuming the rate of degradation, $R(T)$, is proportional to $\exp\left(\frac{-E_a}{kT}\right)$ where E_a the activation energy, accelerated lifetime test conditions are determined by standard parametric modeling [13]. With a chosen accelerated test temperature, T , the acceleration factor, AF , is computed as:

$$AF = \exp\left(\frac{E_a}{k}\left(\frac{1}{T_f} - \frac{1}{T}\right)\right) \quad (2)$$

where T_f is the final use, or service, temperature. A scale-accelerated failure time model, referred to as SAFT model, can be used to determine the equivalent test time at the service temperature T_f by the linear relationship

$$L(T_f) = AF \cdot L(T) \quad (3)$$

where $L(T)$ and $L(T_f)$ are the lifetimes, respectively, at the test and service temperatures.

3 DESIGN AND FABRICATION

The key idea of the PPhC design is a patterned subsurface but a geometrically flat surface, which can be fabricated by plugging the micro- and nano-patterned surface cavities of a PhC with an oxide ceramic. The critical requirements of the ceramic plug are: infra-red (IR) transparency, serve as inter-diffusion barrier between functional layers, and compatible thermal expansion with W substrate to prevent cracking and debonding of the plug. For a W PhC, hafnium oxide (HfO₂) is selected because of its IR transparency, compatible thermal expansion coefficient, and thin-film manufacturability via sol-gel deposition process. Based on an earlier study, an inter-diffusion barrier of ≈5 nm of oxygen-stuffed titanium nitride (TiN) imparts both oxidation resistance to tungsten and also serves as an adhesion layer between W and hafnium oxide [3].

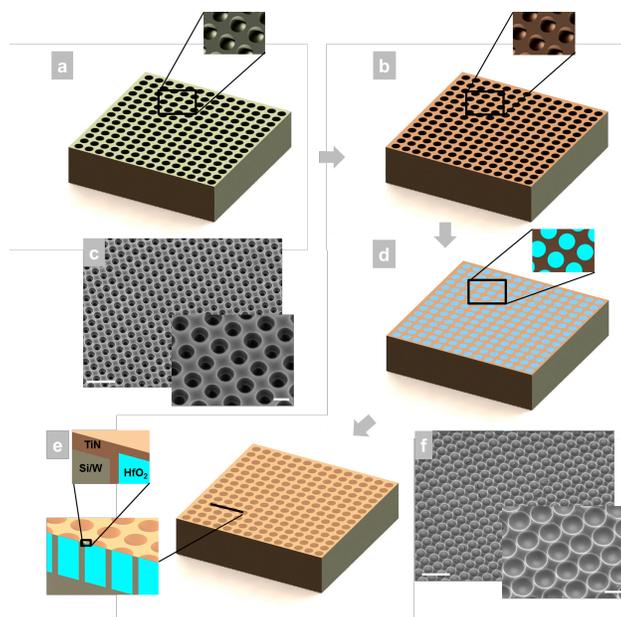


Figure 3: Schematic of PPhC fabrication process (a,b,c,e). a, 2D PhC structure etched into substrate. (b), Thin TiN inter-diffusion barrier layer deposited. (d), PhC cavities filled with HfO₂ and surface planarized. (e), Additional thin TiN oxidation barrier layer deposited. Final device cross-section renderings shown in insets (e). (c) Scanning electron microscope images of the Si PPhC after etching and (f) after HfO₂ plugging. Scale bars in large images and insets in (c) and (f) indicate 5 μm and 2 μm, respectively. Note the high yield of the HfO₂ coating process with ≈90% crack-free plugs.

The construction of the PPhC is shown in Fig. 3, and begins with patterning and etching the photonic crystal structure. Masks for the nano-scale surface features were prepared via a multi-step interference lithography (IL) process. The features are then patterned on the Si substrate using standard photolithography techniques and etched via

deep reactive ion etching. An adhesion/surface diffusion barrier layer of TiN is then added via RF sputtering, and vacancies are filled with oxygen through heating at 300°C for 30 min on a hot plate in air. The ceramic plugs are created using a water-based HfO₂ solution that is deposited via a sol-gel technique following [14]. Multiple annealing steps are added after spin coating and pyrolysis of 3-5 layers to improve film quality and prevent cracking, and the process is repeated until the etched pattern is filled.

4 RESULTS

Before and after firing tests on the fabricated Si PPhC, Fourier transform infrared (FTIR) spectroscopy was used to determine the emissivity of both plugged and unplugged samples. By Kirchhoff's law, absorptance is equal to emittance in opaque materials [15]. Since there was little difference in the initial emission spectra measurement of the plugged and unplugged samples, the HfO₂ plugging has minimal effect on the emission characteristics of the Si PhC.

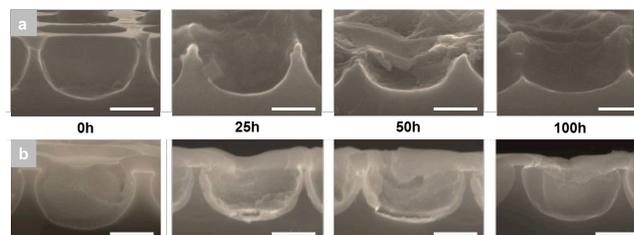


Figure 4: SEM cross-section images taken at times indicated. (a), Si PhC. (b), Hafnia-plugged Si PhC. The samples were fired at 673 K, Th = 0.4. Severe structural degradation of the unplugged Si PhC was observed with longer exposures. Scale bars are 500 nm.

The samples were then fired at 673 K for 100 hours. Thermal degradation was periodically monitored by cross-sectional scanning electron micrographs (Fig. 4). Prolonged high-temperature operation clearly has catastrophic effects on Si PhC without the ceramic plugs where significant degradation of the microstructure was observed (Fig. 4a). By contrast, the hafnia-plugged sample showed almost no degradation (Fig. 4b).

Since the Si PPhC has survived 100 hours of continuous operation at the homologous temperature Th = 0.4 (or 673K), it may be expected, based on the universality of surface diffusion with the homologous temperature, that a W PPhC will survive 100 hours of continuous operation at the same homologous temperature, 0.4 (or 1,500K). Now the lifetime of a W PPhC operating at 1,100K, $L(T_f=1,100\text{ K})$, can be estimated by Eqs. 2 and 3. The activation energy for surface diffusion of Si $E_{a,\text{Si}}=1.7\text{ eV/atom}$, for W diffusion $E_{a,\text{W}}=2.79\text{ eV/atom}$, and the Boltzmann's constant is $8.62 \times 10^{-5}\text{ eV/K}$. Substituting these values in Eq. 2, the acceleration factor, AF, is calculated to be 2,557. Thus $L(T_f=1,100\text{ K}) = 100 \times 2,557 = 255,700\text{ hours}$ or about 30

years. It may be noted, however, that this would be an underestimate, because the firing tests on Si PPhCs were concluded after 100 hours with no discernible damage. It is quite likely that the Si PPhCs would have survived much longer at 673K ($T_h = 0.4$) if the tests were prolonged, and thus a realistic estimate of the lifetime of W PPhC needs to be established by experiments on W PPhCs at higher temperatures and for longer times.

5 CONCLUSIONS

In summary, the concept and results of experiments on Si PPhC are promising. Much more work needs to be done, however, to accurately estimate the structural stability of W PPhCs at the service temperatures for prolonged times. Specifically, tests should be conducted on fabricated W PPhCs at the service temperature, or even at higher temperatures in accelerated testing. Equally importantly, the thermal stability of the HfO₂ plug and the integrity of the inter-diffusion barrier layers at the service temperature for prolonged exposures must be determined. It is hoped that with further advances in PhC bandgap engineering and the long-term thermal stability of the PPhCs the TPV energy conversion technology would advance from the research domain into commercial implementation in the not-too-distant future.

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