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PYROLYZED PARYLENE STRUCTURE AS SELECTIVE EMITTER FOR HIGH-EFFICIENCY THERMOPHOTOVOLTAIC POWER GENERATION

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ABSTRACT

In this report, we propose Si microcavities coated with parylene-pyrolyzed carbon as a selective emitter for high-efficiency thermophotovoltaic (TPV) power generation system. In order to obtain carbon films with uniform thickness on three-dimensional Si structures, we adopt C_xF_y deposition on the top of the parylene film before the pyrolysis. The carbon yield doubles with the C_xF_y deposition. We also demonstrate that the Si microcavities coated with carbon thus fabricated exhibit an emittance peak near the wavelength of 2.6 μm, which corresponds to the characteristic electromagnetic mode of the cavity.

INTRODUCTION

With the development of portable microelectronics devices, micro power generation systems attract significant attention. Thermophotovoltaic (TPV) power generation is a promising candidate of such a system due to its large energy density on the order of 1 W/cm^2 and simple structure with no moving parts.

Our final goal is to develop a micro TPV power generation system as shown in Fig. 1. A micro combustor and an emitter are packaged into a vacuum chamber, and the thermal radiation energy in the infrared region from the emitter is converted into electrical energy with a PV cell. For high-efficiency TPV systems, spectrum control of the thermal emission is the key issue, since the spectral sensitivity of low-band-gap cells (e.g. GaSb) is mismatched with the blackbody spectra of the thermal radiation [1]. Sai *et al.* [2] reported that microcavities on a single-crystalline tungsten surface produce a strong emittance peak and reduce radiation energy in a long-wavelength region. However, they fabricated the tungsten cavities with FAB, which cannot be applied to large surface area. Fabrication with Si technology is preferable, but uniform conductive coating is needed on the surface, since Si is transparent in the infrared region.

In the present study, we propose parylene-pyrolyzed carbon [3] as the coating of the emitter surface, and characterize a prototype emitter with carbon-coated Si microcavities.

CARBON COATING WITH PYROLYSIS OF PARYLENE

Recently, parylene-pyrolyzed carbon attracts much attention for electroconductive MEMS. However, since the melting point of parylene-C (~ 280 °C) is far below its pyrolysis temperature, it is not straightforward to obtain uniform carbon thickness on three-dimensional structures; parylene-C films are melted during the heating-up period, and liquid parylene-C is driven to the corner of the micro structure by the surface tension. As a result, the carbon thickness after pyrolysis becomes highly nonuniform. Figure 2 shows the parylene-pyrolyzed carbon on Si micro structures. Thickness of parylene-C is 2.3 μm, and the pyrolysis temperature is 600 °C. The top edge of the Si cylinder is exposed by the reflow, and the corner of the cylinder is covered with thick parylene-pyrolyzed carbon. Therefore, pre-treatment of parylene-C is needed before pyrolysis [4]. To minimize the reflow, we employ carbon-fluorine polymer (C_xF_y) as the protecting topcoat layer.

PARYLENE-PYROLYZED CARBON WITH C_xF_y TOPCOAT

Firstly, we evaluate the effect of the C_xF_y deposition on the carbon yield. The parylene-C films of various thicknesses were deposited on Si substrates, followed by a deposition of a 110-420 nm-thick C_xF_y film with C_4F_8 plasma. The parylene-C/C_xF_y films were then pyrolyzed in N_2 atmosphere up to 600 °C with a 10 °C/min ramp rate.

Figure 3 shows the carbon thickness versus the thickness of parylene-C/C_xF_y films before pyrolysis. It is apparent that the carbon yield is much increased by the C_xF_y deposition. We assume that the carbon thickness is a linear function of the thicknesses of parylene-C and C_xF_y films, and employ a least square fit to the experimental data shown in Fig. 3. It is found that the thickness ratios defined with the polymer and the carbon thicknesses are respectively 0.59 and 0.20 for parylene-C and C_xF_y. On the other hand, the thickness ratio of a single layer of parylene-C is 0.32. Therefore, when C_xF_y is deposited on parylene-C before pyrolysis, the thickness ratio doubles.

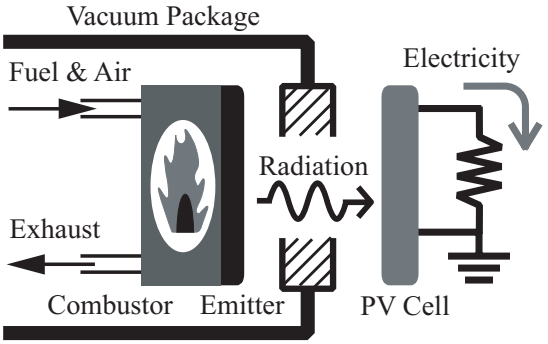

Figure 1. Schematic of a micro TPV power generation system.

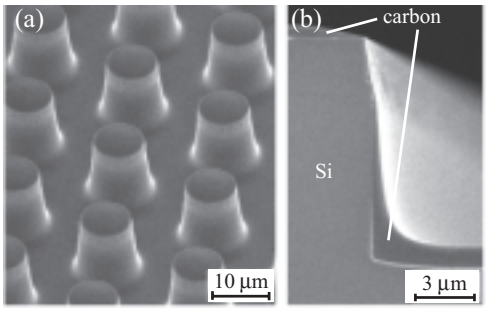

Figure 2. SEM images of Si micro structures with conventional parylene-pyrolyzed carbon coating. (a) Oblique view of micro cylinder array, (b) Cross-sectional view of a trench.

Figure 4 shows the thickness ratio of parylene-C versus the C_xF_y thickness. When the thickness of C_xF_y is larger than 110 nm, the thickness ratio of parylene-C becomes constant at around 0.6. Therefore, the minimum C_xF_y thickness to obtain large carbon yield is around 100 nm.

The effect of the C_xF_y deposition on uniformity of carbon films on 3-D structures was also examined. Figure 5 shows parylene-pyrolyzed carbon on a Si trench. The thickness of parylene-C and C_xF_y are respctively 1.6 μm and 0.18 μm. The carbon coverage on the top edge of the Si wall is better than that shown in Fig. 2, and all Si surface is covered with the carbon. However, the carbon surface has many wrinkles, which are undesirable from the viewpoint of uniform coating.

It is also found that the wrinkles disappear for thinner parylene-C films. Figure 6 shows a carbon film on a Si cavity for 0.27 μm-thick parylene-C and 0.18 μm-thick C_xF_y layers. The reflow of parylene-C is minimized with the C_xF_y coating, and almost uniform thickness without wrinkles has been achieved. Therefore, for the uniform coating of parylene-pyrolyzed carbon, the thickness of parylene-C should be thin.

The Raman spectrum of the pyrolyzed parylene-C/C_xF_y films exhibits a peak at around 1600 cm^{-1}, which is a characteristic wavenumber observed for graphite-like materials (Fig. 7).

DESIGN AND FABRICATION OF MICRO CAVITIES

Maruyama *et al.* [5] reported that the electromagnetic modes Λ inside a conductive cavity are expressed by

$$\Lambda = \frac{2}{\sqrt{\left(\frac{l}{L_x}\right)^2 + \left(\frac{m}{L_y}\right)^2 + \left(\frac{2n+1}{2L_z}\right)^2}}, \qquad (1)$$

where L_x, L_y, and L_z are the cavity dimensions (the aperture size of L_x x L_y with the depth L_z), and l, m, and n are positive integers. The maximum value of Λ corresponds to the cut-off wavelength, where a strong emittance peak appears.

Based on Eq. (1), we designed the cavity dimensions with opening, depth, and pitch of 1.4 μm,

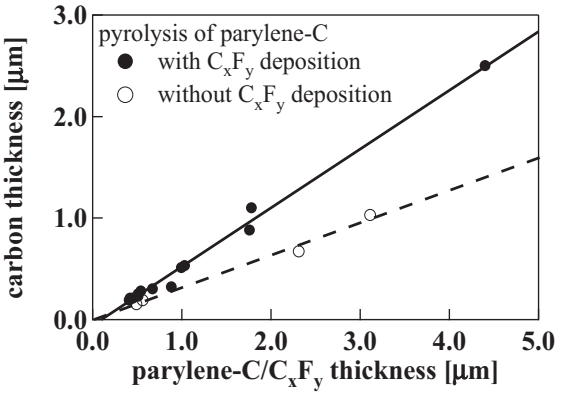

Figure 3. Carbon thickness of pyrolyzed parylene-C films with and without the C_xF_y deposition.

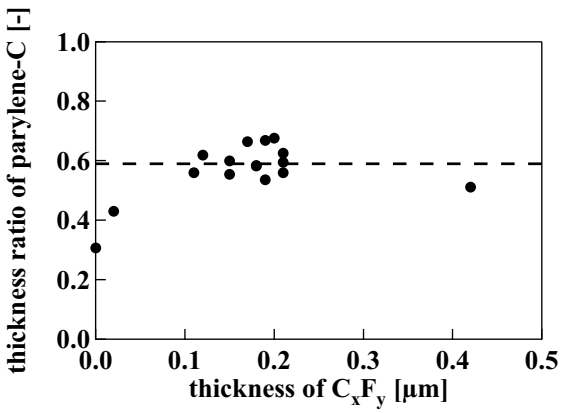

Figure 4. Carbon yield versus the C_xF_y thickness.

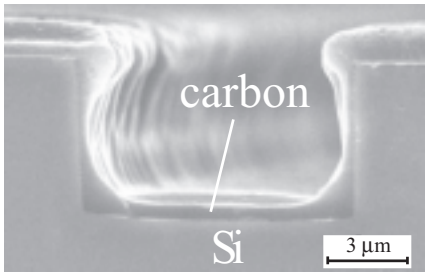

Figure 5. Cross-sectional SEM image of a Si trench with pyrolyzed carbon for 1.6 μm-thick parylene-C and 0.18 μm-thick C_xF_y layers.

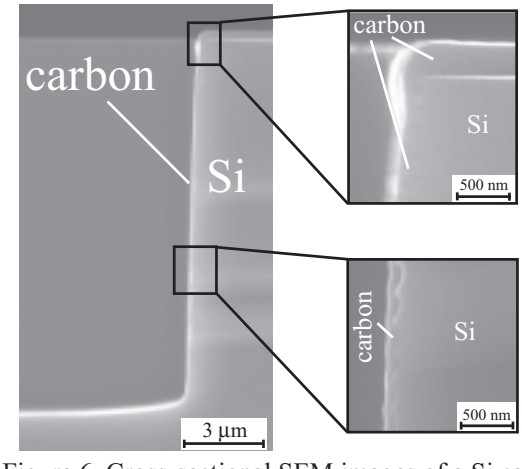

Figure 6. Cross-sectional SEM images of a Si cavity with pyrolyzed carbon for 0.27 μm-thick parylene-C and 0.18 μm-thick C_xF_y layers.

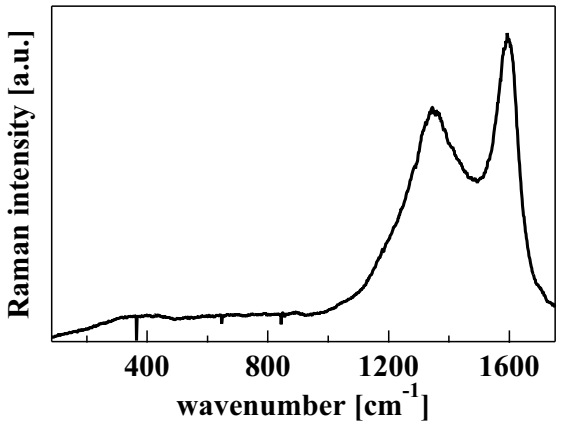

Figure 7. Raman spectrum of parylene-pyrolyzed carbon.

1.4 μm, and 2.0 μm respectively in order to make the emission peak at the wavelength of 2.5 μm.

Microcavities on a Si substrate are fabricated with submicron electron-beam (EB) lithography. Firstly, 400 nm-thick EB resist (ZEP-520A, ZEON Chemicals L. P.) is spun-on at 4000 rpm, and baked at 180 °C for 5 minutes. The resist is then exposed with an EB exposure system (F5112, Advantest Corp.) with a dose of 100 μC/cm^2. After development with ZED-N50 (ZEON Chemicals L. P.), cavities are etched into the substrate using DRIE (MS100SE, Alcatel) with the Bosch process. Next, a 270 nm-thick parylene-C film is deposited, followed by 160 nm-thick C_xF_y deposition with C_4F_8 plasma. Finally, the parylene-C/C_xF_y film is pyrolyzed at 600 °C with a 10 °C/min ramp rate in N_2 atmosphere, which results in a 120 nm-thick carbon film.

Figure 8 shows SEM images of the prototype selective emitter. Almost uniform coating of the carbon film without wrinkles is achieved on the square cavities. As shown in Fig. 9, no peel-off or degradation of the carbon coating contour is observed after heated up to 900 °C at 4x10^{-2} Pa for 2 hours. Note that the carbon thickness is decreased because of the higher temperature [3]. The present findings demonstrate durability of the pyrolyzed carbon device as a selective emitter.

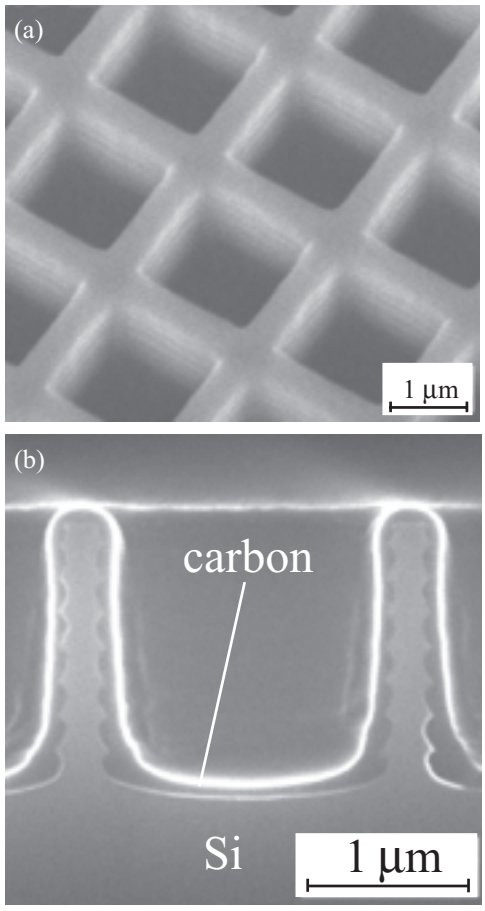

Figure 8. SEM images of the protoype device: (a) Oblique view. (b) Cross-sectional view.

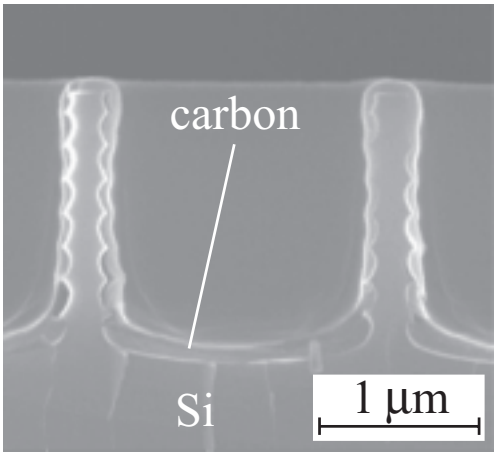

Figure 9. Cross-sectional SEM image of the prototype device after hetaed up to 900 °C at 4x10^{-2} Pa for 2 hours.

RADIATION SPECTRUM MEASUREMENT

Figure 10 shows our experimental setup for radiation spectrum measurements, which consists of a vacuum chamber with a sapphire window, an infrared heat lamp (GVL298, Thermo Riko Co., Ltd.), a sample holder made of amorphous graphite, and an IR spectrometer. Temperature of the holder was measured by a thermocouple inserted into the holder. The samples were heated up to about 900 °C at 4x10^{-2} Pa in the vacuum chamber. The thermal emission from the sample was introduced to the spectrometer using two silver-coated mirrors.

Emittance of the sample (ε_{sam}) was obtained by comparing the radiation energy of the sample (E_{sam}) with that of a reference material (E_{ref}) with known emittance. In the present study, a Si substrate coated with blackbody paint (JSC-3, Japan Sensor Corp.), of which emittance ε_{ref} is 0.94, was employed. All the samples including the reference plate were glued onto the holder using photoresist (AZP4400). When the holder was heated, the photoresist was also carbonized.

The temperature difference between the sample and the reference plate should be compensated. The correction formula based on the Planck's radiation law is as follows:

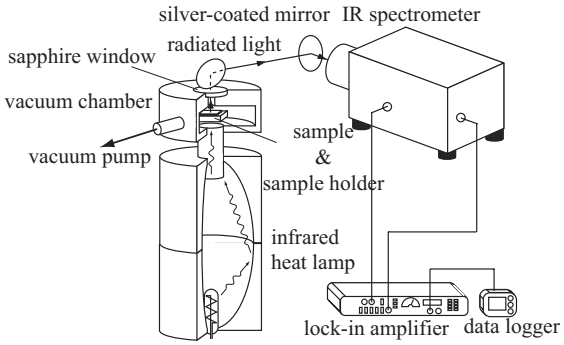

Figure 10. Schematic of the measurement system for the thermal emission spectrum.

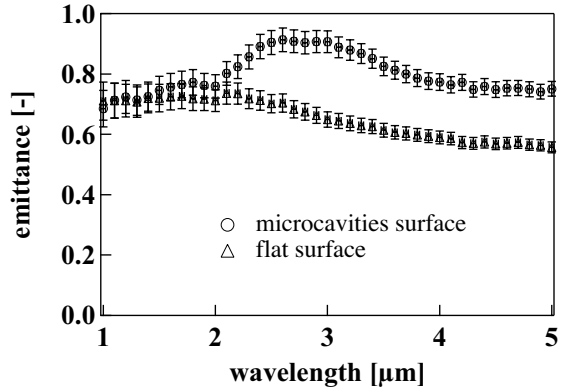

Figure 11. Emittance spectra of microcavities surface and flat surface with parylene-pyrolyzed carbon.

$$\varepsilon_{sam}(\lambda)=\varepsilon_{ref}(\lambda)\frac{E_{sam}(\lambda)}{E_{ref}(\lambda)}\frac{\exp(hc/kT_{sam}\lambda)-1}{\exp(hc/kT_{ref}\lambda)-1}, \quad (2)$$

where λ, h, c, and k are respectively the wavelength, Planck's constant, the light speed, and Boltzmann constant. The temperature T_{ref} was measured by a radiation thermometer (FTZ6-P300-20S22, Japan Sensor Corp.). Since we could not directly measure the temperature of sample with microcavities, T_{sam} was estimated by solving one-dimensional heat conduction equation in the holder and the sample. We assumed that the thermal contact resistance between the holder and the sample is equal for different samples, and calculated the contact resistance from the temperature difference between the reference plate and the holder.

Figure 11 shows the emittance spectra of the microcavities surface and the flat surface. It is apparent that the emittance of the microcavities surface is higher than that of the flat surface. The emittance of the microcavities surface has a peak at the wavelength of 2.6 μm. This is in good agreement with its designed value with Eq. (1). Therefore, we can conclude that Si microcavities uniformly coated with the parylene-pyrolyzed carbon can work as a selective emitter.

CONCLUSIONS

We developed a novel uniform coating method of parylene-pyrolyzed carbon on three-dimensional structures. By employing C_xF_y as the protecting layer, the reflow of the parylene-C film during pyrolysis is minimized and the uniform carbon film has been achieved on three-dimensional Si structures. In addition, with the C_xF_y deposition, the carbon yield doubles.

We also demonstrate that the Si microcavities with the pyrolyzed carbon exhibit an emittance peak near the wavelength of 2.6 μm, which is in good agreement with its theoretical value.

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