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# Patterning of oxide-hardened gold black by photolithography and metal lift-off

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## HIGHLIGHTS

- We report the patterning of oxide-hardened gold black with standard photolithography and metal lift-off.
- The minimum pattern length-scale achieved was less than 10 μm after lift-off.
- Average ~90% absorption in 3–5 μm wavelength window is observed on the patterns.
- For IR array detectors, we provide a method to selectively coat the active regions of individual pixels.
- This method will help improve the sensitivity of current generation micro-bolometers.

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## ABSTRACT

A method to pattern infrared-absorbing gold black by conventional photolithography and lift-off is described. A photo-resist pattern is developed on a substrate by standard photolithography. Gold black is deposited over the whole by thermal evaporation in an inert gas at ~1 Torr. $SiO_2$ is then deposited as a protection layer by electron beam evaporation. Lift-off proceeds by dissolving the photoresist in acetone. The resulting sub-millimeter size gold black patterns that remain on the substrate retain high infrared absorption out to ~5 μm wavelength and exhibit good mechanical stability. This technique allows selective application of gold black coatings to the pixels of thermal infrared imaging array detectors.

## 1. Introduction

In thermal IR sensors (e.g. bolometers), absorptive coatings convert IR incident power into heat. Many different absorber materials have been investigated, including thin metals, SiN films [1], and metamaterials [2]. Gold black is an absorber that has been used for many decades for IR bolometers [3], particularly for dedicated single-use applications such as space missions. This material achieves nearly unity absorption from visible to far infrared [4–7].

Gold black is a nano-crystalline deposit of gold with extremely low density, low heat capacity, and a refractive index close to unity [4]. Broader application to commercial array detectors is hampered by its extreme fragility, which also makes it difficult to pattern. In array detectors, only the sensing element should be coated to avoid thermal and electrical bridging between pixels. Laser ablation has been used in the past to remove coatings deposited between the pixels, but this slow process is unsuited to mass production [8].

Stencil lithography has shown some success at patterning gold black, but stencil mask alignment is tedious, the masks must be cleaned between use, and the edges of the resulting patterns are blurry [9]. The patterns we previously reported [9] were hardened with cyanoacrylate using a fuming apparatus, but the heavy polymer chains collapse the gold black film. The resulting loss of porosity and increase in the refractive index caused an unwanted increase in reflection at the top surface. The smallest feature size achieved by us was ~80 μm. The Geostationary Earth Radiation

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Budget (GERB) instruments launched by the European Space Agency (ESA) achieved patterned stencil deposition on 50 × 50 $\mu m^2$ micro-bolometer pixels, but this gold black was unprotected [10]. In contrast, the new approach presented here using evaporated $SiO_2$ over-coating provides hardening and stabilization together with the opportunity to achieve patterned depositions below 10 μm dimensions via standard lift-off.

In usual metal lift-off, a pattern is prepared by spinning photoresist, exposing this layer to UV through a shadow mask, and developing with solvents to open patterned windows down to the substrate. Then metal is deposited over the entire wafer, which is finally submerged in solvent to remove the remaining photoresist and the metal on top of it. The metal stuck to the substrate remains. Lift off can be performed only if the metal adheres strongly to the substrate and if the metal is not attacked by the solvent. None of these conditions is satisfied by usual gold black, which is immediately washed off in the final lift-off step from all areas of the substrate.

Patterning of gold black on infrared focal plane arrays by conventional lift-off was reported in [11]. However, the reported absorption spectrum was clearly stated to be of unpatterned gold black, and so evidently was the SEM image of gold black. No data characterizing the gold black properties after the lift-off procedure were presented. Our experience is that the porous structure necessary to maintain high absorption cannot withstand immersion or saturation in liquid chemicals of any kind for any amount of time, and there remains no clear published evidence to suggest otherwise.

This paper describes the preparation of mechanically-robust, sub-millimeter scale, gold black patterns having nearly 100% absorption out to mid-infrared wavelengths. The approach is by standard photolithography and metal lift-off, which is made possible by mechanically stabilizing the gold black with an evaporated oxide coating.

## 2. Experimental details

Fig. 1 presents a schematic of the deposition process. Negative photoresist NR1500 PY was spin-coated to thickness 1 μm on silicon substrate. A mask pattern was transferred to the resist using an OAI 200 contact mask aligner. RD6 developer was used to remove the unexposed parts, leaving behind bare silicon substrate, which was further cleaned by an oxygen plasma de-scum.

Gold black was deposited following the method of Harris [4–7]. The sample was placed on a temperature-controlled heat sink in a thermal evaporation chamber. The heat sink temperature was maintained at −13 °C using a Peltier cooler. The chamber was first evacuated to $10^{-5}$ Torr. Then it was brought to 400 mTorr by continuous controlled flow of nitrogen. Gold wire in the amount 85 mg and of 99.9% purity was placed in a molybdenum boat. The current applied to the boat was 65 A for all depositions. The inert gas causes gold atoms to collide and bind with each other to form web-like structures before landing on the sample.

The instability and fragility of gold black make it incompatible with PECVD oxide deposition due to the high temperatures involved. Instead, we deposited $SiO_2$ on the gold black sample by electron beam evaporation. The source was fused silica pellets of 99.99% purity placed in a 7 cc carbon crucible. The chamber was evacuated to $2 \times 10^{-6}$ mTorr and a wide, high-frequency e-beam sweep pattern maintained a deposition rate of 2–3 nm/s. The thickness of the film and rate of deposition were continuously measured by a quartz crystal monitor (Inficon XTC). The sample was placed normal to the target boat at the optimized distance of 30 cm to keep the temperature below 60 °C. A thermocouple monitored the temperature of the substrate holder during the process. The $SiO_2$ film undergoes compressive stress after venting the chamber. The stress reverses to tensile direction logarithmically with time until it reaches a stable state [12]. Therefore, the substrate was kept at atmospheric pressure for more than 10 h to allow it to reach mechanical equilibrium before absorption measurements.

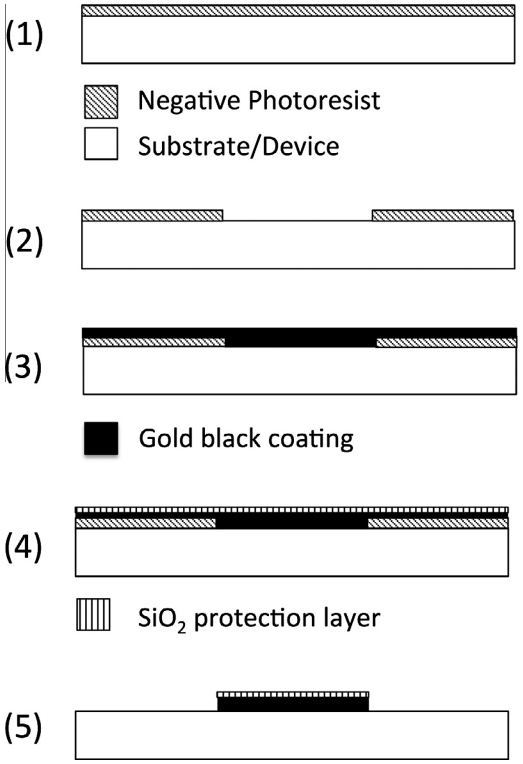

**Fig. 1.** Schematic of processing sequence patterned gold black/$SiO_2$ composites.

Infrared absorption spectroscopy was performed on gold black with and without $SiO_2$ over-coating using a Vertex 80 FTIR equipped with Hyperion 1000 Microscope. The upper aperture in the microscope defines the illuminated sample area, which was chosen to be 3 $mm^2$. For vis–NIR measurements a $CaF_2$ microscope objective (2.4×, NA 0.07), $CaF_2$ beam splitter, tungsten source, and Si diode and mercury–cadmium–telluride (MCT) detectors were used. For the mid-IR range (4000–650 $cm^{-1}$ range), we used a ZnSe microscope objective (2.4×, NA 0.07), Globar source, KBr beam splitter, and 77 K MCT detector. Adequate signal-to-noise ratio was attained by co-adding 128 FTIR scans at 4 $cm^{-1}$ spectral resolution.

For IR imaging micro-spectroscopy with high spatial resolution, we used the Infrared Environmental Imaging (IRENI) beam line at the Synchrotron Radiation Center, University of Wisconsin, Madison [13]. A Brucker Vertex FT-IR spectrometer with Hyperion 3000 IR microscope used multiple combined beams of the synchrotron source to provide up to 1000 times higher brightness than available from a globar. A Focal Plane Array (FPA) detector allowed spectral imaging with better than 1 μm spatial sampling. The spectral resolution was 4 $cm^{-1}$ and the spectral range was 900–3700 $cm^{-1}$. For reflectance measurements, the microscope was equipped with 20×, 0.65 numerical aperture (NA) Schwarzschild objective. IRidys (Infrared Imaging & Data Analysis) program, which runs on the commercial software package IGOR PRO, was used to extract spectra from different pixels [14].

The fraction of light absorbed by the gold black coating is the absorptance $A = (1–T–R)$, where $T$ is the transmittance and $R$ the reflectance. For Vis–NIR, the sample was deposited on an optically thick gold surface, giving $T = 0$. For mid-IR measurements, double-sided polished (DSP) silicon was used as the substrate. Bare DSP Si