Strong infrared absorber: surface-microstructured Au film replicated from black silicon

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Abstract: With quasi-periodic microstructures, great enhancement of infrared light absorption of Au film over a broad wavelength band (2.7~15.1 µm) was realized experimentally for the first time. The microstructured Au film was prepared by replica molding of the surface of femtosecond (fs) laser microstructured silicon (black silicon). This unique absorption characteristic is mainly ascribed to good impedance match from free space to Au film. The surface of the sample was examined by X-ray photoelectron spectroscopy (XPS) and the four peaks of absorptance were ascribed to residual polydimethylsiloxane (PDMS), H2SO4, adsorbed water and CO2 in the air, respectively.

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References and links
1. Introduction

For infrared-thermal application like infrared thermal detectors, thermal imaging, a strong infrared absorber operating over the entire wavelength bandwidth is desired. Metal film can be a wide-band absorber for infrared radiation with a very small heat capacity, compared to previous designs including intrinsic absorber, black coatings, multilayer absorbers and metal-dielectric composite [1–3]. However, it is still a challenge to get high absorption for metal, as is well known that most bulk metals and flat metal films show little transmission or absorption from visible to infrared light. Recently, metal-dielectric nanocoatings with strong broadband and wide-angle absorption (so-called plasmonic blackbody) in the visible range have been demonstrated experimentally by V. G. Kravets et al. [4,5]. For mesoscopic continuous metal films, Rephaeli and Fan proposed a pyramidal structure on the surface of tungsten and performed a three-dimensional finite-difference time-domain (FDTD) simulation [6]. By adjusting both the height and periodicity of the pyramids for optimal impedance match, they achieved broadband absorption for tungsten in the solar light wavelength range theoretically. Nevertheless, the metal films with such fine and periodic microstructures which may result in a great enhancement of infrared light absorption and can be good candidate for infrared light-heat conversion applications, have not yet been achieved experimentally before.

With cumulative femtosecond (fs) pulses irradiation on the surface of silicon in the ambient of SF$_6$, a quasi-periodic micro-sized conical structure can be formed [7]. Around the year of 2000, extremely strong (close to 90%) light absorption of this microstructured silicon surface over a wide wavelength range from 0.25 to 16.7 $\mu$m was discovered [8,9]. Due to its unique absorption property, it is called “black silicon”. Ever since then, a lot of interests have been attracted to go deep into its mechanism or apply it to devices [10–15]. Here, we replicated the conical structure from the surface of a black silicon to a thin Au film. The optical absorption property of three samples with different spike heights (~32, 16, 6 $\mu$m) was measured in the wavelength range of 2.0–15.1 $\mu$m. Our results for the first time revealed broadband strong infrared light absorption of Au film with this structure on the surface. The absorptance of 0.7–0.8 was observed in the wavelength range of 2.7–15.1 $\mu$m for sample with the highest conical structure (~32 $\mu$m). The absorptance becomes stronger when the height of the spike increases, implying that impedance match tends to be optimal, which is consistent with Rephaeli and Fan’s theoretical result.
2. Experimental details

The surface of silicon (100) wafer (undoped, single crystalline, 350 μm thick) was structured in the ambient gas of 70 kPa SF₆ with cumulative pulsed (800 nm, 120 fs) irradiation of fs laser. The focused laser beam was normally incident upon the sample surface. The laser beam was scanned along the surface of silicon wafer at a certain speed to fabricate samples of large area (over 10 × 10 mm²). The irradiation resulted in arrays of conical spikes formed on the surface. In present experiments, three types of samples were prepared. The heights of the spikes are ~32, 16, 6 μm, respectively.

Microstructured Au films were prepared by replicating the surface of fs laser microstructured silicon. Two steps are involved as illustrated in Fig. 1. The first step is similar to the process done by Reinhardt et al. [16]. The casting material used was Sylgard 184 from Dow Corning, Co. The polydimethylsiloxane (PDMS) base and the curing agent were mixed in the weight ratio of 10:1 for 10 min. The mixture was put into a vacuum chamber for 30 min to remove the air contained in it. Then it was poured over the master structure of black silicon placed in a small plastic cup. After another removal of air being trapped in the spikes for 40 min, the samples were heated under the temperature of 65°C for 5 hours. The PDMS mold was carefully peeled off from the black silicon master mold when the sample was cooled for 24 hours. At this stage, a surface replicating the negative-sculpture microstructure of the original master was obtained. During the second step, an Au film with thickness of ~300 nm was deposited onto the PDMS surface by vacuum thermal evaporation (VTE). After that, it was dissolved in oil of vitriol (mass fraction 98.3%) for 12 hours to remove the PDMS. When all PDMS was dissolved, an ultrathin Au film was left floating on the surface of sulfuric acid. With a trap valve, the ultrathin Au film can be transferred to ethanol in a glass culture dish. After being rinsed for several times, it was reversed upside down carefully with a tweezer and placed on an undoped, double-side polished single crystalline silicon substrate.

The total hemispherical (specular and diffuse) reflectance (R) and transmittance (T) of the microstructured Au films were measured over the wavelength range of 2.0–15.1 μm. The absorptance were calculated via the formula $A=1-R-T$ [8]. The absorption spectra of the
substrate (an undoped, double-side polished, single crystalline silicon wafer) and a flat Au film (~300 nm) deposited on the silicon substrate were also measured for comparison. All optical measurements were performed with a Bruker Equinox 55 Fourier Transform Infrared (FTIR) spectrometer equipped with an integrating sphere detector. The incident angle is ~9° to the normal of sample port. The surfaces of samples were examined by X-ray photoelectron spectroscopy (XPS) with an Axis Ultra DLD spectrometer from Kratos, Co.

3. Results and discussion

Figure 2(a) shows the scanning electron microscope (SEM) image of microstructured silicon with the spike height of about 16 µm. It can be seen that micrometer-scale quasi-periodic spike arrays are formed on silicon surface and the side of the spike is covered with nanostructures. Many of them are protuberances. These samples exhibit ultrahigh light absorption in the visible and infrared wavelength range [8, 9]. Figure 2(b) shows the SEM image of microstructured Au film replicated from the above microstructured silicon. It can be seen that the spikes look smoother and there are also some protuberances on each spike, though they are not as dense as those on spikes of microstructured silicon. The average height (16 ± 2 µm) and density of the spike (25 ± 2 per this area) are nearly the same with its counterpart. For the feasibility of this replica molding method, Reinhardt et al. gave a relatively strict experimental demonstration [16].

![Fig. 2. SEM images of (a) the surface of black silicon and (b) the surface of Au film with microstructures replicated from the counterpart. The inset of (a) and (b) show the side of the spike at a smaller scale.](image)

Figure 3 shows the reflectance, transmittance and absorptance spectra of three types of samples (denoted as S1, S2 and S3 corresponding to the spike height of ~32, 16 and 6 µm, respectively), as well as a flat Si substrate and a flat Au film (denoted as Si and Flat Au, respectively) for comparison. In Fig. 3(a), sample 1 shows the lowest reflectance, close to 0.15 and sample 3 shows the highest, close to 0.45 over most part of wavelength range from 2.7 to 15.1 µm. It implies that the height of the spikes plays an important role in the reflectance. Higher spikes result in lower reflectance. There are four valleys over the whole measured wavelength range, which are located at 2.5~3.7 µm, 4.2~4.3 µm, 5.4~6.5 µm and 7.8~10 µm. As for flat Au film and silicon substrate, it is well known that the former exhibits good reflectance higher than 0.9 and the latter is about 0.45 in this wavelength range [3, 17, 18]. From Fig. 3(b), it can be seen that, except the sample Si, all Au samples show nearly zero transmittance in the whole wavelength range. Accordingly, it can be concluded that the microstructured Au film replicated from black silicon is completely continuous. That is to say, there is no hole or slot in the structure otherwise the transmittance would not be so low. Figure 3(c) shows the absorption of all samples calculated with formula A=1-R-T. It can be seen that sample 1 shows the highest absorption of 0.7~0.8 and sample 3 shows the lowest one of about 0.5 over the wavelength range from 2.7 to 15.1 µm. One can also find that higher spikes result in higher absorption. There are four absorption peaks in the wavelength range: 2.5~3.7 µm, 4.2~4.3 µm, 5.4~6.5 µm and 7.8~10 µm, corresponding to the four valleys in the reflectance spectra. Compared to the flat Au film (~0.05 over the whole range), all
microstructured Au films (S1, S2 and S3) exhibit great enhancement in the infrared light absorption. As for the sample of smooth silicon substrate, no absorption can be seen in the whole wavelength range because of the band gap 1.12 eV (corresponding to 1.1 µm) of silicon. Therefore, the influence of the substrate can be neglected in our experiments.

Figure 3. (a) reflectance, (b) transmittance and (c) absorptance spectrum for sample 1, sample 2, sample 3 (denoted as S1, S2 and S3 corresponding to the spike height of ~32, 16 and 6 µm, respectively) and a flat Si substrate, a flat Au film (denoted as Si and Flat Au, respectively) in the wavelength range of 2~15.1 µm.

Figure 4 shows the XPS of sample 3. The results reveal that there are some other substances existing on the surface of the sample, which may affect its light absorption. Most of them are residua yielded during the replicating process. Figure 4(a) gives the O 1s peak and it can be fitted well by two PDMS O 1s peak (533.2 eV and 532.05 eV) [19,20] and one H₂O O 1s peak (534.2 eV) [21]. Figure 4(b) shows the Si 2p peak and it can also be well fitted by two PDMS Si 2p peaks (103.35 eV and 102.45 eV) [19]. Figure 4(c) shows a C 1s peak, which can also be assigned to PDMS (284.6 eV) [20]. Figure 4(d) gives the S 2p peak corresponding to H₂SO₄ (169.5 eV). Then it can be concluded that the residua contain PDMS and H₂SO₄. H₂O should be the adsorbed water on the Au microstructured surface. Thus, two absorption peaks of 2.5~3.7 µm and 5.4~6.5 µm can be ascribed to the absorption of H₂O [22]. The peak of 7.8~10 µm corresponds to the absorption of PDMS [20, 23] and H₂SO₄ [24]. The last small peak of 4.2~4.3 µm should be due to the little absorption of CO₂ in the air [22] because all optical measurements were performed in atmosphere. In addition, it can be seen in Fig. 3(c) that the observed characteristic absorption peaks of PDMS, H₂SO₄ and H₂O are weak, especially in view of surface enhanced infrared absorption (SEIRA) effect. Other discrete characteristic peaks of these materials do not appear at all, implying that the amount of residua is little and can be neglected when one considers the wide band absorption of the surface-microstructured Au film.
In general, the infrared light absorption of bulk metal or smooth metal film is quite low. However, in our experiment, the surface-microstructured Au films show great enhancement of infrared light absorption over such a wide wavelength range (2.0~15.1 µm). Higher spikes on Au film result in lower reflectance and therefore higher absorptance. As for this new characteristic, the impedance match should be the dominating factor according to Rephaeli and Fan's simulation result [6]. We found that the effective impedance of the microstructured Au film changes gradually from ~1.0Z₀ at the peak position of spike to ~0.10Z₀ at the bottom [25], so that light can be easily coupled into the device (since the impedance matches well with air at the device surface) and is then absorbed efficiently inside the medium due to losses of metal. Increasing the height of the spikes provides a longer and more gradual transition region from free space to Au film, which can generally improve absorption characteristic. Although a certain period cannot be fixed for the spike arrays, the distance between two spikes is either smaller than the wavelength or comparable to it, which is crucial to achieve broad band absorption. Numerical simulations show that the absorption effect is rather insensitive to the incident angle. Light trapping resulted from diffuse reflection by spikes and the protuberances on their surfaces may also contribute to the whole band increment [8].

4. Conclusions

In summary, we present the fabrication and infrared characterization of Au films with micro-sized quasi-periodic spike arrays. By using the method of replica molding, we successfully transferred the spike arrays from the fs laser microstructured silicon to Au film. Enhanced broad band infrared light absorption was observed in the wavelength range of 2.7~15.1 µm. This property is clearly different from that of bulk Au or flat Au film. It is mainly ascribed to the good impedance match between free space and surface-microstructured Au film. As a new infrared absorber, this kind of metal film may have some potential applications in infrared thermal sensor, detector, and stealth military technology, etc.

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