銀塩分層型光触媒の合成

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Spectrally Selective Emitters with Deep Rectangular Cavities Fabricated with Fast Atom Beam Etching

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Abstract. Spectral emittance and thermal stability of two-dimensional W surface gratings are investigated to obtain high-temperature resistive selective emitters for TPV applications. Numerical calculations based on rigorous coupled-wave analysis are performed to determine the structural profile of surface gratings. According to the determined parameters, W gratings composed of rectangular microcavities with the period of 1.0 μm are fabricated on single crystalline and polycrystalline W substrates by means of fast atom beam etching technique. The grating shows a strong emission peak which can be explained by the confined modes inside the cavities. The grating made from a single crystalline W shows very high thermal stability up to 1400K, while the polycrystalline grating is deformed at a high temperature because of the grain growth.

INTRODUCTION

With recent developments in micromachining techniques, many researchers have been actively studying on thermal radiation control by means of periodic microstructures, for example, one-dimensional (1D) [1,2] and 2D surface gratings [3-6], and 3D photonic crystals [7,8], to realize ideal spectral emittance or very efficient heat transfer. Greffet et al. have reported on thermal emittance from 1D surface gratings on a SiC substrate, and showed sharp emittance peaks due to the surface phonon polaritons modulated by the grating in the infrared (IR) region [1,2]. Hienzel et al. [3] and Sai et al. [4] have fabricated 2D metallic gratings to develop selective emitters, and demonstrated strong emittance peaks originated from surface plasmon polaritons supported by the gratings in the near IR (NIR) region. The research of Heinzel et al. has been developed in relatively deep gratings by Ferber et al [5]. As another report on 2D gratings, Maruyama et al. [6] has investigated thermal radiation from 2D gratings composed of deep microcavities in the IR wavelengths and discussed the effect of confined modes inside the cavities. On the other hand, Lin et al. [7] and Fleming et al. [8] have reported on thermal emission from 3D photonic crystals with woodpile structure and observed emittance decrease attributed to the photonic bandgap.

Control of thermal radiation by means of periodic microstructures has several advantages such as adjustability of design, applicability to various materials, and so on. All above-mentioned reports have demonstrated that spectral emittance can be
controlled by varying the profile of microstructures and materials. Naturally, anyone expects to apply this method to high-temperature applications where thermal radiation mostly dominates heat transfer phenomena. Thermophotovoltaics (TPV) [9] is a typical application for this technique. Actually, several groups have researched surface gratings intending to develop selective emitters for TPV applications [3-5].

However, thermal stability of such microstructures is supposed to be lower than that of bulk materials, and therefore it is important to investigate the thermal stability of microstructures at high temperatures. Some researchers have fabricated microstructured radiators with refractory metals aiming at high thermal resistibility [3,5,8], but the detailed feature has not been given. In the past publications, the maximum temperature at which thermal emittance is measured has been limited at 1200K [3] as far as authors’ knowledge. Since emitters are operated at over 1300K (1000°C) in ordinary TPV systems, further investigation and development are needed for practical utilization.

The objective of this research is to develop spectrally selective emitters with high thermal stability enough to be used in TPV applications. We have conducted numerical calculations based on rigorous coupled-wave analysis (RCWA) [10] to obtain a reasonable emitter design. Based on the calculated results, we have fabricated 2D surface gratings on single and polycrystalline W substrates by means of electron beam (EB) lithography and fast atom beam (FAB) etching technique [11]. Spectral emittance of the samples has been measured at high temperatures, and evaluated their thermal resistivity.

**NUMERICAL CALCULATIONS**

**Surface Design of Selective Emitters**

In TPV systems, it is necessary that spectral feature of radiators is matched with spectral response of photovoltaic cells. For example, the sensitive spectral band of GaSb cells is about 0.8 to 1.8 μm, and this requires emitters to have a high emittance only within that band and low outside it. To design the grating profile which materializes such spectral features, we have performed RCWA calculations on W gratings varying structural parameters and the state of incident wave. Figure 1 is a schematic drawing of the calculation model of 2D W gratings with rectangular microcavities. All gratings are symmetric to the x- and y- axes. Parameters are defined as periodicity $\Lambda$, aperture size $a$, depth $d$, incident angle $\theta$, azimuthal angle $\phi$, polarization angle $\psi$, and wavelength $\lambda$. With use of optical constants of W at room temperature reported in the literature [12], we have simulated spectral absorbance of W gratings, and regarded it equal to emittance according to Kirchhoff’s law.

Figure 2 (a) shows the calculated normal emittance spectra of 2D W gratings with rectangular cavities with three different $a/\Lambda$. $\Lambda$ and $d/a$ are fixed at 1.0 μm and 1.0, respectively. Spectral emittance of the W gratings increases drastically with increasing $a/\Lambda$ in $\lambda$ of 0.3 to 2.0 μm. In addition, high emittance region broadens
FIGURE 1. Schematic diagram of the calculation model of 2D surface gratings composed of rectangular parallelepiped microcavities.

FIGURE 2. Calculated spectral emittance of 2D W gratings with rectangular microcavities. In all calculations, $A = 1.0 \mu m$, $d/a = 1.0$, $\phi = 0^\circ$ and $\psi = 45^\circ$. (a), Normal emittance of W gratings with the different value of $a$. (b), incident angle dependence of spectral emittance of W grating with $a/A = 0.8$ and $d/a = 1.0$. 

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simultaneously. It is derived from the figure that $a/A$ value of 0.8 to 0.9 is suitable to realize good selective emitters. In Fig. 2 (b), calculated emittance spectra are plotted as a function of $\theta$ with the fixed parameters, $A = 1.0 \, \mu m$, $a/A = 0.8$, $d/a = 1.0$, $\phi = 0^\circ$, and $\psi = 45^\circ$. This figure shows that the spectral profile of the grating doesn’t depend on $\theta$ very much. This result is ideal for TPV applications. It is considered that these emittance enhancements are mainly originated from the resonance between electromagnetic waves and standing wave modes inside the cavities [5] instead of surface plasmon polaritons, because W cannot support surface plasmons strongly in these wavelengths.

**Efficiency and Radiative Power**

Based on the calculated spectra, we have estimated selective emission efficiency $\eta_{se}$ and relative radiative power of microstructured W emitters. $\eta_{se}$ is defined as the ratio of the radiative power emitted in the PV cell’s sensitive wavelengths to the total radiative power. Relative radiative power is also defined as the ratio of the radiative power of selective emitters to that of an ideal blackbody emitter in that region. Here, the region is set to $\lambda = 0.8$ to 1.8 $\mu m$, which corresponds to the sensitive wavelengths of GaSb cells. Angular dependence of emittance is also a significant problem to evaluate them. In this study, we use hemispherical emittance, which is the mean value of emittance in a hemisphere, to estimate reasonable indices in TPV applications. We calculate hemispherical emittance by computing directional emittance from $\theta = 0^\circ$ to 90$^\circ$ at intervals of 15$^\circ$, and averaging them in solid angle. In all calculations, it is supposed that emitters’ spectral feature doesn’t depend on

**FIGURE 3.** $\eta_{se}$ (a) and relative radiative power (b) of 2D W gratings with rectangular cavities as functions of temperature. All plotted data are calculated with the hemispherical emittance simulated under the condition of $A = 1.0 \, \mu m$ and $a/A = 0.8$. 

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temperature.

Figure 3 (a) shows the $\eta_{se}$ of microstructured W emitters for GaSb PV cells as a function of temperature at three different aspect ratio ($d/a$). Other structural parameters are fixed as $A = 1.0$ $\mu$m and $a/A = 0.8$. W emitters possess higher $\eta_{se}$ than the blackbody, and it increases from 0.35 to 0.55 with temperature rising. It can be said from the figure that $\eta_{se}$ does not depend on $d/a$ significantly. Relative radiative power of the W emitters is plotted in Fig. 3 (b) in the same manner as Fig.3 (a). Relatively high energy density up to 0.85 is achieved. It is almost independent from temperature, but improves from 0.71 to 0.85 by increasing $d/a$ from 0.5 to 1.0. However, further increasing of $d/a$ is not effective in raising radiative power.

Although the spectral feature of W emitters has not been optimized for GaSb cells yet, we have chosen $A = 1.0$ $\mu$m, $a/A = 0.8$, and $d/a = 1.0$, which are the best solution obtained in these calculations, as parameters to fabricate samples.

**EXPERIMENTAL**

**Sample Preparation**

2D surface grating have been processed on W substrates by the following procedure. First, a thick resist layer, an Al thin film and an EB resist layer are stacked one after another on a mechanically polished W substrate. The top EB resist is

![SEM images of the 2D W gratings](image)

**FIGURE 4.** SEM images of the 2D W gratings: (a) single crystalline W grating (1: top view, 2: oblique view), (b) polycrystalline W grating (1: top view, 2: oblique view).
exposed by EB lithography system (ELIONICS, ELS-3700) and a grating pattern is drawn. After the development of the pattern, FAB etching with SF$_6$ gas is carried out with a FAB system (EBARA, FAB-60ML) to replicate it on the Al film. Since FAB is electrically neutral atomic or molecular beam, it is possible to obtain fine patterns with nanometer order without deformation of etching shape due to accumulated charge on samples. Next, FAB etching with O$_2$ gas is successively performed to replicate the pattern on the thick resist under the Al film. With this double layer method, we can obtain a deep resist mask. Finally, FAB etching with SF$_6$ is performed again and the grating pattern is transferred on the W substrate consuming the resist mask. The same procedure is used to fabricate mono- and polycrystalline W gratings.

Figures 4 (a) and (b) show scanning electron microscope (SEM) images of 2D W gratings with 1.0 μm periodicity processed on mono- and poly crystalline W substrates. It can be confirmed that 2D array of rectangular microcavities are fabricated on each substrate. $a$ and $d$ are estimated as 0.8 μm and 0.75 μm, respectively, through SEM observations. It is observed that the cross section of a cavity is not a perfect rectangular but a trapezoid whose base length of the bottom is a little bit shorter than that of the top. It is also observed that the walls of each cavity are uneven; however, the roughness is sufficiently smaller than $A$.

**Experimental Setup**

We have measured thermal emittance spectra of the samples with the emission measurement system equipped with an electric heater, a Fourier transform NIR spectrometer with an emission port (Perkin Elmer, GX2000), and some optical elements. The schematic drawing of the experimental setup is shown in Fig. 5. Thermal emission from a heated sample passes through a sapphire window and is focused on a pinhole, which shunts out stray lights, by a CaF$_2$ lens. After that, the emission beam is collimated by another CaF$_2$ lens, and analyzed by the FT-IR. The measured spectra are calibrated and given units by comparing with the emissive spectra of the materials whose emittance has been already known, for example, SiC.

![Schematic drawing of the experimental setup for measuring spectral emittance.](image-url)

**FIGURE 5.** Schematic drawing of the experimental setup for measuring spectral emittance.
During heating samples, 5%H₂-Ar gas is flown inside the heater casing to prevent samples from oxidation. Surface temperature of samples is determined with a radiation thermometer by measuring the temperature of a flat W heated simultaneously with microstructured samples.

RESULTS AND DISCUSSION

Figure 6 shows the normal emittance spectra of the single crystalline W grating shown in Fig. 4 (a) at high temperatures. In the figure, measured emittance and literature data [12] of flat W are added as references. The emittance of the grating increases drastically in $\lambda < 2.0 \ \mu m$. In addition, a significant emission peak is appeared at about 1.3 $\mu m$, which can be explained by the standing wave modes inside cavities [5]. The spectral selectivity of the measured data is somewhat worse than that of the calculated shown in Fig.1. This may be caused by the difference of the cavity shape: smaller $d$ and the tapered walls. Emittance measurement has been carried out varying temperature up to 1400K. The spectral feature of the single crystalline grating has slightly changed with increasing temperature, and this will be explained by temperature dependence of optical constants. On the other hand, that of the polycrystalline grating has been clearly aggravated in the point of spectral selectivity at over 1300K.

After a heating at 1400K for 1h, we have measured reflectance spectra on both samples. The results are plotted in Fig.7 with reflectance spectra measured before the heating. Before the heating, each sample has similar reflectance spectrum as shown in the figure, and shows strong absorption at about $\lambda = 1.3 \ \mu m$, which corresponds to the emission peak in Fig.6. After the heating, however, the reflectance of both samples is

![Figure 6](image_url)

**FIGURE 6.** Measured spectral emittance of the 2D grating fabricated on a single crystalline W substrate shown in Fig. 4 (a) and a flat W measured at 1180K in a reductive atmosphere.
quite different; the single crystalline sample maintains its spectral feature, while that
of the other becomes duller and no clear absorption peak is observed in the NIR region.

SEM observation has been conducted to check surface conditions of the
samples after the heating. Figure 8 shows the SEM images of the W gratings after a
heating at 1400K for 1h in 5%H$_2$-Ar atmosphere. The grating made from single
crystalline W keeps its microstructure almost perfectly. However, a severe
deformation and creation of voids are observed on the polycrystalline W grating, and
this causes the degradation of spectral feature. Significant grain growth is also
observed on the sample. Considering these results and the very high melting point of
W, we regard the deformation of the microstructures on a polycrystalline W is mainly
carried out by the grain growth. In other words, high-temperature resistive microstructures
can be produced by using single crystalline materials.

![Graph showing reflectance spectra of W gratings](image1.png)

**FIGURE 7.** Measured reflectance spectra of the W gratings after a heating at 1400K for 1 hour in a
reductive atmosphere.

![SEM images of W gratings](image2.png)

**FIGURE 8.** SEM images of the W grating made from (a) a single crystalline W and (b)
polycrystalline W after a heating at 1400K for 1h in a reductive atmosphere.
CONCLUSIONS

To obtain high-performance selective emitters for TPV generation, surface design of 2D W surface gratings are investigated with numerical calculation based on RCWA. Although optimization has not been achieved, it is showed that microstructured W emitters can realize good spectral selectivity and high energy density at the same time. According to the calculated results, 2D surface grating with 1.0 μm periodicity composed of rectangular microcavities have been fabricated on both of mono- and polycrystalline W substrates with the combination of EB lithography and FAB etching techniques. The W gratings show a strong emittance peak, which can be explained by the resonance between electromagnetic waves and confined modes inside the cavities. The grating structure on a polycrystalline W is deformed and damaged by a heating at 1400K in a reductive atmosphere. It is speculated that this phenomenon is mainly due to grain growth. On the other hand, the grating structure on a single crystalline W is stable over 1400K. From these results, we conclude that the thermal resistivity of microstructures can be drastically improved by using single crystalline substrates.

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