Gold-black coatings for freestanding pyroelectric detectors*

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Abstract
We describe the process of depositing gold-black on thin, freestanding pyroelectric detector substrates and compare this with previous work documented in the literature. We have evaluated gold-black coatings on thin, freestanding pyroelectric detector substrates by means of scanning electron microscope, Fourier transform infrared spectrophotometer reflectance, and spectral responsivity measurements. Spectrophotometric measurements indicate that reflectance at normal incidence varies by less than 1% at wavelengths shorter than 2.5 μm and by less than 10% at 10 μm. These results are correlated with the spectral responsivity of the detector and demonstrate that radiation not reflected by the gold-black is absorbed by the detector element. We have evaluated gold-black coatings as a function of position at two wavelengths and found variations of less than 1% at 1.25 μm and less than 5% at 10.3 μm, which demonstrates that spatial uniformity can be coating dependent. Gold-black coatings exposed to a 193 nm wavelength excimer laser were evaluated by visual inspection for damage and determined to have a damage threshold of approximately 38 mJ cm^{-2}.

Keywords: gold-black, lithium tantalate, pyroelectric detector, reflectance, spatial uniformity, spectral responsivity

1. Introduction

Pyroelectric detectors exhibit a broad and uniform spectral (spectrally flat) response that is practically limited only by the characteristics of the absorbing material covering the detector's receiving area. We describe the gold-black deposition process using experimental results that demonstrate the behaviour of gold-black as a detector coating. Detectors for optical energy measurements (that is, for use with pulsed lasers) are not the emphasis of this paper; nonetheless, relevant coating experiments are important enough to be included.

In principle the wavelength range of the spectral response of a pyroelectric detector depends on converting the optical energy into heat. A pyroelectric material such as LiTaO$_3$, however, is semitransparent to visible and infrared (IR) radiation [1]; therefore, we rely on one or more coating layers to enhance the absorption. The coating layers include an electrode, which is essential to conduct surface charge generated by the detector, and usually an additional opaque layer to enhance the optical absorption and convert the optical energy to heat. The electrode material is usually a specular metal such as Ni, Cr, Au or a combination thereof. However, the specular metal may introduce undesirable optical properties such as high reflectance or polarization dependence. This shortcoming may be overcome by an additional coating layer such as carbon-based paints or gold-black. Conversely, rather than high absorption efficiency, low absorption and high damage resistance may be desirable for building detectors
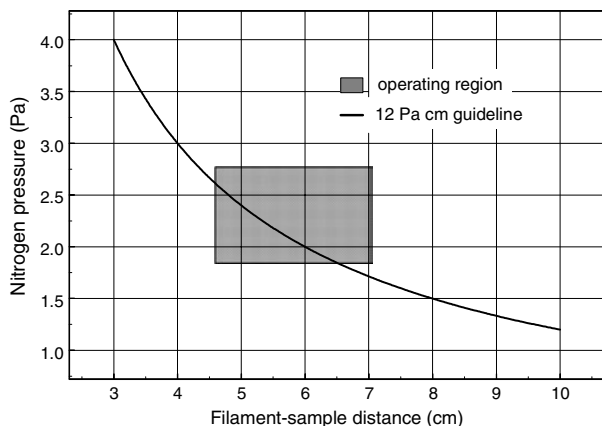
Figure 1. Operating range of the deposition process.

suitable for laser-energy measurements or other high power and energy measurement applications.

There are alternatives to specular metals and gold-black for pyroelectric detector coatings. Proprietary paints such as 3M black and Catalac black are useful and appropriate for some applications requiring a very wide spectral response [2][5]. Other paints and oxide coatings have been developed for damage-resistant coatings for UV measurement applications[6]. Other metal blacks such as silver-black have been used to enhance the IR sensitivity of pyroelectric detectors. Silver-black is comparable to gold-black; the spectral response of pyroelectric detectors coated with silver-black exhibits a gradual decrease of approximately 2% as the wavelength decreases from 2.5 to 1 μm. Platinum-black is deposited using a wet (electrochemical) process and is being used as a coating for pyroelectric detectors by GEC Marconi[7].

2. Gold-black coatings for wavelength-independent responsivity

Pyroelectric detectors are available commercially with a variety of coatings to enhance the absorption and to reduce the variation of absorption as a function of wavelength. As with any engineering challenge there are trade-offs for choosing the best coating for a particular application. Gold-black has been used for a variety of sensors, not just pyroelectric detectors, because it potentially has very low reflectance (high absorption, negligible transmittance) over a range of wavelengths from less than 1 μm to more than 50 μm [3]. Even though metal blacks were first demonstrated in the 1930s [4], and the process has remained relatively unchanged since the 1950s [5], gold-black-coated detectors are relatively uncommon. The work we describe is unique because depositing gold-black on a thin, freestanding, dielectric material presents challenges beyond the basic process. The ability to conduct heat away from the crystal is crucial during

the deposition, but a uniform and substantial heat sink (without contact resistance) is difficult to attach without scratching or breaking the detector plate.

In addition to providing broad and uniform absorptance, gold-black has relatively low thermal mass (compared to black paints, for example) and high thermal conductivity, and can be deposited to be spatially uniform [5]. On the other hand, gold-black is fragile and may be crushed or scratched easily and removed with a breath of air. It is also easily destroyed when wetted and may be difficult to produce consistently. As a result gold-black is typically seen in limited production scientific applications such as space-based sensors, and with only a few exceptions is produced commercially[8].

Successful gold-black deposition depends on a few important variables. The process by which the gold-black is deposited is similar to that documented by others, most notably Blevin and Brown in 1966 [6], but not substantially different from that documented by Harris *et al* in 1948 [5]. Our process depends on the product of the pressure of the nitrogen environment in which the gold is evaporated, and the distance from the filament source and the target (the nickel-coated LiTaO$_3$ or LiNbO$_3$ plate). We follow a guideline adapted from our own work and the results of other authors [5, 6], which we state as 10 Torr cm (12 Pa m), which means that the product of the pressure of nitrogen during deposition (measured in torr) and the distance between the sample and the source (measured in centimetres) is 10. This rule of thumb in SI units is $P = \psi/l$, where l is the distance between the filament and the sample, P is the deposition pressure and $\psi \cong 12$ Pa m. This guideline is plotted for a range of distances and nitrogen pressures in figure 1. The most recent publications by Becker *et al* [7] indicate that their preferred distance is 7 cm, and ever-higher pressures result in lower reflectance in the far IR. The trade-off for higher pressure is slower deposition, which increases the period during which the sample is exposed to the hot filament, which in turn tempers the black structure. The deposition rate (gold evaporation rate) is 3 mg s^{-1}, which is also comparable with the rate given by previous authors [5].

3. Experiments with coatings

An indication of the quality of gold-black is the appearance of the percolated structure, which we can correlate with the experimentally measured reflectance [7]. In order to scale the properties of the percolated structure, it is necessary to view the gold-black using a scanning electron microscope (SEM). The optical nature of the gold-black is such that it is impossible to perceive depth or dimensions of the structure by use of an optical microscope. However, because the gold remains electrically conducting in the form of a percolated metal, useful images are easily obtained with the SEM. For the SEM images, 1 cm samples consisting of Ni-coated 60 μm thick LiTaO$_3$ pyroelectric detectors were prepared. Viewing the gold-black with the SEM is in itself not novel. Our contribution is the introduction of additional steps that allow us to correlate images from coated detectors that are evaluated for reflectance and responsivity, rather than simply reflectance of substrate samples.
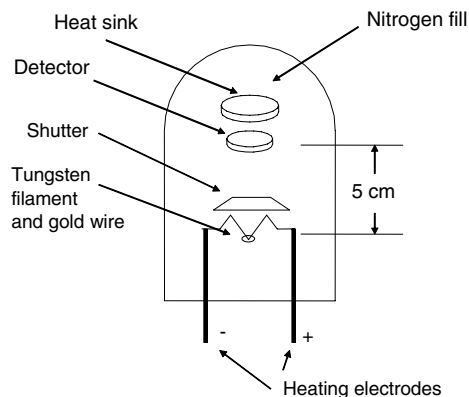
Figure 2. Schematic representation of the gold-black deposition system.

In principle the reflectance measurement is a valid prediction of the relative spectral responsivity if we assume that all of the optical energy absorbed by the gold-black is converted to heat and is absorbed entirely by the detector material. Past results are given in the form of reflectance as a function of wavelength acquired from a gold-black sample deposited on a relatively massive substrate [3]. In the present case, the reflectance measurements were performed by Fourier transform infrared (FTIR) spectrophotometry [8] on detector samples that were prepared using process parameters identical to those for samples prepared for the SEM images.

We are also interested in the detector's responsivity as a function of wavelength and position. Therefore, in addition to SEM images and reflectance measurements, we measured the detector's spectral and spatial responsivity. These measurements were done using a broadband lamp and a monochromator as a selectable-wavelength radiation source over a range of wavelengths from 1 to 25 μm. In the case of the responsivity measurements, the detector was evaluated by comparison with another thermal detector traceable to national (UK) standards [9].

4. Gold-black deposition apparatus and procedure

The essential elements of the gold-black deposition apparatus include a vacuum chamber, a thermal evaporation source and a heat sink on which the deposition sample is attached. A schematic representation of the apparatus is shown in figure 2. The detector or deposition sample is attached to the heat sink in such a way that there is minimal thermal resistance between the sample and the heat sink, but without exerting enough mechanical pressure to damage the sample.

The procedure for the deposition is as follows. The sample to be coated is attached to the heat sink by means of finger-like spring retainers. A 1.5 mm diameter, 30 mm long piece of gold wire is wrapped onto a tungsten filament. The vacuum system containing the filament and sample is closed and evacuated to a pressure of 5×10^{-6} mbar[9]. Then, nitrogen gas (purity $\sim$99.9%) is continuously leaked into the vacuum chamber. In order to achieve the desired nitrogen pressure a combination of adjustments are made: partially closing a gate valve situated

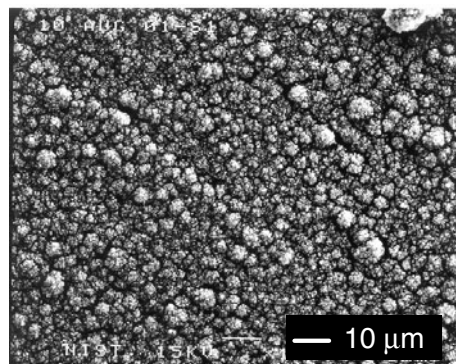[9] The units of bar are non-SI units currently accepted for use with the International System [10].

Figure 3. SEM micrograph of gold-black structure deposited at low nitrogen pressure (1.3 mbar).
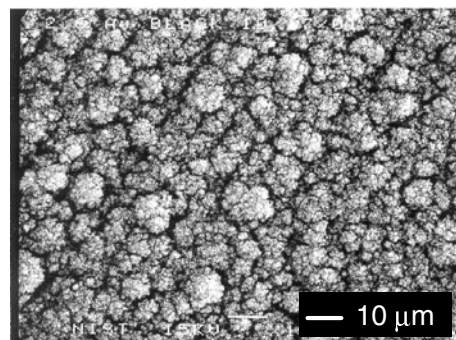

Figure 4. SEM micrograph of gold-black structure deposited at higher nitrogen pressure (2.6 mbar).

between the vacuum pump and the vacuum chamber; adjusting the nitrogen flow rate; and slowing the vacuum-pump speed. The gold wire is then melted to form a molten ball on the tungsten filament, and a manual shutter between the melted gold and the detector is opened. The gold ball evaporates as it is electrically heated at a constant current of 23 A (8 V source). The evaporation continues for approximately 90 s or until the gold ball disappears and the filament appears only wetted. From direct thermometry, we found that the sample temperature reaches approximately 80 °C during the 90 s deposition.

5. Spectral uniformity of gold-black

We have evaluated the spectral properties of the gold-black coating on an LiTaO$_3$ pyroelectric by SEM micrographs, reflectance measurements ranging from 1 to 20 μm, and spectral responsivity measurements from 2 to 10 μm.

Two SEM micrographs are shown in figures 3 and 4. The first image is from a coating prepared at a nitrogen pressure of 1.3 mbar, with a sample-filament spacing of 5 cm. The gold-black structure is globular with varying feature sizes up to approximately 10 μm in width and gaps a fraction of the globule size. From spectral responsivity measurements of a detector prepared at a nitrogen pressure of 1.3 mbar, we found that the relative spectral responsivity decreased monotonically from 1 to 0.7 over the wavelength range from 1 to 10 μm.

The second image was acquired from a coating prepared at a nitrogen pressure of 2.6 mbar, with the distance between the
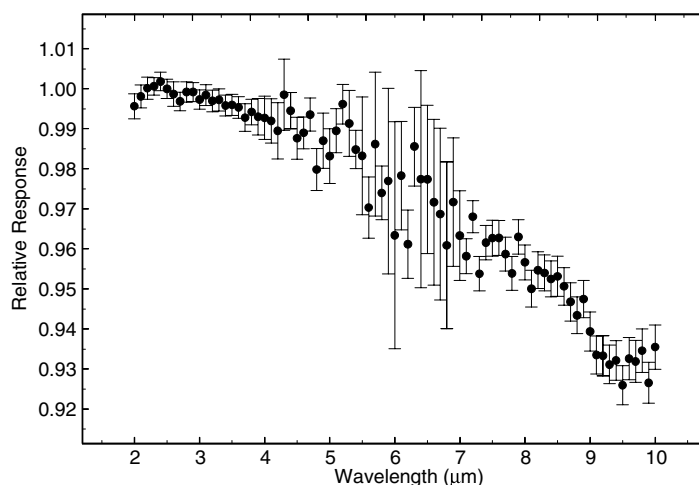
Figure 5. Relative spectral response of a gold-black-coated LiTaO$_3$ pyroelectric detector prepared at 2.6 mbar. The confidence interval for the error bars is approximately 68%.

sample and filament (5 cm) the same as for the 1.3 mbar sample. Again the gold-black structure is globular, but with larger feature sizes than before. In this instance 10 μm wide globules are prevalent. From spectral responsivity measurements of a detector prepared at a nitrogen pressure of 2.6 mbar, we found that the relative spectral responsivity decreased monotonically from 1 to 0.9 over the wavelength range from 1 to 10 μm. The spectral responsivity measurement results are shown in figure 5.

Reflectance measurements of gold-black samples prepared at 2.6 mbar, shown in figures 6 and 7, corroborate the findings in figure 5. The relative expanded uncertainty of the IR reflectance measurements ranges from 0.2% near 0.01 reflectance level to 3% at the 0.5 reflectance level. The level of confidence for the relative expanded uncertainty is approximately 95%. These results imply that the optical energy absorbed by the gold-black is converted to thermal energy that is absorbed by the detector. Therefore, in the absence of spectral responsivity measurements the reflectance measurements can be used to determine the expected relative spectral responsivity. The absolute responsivity must still be confirmed by comparison with an optical detector having known absolute responsivity. The advantage of knowing this result is that, if necessary, the absolute responsivity may be inferred over a range of wavelengths by measuring the reflectance to provide the relative responsivity, and then also measuring the absolute responsivity at a few wavelengths with laser sources and without relying on a broadband source and monochromator.

According to Becker *et al* [7] the optimal distance between the sample and the thermal evaporation source is 7 cm, and higher nitrogen pressure results in coatings having lower reflectance. On the other hand, Blevin and Brown [6] indicate that coatings deposited at higher pressure have high values of thermal resistance. In general we prefer lower reflectance if the spectral responsivity measurements indicate that the gold-black reflectance and the detector absorption are complementary. In other words, we can accept the possibility of higher thermal resistance if the reflectance measurements and spectral responsivity measurements indicate that radiation

that is not reflected by the gold-black is absorbed by the detector.

6. Spatial uniformity of gold-black

We undertook measurements of spatial uniformity of a pyroelectric detector to demonstrate that spatial uniformity variations can be coating dependent. Other than SEM-based interrogations, which are qualitative, there are limited means to investigate wavelength dependence of gold-black as a function of position. Several groups have made indirect measurements of the thickness of gold-black coatings [3], but direct measurements are difficult because the coating is easily damaged by applied force, and optical methods are limited by the profound optical absorption of the coating. Spatial uniformity measurements also do not provide a means of directly measuring thickness, but provide another indication in the variability and wavelength-dependent behaviour of the coating, which is possibly related to variation in coating thickness.

A gold-black-coated pyroelectric detector was prepared on a 1 cm diameter, 60 μm thick, z-cut LiTaO$_3$ pyroelectric detector. The spatial uniformity was measured at two wavelengths, 1.25 and 10.3 μm, as described previously. The data from this measurement are presented in two ways. First, contour plots of the data are shown followed by a cross section of each contour plot to emphasize the difference between spatial uniformity at 1.25 μm and that at 10.3 μm.

Figure 8 is map of the detector response at 10.3 μm with 1% contour intervals. Figure 9 is a map of the detector response at 1.25 μm at 1% contour intervals. The data for the first instance appear to have variations as large as a few per cent and a sloping variation across the detector. The variation in the second instance is smaller, and any variability across the detector is less than the 1% contour. The two measurement results were directly compared by plotting a cross section of each on a two-dimensional graph as shown in figure 10.

The spatial uniformity variation of nearly 5% measured at 10.3 μm could be attributed to variation in the percolated structure of the gold-black, in the thickness, or both. Lacking
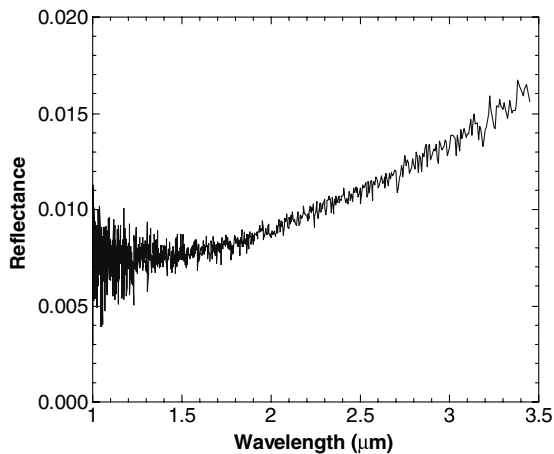
Figure 6. Reflectance measurements of a 2.6 mbar gold-black-coated LiTaO$_3$ pyroelectric detector evaluated over the wavelength range from 1 to 3.5 μm.
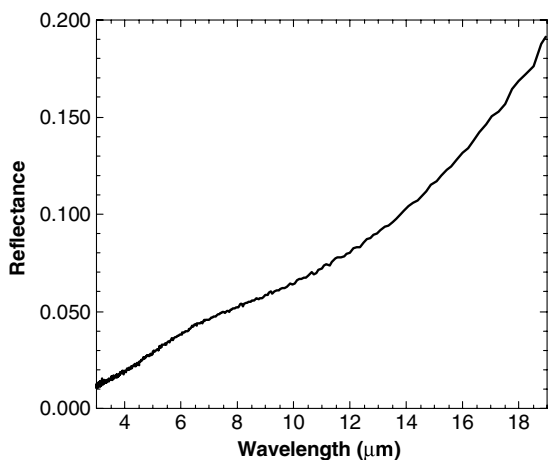

Figure 7. Reflectance measurements of a 2.6 mbar gold-black-coated LiTaO$_3$ pyroelectric detector evaluated over the wavelength range from 3 to 20 μm.

quantifiable evidence in either case, we could attribute the variation to at least two aspects of the deposition process:

(1) the distance from the evaporation filament and the detector surface;
(2) uniformity of thermal contact between the back of the detector and the heat sink on which it is mounted.

In the first case the gold diffuses from the evaporation source radially, while it intersects the planar detector surface. Considering the guideline that the gold-black reflectance depends on the nitrogen pressure and filament distance, we expect the reflectance to change over the area of the detector. The detector surface is oriented to be perpendicular to an imaginary line between the centre of the evaporation source and the centre of the detector plate. Therefore the perimeter of the detector plate is farther from the filament than is the centre of the detector, as depicted in figure 11. If the radial-diffusion dependence were significant, we would expect the uniformity variation to be symmetric about the centre of the detector area. The gold-black would be denser in the centre of the detector area and gradually less dense near the perimeter. The
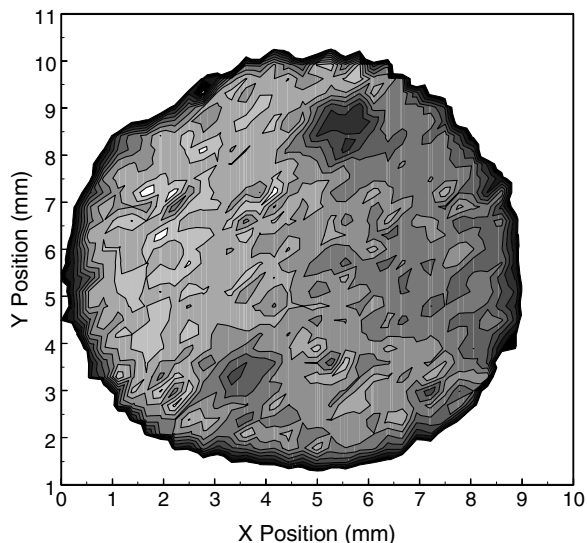
Figure 8. Contour plot of the detector response as a function of position acquired at 10.3 μm wavelength. The relative response values range from 0.95 to 1. The contour intervals represent changes in response of 1%. The relative uncertainty of the response is 0.5% with a confidence interval of approximately 68%.

Figure 9. Contour plot of the detector response as a function of position acquired at 1.25 μm wavelength. The relative response values range from 0.95 to 1. The contour intervals represent changes in response of 1%. The relative uncertainty of the response is 0.5% with a confidence interval of approximately 68%.
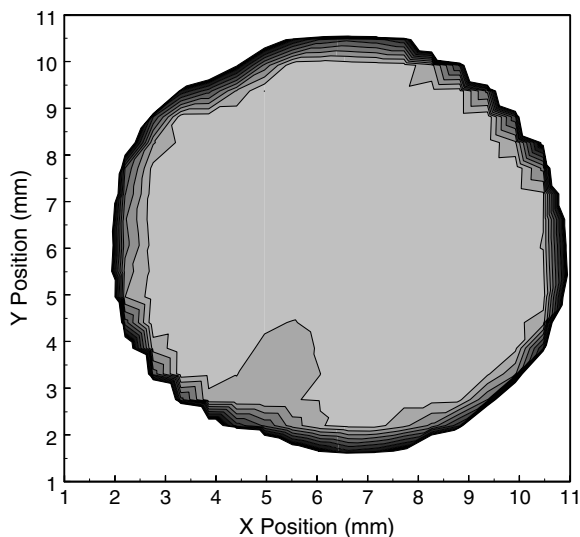
density change would manifest itself in the spatial uniformity measurements with a contour map that appeared convex and a cross-sectional plot in the form of a radial arc centred at the detector centre.

In the second case the percolated structure, on which the low reflectance properties are based, is temperature dependent. The limiting case is the observation that gold-black returns to its familiar yellow and specular appearance when heated. Aging studies by Advena *et al* [3] demonstrate increased reflectance as a result of changing the substrate temperature between 70 and 120 °C (the range in which the estimated substrate temperature lies). The detector crystal is mounted on a heat sink by means of flexible spring retainers. We
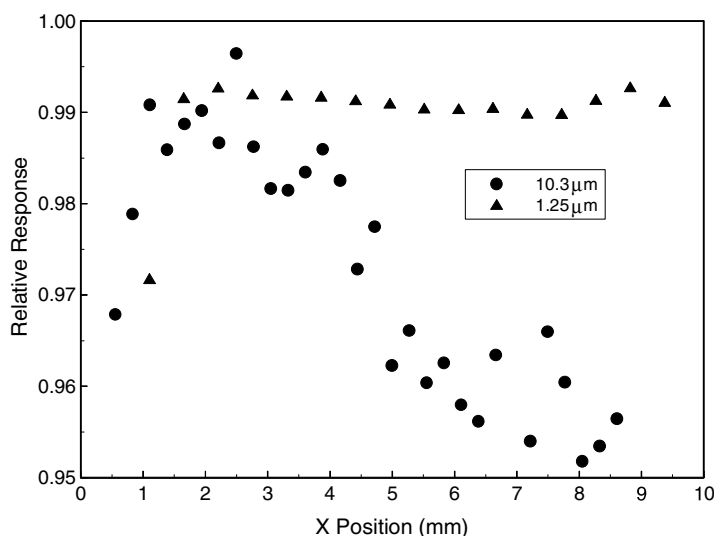
Figure 10. Comparison of a cross section of the detector spatial uniformity at 10.3 and 1.25 μm.
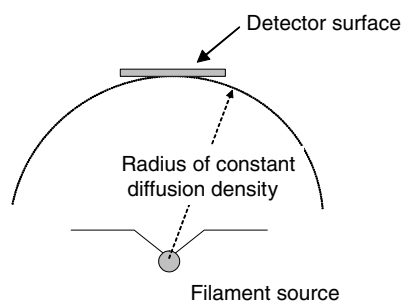

Figure 11. Schematic drawing of the relationship the planar detector surface and radial diffusion.

expect the distribution of force near the retainers to be greater because the crystal and the brass ring on which the crystal is mounted are not perfectly rigid. Where the force of contact is least, we expect the thermal contact to be less. Therefore the thermal contact is not uniform, the temperature of the substrate is not uniform, and the resulting gold-black reflectance is not uniform. Rather than analyse the distribution of force and the thermal contact, our future work will be directed at improved packaging and mounting of the detector crystal.

7. Damage experiments with nickel and gold-black

Experiments to determine the damage-resistance threshold of gold-black and specular Ni coatings were undertaken with a 193 nm wavelength excimer laser operating with a pulse width of approximately 15 ns and a repetition rate of 100 Hz. In these experiments the energy per pulse was monitored while the beam size on the sample was varied. The first samples tested were a single deposition of gold-black on top of 25 nm thick Ni electrodes on 250 μm thick LiNbO$_3$. The second samples tested were 25 nm thick Ni, also deposited on LiNbO$_3$.

As the gold-black was irradiated by the excimer laser, the appearance of the coating changed from black to brown. The colour change is the result of the collapse of the percolated structure of the gold-black, the limit of which is melting the gold until it appears nearly yellow and specular. The collapse and colour change were witnessed at a beam size of

approximately 2 mm $\times$ 4 mm at 3 mJ, resulting in an energy–density threshold of approximately 38 mJ cm^{-2}.

By the same process of varying the beam size while maintaining a constant pulse energy, we found that a 25 nm thick Ni coating (25 nm thick deposited on LiNbO$_3$) had a damage threshold approximately two times higher. In this case, damage appeared as the laser energy visibly ablated the coating.

The colour-change criterion for gold-black damage is qualitative and does not address the likelihood that there is damage to the gold-black at a slightly lower damage threshold. The colour change also implies that the damage is wavelength dependent, or in other words damage that appears as a change in reflectance at 10 μm may not manifest itself as a change in reflectance at 1 μm. A more rigorous evaluation would include the SEM investigations, reflectance and spectral responsivity measurements along with a laser-beam profile measurement and record of dose accumulation over time.

The uncertainty of these measurements is contingent largely on knowing the beam size, the beam profile and our somewhat informal definition of damage; therefore, we must assign a large uncertainty to the results. No long-term ageing studies were undertaken. Based on repeated visual inspection and measurement of the beam size by measurement of the damage area, we assign a type B uncertainty of 10% ($k = 1$) to the stated values [11]. If the beam profile has circular symmetry and is predominantly Gaussian, then the peak irradiance or fluence of the beam can be calculated from the energy of the beam divided by the cross-sectional area at the 1/e irradiance points (the points where the irradiance has dropped from a maximum to a value approximately 37% times the maximum). If the beam has irregular regions of high intensity or an asymmetrical irradiance profile, then the calculations are more difficult and must be handled on an individual basis.

The nickel damage is somewhat lower than other published values of the damage threshold for nickel-plated coatings [12]. For nickel-on-copper and nickel-on-sapphire for 100 Hz pulse repetition rates, the damage threshold is 150 mJ cm^{-2}. The difference between our measured values for

nickel-on-LiTaO$_3$ and those for nickel-on-copper is most likely due to the adhesion of Ni deposited by thermal evaporation being less than adhesion of Ni deposited by plating.

8. Summary and conclusions

The gold-black deposition process has changed very little over the last 50–80 years, but consistent production of low-reflectance gold-black coatings is uncommon. We have evaluated gold-black coatings on thin, freestanding pyroelectric detector substrates by means of SEM, FTIR spectrophotometer reflectance and spectral responsivity measurements. Gold-black-coated pyroelectric detectors may be fabricated having reflectance variations at normal incidence (and hence spectral responsivity) decreasing to less than 1% at 2.5 μm, 10% at 10 μm, and 20% at 20 μm. Such low reflectance on thin, freestanding pyroelectric detectors is apparently not documented in the literature. We have evaluated the spatial uniformity of gold-black coatings as a function of wavelength and found variations of less than 1% at 1.25 μm and less than 5% at 10.3 μm. Process variables such as filament distance and substrate temperature point to strategies for improvement (smaller variations). Gold-black coatings exposed to a 193 nm wavelength excimer laser were evaluated by visual inspection for damage and determined to have a damage threshold of approximately 38 mJ cm^{-2}. Future work will be directed toward experiments with higher nitrogen pressure and thermal shielding between the evaporation source and the detector crystal.

Acknowledgment

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