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High-temperature tantalum tungsten alloy photonic crystals: Stability, optical properties, and fabrication

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We demonstrate tantalum-tungsten (Ta-W) solid solution alloy photonic crystals (PhCs) as spectrally selective components for high temperature energy conversion. The thermo-mechanical properties of the alloy are tuned by the Ta-W ratio. A 2D PhC was designed as a selective emitter, fabricated on a Ta3%W substrate, and optical properties and thermal stability were characterized. A thin layer of HfO₂ was deposited for thermal stability. The PhCs show outstanding emittance selectivity, well preserved after annealing for 24h at 1200 °C. The structure is preserved as shown in cross-sectional images, demonstrating that the coating effectively prevents degradation due to surface diffusion at high temperatures. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4821586>]

An increased interest in thermophotovoltaics (TPV), solar TPV, and solar-thermal energy conversion systems in general has led to new investigations of photonic crystals (PhCs) as selective emitters/absorbers made from refractory metals that can maintain optical properties at high temperatures over operational lifetime. These two-dimensional (2D) PhCs are fabricated by etching a periodic pattern into a metallic substrate, such as tungsten (W)^{1–6} or tantalum (Ta)⁷ which are suitable substrates for PhCs for energy applications due to their high long-wavelength reflectance as well as high melting point and low vapor pressure. These metallic 2D PhCs can be designed to exhibit precisely tailored optical properties at high temperatures (>900 °C) and produce spectrally confined selective emission of light.^{2,3,6–8} High reflectance, i.e., low emittance, in the infrared (IR) wavelength range of the substrate material is critical for high-temperature nano-photonic devices, to reduce losses due to waste heat at wavelengths longer than the bandgap of a TPV cell (typically 2–3 μm). Similarly, for selective solar absorbers, low emittance at long wavelengths minimizes re-radiation. In advanced TPV or solar TPV systems, selective absorbers/emitters have to be integrated into the system (e.g., by welding onto the heat source/sink). The heat source can be a micro-reactor fueled by hydrocarbon combustion,⁹ a radio-isotope general purpose heat source (GPHS),¹⁰ or thermal fluid in the case of a solar absorber.

In this paper, we investigate a tantalum tungsten solid solution alloy, Ta 3% W, as a substrate for a 2D PhC for high-temperature high-efficiency TPV. The Ta 3% W alloy presents critical advantages compared with non-alloys as it combines better thermo-mechanical properties of W with the more compliant material properties of Ta, allowing a direct system integration path, i.e., machining and welding. In addition, the mechanical stability of the selective emitters, as part of a high temperature system, is greatly enhanced using Ta W alloy substrates as opposed to pure Ta, which is beneficial for the overall system stability where degradation, such

as creep and deflection, can play a critical role in system failure. A 2D PhC on a pre-annealed polycrystalline Ta 3% W alloy substrate was designed using finite-difference time-domain (FDTD) numerical simulations¹¹ and fabricated using standard semiconductor processes.¹² The emittance of Ta 3% W was obtained from near-normal reflectance measurements at room temperature (RT) before and after annealing at 1200 °C for 24 h in vacuum with a protective dielectric coating of 40 nm HfO₂. A slight degradation of the initial high spectral selectivity of the emittance spectrum after anneal was attributed to the beginning of carbide formation on the surface of the HfO₂ coating, which is greatly decelerated in contrast to the surface reaction on Ta without the coating.¹³ Scanning electron microscope (SEM) images of the cross section of the PhC prepared by focused ion beam (FIB) milling compared before and after anneal confirm the structural stability of the HfO₂ coated Ta 3% W PhC. No degradation (i.e., rounding of the sharp features) was observed, which confirms that the coating effectively prevents structural degradation due to surface diffusion.

The emittance spectrum of the 2D PhC is tailored so that the cut-off wavelength λ_{cutoff} of the high emittance band matches the bandgap λ_{PV} of a PV cell for TPV applications, maximizing the efficiency of the system. The PhC consists of a periodic array of etched cylindrical cavities with period a , radius r , and depth d in the substrate (Ta 3% W). The geometric parameters of the cavity array define the cut-off wavelength which is tuned by selecting the appropriate r and d . Prior to fabrication, the PhCs are simulated and the geometric parameters are optimized using a FDTD algorithm¹⁴ implemented in Meep.¹¹ For the optimized set of parameters r and d , the quality (Q) factors of the radiative and absorptive modes of the PhC are matched so that the emittance below the cut-off wavelength is maximized.^{6,8} At the same time, the emittance above the cut-off wavelength is kept low in order to minimize losses in the IR due to waste heat and to achieve high selectivity with a sharp cut-off between the two regions. The optical dispersion of the substrate is taken

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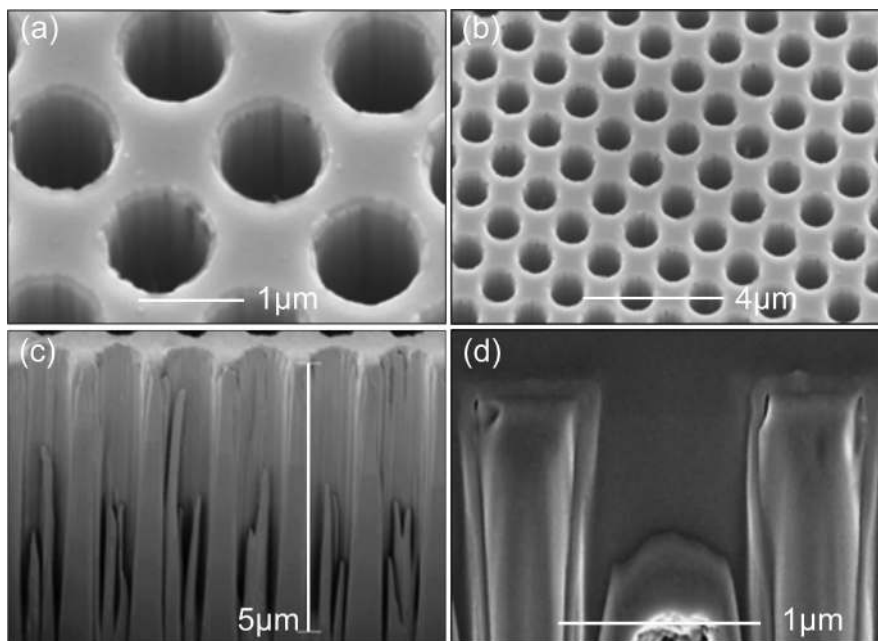


FIG. 1. (a) and (b) SEM top views of the Ta 3% W PhC. (c) and (d) FIB cross sections of the PhC without and with platinum (Pt) deposition, respectively.

into account in the simulation using a Drude-Lorentz model fit to the measured reflectance of polished Ta 3% W, which is almost identical to that of a pure Ta substrate.

The PhC fabrication process is very similar to the one developed for non-alloy substrates using interference lithography (IL) and reactive ion etching (RIE) of a hard mask and a subsequent deep RIE (DRIE) of Ta.^{5,6,12} The Ta 3% W PhC is designed for a cut-off wavelength $\lambda_{cutoff} = 2 \mu\text{m}$ which corresponds to a band gap of 0.62 eV (InGaAs TPV cell). The optimized geometrical parameters for this case are a period $a = 1.3 \mu\text{m}$, radius $r = 0.54 \mu\text{m}$, and cavity depth $d = 8 \mu\text{m}$. In the optimization, fabrication constraints were taken into account by ensuring a minimum space between the cavities and limiting the cavity depth. The benefit of increased selectivity of the emittance diminishes for cavity depths above $d \sim 8.0 \mu\text{m}$. The measured cavity radius of the fabricated PhCs was $r = 0.53 \mu\text{m}$, with a period $a = 1.37 \mu\text{m}$ (Fig. 1). The depth is experimentally measured by milling into the substrate using a FIB microscope. In order to achieve a cleaner cross-section, the cavities are filled with Pt and then milled. The etch depth measured by FIB was $6 \mu\text{m}$ on average, corresponding to an aspect ratio of 6 to 1, as shown in Fig. 1(d). Note that there is a grass formation inside the cavity that can be reduced by optimizing the etch parameters of Ta, but its influence on the emittance spectrum of the PhC is minimal. The simulation using the measured cavity radius and period of the fabricated PhC and a cavity depth of $d = 6.7 \mu\text{m}$ shows good agreement to the emittance obtained from room temperature reflectance measurements as shown in Fig. 2(a) with a cut-off wavelength of about $\lambda_{cutoff} = 2.0 \mu\text{m}$, demonstrating high emittance below the cut-off wavelength while maintaining low emittance above, with a steep cut-off between. The spectral efficiency (defined as the ratio of useful emission to total emission) can be found from the simulated hemispherical data using high temperature material properties. Very good selectivity is observed for the PhC emitters which increases with temperature as expected. The total calculated hemispherical spectral

efficiency is found to be greater than 50% above $\sim 1100^\circ\text{C}$. System modeling shows that the expected TPV thermal-to-electrical efficiency using an InGaAsSb TPV cell and a matched PhC emitter (with no further spectral components, such as filters) can reach 29.1% for ideal TPV cell properties, and 13.0% for actual measured TPV cell properties, both at an operating temperature of $\sim 1170^\circ\text{C}$.¹⁵

The intended use of the selective emitters in high-temperature energy conversion applications with target operating temperatures $> 900^\circ\text{C}$ and expected lifetimes of years imposes 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.

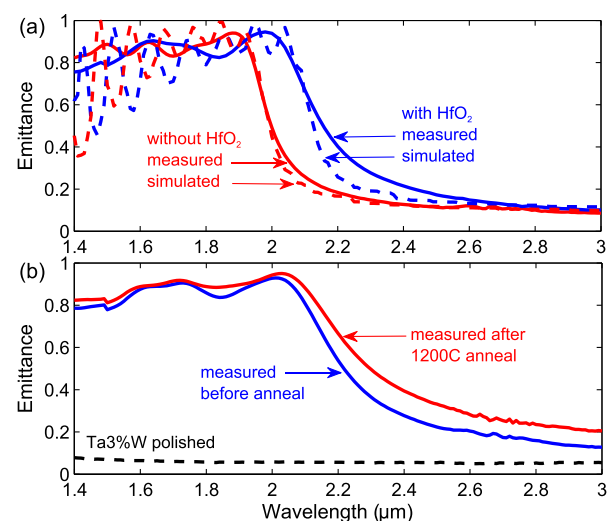


FIG. 2. (a) Comparison of the emittance obtained from reflectance measurements at RT of the Ta 3% W PhC without and with an HfO_2 coating of 40 nm thickness, and simulations using a period $a = 1.37 \mu\text{m}$, cavity depth $d = 6.7 \mu\text{m}$, and radius $r = 0.53 \mu\text{m}$ and radius $r = 0.57 \mu\text{m}$, respectively, for the uncoated and coated PhC. (b) Comparison of the emittance of the Ta 3% W PhC with an HfO_2 coating before and after anneal at 1200°C for 24 h in a vacuum furnace with the emittance of the polished substrate.

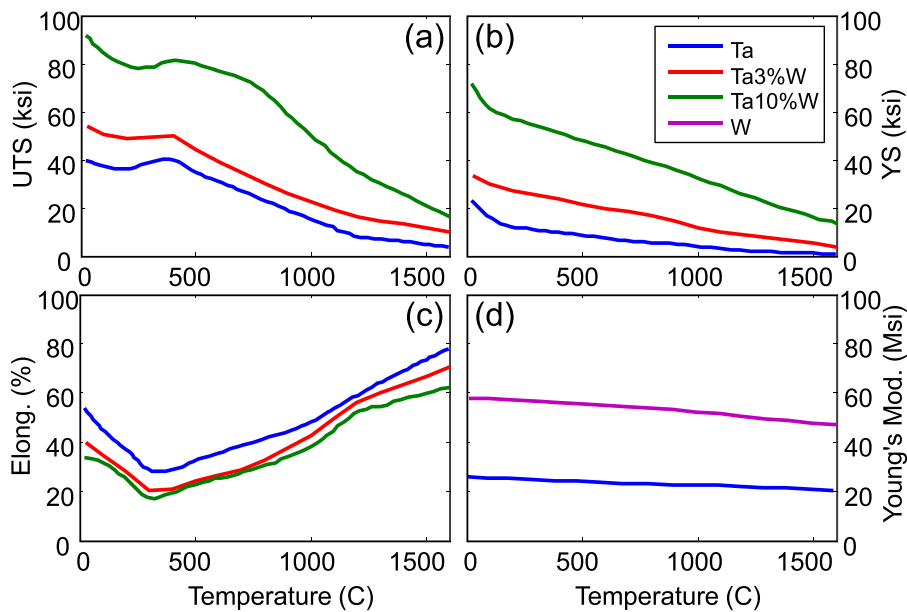


FIG. 3. Comparison of (a) ultimate tensile strength (UTS), (b) YS, and (c) percent elongation of Ta, Ta 3% W, and Ta 10% W and their dependence on temperature. (d) Comparison of Young's modulus of Ta and W.

Refractory metals are preferred at high temperatures due to their high melting point, low vapor pressure, and advantageous high reflectivity in the IR. W has high yield strength (YS) and Young's Modulus, however it is very brittle and therefore hard to machine or weld. Ta on the other hand is soft and more compliant, in addition to being easily weldable and machinable. In order, however, for a Ta based system to achieve the same mechanical stability as for a W based system, a thicker substrate is required due to Ta's softness, which in turn adds to the system weight and cost. The use of Ta W alloys allows one to achieve the same thermo-mechanical stability while keeping the required material thickness low. Fig. 3 illustrates the mechanical properties of Ta, Ta 3% W, and Ta 10% W and their dependence on temperature and shows the increasing mechanical stability with increasing W content of the alloy for all temperatures.¹⁶

Surface diffusion and surface chemical reactions are known high-temperature PhC degradation mechanisms. Previous studies have shown that the addition of a protective dielectric coating, such as HfO₂ by Atomic Layer Deposition (ALD), onto the fabricated selective emitters prevented both structural degradations by surface diffusion and grain boundary grooving as well as surface reactions, such as the formation of Ta carbide on the surface of the PhC at high temperatures.^{13,17,18} In this study, we use a protective coating of 40 nm HfO₂ for this purpose. Coating by ALD ensures a completely conformal deposition in the high-aspect ratio cavities. While the additional layer influences the emittance, causing the cut-off wavelength to shift slightly to a higher wavelength, the sharp cut-off, low emittance at longer wavelengths, and high selectivity are preserved. Fig. 2(a) shows the emittance of the fabricated PhC with and without the coating as obtained from RT reflectance measurements, showing a shift of the cut-off from 2.0 to 2.15 μm . This shift of the cut-off wavelength is reproduced by simulations of the PhC with the coating. For simplification, it can be taken into account in the simulations by using a larger cavity radius r as the optical path length in the cavity is effectively increased by the addition of a high index material ($n \sim 1.8$).

Thus, to achieve the target cut-off wavelength with the coated PhC a slightly smaller cavity radius has to be fabricated than given by the optimization without the coating.

To study the thermal stability, the fabricated PhCs were annealed at 1200°C for 24 h in a vacuum setup under Ar atmosphere (10^{-7} Torr base pressure, 10^{-4} Torr flowing UHP Ar). To prevent convection and conduction losses, as well as oxidation and degradation of the microstructured materials, any high-temperature TPV system is preferably run under vacuum. The reflectance of the Ta 3% W PhCs with the HfO₂ ALD coating was obtained experimentally at RT before and after annealing by spectroradiometric measurement. Note that the emittance can be obtained from the measured reflectance by using Kirchhoff's law ($E = 1 - R$ for non transmitting substrates). As shown in Fig. 2(b), the spectral emittance of the Ta 3% W PhC and its selectivity are essentially preserved after the 24 h anneal at 1200°C. A small degradation of the cut-off tail is observed after anneal, as well as a slight increase of the emittance above the cut-off wavelength. The furnace used was limited to 1200°C preventing us to go to higher temperatures, but longer term annealing studies are under way.

As previously mentioned, thermal degradation of the reflectance spectra could be due to a rounding of structure profiles due to surface diffusion or surface reactions like carbide formation, as observed in a previous study on Ta samples without coating.¹³ The structural stability of the Ta 3% W PhC with the HfO₂ ALD coating was studied through the FIB cross sectional images before and after annealing. Very little change was observed after annealing at 1200°C for 24 h under Ar atmosphere, as shown in Fig. 4. Therefore, we conclude that surface diffusion was effectively prevented by the HfO₂ coating at least for the observed time and temperature scale. We could, however, observe the beginning of localized carbide formation on the surface of the HfO₂ coating, as confirmed by Auger spectroscopy. This is the reason for the degradation of the emittance spectrum of the PhC and thus a surface passivation carbide barrier is needed. Although the reaction is significantly slower than on the Ta

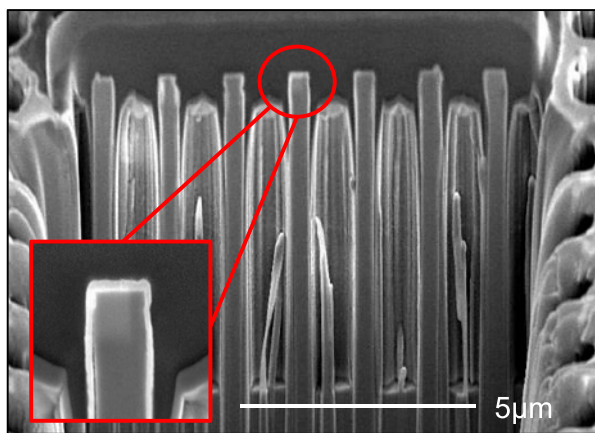


FIG. 4. FIB cross section of the Ta 3% W PhC after 24 h anneal at 1200 °C for 24 h in a vacuum furnace. Note that Pt was deposited prior to FIB milling in order to improve the cross-sectional imaging. The inset is a close up of the cavity wall.

surface (without the coating), the carbide formation at higher temperatures could eventually compromise the spectral selectivity of the emitter. Further investigation on the source of carbon and the prevention of this reaction is under way.

In conclusion, in this paper, we investigated a tantalum tungsten solid solution alloy, Ta 3% W, as a substrate for 2D PhCs for high-temperature energy applications. The Ta 3% W alloy presented advantages compared with the non-alloys as it combined better high-temperature thermo-mechanical properties of W with the more compliant material properties of Ta, allowing for a direct system integration path. A 2D PhC on a Ta 3% W alloy substrate was designed using FDTD numerical simulations and fabricated. The PhC design and fabrication process remained the same for Ta 3% W as for Ta. The mechanical stability of the selective emitters as part of a high temperature system was found to be greatly enhanced using the Ta W alloy substrates instead of pure Ta, reducing potential degradation, such as creep and deflection which can play a critical role in system failure. Furthermore, the thermo-mechanical properties can be tuned by the W content. The emittance of Ta 3% W was obtained from near-normal reflectance measurements at RT before and after annealing at 1200 °C for 24 h in vacuum with a protective dielectric coating of 40 nm HfO₂, showing high spectral selectivity as predicted by simulations. A slight degradation of the emittance spectrum was attributed to the beginning of carbide formation on the surface of the HfO₂ coating, which is greatly decelerated in contrast to the surface reaction on Ta without the coating. While it appears that the observed surface degradation is only due to contamination, further tests are being conducted for longer anneal times at high temperature. Scanning electron microscope images of the cross section of the PhC prepared by focused ion beam milling compared before and after anneal confirm the structural stability of the HfO₂ coated Ta 3% W PhC and no degradation, i.e., rounding of the profile, was observed, which

confirms that the coating effectively prevents structural degradation due to surface diffusion. Overall, these results confirm that Ta 3% W based PhCs with an HfO₂ coating are a promising solution for spectrally selective optical components for high-temperature applications.

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