Final Report

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I. Background

Photonic crystals are materials that are periodically structured on an optical length scale. It was previously demonstrated that the glow, or thermal emission, of tungsten photonic crystals that have a specific structure – known as the “woodpile structure” – could be modified to reduce the amount of infrared radiation from the material. This ability has implications for improving the efficiency of thermal emission sources and for thermophotovoltaic devices. The study of this effect had been limited because the fabrication of metallic woodpile structures had previously required a complex fabrication process. In this project we pursued several approaches to simplify the fabrication of metallic photonic crystals that are useful for modification of thermal emission. First, we used the self-assembly of micrometer-scale spheres into colloidal crystals known as synthetic opals. These opals can then be infiltrated with a metal and the spheres removed to obtain a structure, known as an inverse opal, in which a three-dimensional array of bubbles is embedded in a film. Second, we used direct laser writing, in which the focus of an infrared laser is moved through a thin film of photoresist to form lines by multiphoton polymerization. Proper layering of such lines can lead to a scaffold with the woodpile structure, which can be coated with a refractory metal. Third, we explored a completely new approach to modified thermal emission — thin metal foils that contain a simple periodic surface pattern, as shown in Fig. 1. When such a foil is heated, surface plasmons are excited that propagate along the metal interface. If these waves strike the pattern, they can be converted into thermal emission with specific properties.

Fig. 1 Electron micrograph of a bull's eye patterned on a tungsten film. The periodicity and depth of the grooves are 3.5 μm and 160 nm, respectively. The total diameter of the bull's eye is 2 mm. When heated this film can project a beam of thermal emission [Ref. 8].

II. Accomplishments

Below we describe the main accomplishments of this project in the three areas of research described above: inverse opals, direct laser writing, and plasmonic films.

A. Inverse Opals

1. Avoiding Strong Absorption: Previous experiments on tungsten inverse opals revealed that these structures suffered from extremely strong optical absorption. Essentially, when light propagates inside the structure, it is absorbed before it is influenced by the periodic bubbles, eliminating the influence of the photonic crystal. In this case, modification of thermal emission would not be expected. Consequently, these materials had largely been abandoned because they were believed to be ill-suited to study this effect.

Surprisingly, we found through a detailed examination of the physics of self-assembled photonic crystals that this conclusion was incorrect. Small, experimentally realizable changes to the structure can provide suitable materials. Our theoretical analysis showed that severe absorption is not intrinsic to these materials but rather can be moderated by properly tailoring the structure. Indeed, slight alterations to the tungsten inverse opal can lead to optical properties that are very similar to the tungsten woodpile that had previously shown modified thermal emission. Specifically, we found that the inverse opal structure must be more “open.” By inserting “air-cylinders” at the contact points between the bubbles in the inverse opal, we obtained crystal structures where the absorption was moderated. An important guiding principle during all of our analyses was to make sure that our structures could be achieved in experiment. Indeed, we demonstrated a fabrication approach in Ref. 1 (see Fig. 2). This work was further highlighted in a review article written by our team (Ref. 2). Our final theoretical structure, which was published

Fig. 2 Realization of the “open” tungsten structures that our analysis predicted should exhibit moderated absorption. These structures were synthesized in “bulk” form. This work was reported in Ref. 1.

Fig. 3 We predicted that this self-assembled photonic crystal will exhibit modified thermal emission. The structure was tailored to moderate absorption, a severe limitation in previous self-assembled tungsten photonic crystals. Details were reported in Ref. 3.

in *Physical Review Letters* (Ref. 3), is shown in Fig. 3.

2. Thermal Stability of Tungsten Inverse Opals: Although not addressed in the prior literature on metallic photonic crystals, several critical challenges must be faced when heating such a structure to high temperature. One must avoid undesirable processes such as melting, evaporation, grain coarsening, and recrystallization of the metal. To date, tungsten has been the choice for both metallic photonic crystals and incandescent light bulbs because of its high melting temperature and low vapor pressure. In tungsten wire filaments for incandescent lighting, grain coarsening and recrystallization are restrained by the addition of dopants such as Al, Si, and most notably K. When structural dimensions are reduced from 10-100 μm in a traditional filament to 50–100 nm in the walls of inverse opals and $\sim 1\ \mu\text{m}$ in the woodpile structure, the potential for physical changes increases. At these small dimensions, higher surface-to-volume ratios of tungsten particles increase the reactivity of the metal and may lower its melting point. If the photonic crystal structure is altered as a result of thermal emission, optical properties will change.

We completed a detailed study of these issues. In general, unless strategies to stabilize the structures were employed, we observed vapor transport and grain coarsening at temperatures as low as 800 $^{\circ}\text{C}$. In particular, we found that tungsten needles grew due to the chemical vapor transport involving the volatile $\text{WO}_2(\text{OH})_2$ phase produced when the hot tungsten photonic crystal reacted with residual water on its surface or in the device atmosphere. If water was removed, we showed that this effect could be avoided.

However, grain growth remains an issue even when water is excluded. Therefore, we explored the possibility of using tungsten doped with molybdenum. Molybdenum doping had previously been shown to reduce chemical vapor transport in bulk tungsten. Thus, we believed that it could help mitigate the problems of needle formation and grain growth. After modifying our synthetic procedure to synthesize inverse opals as alloys of tungsten with molybdenum, we confirmed that molybdenum mitigated chemical vapor transport reactions. Furthermore, the periodic structure was maintained in these alloys even after heating at 800 $^{\circ}\text{C}$ for 4 h, as shown

Fig. 4 Electron micrograph of one of our tungsten inverse opals doped with molybdenum. The sample was heated under flowing nitrogen at 800 $^{\circ}\text{C}$ for 4 hours. By using the W-Mo alloy, the formation of needles and the coarsening of the grains could be greatly reduced. See Ref. 4 for details.

in Fig. 4. Grain sizes remained approximately constant. After heat treatment at 1000 $^{\circ}\text{C}$ for 30 minutes, some sintering was observed, but the change was significantly less than in the molybdenum-free samples. These results were reported in *Chemistry of Materials* [Ref. 4].

To understand the coarsening in more detail, we also completed *in-situ* heating experiments in a transmission electron microscope (TEM) to record the grain growth in real time. These experiments were reported in the *Journal of Materials Chemistry* [Ref. 5]. For example, Fig. 5 shows a tungsten inverse opal both before and after heating to 1000 $^{\circ}\text{C}$. With heating, coarsening could be followed in the TEM. The images reveal a smoother surface structure in the sample after 30 minutes at 1000 $^{\circ}\text{C}$, but the structure was also comprised of fewer grains. In fact this coarsening may actually improve the photonic

Fig. 5 TEM images of W inverse opals before (top) and after (bottom) *in-situ* heating to 1000 °C with a dwell time of 30 min.

properties of the sample. However, heating for longer times at 1000 °C causes the structure to be lost. Similar experiments have been completed on a variety of W and W-Mo inverse opals to confirm that grain coarsening is impeded on a nanometer scale in inverse opals made from tungsten-molybdenum alloys. Our results provide an important and general strategy for maintaining periodic structure in metallic photonic crystals for thermal emission modification. These issues must be considered not just for inverse opals, but all periodic structures.

3. Carbon Inverse Opals as High Temperature Supports:

Even with the strategies employed above, the thermal stability of nanostructured metallic photonic crystals is inherently limited. Therefore, we also investigated an alternative approach to improving their high temperature stability. We deposited a thin layer of a refractory metal on the surface of an inverse opal composed of carbon, which is known to maintain its structure up to at least 2200 °C. A conformal metal layer will endow the surface with the optical properties of the metal, while carbon provides a thermally stable scaffold. Metal coatings thicker than ~50 nm prevent any interaction of light with the scaffold, and keep the open structure intact. Thus, these composite structures are expected to emit light like pure metallic inverse opals, while displaying enhanced thermal stability.

We deposited the refractory metals tungsten, molybdenum, or tantalum on thin-film carbon inverse opals or thicker monolithic carbon inverse opals by

chemical vapor deposition (CVD). The distribution of tungsten on the carbon surface was evaluated and the thermal stability tested up to 1000 °C. The thin carbon films (10–20 pore layers thick) were synthesized by infiltration of polymer opal templates with a resorcinol-formaldehyde precursor and carbonization in nitrogen at 900 °C, following a previously developed procedure. This process yields a glassy carbon phase. To improve the metal adhesion on the carbon scaffolds, these were coated with hafnium oxide (melting point 2758 °C) by atomic layer deposition (ALD). Figure 6 shows electron micrographs of a carbon inverse opal and one coated with tungsten, demonstrating that uniform metal deposition was possible over large areas. A manuscript describing these results is in preparation.

B. Direct Laser Writing

1. Inorganic Photoresists for Thermally Stable Woodpile Templates: Previously, we developed a methylsilsesquioxane ($\text{CH}_3\text{SiO}_{1.5}$, MSQ) based inorganic-organic hybrid photoresist to incorporate local structural defects in self-assembled photonic crystals with direct laser writing.

Fig. 6 (a) Carbon inverse opal made using monodisperse PMMA spheres as a template, followed by oxygen plasma to tailor the surface termination and fill fraction. (b) Top side of the self-assembled tungsten-coated inverse opal. A manuscript describing these results is in preparation.

In our DOE project, we wanted to use this photoresist not just to define local defects, but to define the entire metallic 3D photonic crystal. Therefore, we examined whether the photoresist could be combined with direct laser writing. As can be seen in Fig. 7, we successfully achieved woodpile structures with this approach. Moreover, the thermal stability of these structures was also tested. The woodpile in Fig. 7 was heated for 7 h at 550°C in air. Air presents the most challenging environment because it leads to a lower decomposition temperature and higher weight loss of the MSQ. Even under these severe conditions, the structure did not crack. Shrinkage in the plane of the substrate was very small (~1.5%). However, contraction did occur in the width and height of the lines, which led to a shrinkage of ~40% in the direction perpendicular to the substrate. However, when similar structures were heated under nitrogen, they showed almost no structural changes. For example, shrinkage of the woodpile in the direction perpendicular to the substrate was ~5% after 4 h under nitrogen at 550 °C.

The demonstration of a photoresist that can produce thermally stable scaffolds is an important development for this project. Because the MSQ converts to silica at elevated temperatures, it provides a flexible route to SiO₂ templates that can be used for a variety of fabrication approaches. These results were reported in *Advanced Materials* [Ref. 6].

2. Examination of Thermal Emission from Metallic Woodpile Photonic Crystals: Utilizing the MSQ-based photoresist described above, we produced silica woodpiles and then coated them with either tungsten or molybdenum using a simple CVD process. We then tested the thermal stability of such structures at elevated temperatures. In particular, for studying modification of thermal emission, the structures cannot suffer from grain growth at the temperature of interest. Figure 8 presents a molybdenum-coated silica woodpile that was heated for two hours under

Fig. 7 Electron micrographs of an 8-layer woodpile structure created from our MSQ photoresist. This structure was heated in air for 7 h at 550 °C without cracking and thus has sufficient thermal stability for coating with metal. The scale bars are 20 (left) and 2 (right) μm. See Ref. 6 for details.

inert gas at 650°C. No metal grain growth was observed due to the heating. (The small metal flakes on the top surface of the sample were deposited prior to the heat treatment due to the simplicity of our CVD apparatus.)

We designed these structures to study their applicability in solar thermophotovoltaics. Although the conversion of solar energy directly into electricity (*i.e.*, photovoltaics) has received significant attention, the ability of new photonic structures to impact thermophotovoltaic (TPV) devices has not been widely appreciated. A TPV device transforms sunlight first into low energy photons, which can then be converted into electricity. To be efficient, this process requires a material that absorbs solar energy and then thermally emits a narrow band of infrared light that is well-matched to a conventional photocell. This approach can in principle reach conversion efficiencies above 50%. However, it has been limited in part by the thermal emission behavior

of real materials. We demonstrated that our structures can provide efficient thermophotovoltaic emitters that operate at relatively low temperatures. After fabricating our woodpiles, we analyzed their optical properties and compared them with theoretical predictions. We measured thermal emission spectra with an apparatus constructed during the first year of the project. Initially, we planned to heat the structures through Joule heating. However, because this introduced significant inhomogeneities in the sample temperature, we purchased a heating stage with project funds (Linkam TS1500). Based on the resulting measurements, we then extracted optical-to-electrical conversion efficiencies for TPV. If our structures were coupled to InGaAsSb photocells developed recently, conversion efficiencies over 30% are predicted. Because this could be achieved at low temperatures (650°C), our results have implications not just for solar energy, but also heat recovery from geological or industrial sources. Thus, these structures can impact several sources of energy production. This work was reported in *Nano Letters* [Ref. 7].

C. Plasmonic Films

1. Metallic Bull's Eyes: Our work on three-dimensional metallic photonic crystals led us to consider whether simple metallic surface patterns could also provide useful thermal emission. In particular, we were interested if they could control the direction of the emission. If such an effect was possible, this could have implications for thermophotovoltaics. In such devices, thermal emission must be collected by a photocell and converted into electricity. However, because this emission is not directional, the collection can be difficult in real TPV devices. Thus, it would be highly desirable to discover a structure that controlled not only the spectrum but also the direction of the thermal emission. The emission could then be “beamed” efficiently to the photocell and converted to electricity.

We found that a very simple patterned metal can produce this behavior. Namely, a tungsten bull's eye structure (Fig. 1), in which the surface of a tungsten film is patterned with a series of

Fig. 8 Electron micrograph of an 8-layer molybdenum woodpile structure. A silica woodpile was created using our MSQ photoresist and then coated with molybdenum using chemical vapor deposition. This structure was heated under inert atmosphere for 2 h at 650 °C. See Ref. 7 for details.

circular concentric grooves, can produce a beam of thermal emission that is narrow both in its spectrum and angular divergence. We have shown this both through simulations and preliminary experiments. Amazingly, the emission is predicted to have spectral and angular linewidths as narrow as ~ 0.1 nm and $\sim 0.1^\circ$, respectively. Further, this effect is not limited to W, but can also occur in other refractory metals such as Ta and even Ag. By tailoring both the spacing between the grooves and the metal, the emission wavelength can be tuned. Therefore, we discovered a very simple surface structure that can produce a directional, narrow bandwidth thermal emission source. A paper describing these results appeared in *Optics Express* [Ref. 8]. The University of Minnesota also filed a provisional patent application related to this discovery [Patent P1].

2. Fabrication of Ultrasmooth Patterned Films for Plasmonics: While we initially fabricated the bull's eyes with optical lithography and reactive ion etching (see Fig. 1), the optical properties were affected by the interface roughness of the metal. Thus, we needed a different technique to produce smooth, patterned metal foils. During our efforts to make such structures, we developed an extremely simple, general technique for producing ultrasmooth patterned metal surfaces (see Fig. 9). It also provides a high-throughput fabrication procedure that can produce wafer-scale films. Surprisingly, no techniques existed previously to obtain such structures. Metal films deposited by evaporation are inherently rough due to polycrystallinity. Moreover, when such films are patterned, for example by focused ion beam or reactive ion etching, this roughness is increased as the grains are exposed. When this roughness is present, effects such as our thermal beaming effect can be diminished. More generally, surface roughness in patterned metal films has been a serious problem for the field of plasmonics. Because our approach can eliminate this roughness, it can impact not only our research on bull's eyes for the modification of thermal emission, but also more broadly. A paper describing our fabrication approach was reported in *Science* [Ref. 9]. The University of Minnesota also filed a provisional patent application related to our method for fabrication of ultra-smooth metals [Patent P2]. This work was completed in collaboration with Prof. Sang-Hyun Oh's group at UMN.

Fig. 9 Electron micrograph of a silver bull's eye. We developed a simple, high-throughput technique for generating ultrasmooth patterned metal films. This approach has implications for the field of plasmonics. See Ref. 9 for details.

While our procedure was initially limited to noble metals, such as Ag and Au, we recently extended the process to refractory metals, such as W and Ta. Therefore, we have recently fabricated ultrasmooth W bull's eyes for thermal emission modification. A manuscript is in preparation that describes this extension of the original fabrication process.

3. Plasmonic Focusing: Because our fabrication procedure is not limited to bull's eyes, we also fabricated silver pyramids that have sharp tips (see Fig. 10). If patterned appropriately, such structures can focus optical energy at a nanoscale hot spot near the tip, which can be useful for a broad range of applications. In collaboration with Prof. Sang-Hyun's group at UMN, we prepared such structures and demonstrated optical nanofocusing. Previous efforts in the literature

Fig. 10 (a) Sideview and (b) top-view electron micrographs of a silver pyramid patterned with a set of asymmetric grooves. (c) top-view and (d) side-view scanning confocal Raman images of a smooth template-stripped asymmetrically patterned silver pyramid. The enhanced optical field at the tip is clearly distinguishable, and the signal from the gratings is very weak. The dashed lines depict the location of the pyramid. Scale bars: (a) 200 nm; (b) 1000 nm; (c) 500 nm; (d) 1000 nm.

to demonstrate this effect were limited by surface roughness. In Fig. 10, we use confocal Raman microscopy to show the optical hot spot that forms at the tip of a patterned pyramid. Such a hot spot forms when the pyramid is illuminated with light of the appropriate wavelength. Our control structures, which were prepared according to conventional methods, did not exhibit nanofocusing due to surface roughness. Our results on this topic were reported in *Nano Letters* [Ref. 10].

III. Personnel Trained

A. Graduate Students

Name	Period on Project	Other Support
Mr. Nick Denny	08/06-08/09 (Ph.D.)	TA
Mr. Sang Eon Han	08/06-03/09 (Ph.D.)	Fellowship
Mr. Prashant Nagpal	08/06-01/10 (Ph.D.)	TA and Fellowship
Ms. Kasia Kobeszko	05/07-08/08	
Mr. Won Cheol Yoo	05/07-07/08	
Mr. Jong Hyuk Park	01/09-08/10	TA
Mr. David Josephson	05/09-02/11	TA
Mr. Sriharsha Jayanti	01/10-08/10	Fellowship

B. Postdoctoral Scholars

Name	Period on Project	Other Support
Dr. Shaibal Sarkar	08/07-08/09	U. Colorado/NREL

IV. Publications and Patents for This Project to Date

A. Publications:

1. Denny, N. R.; Han, S.; Turgeon, R. T.; Lytle, J. C.; Norris, D. J. & Stein, A.; "Synthetic approaches toward tungsten photonic crystals for thermal emission," *Proc. SPIE-Int. Soc. Opt. Eng.* **6005**, 600505, 13 pages (2005).
2. Stein, A.; Li, F. & Denny, N. R.; "Morphological control in colloidal crystal templating of inverse opals, hierarchical structures, and shaped particles," *Chem. Mater.* **20**, 649-666 (2008).
3. Han, S. E.; Stein, A. & Norris, D. J.; "Tailoring self-assembled metallic photonic crystals for modified thermal emission," *Phys. Rev. Lett.* **99**, 053906, 4 pages (2007).
4. Denny, N. R.; Han, S. E.; Norris, D. J. & Stein, A.; "Effects of thermal processes on the structure of monolithic tungsten and tungsten alloy photonic crystals," *Chem. Mater.* **19**, 4563-4569 (2007).
5. Denny, N. R.; Li, F.; Norris, D. J. & Stein, A.; "In situ high temperature TEM analysis of sintering in nanostructured tungsten and tungsten-molybdenum alloy photonic crystals," *J. Mater. Chem.* **20**, 1538-1545 (2010).
6. Jun, Y.; Nagpal, P. & Norris, D. J.; "Thermally stable organic-inorganic hybrid photoresists for fabrication of photonic band gap structures with direct laser writing," *Adv. Mater.* **20**, 606-610 (2008).
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8. Han, S. E. & Norris, D. J.; "Beaming thermal emission from hot metallic bull's eyes," *Opt. Express* **18**, 4829-4837 (2010).
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12. Aguirre, C.; Reguera, E. & Stein, A.; "Colloidal photonic crystal pigments with low angle dependence," *ACS Appl. Mater. Interfaces* **2**, 3257-3262 (2010).
13. Li, F.; Josephson, D. P. & Stein, A.; "Colloidal assembly: The road from particles to colloidal molecules and crystals," *Angew. Chem. Int. Ed.* **50**, 360-388 (2011).
14. Nagpal, P.; Josephson, D. P.; Denny, N. R.; DeWilde, J.; Norris, D. J.; Stein, A.; "Fabrication of Carbon/Refractory Metal Nanocomposites as Thermally Stable Metallic Photonic Crystals", *J. Mater. Chem.* **21**, 10836-10843 (2011).
15. Rudisill, S. G.; Wang, Z.; Stein, A.; "Maintaining the Structure of Templated Porous Materials for Reactive and High Temperature Applications", *Langmuir* **28**, 7310-7324 (2012).
16. Park, J. H.; Nagpal, P.; Oh, S. H.; Norris, D. J.; "Improved Dielectric Functions in Metallic Films Obtained via Template Stripping", *Appl. Phys. Lett.* **100**, 081105, 4 pages (2012).
17. Park, J. H.; Ambwani, P.; Manno, M.; Lindquist, N. C.; Nagpal, P.; Oh, S.-H.; Leighton, C.; Norris, D. J.; "Single-Crystalline Silver Films for Plasmonics", *Adv. Mater.* **24**, 3988-3992 (2012).

B. Patents:

- P1. D. J. Norris, S. E. Han, and A. Bhan; "Creation of light and/or surface plasmons with heated metallic films," U.S. Provisional Patent Application filed on November 25, 2008.
- P2. D. J. Norris, P. Nagpal, M. Manno, C. Leighton, and S.-H. Oh; "Creation of light and/or surface plasmons with heated metallic films," U.S. Provisional Patent Application filed on January 2, 2009.