

Thermal Stability of Nano-Structured Selective Emitters for Thermo Photovoltaic

H. Lee, S. Bathurst and S.-G. Kim

Massachusetts Institute of Technology, Cambridge, MA, USA,
heonju@mit.edu, bathurst@mit.edu, and sang-kim@mit.edu

ABSTRACT

This study aims to provide the high temperature stability of tungsten selective emitters for thermophotovoltaic (TPV) systems. Photonic crystals have periodic nano-structures that are designed to control the motion of photons at certain wavelengths, giving off light radiation at favorable wavelengths to be absorbed by the adjacent PV cells. However, nano-structures would lose their structural integrity at high temperatures, disrupting the tight tolerances required for the spectral control of the light radiation. We studied four major mechanisms of thermal degradation by which tungsten nano-structures change their geometry when heated over 800oC. Observed degradation modes are recrystallization/grain growth, oxidation, surface diffusion, and evaporation/condensation. Identification of degradation modes and the thorough understandings of each degradation phenomenon is performed experimentally and analytically.

Keywords: thermal stability, micro-structures, nano-structures, selective emitters

1 INTRODUCTION

Periodically patterned sub-micron structures are widely used for functional surfaces, such as anti-reflective surface, self-cleaning surface, and selective emitters. These surfaces have been developed for years, but the durability is still the biggest issue to utilize these surfaces to the commercial products. One of the major surface degradation types is thermal degradation. For example, photonic crystals, which can be used for selective emitters or selective absorbers, are periodic micro/nano-structures that are designed to affect the motion of photons at certain wavelengths. The general operating temperature of tungsten selective emitter is above 1,000 oC. These structures, however, lose their structural integrity at high temperature, which disrupts the tight tolerances required for spectral control of the thermal emitters [1-2].

In this paper, we are focusing on the degradation modes of 2-D sub-micron structures on smooth surface. Polycrystalline tungsten, single crystal tungsten and silicon substrates are used for experiment and firing temperature of 1200 °C for tungsten and 850 °C for silicon, which is equivalent temperature for tungsten at 1,500 to 1,600 °C.

2 THERMAL DEGRADATION MODES

From experimental observation, we found four main modes by which micro/nano-structures can be reformed when heated: recrystallization and grain growth, oxidation, surface diffusion and evaporation/re-condensation. These modes are further investigated with modeling and simulation.

2.1 Recrystallization and/or grain growth

Recrystallization occurs when previously deformed grains reform a new energetically more favorable grain structure. When new crystal grains have stored energy due to deformation, such as after cold rolling, that energy will be released when the material is heated and new grains will nucleate. After a brief nucleation period grains will grow at a roughly constant rate until a maximum grain size is reached. Recrystallization is influenced by many factors, but is mainly thermally driven and is triggered when a critical temperature is reached. It is also important to note that grain growth may occur without recrystallization if there is no stored energy. To determine the effect of recrystallization and grain growth on a metal surface is important to understand the amount of energy stored in the material and the critical recrystallization temperature.

10 mm by 10 mm polycrystalline tungsten sample is prepared by mechanical polishing. Surface roughness is less than 0.5 μm and its thickness is 300 μm . First, we drilled 20 (array of 4 by 5) of 5 μm -diameter-holes using focus ion-beam milling.

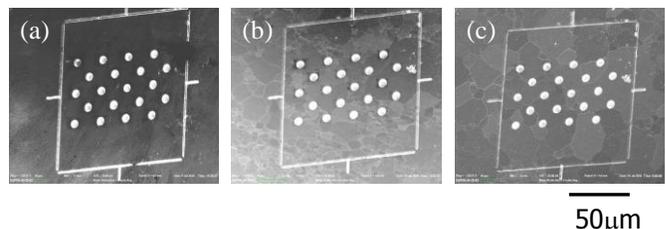


Figure 1: Thermal stability test of micro holes on tungsten surface (a) polished surface with focused ion-milled 5 μm diameter and 2 μm deep trenches, (b) 50 hours annealing at 1,200 °C, and (c) 100 hours annealing at 1,200 °C (Grain growth is observed, SEM images are 30 degree titled view)

Spacing between each hole is 20 μm and its drilled depth is 5 μm . as shown in the Figure 1. The sample is fired in oxygen free condition at 1200 $^{\circ}\text{C}$ for 100 hours total.

We observed sample using SEM at 50 hours and 100 hours later. The temperature gradually increased to 1200 $^{\circ}\text{C}$ at the rate of 3 $^{\circ}\text{C}/\text{min}$ and stayed for 50 hours. To remove possible oxygen molecules on the surface, the forming gas, hydrogen (5%) and nitrogen (95%) areflow in 150 sccm. Hot sample cools down to room temperature at the rate of 3 $^{\circ}\text{C}/\text{min}$ under same forming gas flown. SEM images obtained at this point. We repeated the same procedure for additional 50 hours to obtain 100 hours firing results. Closer look to the micro holes showed us the recrystallization along with surface diffusion, Figure 2.

However, this recrystallization and/or grain growth can be minimized by pre-annealing the sample prior to drill the micro/nano-holes. Primary recrystallization and grain growth occurred when the material have stored energy due to deformation, such as after cold rolling. If we relaxing these stresses by pre-annealing process, we can recrystallize small grains to the certain level of stable size and minimize the effect of grain growth. With 100 hours pre-annealing sample at 1200 $^{\circ}\text{C}$, the grain structure observed after additional 40 hours annealing at 1,200 $^{\circ}\text{C}$, Figure 3. The grain boundary does not move significantly, means the grain size does not changed much during additional 40 hours.

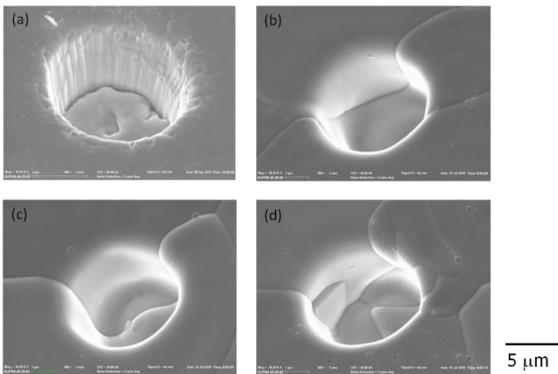


Figure 2: Thermal stability test of micro holes on tungsten surface (a) polished surface with focused ion-milled 5 μm diameter and 2 μm deep trenches, (b), (c) and (d) 100 hours annealing at 1,200 $^{\circ}\text{C}$ (Grain growth and surface diffusion are observed)

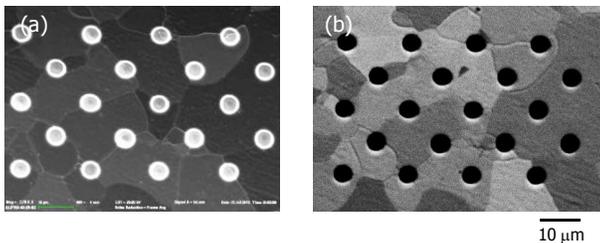


Figure 3: (a) 100 hours annealed at 1,200 $^{\circ}\text{C}$ and (b) additional 40 hours annealing at 1,200 $^{\circ}\text{C}$.

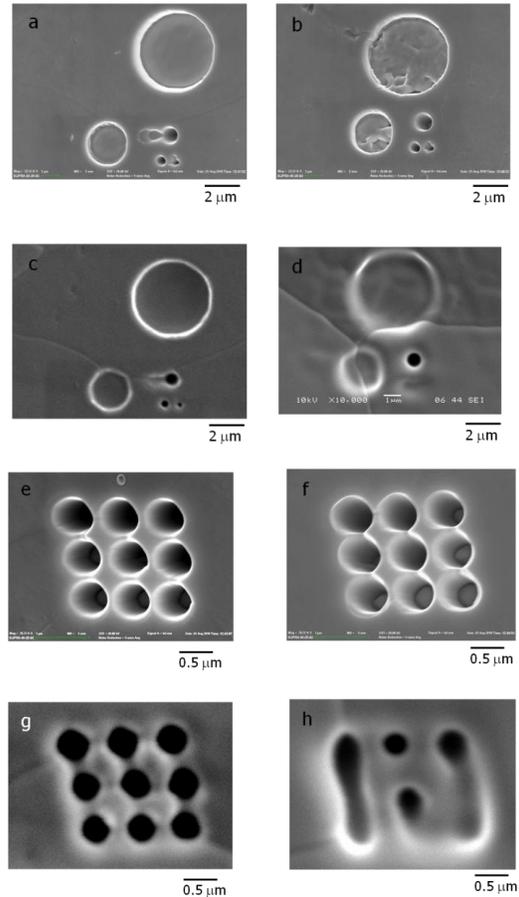


Figure 4: (a) 100 hours pre-annealed at 1200 $^{\circ}\text{C}$ before drilled the holes, (b) non-treated polished tungsten with drilled holes, (c) and (d) 100 hours firing at 1200 $^{\circ}\text{C}$ in oxidation free condition. (e) and (f) are treated same method with (a) and (d) but nano-scale holes, diameter of 300 nm, (g) and (h) are images after 100 hours firing at 1200 $^{\circ}\text{C}$.

We tested two polycrystalline tungsten samples. One is pre-annealed and another is just drilled. Pre-annealing condition is 1,200 $^{\circ}\text{C}$ for 100 hours and ramping up and ramping down speed was 3 $^{\circ}\text{C}/\text{min}$. The samples put together into the furnace without having any chance of oxidation and observed during the next 100 hours. As it can be seen from Figure 4, we noticed that pre-annealing effectively prevent the degradation by grain growth

2.2 Oxidation

Oxidation may impact both the density and geometry of micro/nano-structures on the surfaces and, in the case of selective emitters, chemical changes 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 $^{\circ}\text{C}$. Tungsten trioxide (WO_3) is permeable to oxygen and the oxide layer quickly grows. If the tungsten is heated further sublimation will

begin around 730 °C. It is therefore critical to understand the exact relationship between the oxidation rate, the partial pressure of oxygen, and the temperature [3]. We estimated that even at a very low partial pressure of oxygen of 10^{-12} mmHg and a temperature of 1,100 °C, the surface will oxidize at a rate of approximately 8 nm/day.

We found even at a controlled condition with forming gas supply, oxidation occurred. Tungsten trioxide (WO_3) is verified by XRD measurement the samples between 10 hours and 20 hours run, Figure 5.

Diffusion barrier coating, which is TiN layer coated by sputtering, can be a solution for preventing oxidation. It is also reported that oxygen stuffing on sputtered TiN enhanced the diffusion barrier quality since sputtered TiN has columnar structure and oxygen can fill the gap between grains by stuffing method [4]. Figure 6 and 7 also shows the effect of oxygen stuffing, TiN film (with O_2 stuffing) coated sample didn't show significant oxidation after 30 hours of firing test at 1200 °C. The coating of TiN (5-7 nm) was very effective as shown in Figure 6 and 7 where micro- and nano-holes without the barrier were completely destroyed. TiN coated by sputtering at 400 °C and then baked at 300 °C for 30 min in air for stuffing oxygen.

2.3 Surface Diffusion

Thermally driven diffusion of atoms is constantly occurring in all materials. While it tends to be negligible in solids at low temperatures, as the temperature increases the rate at which diffusion occurs may begin to dominate the evolution of the material geometry. In the case of micro/nano-scale structures surface diffusion tends to dominate bulk diffusion. Surface diffusion may be thought of as random thermal motion of atoms along a surface. However, because the amount of surface atoms varies based on the geometry of the structure, some areas of a surface may experience more diffusion than others and a net material flow occurs.

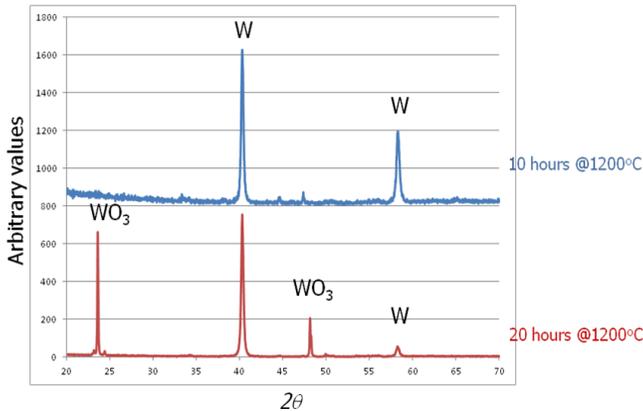


Figure 5: XRD data from tungsten sample which is fired for 10 hours at 1200 oC and 20 hours at 1200 oC. In between 10 hours and 20 hours, there were chance of leakage of ambient air and samples oxidize.

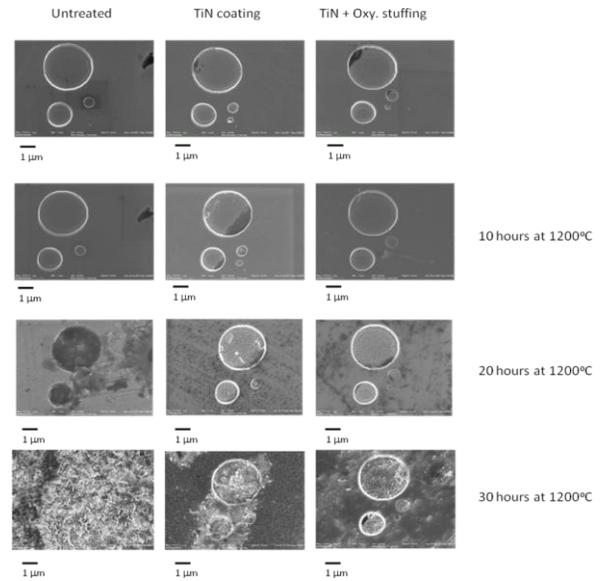


Figure 6: Oxidation on tungsten surface. (a) untreated sample, (b) TiN coated and (c) TiN coated and oxygen stuffed. Images captured every 10 hours after firing at 1200 oC.

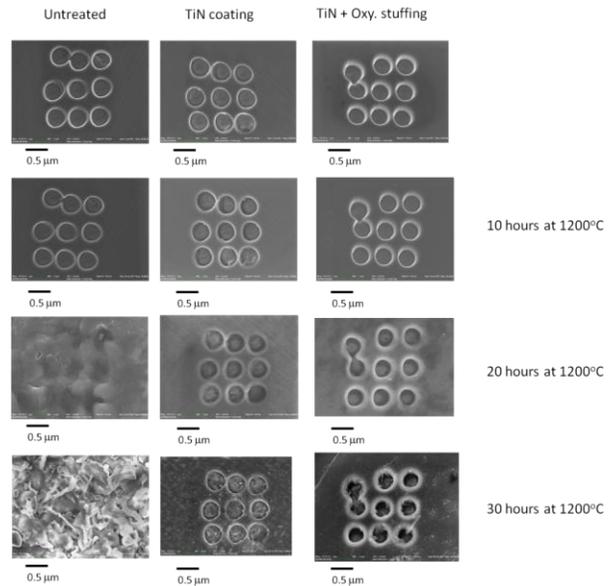


Figure 7: Oxidation on tungsten surface. (a) untreated sample, (b) TiN coated and (c) TiN coated and oxygen stuffed. Images captured every 10 hours after firing at 1200 oC, same test sample but nano-scale structures.

We observed this phenomenon with silicon micro trench. The trenches are fabricated with using lithography and deep reactive-ion-etching (Deep-RIE), Figure 8. Then the sample was fired for 25 hours at 850 °C. As it can be seen from Figure 8, surface diffusion occurred.

To investigate surface diffusion further, we made a theoretical modeling of thermal degradation of the micro/-

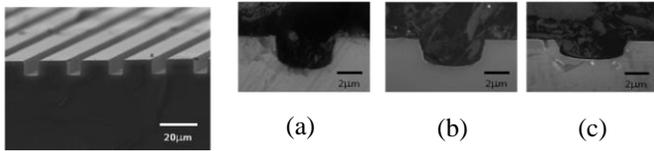


Figure 8: Fabricated silicon trench and its cross-sectional view after (a) 0 hour, (b) 1 hour, and (c) 25 hours of firing at 850 °C

nano-structures. Based on Mullin’s analysis, equation (1), the second derivative of the curvature along the surface, the coefficient of surface diffusion, the interfacial free energy are the key parameters that affect the spatial distribution of surface diffusion. However, for a given operation conditions, generally isothermal and isobaric, surface diffusion fully determined by the second derivative of curvature. This is because all the other parameters are identical for same temperature, pressure and material

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

Where, v_n is the velocity of the surface in the normal direction, γ is the interfacial free energy, Ω is the atomic volume, and n is the number of atoms per unit area. D_s is the coefficient of surface diffusion, k is Boltzmann constant, T is absolute temperature, and $\partial^2 K / \partial s^2$ is the second derivative of the curvature along the surface.

We were also able to simulate the degradation of the 2-D trench tungsten holes using a method called the level-set method, Figure 9.

2.4 Evaporation and Re-condensation

The final mechanism for surface evolution that we will

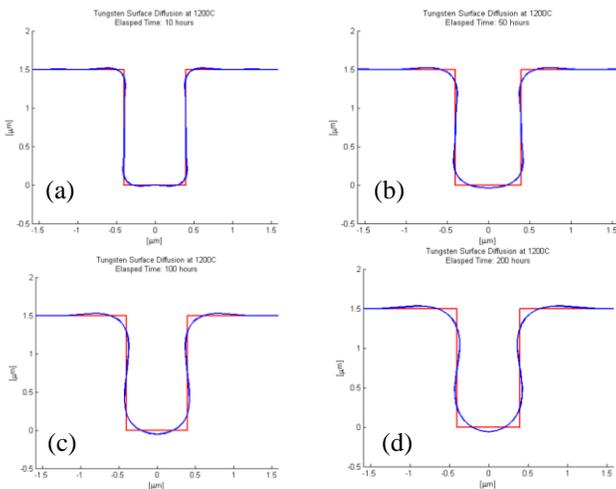


Figure 9: 2-D surface diffusion modeling of tungsten at 1200 °C (a) 10 hours, (b) 50 hours, (c) 100, and (d) 200 hours later.

consider is that of evaporation and condensation. At high temperatures, the amount of material that is vaporized at a solid surface can be significant. This gas creates a locally high vapor pressure and re-deposits on the surface nearby. In *Kinetics of Materials*, R. W. Balluffi et. al. show how the normal surface velocity that results from this redistribution of material is, in general, proportional to curvature of the surface and the ambient (non-local) vapor pressure of the material [5].

$$V_n = A \cdot P^{amb} \cdot K \quad (2)$$

Depending on the application, this material flux may be controlled by lower the ambient vapor pressure. Knowledge of this vapor pressure and the various elements that make up the constant of proportionality are required to determine the relative importance of condensation and evaporation.

3 SUMMARY AND CONCLUSIONS

There are four main modes by which micro/nano structures can be reformed when heated: recrystallization and grain growth, oxidation, surface diffusion and evaporation/condensation.

Recrystallization and grain growth occurred when the material have stored energy due to deformation, such as after cold rolling. If we relax these stresses by a pre-annealing process, we can recrystallize small grains to certain level of stable size and minimize the effect of grain growth. Oxidation may impact both the density and geometry of nano structures on that surface. We found that dense TiN film (with O₂ stuffing) coated can prevent oxidation at 1200 °C. Surface diffusion is another mode of thermally driven degradation. In the case of micro/nano-scale structures surface diffusion tends to dominate bulk diffusion. The key parameter for surface diffusion is the structure’s geometry, the curvature. Evaporation and re-condensation is another issue to be avoided for maintaining the micro/nano-structures.

ACKNOWLEDGMENTS

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