Patterning and hardening of Gold Black infrared absorber by shadow mask deposition with Ethyl Cyanoacrylate

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ABSTRACT

Patterning of gold-black infrared absorbing films by stencil lithography and hardening by polymer infusion is reported. Gold black nano-structured films are deposited through a thin metal shadow mask in a thermal evaporator in ~400 mTorr pressure of inert gas, followed by ethyl cyanoacrylate fuming through the same mask to produce rugged IR absorptive patterns of ~100 micron scale dimensions. Infrared absorptivity is determined by transmission and reflectivity measurements using a Fourier spectrometer and infrared microscope. Results indicate that the optimized hardening process reduces the usual degradation of the absorptivity with age. This work has potential application to infrared array bolometers.

Keywords: goldblack patterning, shadow mask, polymer infusion, absorptance, aging effect studies

1. INTRODUCTION

Gold black is a well-studied nano-structured metal film that shows strong broad band absorption throughout the visible to far-infrared range [1-6]. As such it has found wide application as a coating for infrared bolometers to improve their responsivity. Examples include the Geostationary Earth Radiation Budget (GERB) instrument launched by the European Space Agency (ESA) and CASSINI spacecraft of the National Aeronautics and Space Administration (NASA)[6-7].

Gold black has a number of limitations that this paper addresses. It is very porous and fragile, so that it is easily damaged by contact, shock, or air currents. The deposition process tends to cover large areas, so that it has usually been applied only to single element detectors. It cannot be patterned at sub-mm scale by traditional metal lift-off using photoresist and solvents, because it tends to clump and return to its non-absorbing bulk gold state. It cannot endure elevated temperatures without similarly reverting. It suffers deleterious aging effects.

Alternatives to gold black exist. For some infrared bolometers, combinations of Ni and SiN thin film are used as absorbing coatings.[8] However, to achieve sufficient absorption, the thickness of the SiN film must exceed a micron since the value of its IR extinction coefficient is small. This results in excessive thermal mass that limits bolometer response time and achievable frame rates. In contrast, with a density that is only 0.02% of bulk gold, gold black has a correspondingly low heat capacity.[9] Hence, gold black remains of significant interest for applications if its patterning and stability limitations can be overcome.

Opportunities for patterning and stabilization are explored here. Patterning with ~100 micron length scales is achieved by deposition through a shadow mask. Such dimensions are suitable for the characteristic pitch of most long-wave to far-IR array bolometers. Stabilization is achieved by subsequent fuming with ethyl cyanoacrylate (trade name "Superglue™").

2. EXPERIMENT

Gold black is deposited by the method of Harris.[1] Thick, porous films of gold black with high packing fraction were deposited on a double-side polished silicon substrate by thermal evaporation in a chamber that was back-filled to ~ 400 mTorr with N_2. A thermoelectric cooler is used to keep the substrate at -13 C.

Molybdenum boats with dimensions of 12 mm x 5 mm x 1 mm deep were filled with 99.9% gold wire of diameter 0.8 mm with length varying from 0.1 to 0.5 mm during different experiments.

A stencil shadow mask is held at sub-millimeter distances from the substrate by using layers of cellophane tape (“Scotch™”) as spacers. Such tape has poor thermal conductivity, so that the mask is radiantly heated by the hot evaporation boat during the deposition while the substrate remains cold. This insures that the deposition occurs preferentially on the substrate through the stencil windows. Nevertheless, gold black also accumulates around and inside the aperture of the stencil mask, which eventually clogs the openings. To prevent this, the mask was cleaned in acetone after each use. Various stencil patterns with different opening sizes were investigated. Fig. 1 presents a schematic of the process.

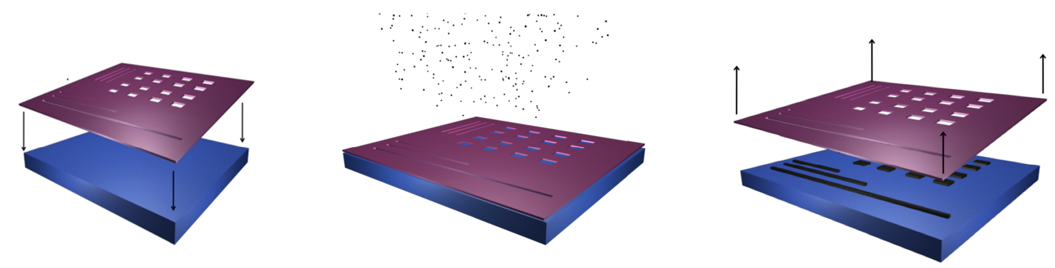


Fig 1. Schematic diagram of stencil lithography method. Alignment of the shadowmask (left) is followed by deposition of gold black (middle). Then the mask is lifted leaving the gold-black pattern (right).

Polymer infusion by cyanoacrylate fuming was performed at atmospheric pressure in a fuming chamber. The gold black sample was placed 100 mm above an electric hot plate at 100 C. An aluminum foil dish containing 2 mL of cyanoacrylate was placed on the hot surface. We reported this process previously for un-patterned depositions.[12] In this paper, the cyanoacrylate is deposited through the realigned shadow mask to produce a patterned deposition that coincides with the gold black pattern.

To observe changes in gold black structure with aging and polymer fuming, a Zeiss Ultra Scanning Electron Microscope was also used to image the gold black film.

Spectral measurements were performed with a Brucker Vertex 80v FTIR Spectrometer interfaced with a Hyperion infrared microscope. Double side polished silicon was used as a reference for transmittance measurements. An evaporated optically-thick smooth gold layer served as the reference for reflection measurements at normal incidence.

To measure the conductivity of gold black thin film, four parallel gold strip electrodes of 250 μm width and 500 μm separation were photo-lithographically deposited on a non-conductive substrate and goldblack was deposited on top of these electrodes. Since the thickness of the gold black deposit is negligible compared to the separation between the electrodes, the sheet resistance is[10]

$$R_s = 4.53 \times \left(\frac{V}{I}\right) \quad , \qquad (1)$$

where voltage (V) and current (I) is measured between inner and outer pairs of electrodes, respectively.

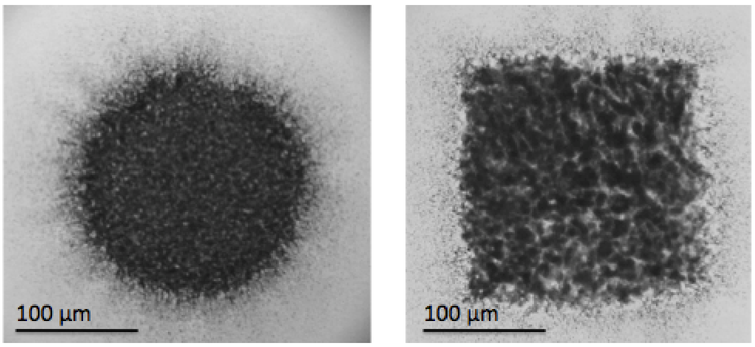
Gold black showed constant conductivity for different applied current values up to 2 mA. Higher currents caused interesting changes in sheet resistance due to thermal breakdown and transformation of the film. These effects are outside the scope of this paper and will be presented elsewhere.

3. RESULTS & DISCUSSION

3.1 Patterning of Gold Black

We first attempted to pattern gold black by standard photolithography and lift-off in acetone. The color of the film changed from black to brownish. The reflectivity of the sample increased from 1% up to 40 %. Similar effects occur when gold black is annealed over 150 C for an hour, which is attributed to collapse of the gold black structure from fluffy and porous back toward bulk gold. We conclude that gold-black cannot be patterned by conventional metal lift-off.

Next we pursued deposition of gold black through a shadow mask. When placed at optimum height above the substrate, well-defined and reproducible patterns were obtained. Fig. 2 presents optical microscope images of two different patterns achieved with shadow mask kept at (a) 0.9 and (b) 0.6 mm heights. For each pattern, the mass of gold, deposition rate, and inert gas pressure were 121 mg, 0.33 mg/s, and 400 mTorr, respectively. Even though deposition parameters were similar for both patterns, there resulted significant differences in thickness, morphology, and edge definition. The pattern in Fig 2(a) has thickness less than 500 nm, a fine grained structure, and hazy edges. The pattern in Fig. 2 (b) exceeds 10 µm thickness, its structure is more coarse, and its edges sharper. In other words, the closer the shadow mask is to the substrate, the sharper are the edges and the thicker is the resulting pattern. To avoid damage to sensitive bolometer structures, actual contact would usually be prohibited.



(a) (b)

Fig 2. Optical image of gold black patterns produced at different heights (a) 0.9 mm and (b) 0.6 mm of the shadow mask above the substrate.

Compared with coatings prepared without a mask, the patterned gold black density was much higher, but the thickness was much lower. In each case, the substrate is cooled to -13 C, according to a thermocouple located below the substrate. However, the mask partially shields the substrate from radiant heating by the evaporation boat, so that the actual substrate surface temperature may be lower when using a mask, causing more accumulation by “cryo-pumping” effect. Also, the relative warmth of the mask aperture may focus the deposition, so that the gold-black flux is higher through the aperture than the flux would be in the same area without the mask. That the films are thinner but more dense may be due to the exclusion by the mask of long chains of gold black particles that link together before reaching the sample. The smaller chains that make it through the aperture are able to pack more closely together, a scenario similar to the computer game “Tetris”. When thermally conducting spacers are used to separate the mask from the substrate, which allows lower mask temperatures, the patterns produced are very sparse and discontinuous, and the mask itself collects heavy gold black depositions.

SEM images of a gold black pattern produced with the mask and substrate separated by 0.3 mm are presented in Fig. 3. The edges are blurred over lateral distances of about 10 µm. This can be attributed to lateral diffusion of the cloud of gold particles between the time that the particles pass the aperture until they land on the substrate.

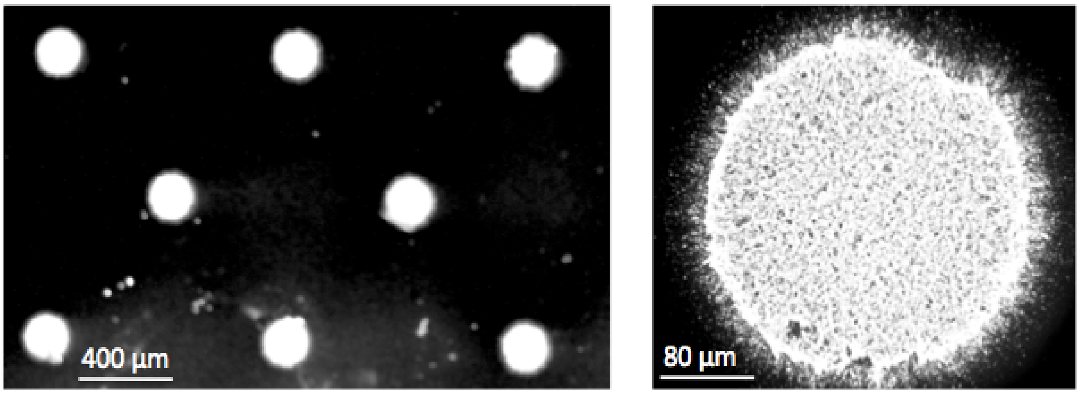


Fig 3. SEM images at two different magnifications. The bright gold black patterns were formed with stencil mask held 0.3 mm above the substrate.

For mask-substrate separations exceeding ~3 mm (obtained using plexiglass spacers), we obtain loose patterns with unusual morphology. Fig. 4 presents an SEM image with field of view limited to several microns linear dimension. Individual clumps of gold black are observed in the form of loose strands of ~ 1 micron length and separated from each other by comparable distances. The blurring of the pattern edges was so extensive, that the pattern is barely discernable. Such large mask separations are therefore useless for fine patterning, but the unusual morphology obtained may nevertheless have application, e.g. for plasmonic enhancement of solar cell efficiency.[11-12]

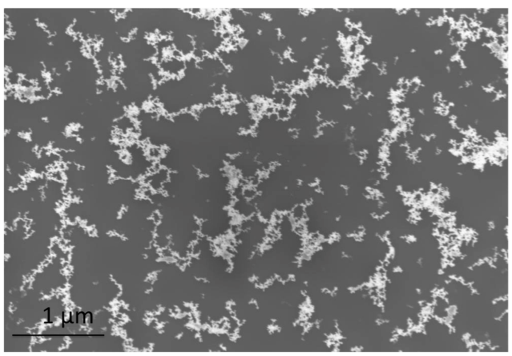


Fig 4. SEM image of gold black pattern deposited through a stencil mask separated from the substrate by 3.3 mm.

3.2 Polymer Infusion

To improve mechanically stability, we infused gold black patterns with ethyl cyanoacrylate.[13] This fuming was performed through the shadow mask, which was re-aligned to the gold-black pattern using an optical microscope. Fig. 5 presents an optical micrograph a gold black pattern before and after polymer infusion. To prevent lateral spread and staining of the substrate during cynoacralate-fuming, the mask-substrate separation could not exceed 0.3 mm.

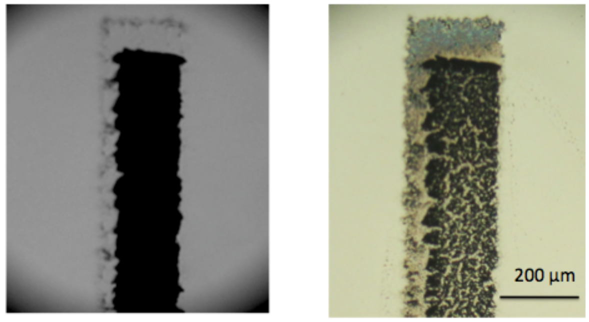


Fig 5. (left) Gold black pattern. (right) After cyanoacrylate fuming.

Fig. 6 presents reflectivity spectra of gold black films before and after fuming for three different fuming times. Before fuming, the reflectivity is already low for all three samples, though it is not equally low, due to imperfect control of deposition conditions. There is a tendency for increased reflectivity at the lower wavenumbers. Long fuming time results in a thick ethyl cyanoacrylate coating. This expected result is confirmed by the growth of a sharp ethyl cyanoacrylate absorption band at ~1755 cm^{-1}. As the thickness of this polymer increases, the reflectivity also increases. The sample with just 2 minutes of fuming shows little spectral change, and fortunately this sample already shows much improved resistance to mechanical damage. It was stable against a stream of nitrogen gas coming out of 4 mm internal diameter nozzle at 70 liters/min flow rate from a distance of approximately 3 cm. Thus, the minimum fuming time of 2 minutes provides significant mechanical stabilization without degradation of the desired absorptivity.

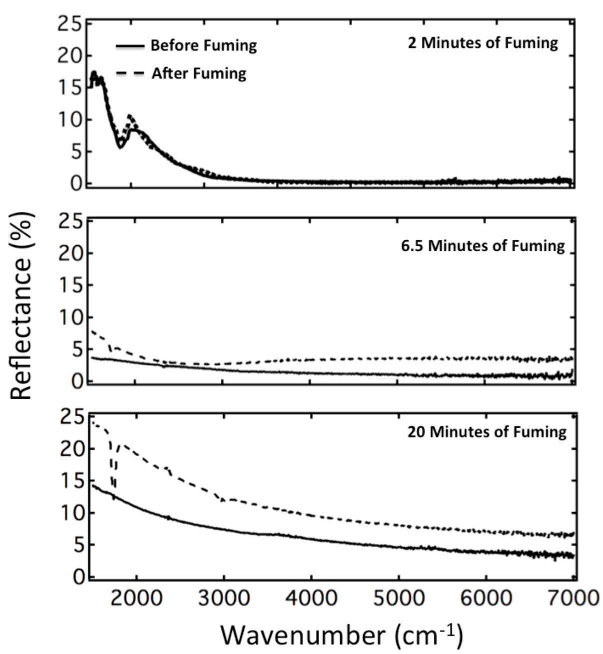


Fig. 6. Reflection spectra of gold black films before and after polymer infusion for three different fuming times as indicated.

With a density just 0.02% of bulk gold, gold black has an index close to unity[6]. Fuming increases the optical density of the film. Therefore higher reflectance is expected at the interface with air after fuming.

Fig. 7 presents SEM cross sections of gold black film before and after cyanoacrylate fuming for 2 minutes. The fumed cyanoacrylate immediately polymerizes inside the gold-black spider web in the presence of a weak base such as water vapor in the atmosphere. The polymer chains cause the gold black structure to compress and stabilize. However the film undergoes only 30% compression for 2 minutes of fuming and as seen in Fig. 7, and the reflectance apparently is unaffected by this much compression.

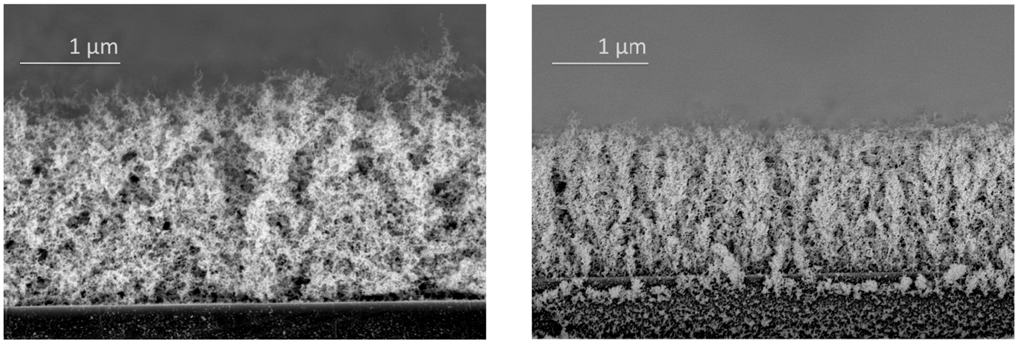


Fig 7. Gold black film cross section before (left) and after fuming for 2 minutes (right)

Fig. 8 shows that 20 minutes of fuming compresses the film by a factor of about 3, which increases the reflectance by more than 5% (Fig. 6).

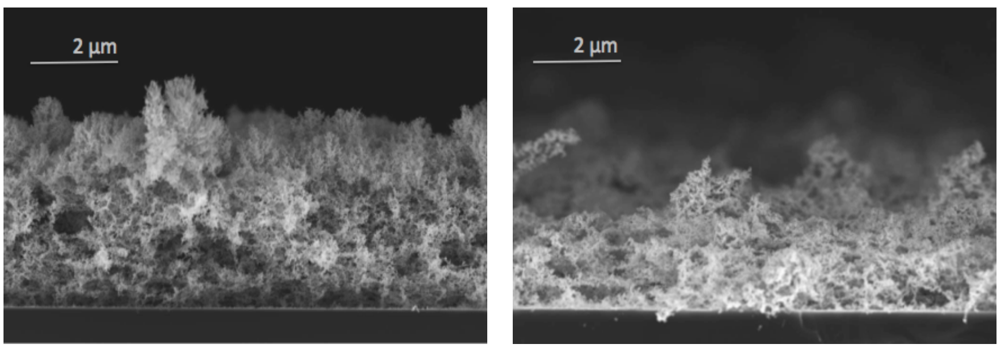


Fig 8. Gold black film cross section before (left) and after (right) 20 minutes of fuming.

3.3 Aging Effects

Fragility of gold black makes it vulnerable to structural changes with time. Hence, it is important to characterize and understand aging effects in gold black. To this end, we studied the sheet resistance and spectra over time for samples without and with cynoacralate fuming. We conducted our aging experiments for fuming times of 2 minutes and 20 minutes.

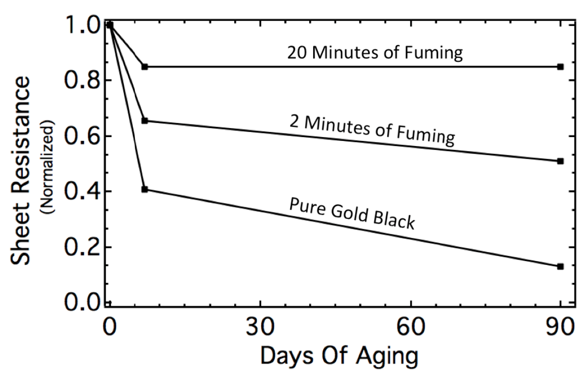


Figure 9. Aging effect on sheet resistance of gold black samples with different fuming times.

Advena showed that the resistivity of the gold black film decreases over time.[9] Fig. 9 presents our own observations of this effect for three samples with different fuming times. We find that after 7 days, the resistivity of our as-deposited gold black drops by a factor of 2.5 to 3. After 90 days, the resistivity has decreased by nearly a factor of 10. Resistivity becomes increasingly stable against aging the more fuming it receives. The 2 minutes fuming sample's resistivity decreases by only a factor of 2 in 3 months. However, the samples with 20 minutes of fuming dropped only 15% in 7 days and showed no further decrease for longer times.

Absorptance (1-R-T) for high quality films is observed to be spectrally flat in the range 500 to 4000 cm^{-1}. Thus, we may take the average absorptance over this range to study small aging effects. Fig. 10 presents these data as a function of time from 0 to 60 days for three different fuming conditions. All samples showed stable absorptance within experimental uncertainty.

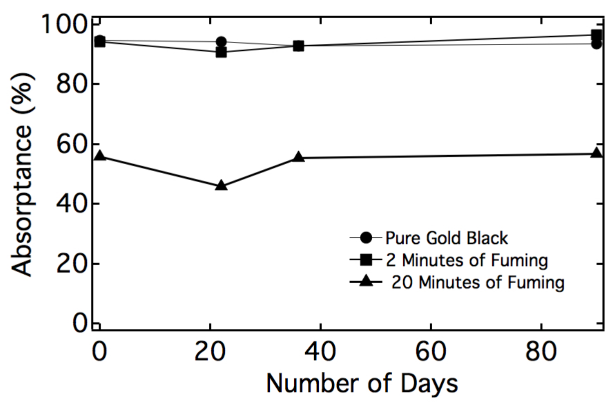


Fig 10. Spectrally averaged absorptance as a function of time for three different fuming conditions

CONCLUSIONS

We presented results of patterned gold black depositions with ~100 micron length scales using stencil lithography. Ethyl cyanoacrylate infusions with short fuming times (2 minutes) adequately improve mechanical stability without compressing the film or reducing its absorptivity much. Such fuming also decreases conductivity rise with aging.

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