Manufacture and Characterization of Gold-Black and Prediction and Measurement of its Directional Spectral Absorptivity

Nazia Binte Munir

Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

In

Mechanical Engineering

James R. Mahan. Chair
Kory J. Priestley. Co-Chair
Brian Vick.
Vinh Nguyen.
Mehdi Ahmadian.

December 14, 2020
Blacksburg, Virginia

Keywords: Gold-Black, Spectral Directional Absorptivity, Bidirectional Reflectance Distribution Function
Gold-black has emerged as a popular absorptive coating for thermal radiation detectors in aerospace applications. The performance and accuracy of thermal radiation detectors largely depends on the surface optical properties of the absorptive coating. If the absorptivity of the layer is directional or wavelength dependent, then so will be the detector gain itself. This motivates our interest in the manufacture, physical characterization, and study of the wavelength and polarization sensitivity of the directional spectral absorptivity of gold-black. A first-principle model based on lossy antenna theory is presented to predict the polarization dependent directional spectral absorptivity of gold-black in the visible and near infrared. Results for normal spectral absorptivity are in good agreement with measurements reported in the literature. However, suitable experimental data were not available to validate the theory for directional spectral absorptivity. Therefore, an experimental campaign to fabricate and measure the directional spectral behavior of gold-black had to be undertaken to validate the first-principle model. New in-plane bidirectional reflectance distribution function (BRDF) measurements for two thicknesses (~4 μm and ~8 μm) of gold-black laid down on a gold mirror substrate are reported in the visible (532 nm) and near-infrared (800 and 850 nm) for p- and s-polarizations. The investigation is then extended to a three-layer sample, which is shown to exhibit off-specular reflectivity. Described are processes for laying down gold-black coatings and for measuring their in-plane BRDF as a function of thickness, wavelength, and polarization state. A novel method
for retrieving the directional absorptivity from in-plane BRDF measurements is presented. The influence of polarization on directional absorptivity is shown to follow our earlier theory except at large incident zenith angles, where an unanticipated mirage effect is observed.
Manufacturing and Characterization of Gold-Black and Prediction and Measurement of its Directional Spectral Absorptivity

Nazia Binte Munir

GENERAL AUDIENCE ABSTRACT

Instruments called thermal radiation detectors play an important role in monitoring the global climate from space. Gold-black is often used as an absorptive coating to enhance the performance of these instruments. Users need to know how gold-black coatings influence instrument performance. In general, coating properties depend on the wavelength and direction of incident radiation, as well as on an optical phenomenon called polarization. This dissertation investigates the relationship between the creation of gold-black coatings and their performance. A physical model is postulated for predicting the optical behavior of gold-black in the visible and near infrared. The model produces results that are in good agreement with measurements reported in the literature. However, suitable directional measurements were not available to validate the theory. Therefore, an experimental campaign was mounted to fabricate gold-black coatings and measure their optical behavior in order to validate the mathematical model. We observed the optical behavior of several of our gold-black samples of various thickness and over a range of wavelengths. We also studied a three-layer sample which was found to exhibit an unexpected behavior called off-specular reflectivity. Described are processes for creating gold-black coatings and for measuring and explaining their optical performance. During the course of this investigation an unanticipated mirage effect was observed for the first time.
Dedication

To my parents, who are behind each and every success of my life

Md. Munir and Shuriya Zaman

“Dad,
I am sorry I could not make it in time. I hope you know your daughter fulfilled your dream.”
Lament

GOLD-BLACK is an enigma. It guards many secrets. This dissertation is my humble attempt to steal some of them.

The Professor challenged me: “Daughter, if you cannot model the behavior of gold-black, you do not understand it.”

So I set out to model the optical behavior of gold-black.

Having succeeded, the Professor then mocked me in my naïveté: “But, Daughter, how do you know your model is correct?”

So I set out to measure the optical behavior of gold-black.

But then I discovered that gold-black cannot be purchased.

So I set out to manufacture my own samples.

But then I discovered that the formula for gold-black is one of its best-kept secrets.

So I despaired… .
Acknowledgements

First of all, I want to thank the Almighty for showering blessings on me and being my strength throughout my PhD journey.

Words cannot express my heartfelt gratitude to my supervisor and committee chair Dr. J. R. Mahan for all his support and guidance throughout my four-year PhD journey. Without his wisdom and guidance, it would not have been possible for me to finish my research. Looking back, I can see myself as a naïve girl in Radiation Heat Transfer who started her research without sufficient knowledge in that field but who slowly earned her confidence in the field by the prudent guidance of Dr. Mahan. I want to thank him for being patient with me and keeping trust in me.

I also want to convey my gratitude to my co-chair, Dr. Kory J. Priestley, of NASA’s Langley Research Center for the role he played in NASA’s continuing support of the Thermal Radiation Group at Virginia Tech. Without his support this effort would not have been possible.

I would like to convey special thanks to Dr. Vinh Nguyen. Without his support and guidance, it would not have been possible for me to perform the optical testing of my sample within a reasonable period of time. I also want to convey my gratitude to the all students of the Optics Lab in the Physics Department for extending their helping hands during my association with their lab.

Furthermore, I want to convey my gratitude to Dr. Mehdi Ahmadian, my committee member, for his tremendous support in my early days at Virginia Tech, and to Dr. Brian Vick for serving on my advisory committee and providing valuable guidance and support.
I would like to thank the management and staff of the Virginia Tech Clean Room facility for helping me by sharing their technical knowledge. I want to express my gratitude to the Virginia Tech Cook Counseling Center for providing valuable mental health support to graduate students when needed.

Finally, I want to thank all my lab mates for their support throughout my research journey. I would love to express my gratitude to my friends in Blacksburg for their tremendous emotional support throughout my journey.

Last but not the least, I want to express my heartfelt gratefulness to my family for their unconditional support throughout my PhD journey. Without their love and support it would not be possible.
# Table of Contents

Chapter 1: Introduction ................................................................. 1
  1.1 Motivation ................................................................................. 1
  1.2 The Role of Gold-Black in Bolometer Performance ....................... 5
  1.3 Objectives .................................................................................. 7
  1.4 Organization .............................................................................. 9

Chapter 2: History of Gold-Black ......................................................... 10

Chapter 3: Manufacture of Gold-Black .................................................. 19
  3.1 Design of the Gold-Black Manufacturing Process ............................ 20
  3.2 Evolution of Our Gold-Black Manufacturing Cell .......................... 22
    3.2.1 Preliminary Evolutionary Stage .............................................. 23
    3.2.2 Final Evolutionary Stage ...................................................... 32
  3.3 Gold-Black Manufacturing Process .............................................. 37
    3.3.1 Gold-Black Sample Preparation ........................................... 37
    3.3.2 Gold-Black Deposition on Various Substrates ......................... 39
    3.3.3 Substrate Preparation ........................................................ 41
  3.4 Chapter Summary ....................................................................... 42

Chapter 4: First-Principle Model for the Directional Spectral Absorptivity of Gold-Black in the Near Infrared .................................................. 43
  4.1 Manufacture and Micro-Morphology of Gold-Black Coatings .......... 43
  4.2 Model for the Absorption of EM Radiation by a Single Gold-Black Filament ................................................................. 48
  4.3 Spectral Absorptivity of a Single Gold-Black Filament ........................ 55
  4.4 Conversion of Single-Filament Spectral Absorptivity into Gold-Black Layer Directional Spectral Absorptivity .................................................. 64
  4.5 Results and Discussion ................................................................ 74
  4.6 Conclusions and Recommendations .............................................. 78

Chapter 5: Gold-Black Directional Absorptivity in the Visible and Near Infrared .................................................. 80
  5.1 Follow-Up of the First-Principle Theory Presented in Chapter 4 .......... 80
  5.1 Measurement of Gold-Black BRDF .............................................. 82
    5.1.1 Definition of the bidirectional reflectance distribution function (BRDF) .................................................. 82
    5.1.2 Apparatus for Measuring In-Plane BRDF ................................ 84
    5.1.3 Procedure for Measuring and Computing the BRDF ............... 88
  5.2 Results and Interpretation ........................................................... 90
    5.2.1 Results ................................................................................. 90
    5.2.2 Interpretation of Results ...................................................... 101
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3 Directional Absorptivity of Gold-Black</td>
<td>107</td>
</tr>
<tr>
<td>5.4 Conclusions and Recommendations</td>
<td>119</td>
</tr>
<tr>
<td>Chapter 6: Off-Specular Reflectance in Multilayer Gold-Black Coatings</td>
<td>121</td>
</tr>
<tr>
<td>6.1 Motivation</td>
<td>121</td>
</tr>
<tr>
<td>6.2 Manufacture of Multilayer Gold-Black Coatings</td>
<td>122</td>
</tr>
<tr>
<td>6.3 Results and Interpretation</td>
<td>124</td>
</tr>
<tr>
<td>6.3.1 Results</td>
<td>124</td>
</tr>
<tr>
<td>6.3.2 A Theory for Off-Specular Peaking</td>
<td>130</td>
</tr>
<tr>
<td>Chapter 7: Summary, Conclusions, and Recommendations</td>
<td>135</td>
</tr>
<tr>
<td>7.1 Summary</td>
<td>136</td>
</tr>
<tr>
<td>7.2 Conclusions</td>
<td>137</td>
</tr>
<tr>
<td>7.3 Recommendation</td>
<td>139</td>
</tr>
<tr>
<td>Work Cited</td>
<td>140</td>
</tr>
<tr>
<td>Appendix A</td>
<td>147</td>
</tr>
<tr>
<td>Appendix B</td>
<td>150</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1. 1 The four components of the Earth’s energy balance [1]. .......................... 3
Figure 1. 2 Absorption layer on (a) a generic thermistor bolometer [11] and (b) the thermopile bolometer proposed for Demeter [15]. .......................................................... 6

Figure 3. 1 The original MTI GSL-1700 X-SPC-2 evaporative coater as presented in the users’ manual [42]........................................................................................................ 23
Figure 3. 2 Cold finger assembly showing the internal coolant passage. (All dimensions in inches.) .................................................................................................................. 24
Figure 3. 3 (a) Cold finger assembly with lid, and (b) cold finger assembly in vacuum chamber.................................................................................................................. 25
Figure 3. 4 Across International recirculating chiller. .................................................... 26
Figure 3. 5 The preliminarily modification of the gold-black manufacturing cell. ....... 27
Figure 3. 6 (a) A thin gold-black film on the interior wall of the vacuum chamber, and (b) on cellophane tape affixed to the top and lateral surfaces of the cold finger............. 30
Figure 3. 7 (a) Microscope glass slide taped in place, (b) gold foil and aluminum foil taped in place, and (c) cold finger covered with gold and aluminum foil placed in the vacuum chamber. ........................................................................................................ 31
Figure 3. 8 Gold-black formation on (a) a microscope glass slide, (b) gold foil, (c) aluminum foil, and (d) cellophane tape. ............................................................................. 31
Figure 3. 9 SEM studies of the gold-black sample formed on cellophane tape. The red boxes indicate the region of the SEM image. ................................................................. 32
Figure 3. 10 The modified chamber lid. ........................................................................ 33
Figure 3. 11 (a) Frost layer forming on the Peltier refrigerator during testing, and (b) the Peltier refrigerator and cold finger assembly installed in the vacuum chamber............ 34
Figure 3. 12 (a) Heating arrangement in our preliminary design where gold pellets were placed in a crucible wrapped with a tungsten filament, and (b) heating arrangement cited in the literature [17-19, 21] where gold wire is wrapped on a free standing “V”-shaped tungsten coil ........................................................................................................ 35
Figure 3. 13 Final version of the vacuum chamber with its modified lid and heating source. ..................................................................................................................... 36
Figure 3. 14 Final evolution of our gold-black manufacturing cell, including the turbo-molecular vacuum pump and the revised heating scheme.......................................................... 36

Figure 3. 15 (a) Gold wire is wrapped on the tungsten filament and substrates are attached to the lower surface of the cold finger, (b) gold has melted to form a bead, (c) the onset of evaporation and gold-black formation, (d) the apparatus at the end of a gold-black manufacturing run, and (e) gold-black deposit formed on the left side of the lower surface of the cold finger and a crescent-shaped sample (a second sample originally taped on the right-hand side has been removed). ......................................................................................... 38

Figure 3. 16 Gold-black deposition on (a) the bare copper cold finger, (b) cellophane tape, (c) a microscope glass slide, and (d) a microscope cover slip. ................................................. 40

Figure 3. 17 Gold-black deposit on (a) a microscope glass slide, and (b) SEM images at two different magnifications................................................................................................................. 40

Figure 3. 18 (a) PVD facility available in the Virginia Tech clean room, (b) a gold coated silicon wafer, and (c) gold coated substrates stored in a sealed container....................... 42

Figure 4. 1 (a) Schematic representation and (b) photo of a gold-black manufacturing cell................................................................................................................................. 44

Figure 4. 2 Scanning electron microscope (SEM) images of the same gold-black layer obtained at three different magnifications; (a) ×500, (b) ×2000, and (c) ×5000 [35]..... 46

Figure 4. 3 SEM images obtained at the same magnification of three different gold-black layers created using different gold evaporation rates; (a) 25 µg/s, (b) 0.5 µg/s, and (c) 0.4 µg/s [23]................................................................................................................................. 46

Figure 4. 4 Physical models for a single strand of gold filament forming the basis for (a) the finite-difference time-dependent (FDTD) solution of the one-dimensional lossless wave equation, and (b) the corresponding lossy transmission line model............................................. 49

Figure 4. 5 Real parts of (a) the dielectric function, (b) the refractive index, and (c) the electrical conductivity of single-crystal pure gold (Experimental results replotted from Ref. 49). ...................................................................................................................................... 54

Figure 4. 6 The initial condition for all cases. ......................................................................................... 56

Figure 4. 7 Decay of the initial EM wave within the gold-black filament (L = 1.0 µm). ............................. 58

Figure 4. 8 Exponential decay of quarter-wave, half-wave, and full-wave excitation of gold-black nanofibers for filament effective lengths (a) 0.7, (b) 0.9, (c) 1.1, (d) 1.4, (e) 1.6, and (f) 1.7 µm. The symbols correspond to solution of Eqs. (18) and (19), and the curves are exponential fits to the symbols. ....................................................... 59

Figure 4. 9 Evolution with time of the EM energy remaining in a filament of length L = 0.75 µm for wavelength λ = 1.5 µm......................................................................................... 62

Figure 4. 10 Variation of the single-filament spectral absorptivity with filament length and wavelength predicted using Eq. (4.29). ................................................................. 64
Figure 4.11 DLA simulation of gold-black dendrite growth generated by five million walkers on a two-dimensional rectangular grid using six different random number sequences. ................................................................. 65

Figure 4.12 Frequency of occurrence of (a) horizontal and (b) vertical filament lengths as a function of filament length for the six views of the simulated gold-black dendrite growth fields illustrated in Fig. 4.11 ................................................................. 67

Figure 4.13 Resolution into vertical and horizontal components of the electric field $E$ of a p-polarized EM wave carrying power $P$ incident to the gold-black layer with zenith angle $\theta$. ........................................................................................................ 68

Figure 4.14 (a) DLA model of a gold-black layer and distribution of (b) horizontal and (c) vertical branches in each of four equal-thickness sublayers numbered 1, 2, 3, and 4. 73

Figure 4.15 (a) Normal (\(\theta = 0\)) spectral absorptivity of gold-black as predicted using Eqs. (4.29) and (4.43) with the horizontal effective length frequency data from Fig. 412(a), and (b) experimental results obtained by Nelms and Dowson [23]. ............... 75

Figure 4.16 Relative response of a gold-black-coated pyroelectric detector as measured by Lehman et al. [24] (symbols) compared with the theoretical response (curve) predicted using the current theory. .................................................................................................................. 76

Figure 4.17 Directional spectral absorptivity of gold-black for p-polarized radiation (a) as a function of wavelength for incident zenith angles of 0, 20, 40, 60, and 80 deg, and (b) as a function of incident zenith angle for wavelengths of 2, 3, 4, 5, 6, and 7 \(\mu\)m; and for non-polarized radiation (c) as a function of wavelength for incident zenith angles of 0, 20, 40, 60, and 80 deg, and (d) as a function of incident zenith angle for wavelengths of 2, 3, 4, 5, 6, and 7 \(\mu\)m. ................................................................. 78

Figure 5.1 Gold-black samples of (a) 8-\(\mu\)m thickness and (b) 4-\(\mu\)m thickness. ............ 81

Figure 5.2 Geometry and nomenclature corresponding to Eq. (5.1). .............................. 82

Figure 5.3 (a) Photo of the automated gonioreflectometer used to measure the BRDF of our gold-black samples, and (b) the corresponding schematic layout [55]. ......................... 85

Figure 5.4 (a) Half-wave plate mounted on the laser source, (b) polarizing beam splitter in the visible and (c) the near infrared. ........................................................................................................ 86

Figure 5.5 (a) Sample and photodetector mounted on the reflectometer, (b) field-stop used as an entrance aperture on the detector, and (c) rotating-disc chopper synced with lock-in amplifier to modulate the signal intensity. ................................................................. 87

Figure 5.6 (a) Beam steering mirrors, (b) iris diaphragms, (c) periscope ............................. 87

Figure 5.7 Two views of the gold-black sample mounted on the sample holder and ready for BRDF measurement. .................................................................................................................. 89

Figure 5.8 BRDF of the gold-plated silicon substrate at \(\lambda = 532\) nm for (a) p-polarization and (b) s-polarization ................................................................. 90
Figure 5. 9 Measured noise-equivalent BRDF of the 532-nm (p-polarization) substrate set-up. ................................................................. 91

Figure 5. 10 (a) Plan SEM image with 10,000× and (b) 50,000× and (c) elevation SEM image with 10,000× of an approximately 8-μm-thick sample of gold-black. .......................... 92

Figure 5. 11 BRDF of the approximately 8-μm-thick gold-black sample at λ = 532 nm for (a) p- and (b) s-polarization. ................................................................. 93

Figure 5. 12 (a) Plan SEM image with 10,000× and (b) 50,000× and (c) elevation SEM image with 10,000× of an approximately 4-μm-thick sample of gold-black. .......................... 94

Figure 5. 13 BRDF of the approximately 4-μm-thick gold-black sample at λ = 532 nm for (a) p- and (b) s-polarization. ................................................................. 94

Figure 5. 14 BRDF of the gold-plated silicon substrate at λ = 800 nm for (a) p- and (b) s-polarization. ................................................................. 95

Figure 5. 15 Measured noise-equivalent BRDF of the 800-nm, s-polarization, substrate set-up ................................................................. 96

Figure 5. 16 BRDF of the approximately 8-μm-thick gold-black sample at λ = 800 nm for (a) p- and (b) s-polarization. ................................................................. 97

Figure 5. 17 BRDF of the approximately 4-μm-thick gold-black sample at λ = 800 nm for (a) p- and (b) s-polarization. ................................................................. 98

Figure 5. 18 BRDF of the gold-plated silicon substrate at λ = 850 nm for (a) p- and (b) s-polarization. ................................................................. 99

Figure 5. 19 Measured noise-equivalent BRDF of the 850-nm (s-polarized) substrate set-up ................................................................. 99

Figure 5. 20 BRDF of the approximately 8-μm-thick gold-black sample at λ = 850 nm for (a) p- and (b) s-polarization. ................................................................. 100

Figure 5. 21 BRDF of the approximately 4-μm-thick gold-black sample at λ = 850 nm for (a) p- and (b) s-polarization. The unexpectedly low peak in (a) corresponding to an incident zenith angle of 80 deg is thought to be erroneous. ................................................................. 100

Figure 5. 22 Ratio of gold-black peak BRDF to gold substrate peak BRDF as a function of incident zenith angle for 4-μm-thick (circles) and 8-μm-thick (squares) gold-black coatings for p-polarized radiation at λ = 532 nm (visible). ................................................................. 102

Figure 5. 23 Ratio of gold-black peak BRDF to gold substrate peak BRDF as a function of incident zenith angle for 4-μm-thick (circles) and 8-μm-thick (squares) gold-black coatings for s-polarized radiation at λ = 532 nm (visible). ................................................................. 102

Figure 5. 24 Ray paths through gold-black follow one of two regimes depending on the angle of incidence. In (a) radiation incident at small-to-intermediate zenith angles penetrate to the substrate surface and are specularly reflected back out of the gold-black layer with attenuation which increases with optical path length, while in (b) radiation incident at large incident zenith angles follows a curved path that never intersects the substrate, as in the case of classical road “mirage.” ................................................................. 104
Figure 5. 25 Ratio of gold-black peak BRDF to gold-plated silicon substrate peak BRDF as a function of incident zenith angle for ~4-μm-thick (circles) and ~8-μm-thick (squares) gold-black coatings for p-polarized radiation at λ = 800 nm (near-IR). .......................... 105

Figure 5. 26 Ratio of gold-black peak BRDF to gold-plated silicon substrate peak BRDF as a function of incident zenith angle for ~4-μm-thick (circles) and ~8-μm-thick (squares) gold-black coatings for s-polarized radiation at λ = 800 nm (near-IR). .......................... 105

Figure 5. 27 Ratio of gold-black peak BRDF to gold-plated silicon substrate peak BRDF as a function of incident zenith angle for ~4-μm-thick (circles) and ~8-μm-thick (squares) gold-black coatings for p-polarized radiation at λ = 850 nm (near-IR). The solid symbol is thought to be erroneous. .......................................................................................... 106

Figure 5. 28 Ratio of gold-black peak BRDF to gold-plated silicon substrate peak BRDF as a function of incident zenith angle for ~4-μm-thick (circles) and ~8-μm-thick (squares) gold-black coatings for s-polarized radiation at λ = 850 nm (near-IR). .......................... 107

Figure 5. 29 Illustration of the aureole surrounding a narrow beam; (a) its development by forward scattering as the beam transits the gold-black layer, (b) its radial power distribution viewed from the perspective of the detector, and (c) its BRDF profile. ..... 109

Figure 5. 30 Schematic cross-section of the gold-black in-plane BRDF showing its three components for the case of incident zenith angles producing a strong specular peak. The noise-equivalent BRDF is represented by the broken line. .................................................. 110

Figure 5. 31 Intersection between a unit sphere centered at (x0, 0, z0) and a cone whose vertex is at (0, 0, 0). The cone has an opening angle 2α, and is coaxial with the z-axis. The y- and y’-axes are into the page (i.e., both coordinate systems are right-handed). 111

Figure 5. 32 Contours on the unit sphere defined by the intersection of the sphere tilted an angle of θ = −25 deg with respect to the cone axis for cone half-angle α = 1.0, 2.5, 5, 10, 15, 20, and 25 deg. (b) Projection of contours on the x’, y’-plane. .......................... 114

Figure 5. 33 The value of the integral ∫f defined by Eq. (5.12) as a function of viewing zenith angle for a reflected peak angle φp of 50 deg. .................................................. 115

Figure 5. 34 Measured diffuse components of directional absorptivity for the ~8-μm-thick gold-black sample in the visible (532-nm) and near infrared (800 and 850 nm). 118

Figure 5. 35 Comparison of overall directional absorptivity for p- and s-polarized light. ....................................................................................................................................... 118

Figure 6. 1 Elevation SEM image of the three-layered gold-black sample showing that the bottom layer is thinner than the top two. ........................................................................................................... 123

Figure 6. 2 BRDF of the three-layer gold-black sample illuminated with p-polarized light at a wavelength of 532 nm. ........................................................................................................... 124

Figure 6. 3 BRDF of the three-layer gold-black sample illuminated with s-polarized light at a wavelength of 532 nm. ........................................................................................................... 125

Figure 6. 4 BRDF of the three-layer gold-black sample illuminated with p-polarized light at a wavelength of 800 nm. ........................................................................................................... 126
Figure 6.5 BRDF of the three-layer gold-black sample illuminated with s-polarized light at a wavelength of 800 nm. .................................................................................................................. 127

Figure 6.6 BRDF of the three-layer gold-black sample illuminated with p-polarized light at a wavelength of 850 nm. .................................................................................................................. 128

Figure 6.7 BRDF of the three-layer gold-black sample illuminated with s-polarized light at a wavelength of 850 nm. .................................................................................................................. 129

Figure 6.8 Idealization of the upper two gold-black layers with the intervening air gap (thickness exaggerated). .................................................................................................................. 131

Figure 6.9 Off-specular peaking zenith angle as a function of incident zenith angle for the three-layer coating at 800 and 850 nm, p- and s-polarization. ........................................................................... 132
List of Tables

Table 3. 1 Gold-black manufacturing conditions reported in the literature.................... 22

Table 4. 1 Results for relaxation time $\tau R$ and single-filament spectral absorptivity $\alpha L \lambda$ based on solution of Eqs. (4.18) and (4.19). .............................................................. 60

Table 5. 1 Directional-hemispherical reflectivity and directional absorptivity of the approximately 8-µm-thick gold-black sample in the visible ($\lambda = 532$ nm). and near-IR ($\lambda = 800$ and 850 nm). ................................................................................................................................. 117
Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BRDF</td>
<td>Bidirectional Reflectance Distribution Function</td>
</tr>
<tr>
<td>DLA</td>
<td>Diffusion-Limited Aggregation</td>
</tr>
<tr>
<td>EM</td>
<td>Electromagnetic</td>
</tr>
<tr>
<td>ERB</td>
<td>Earth Radiation Budget</td>
</tr>
<tr>
<td>FDTD</td>
<td>Finite-difference Time-Domain</td>
</tr>
<tr>
<td>PCB</td>
<td>Printed Circuit Board</td>
</tr>
<tr>
<td>PID</td>
<td>Proportional-Integral-Derivative</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

In this chapter we state the motivation for the effort described in this dissertation. This requires understanding the importance of monitoring the Earth’s radiation balance and its impact on the evolution of the planetary climate. Finally, the essential role played by absorption coatings on thermal radiation detectors is established. The organization of the dissertation is also laid out in this chapter.

1.1 Motivation

Thermal radiation detectors may be divided into two categories based on their operating principles. Photon-detectors are based on the photoelectric principle in which incident photons are directly converted into electrical current by raising electrons from the valence band to the conduction band of a suitably biased semiconductor. In photon devices the active face of the detector is typically the uncoated semiconductor itself. Thermal detectors, or bolometers, convert electromagnetic energy into sensible heat, thereby producing a temperature rise. In the case of
thermistor bolometers, the temperature rise produces a concomitant increase in electrical resistivity which is sensed by a resistance bridge, and in the case of a thermopile bolometer the temperature rise is sensed directly as an increase in voltage.

For a variety of reasons, thermistor and thermopile bolometers have emerged as the detectors of choice for monitoring the planetary radiant energy budget from low Earth orbit (LOE). This is partly because they are stable and durable legacy devices with a long and proven record of service in the space environment. In addition, their responsivity is relatively insensitive to wavelength between the ultraviolet and the mid-range infrared and, after suitable calibration, their performance can be accurately predicted using well-understood first-principles models.

The Earth radiation budget (ERB) refers to the balance that exists between energy from the sun intercepted by the Earth’s cross-section, on the one hand, and, on the other hand, the sum of incident radiation reflected from the Earth (albedo) and the thermal radiation emitted from the Earth. The four main components making up this balance are solar incident, solar reflected, Earth absorbed, and Earth emitted energy, as depicted in Fig. 1.1. According to conservation of energy, this balance is only achieved if the Earth emits the same amount of energy as it absorbs from the Sun over a sufficiently long period of time. This balance is very important for maintaining a constant temperature in the Earth’s troposphere, which is the prime condition for ensuring a stable long-term healthy global climate.
Figure 1. 1 The four components of the Earth’s energy balance [1].

However, since the beginning of the industrial revolution a number of processes, especially human activities such as fossil-fuel combustion, have augmented the greenhouse gas concentrations in the atmosphere. This leads to an increase in radiation emitted from the surface that subsequently becomes trapped in the atmosphere. When this happens, the effective temperature at the surface must increase to maintain the balance. The international scientific community has warned of the serious climatic consequences [2] of man’s continued exploitation of fossil fuels to meet the world’s ever-increasing demand for energy. As a result, several governmental authorities including the National Aeronautics and Space Administration (NASA) and the National Oceanic and Atmospheric Administration (NOAA) in the U.S., and the European Space Agency (ESA), the Japan Aerospace Exploration Agency (JAXA), and the National Institute of Information and Communications Technology (NICT) in Japan, are pursuing programs for long-term monitoring of the Earth’s radiation budget.
Efforts have been underway at NASA for decades to develop advanced instrumentation for monitoring the Earth radiation budget in an effort to increase knowledge about atmospheric physics [3, 4, 5]. An important early program was the Earth Radiation Budget Experiment (ERBE), which was initiated in 1979 to monitor the long-term balance between radiation arriving at the Earth from the sun and radiation reflected and emitted from the Earth [6, 7, 8]. The ERBE mission consisted of three spacecraft placed in LOE in 1984 and 1986. NASA’s most recent program, dating from 1997, is the Clouds and the Earth’s Radiant Energy System (CERES) [9-12]. The CERES broadband scanning thermistor bolometer radiometers were an improved version of those embarked on ERBE. The principle aim of CERES is to study the interactive role of clouds and radiation in establishing the Earth’s climate.

In addition to NASA, ESA, in collaboration with JAXA and NICT, is pursuing a satellite-based program called EarthCARE [13]. The aim of EarthCARE is to observe the effects of clouds, radiation, and aerosols on the Earth’s climate by measuring the reflected solar radiation and infrared radiation emitted from the Earth. The broadband radiometer detector consists of a focal-plane array (FPA) consisting of a linear array of 30 thermistor micro-bolometers.

Instruments embarked on both ERBE and CERES are based on thermistor bolometer technology, while the proposed but ultimately deselected Radiation Budget Instrument (RBI) scanners [9] were to be based on thermopile bolometry. The European EarthCARE instrument is based on thermopile micro-bolometer technology. The instruments embarked on ERBE, CERES and EarthCARE are similar in that they operate by converting incident radiation into sensible heat which then provokes a concomitant increase of temperature that can be accurately measured. This
will no doubt also be the operating principle of the next generation of thermal radiation detectors intended for ERB monitoring applications. The performance of these instruments depends directly on their ability to absorb incident radiation. It is essential that their absorptivity be well characterized over a wide wavelength interval—0.1 µm to about 100 µm. Furthermore, the effects of aging on their performance must be well understood. Comprehensive electro-thermal modeling and testing programs are therefore required for proper characterization of the performance of such detectors, whether they are based on thermistor bolometer technology as in ERBE and CERES, or thermopile technology as in RBI and EarthCARE.

The absorber layer that converts incident radiation into sensible heat is obviously a key component of any thermal radiation detector. If the absorptivity of the layer is directional or wavelength and polarization dependent, then so will be the detector gain itself. Both the microbolometer in EarthCARE and the thermopile-based radiometer under consideration for Demeter [14], a possible CERES follow-on, use a gold-black coating to convert incident EM radiation into sensible heat. This is the chief motivating factor behind our interest in the manufacture, characterization, and study of the directional spectral absorptivity of gold-black.

1.2 The Role of Gold-Black in Bolometer Performance

The performance of thermistor- or thermopile-based bolometers clearly plays a vital role in accurate measurement of incident radiant energy. Extensive thermal modeling and testing programs are required for understanding and functional design of a bolometer. A typical microbolometer consists of an array of pixels, with each pixel made up of several layers. Figure 1.1 is a
cross-sectional view of the type of thermistor bolometer used in CERES and a thermopile bolometer proposed to use in RBI.

Figure 1.2 Absorption layer on (a) a generic thermistor bolometer [11] and (b) the thermopile bolometer proposed for Demeter [15].

The thermistor bolometer in Fig. 1.2(a) consists of a thermistor mounted on an aluminum heat sink, which is maintained at a constant temperature. A thermal impedance layer between the thermistor and the heat sink produces a temperature rise in the thermistor which is proportional to the radiation incident to the absorber layer. The electrical resistance of the thermistor, which is highly sensitive to its temperature, is sensed by a bridge circuit. To enhance the absorptivity of the thermistor, it is coated with a high-absorptive material; the commercial aerospace coating Z306, enhanced with microspheres, is used in the case of CERES [11]. This emphasizes the essential role of the absorptive coating.

In the thermopile bolometer proposed for RBI, illustrated in Fig. 1.2(b), a thermopile fence is placed between an absorber and a silicon-nitride printed-circuit board (PCB). The thermopile fence
produces a voltage proportional to the temperature difference between the absorber and the PCB. A high-absorptive material, in this case gold-black, is deposited on a thin layer of pure gold. Radiation absorbed in the gold-black layer is conducted laterally through the gold shunt to the thermopile. It this arrangement the PCB board acts as the heat sink. This once again establishes the important role played by the absorber.

An ideal absorption layer should absorb all incident radiation regardless of wavelength, incident angle, and state of polarization. However, an absorber should have additional properties in order to qualify as a thermal detector coating. These include, among others, low thermal mass. This is a desirable property because it favors both maximum sensitivity and minimum response time. Several absorber materials have been investigated [17]; however, gold-black satisfies almost all of these requirements. Gold-black is a very low density and highly porous material which endows it with a low thermal mass. Moreover, it has an absorptivity very close to unity in the visible and infrared. Due to these favorable properties, gold-black has emerged as a popular coating for thermal radiation detectors in aerospace applications.

### 1.3 Objectives

In spite of its suitability for the thermal radiation detector applications, the directionality of gold-black absorptivity has not been the subject of previous investigations. This could be relevant in the case of wide field-of-view detector arrays such as under consideration for Demeter. The goal of this dissertation is to investigate the directional, spectral, and polarization sensitive absorptivity of gold-black. An experimental campaign to fabricate and measure the directional spectral behavior of gold-black is pursued, as is the search for a corresponding theory.
Gold-black coatings are formed by evaporation and subsequent sublimation of pure gold in an inert low-pressure atmosphere. Previous attempts to predict the spectral absorptivity of gold-black coatings have often assumed a granular continuum with effective bulk optical properties [17-22]. Early in the current effort the need for a first-principle model based on the known microstructure of gold-black was recognized. This led to a contribution to the technical literature [25] in which gold-black was treated as an array of lossy dipole antennas formed by dendritic gold nanostructures. Reported results for normal spectral absorptivity based on this interpretation are generally in good agreement with measurements reported in the literature [23, 24]. However, suitable experimental data were not available to validate the predicted polarization sensitive directional absorptivity.

The resulting experimental campaign involved the design and fabrication of a novel gold-black manufacturing cell that permitted the successful creation of the gold-black samples required for verification of the model. New in-plane bidirectional reflectance distribution function (BRDF) measurements for two thicknesses (~4 μm and ~8 μm) of gold-black in the visible (532 nm) and near-infrared (800 and 850 nm) were performed for p- and s-polarizations. The investigation was subsequently extended to a three-layer sample. The equipment and procedure used to create the gold-black samples and to perform the BRDF measurements are described in sufficient detail to permit later investigators to duplicate the results reported here.

A novel approach is then developed for converting in-plane BRDF measurements to directional absorptivity. Experimental results are found to be in good agreement with those anticipated by our
earlier theory [25]. Specifically, reported measurements verify that gold-black absorbs p-polarized light more efficiently than s-polarized light. Furthermore, an unanticipated mirage effect at large incident zenith angles is discovered, which led to the need for additional theoretical effort.

The discoveries reported in this dissertation should play a valuable role in the design of next-generation thermal radiation detectors.

1.4 Organization

This dissertation is divided into seven chapters:

Chapter 1 presents the motivation and goals.

Chapter 2 presents a brief history of gold-black from its accidental discovery until its emergence as a popular coating in aerospace applications.

Chapter 3 presents the design and fabrication of a novel gold-black manufacturing cell and establishes a protocol for using it to produce gold-black.

Chapter 4 presents a new theory for predicting the directional absorptivity of gold-black coatings as a function of wavelength and polarization.

Chapter 5 presents the measurement of gold-black in-plane BRDF as a function of coating thickness, wavelength and polarization, and a novel approach is described and demonstrated for converting the in-plane BRDF to directional absorptivity.

Chapter 6 presents the in-plane BRDF measurement of a multilayered gold-black coating and interprets its surprising behavior (off-specular peaking).

Chapter 7 offers conclusions and recommendations for future effort.
Chapter 2: History of Gold-Black

In this chapter we delve into the history of gold-black from its accidental discovery in 1930 to its emergence as a highly appreciated coating for thermal radiation detectors.

Metal-black was first reported in 1930 when Pfund [26] accidently discovered a strange characteristic of bismuth. He found that if bismuth is evaporated from a hot tungsten filament under high vacuum and allowed to condense on a cold substrate, it normally creates a smooth bright layer. On the other hand, if the pressure is raised to 250 mTorr in an inert atmosphere, he found that the bismuth is deposited as an intensely black and fluffy layer, which he named “bismuth-black”. This bismuth-black was seen to be quite opaque in the visible and infrared; in fact, it was found to behave very nearly like an ideal blackbody. In the infrared it exhibited only one percent transmission and reflection over the wavelength range of 0.3 to 15 μm. Pfund suggested that it should not be assumed that only bismuth can produce a black layer; in fact, he predicted that other metals should yield metal-blacks. In 1933, Pfund [26, 27] extended his research to metals such as gold, copper, zinc, silver, lead, cadmium, nickel, antimony, tellurium,
and selenium, and demonstrated that these metals could also be used to produce metal blacks. Since then, metal blacks have generated a great deal of interest in the scientific community, with gold-black gaining more attention due its chemical stability.

In the period between 1948 and 1956, Harris with his co-workers carried out an intensive investigation of gold-black production and the properties of gold-black [17-19, 28, 29]. They explored the effect of pressure of the inert atmosphere, purity of the body gas, gold evaporation rate, and distance between the melt and deposition surface, on the formation of gold-black, and correlated these parameters with its surface properties [28]. In this dissertation, as in the cited contribution, the surface properties of interest are the absorptivity, the reflectivity, and the transmissivity. Harris et al. [28, 29] also studied the effect of trace oxygen in the otherwise inert atmosphere, and observed the nanostructure in gold-black formation under different experimental conditions. High absorptivity in the infrared was observed for coatings created in a pure nitrogen environment. On the other hand, the microstructure obtained in the presence of trace oxygen resulted in lower absorptivity beyond one micrometer while retaining high absorptivity in the visible [28]. However, much of the effort reported by Harris and his collaborators is aimed at explaining the electrical and surface properties of gold-black on the basis of classical electromagnetic theory [17, 18, 19]. In their theory, Harris and his associates considered gold-black deposits as a homogeneous medium having an effective electrical conductivity, and established an expression relating the conductivity of gold-black to the absorptivity and transmissivity in different parts of the infrared spectrum [17, 18, 19]. According to their model, the effective electrical conductivity varies with wavelength, and for wavelengths longer than 105 µm this variation can be attributed to a relaxation effect [18]. According to the Drude-Zener model, electrons have a finite relaxation time, which causes them to lag behind the imposed emf. This lag
increases with increasing frequency of the imposed field. This “relaxation effect” causes the effective conductivity to increase with increasing wavelength of the incident radiation. The authors also performed a comparative study between gold-black and other low-reflectance materials for a spectral range of 254 µm to 1100 µm [19].

Although gold-black has been known for nearly 90 years, the process for its creation pioneered by Pfund [26, 27] continues to be practiced with only minor modifications. The technical literature is relatively sparse on the subject of theory and models for optical performance prediction. During 1971-1972, G. Zaeschimar and A. Nedoluha, developed a theory referred to as the “capacitor model” [20]. They anticipated that the properties of gold-black mainly depend on the preparation process. They used the vast database created by Harris and his co-workers [17-19, 28, 29] to establish and validate a model in which they consider gold-black as a chain of interconnected spheres forming conducting/capacitive strands. This homogeneous-strand-structure assumption provides good agreement between theory and experiment in the spectral range of 3 to 100 µm, but diverges in the solar spectrum (0.3 to 2.5 µm).

McKenzie [30] performed a comprehensive study of the optical, electrical, and structural properties of gold-black formed in the presence of different trace amounts of oxygen. He attempted to explain all these properties in terms of existing theoretical models. He claimed that the presence of oxygen during the formation of gold-black gives rise to electrical resistance due to the formation of oxides of gold. As a result, the spectral reflectance of gold-black is affected. He used Mie theory to establish the model for explaining the optical properties of gold-black with oxide contamination. However, he was not able to explain the optical behavior of pure gold-black with his model. He
concluded that the “capacitor model” established by G. Zaeschimar and A. Nedoluha [20] should be more applicable for pure gold-black.

During 1977-1978 O’Neill et al. [21, 31] attempted to establish the relationship between the absorptivity of gold-black and the particulate nature of the material. They produced gold-black samples under a variety of laboratory conditions and concluded that the manufacturing conditions play a vital role for determining the particulate structure of the deposit, and as a result the absorptivity is also affected. In general, the absorptivity shows an increasing trend with the decrease of the particle size. From their observations they concluded that modifications of the previously established capacitor model were required. They suggested that each gold strand (chain of spheres) should be considered as a spheroid with a specified semi-major-to-semi-minor axis ratio [31]. They imagined a distribution through the gold-black film of this axis ratio, resulting in a distribution of various spheroid sizes. They applied the theoretical model presented by Genzel and Martin [32] to attribute the optical performance to this spheroid structure. However, although this model showed good agreement with the experimental results in the solar part of the electromagnetic spectrum, discrepancies are observed in the infrared.

Subsequent to the effort of O’Neill and his colleagues, most of the extant literature is concentrated mainly on investigation of metal-blacks to assess their optical performance and to develop a well-defined process for the production of gold-black [16, 22, 24, 33-35]. The cited authorities observe that the absorptivity of gold-black depend highly on the manufacturing parameters such as pressure, temperature, evaporation rate, and so forth. The microstructure as well as the absorptivity of the gold-black are reported to vary in a way that depends on these parameters. Therefore, a significant amount of research has been performed to determine the
effects of these parameters on the performance of gold-black as an absorber of electromagnetic energy. In 1992, Lang et al. [16] performed a comparative study of the absorptivity of different metal-blacks produced in different deposition processes. They also explored the problem of finding the critical coating thickness in order to obtain maximum absorption. An extensive study of chamber pressure to determine the optimum value was also carried out. In their comparative study of various deposition processes, a thin film of gold was prepared by sputtering from a gold target in an argon atmosphere, a highly porous platinum-black was formed by adding lead to a platinum electrolyte solution, and an absorption layer was produced by evaporating gold in a nitrogen atmosphere to produce gold-black. The transmissivity and reflectivity of the samples produced were then measured for wavelengths ranging from 2 to 20 µm. It was observed that porous metal deposited by evaporation in a nitrogen atmosphere yields the highest infrared absorptivity. A similar evaporating process was used to produce metal-blacks from pure silver, aluminum and bismuth. Silver-blacks showed the highest absorptivity in the infrared range. However, gold-black was deemed preferable for practical application because of its chemical stability.

Becker et al. [22, 33] performed a thorough study on the applicability of gold-black as a thermal detector coating in the far infrared. They followed the path of earlier investigators with emphasis on gold-black manufacturing conditions. They investigated the effects of vacuum pressure on gold-black formation, and provided a useful detailed description of their experimental apparatus [22]. From their observations, they concluded that the absorptivity of gold-black depends mostly on the chamber vacuum pressure. They reported that, up to a certain value of increasing pressure, the reflectivity of gold-black decreases. The chamber pressure affects the deposition rates of gold-black, affecting the microstructure and thus the surface properties. They also studied the effects of annealing the gold-black at 110 °C and 130 °C, observing that annealing the sample decreases its
absorptivity. Their explanation was that the electrical conductivity of gold-black changes with the change in annealing temperature, which plays a vital role in determining the absorptivity. They also claimed that the absorptivity can be controlled by controlling the electrical conductivity of the gold-black layer [33]. They emphasized that the peak of absorptivity for a given thickness of the gold-black layer is a different function of conductivity for each wavelength. Therefore, it is very difficult to optimize the absorptivity over a large spectral range.

Lehman and his collaborators [24] studied gold-black deposition on a freestanding pyroelectric detector substrate. They developed an empirical correlation between the nitrogen pressure inside the vacuum chamber during evaporation and the distance between the melt and the substrate. They suggested, as a rule of thumb for determining the chamber nitrogen pressure, that the product of the nitrogen pressure during deposition and the melt-to-substrate distance should be 10 torr·cm (12 Pa·m). From their observations they concluded that the higher the pressure inside the vacuum chamber, the lower the deposition rate. This is consistent with the idea that increased exposure of the gold-black deposit to the hot melt results in increased annealing of the gold-black. They also studied the spatial uniformity of the gold-black coating and concluded that it depends on the deposition process. They also attempted, for the first time, to perform a damage test on gold-black. Any kind of damage test for gold-black is very difficult to quantify due to its inherent fragility. However, they visually evaluated damage resulting from exposure of the gold-black coating to a 193 nm laser excimer and determined the damage threshold to be approximately 38 mJ·cm⁻².

Nelms and Dowson [34] contributed to the design of a new gold-black production apparatus and have documented extensive characterization of the production process to ensure repeatability of optical performance of the coating in the mid-infrared. They also attempted to optimize the
parameters affecting gold-black production such as gold melt mass, cell pressure during evaporation, evaporation rate, and substrate temperature. They suggested that high absorption at longer wavelengths depends on coating uniformity. On the other hand, the coating uniformity itself was found to be dependent on deposition rate and evaporation pressure. They attempted to establish a relationship between absorptivity and the deposition rate. Through their experimental results and observations, they defined an optimized gold-black production process that provides higher absorptivity in the mid-infrared.

Like Nelms and Dowson, Ilias et al. [35] also studied the design and optimization of a new apparatus for producing a gold-black coating with good performance in a relatively broad wavelength range extending from the ultraviolet to the far infrared. They tried to establish a correlation between the layer thickness and its absorptivity. They concluded that a critical thickness produces maximum absorptivity. They built a laser trimming apparatus (an excimer) to define the blackened infrared detector pixels. This apparatus ablates channels through the gold-black coating thickness while preserving the pixel and gold-black deposit integrity.

Eventually, gold-black became a popular coating for aerospace applications. Wang et al. [36] developed a deposition process for gold-black suitable for microbolometer applications. They performed a comparative study of microbolometer performance with and without a gold-black absorption layer, and showed that a microbolometer coated with a gold-black absorption layer exhibits improved performance without a significant increase in thermal mass. They also studied the effect of nitrogen pressure on gold-black formation and concluded that it influences the density and porosity of the gold-black layer. As a result, film thickness, density, and finally the absorptivity of the gold-black are affected.
With the recent adaption of gold-black coatings on thermal detectors, especially in aerospace applications, concern has turned to the inherent fragility of gold-black. Besides optimization of the production process, recent research explores different technologies for overcoming the handling difficulty of gold-black [37-41]. Qian et al. [37] investigated the optimization of a gold-black layer on infrared detectors in the near-infrared, and engineered a solution to the long-standing problem of the adherence of gold-black to the substrate. They suggested fuming a low viscosity ethyl-based cyanoarylate adhesive (commercially known as 502 superglue) into the gold-black layer for increased adherence, and demonstrated that the resulting absorptivity is not significantly reduced in the near-infrared. They also attempted to define the nitrogen vacuum pressure that maximizes the absorptivity in the near-infrared.

Panjwani et al. [38-40] also studied the applicability of gold-black for enhancing the absorptivity of uncooled infrared detectors such as microbolometers. They used a stencil mask to create patterned gold-black layers to address the difficulty of integrating the extremely fragile gold-black coating with the microbolometer array. Using SEM images, they demonstrated that the patterned gold-black layer density increased over layers created using the unmasked gold-black deposition process [39]. However, while this process preserves the absorptivity of gold-black in the LWIR, it does not do so in the MWIR. In the end they suggested a new design of patterned gold-black featuring a technique called lift-off, where SiO₂ is evaporated as a protection layer. They noted that with this approach the coating retains its high absorptivity in both the MWIR and the LWIR ranges [40].

Ng et al. [41] investigated the applicability of gold-black in photonic-related applications such as the production of “solar fuel” and in photodetector and photovoltaic production. They developed
a model to explain the optical performance of gold-black deposits consisting of nanotubes having high aspect ratios. According to their model, these tapered nanotubes are responsible for a graded refractive index which suppresses Fresnel reflections over a broad range. They also suggested that Fabry-Perot resonances of gap-plasmon modes between the nanotubes are responsible for the suppression of reflections. They developed a finite-element model for their nanostructure in a successful attempt to validate their theory.
Chapter 3: Manufacture of Gold-Black

In this chapter we follow the long and torturous journey that takes us from a commercially available gold mirror coater to a custom-made gold-black manufacturing cell. The difference between the two devices proves to be the elusive protocol that must be adhered to in the latter’s operation.

The manufacture of metal-blacks has changed little since the early 1930s when Pfund [26] first produced bismuth-black by evaporating pure bismuth from an electrically heated tungsten filament \textit{in vacuo} and allowing it to sublime on a cold surface. In general, the process involves evaporation of a noble metal in a vacuum ranging from 0.01 to 0.1 torr, followed by sublimation. A suitable vacuum chamber having a low leakage rate is required. Under high vacuum, evaporated metal
molecules travel with high kinetic energy in a straight line until they encounter a surface where they condense to a liquid before solidifying under the action of surface tension into a smooth shiny surface. However, as explained in Ref. [25], when the vacuum chamber is back-filled with an inert gas, the speed of the metal molecules is moderated by collisions with the inert gas molecules. When the chamber back-pressure is sufficiently high and the melt-substrate distance is adequate, the molecular flow transitions from momentum-dominated to diffusion-dominated, thus favoring sublimation and the formation of crystal-like dendrites on the surface. On a macroscopic level, the resulting coating appears to be a fuzzy black layer, reminiscent of black hoarfrost.

Several gold-black investigators [16-24, 26-41] have observed that the overall conditions during the evaporation process; such as gold quantity, chamber pressure, evaporation rate, substrate temperature, melt-substrate distance, and type of inert gas, influence the microstructure of the deposited coating. Different microstructures result in different coating optical performance as evidenced by its absorptivity, reflectivity, and transmissivity. Generally, gold-black shows good absorptivity in the visible and near-infrared; however, depending on the manufacturing conditions, wide variations in absorptivity are observed. Therefore, it is of interest to determine the manufacturing conditions that maximize absorptivity over a desired wavelength range.

3.1 Design of the Gold-Black Manufacturing Process

A thorough and wide-ranging study of the pertinent literature was essential before undertaking the design of a gold-black manufacturing cell and its operation. While information concerning the choice of an inert body gas, chamber pressure, melt-to-substrate distance (and geometry), substrate
temperature, and evaporation rate is widely available, it is spread across many sources, is occasionally contradictory, and is generally reticent on the step-by-step manufacturing procedure. Choosing the point of departure for the design and the critical operating parameters proved to be a challenging task. As already discussed in Chapter 2, the extant literature provides a dauntingly wide range of manufacturing conditions, each producing an equally wide variety of coating microstructures and optical behavior. However careful study of the literature permits identification of the key parameters and procedures that play a significant role in determining the microstructure and optical behavior:

1. Choice of inert body gas
2. Procedure for purging the chamber of oxygen
3. Evaporation pressure
4. Evaporation rate profile
5. Substrate material
6. Substrate temperature
7. Melt-to-substrate distance
8. Orientation of the substrate vis-à-vis the melt

Conditions gleaned from the literature, summarized in Table 1, provide guidelines for the design and operation of an apparatus for the manufacture of gold-black. The many empty cells in Table 1 are testimony to the sparsity of detail about gold-black manufacturing available in the open literature.
Table 3.1 Gold-black manufacturing conditions reported in the literature.

<table>
<thead>
<tr>
<th>Source</th>
<th>Substrate Temperature (°C)</th>
<th>Chamber Pressure (torr)</th>
<th>Inert Body Gas</th>
<th>Evaporation Rate (mg/s)</th>
<th>Melt-to-Substrate Distance (cm)</th>
<th>Wavelength (µm)</th>
<th>Substrate Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Becker et al. [22, 33]</td>
<td>10</td>
<td>0.75 - 11.25</td>
<td>Nitrogen</td>
<td>0.7, 1</td>
<td>5</td>
<td></td>
<td>Cellulose nitrate films</td>
</tr>
<tr>
<td>Ilias et al. [35]</td>
<td></td>
<td>0.75 - 7.5</td>
<td>Nitrogen</td>
<td></td>
<td></td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Nelms and Dowson [23]</td>
<td>−55</td>
<td>7.5</td>
<td>Nitrogen</td>
<td></td>
<td></td>
<td>10</td>
<td>Visible to mid-Infrared &lt; 40 µm Chromium and gold coated glass</td>
</tr>
<tr>
<td>Harris et al. [17-19, 28, 29]</td>
<td></td>
<td>0.97508</td>
<td>Nitrogen</td>
<td>Between 0.5 and 3.3</td>
<td>7</td>
<td>100</td>
<td>Cellulose nitride film</td>
</tr>
<tr>
<td>O’Neill et al. [21, 31]</td>
<td>1-20</td>
<td>1.2</td>
<td>Helium</td>
<td></td>
<td>0.35 - 2.4 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lang et al. [16]</td>
<td>0.75</td>
<td>Argon/ Nitrogen</td>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>Glass, silicon, silicon oxide, silicon nitride, aluminum, ceramics and epoxy</td>
</tr>
<tr>
<td>Panjwani et al. [38-40]</td>
<td>−13</td>
<td>1st: below 10 - 5</td>
<td>Nitrogen</td>
<td></td>
<td>10</td>
<td>2 - 125</td>
<td>Polished silicon substrate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2nd: back-filled to 0.30 - 3.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lehman et al. [24]</td>
<td></td>
<td>Evacuated to 3.75 × 10⁻⁶</td>
<td>Coat at 0.9751</td>
<td></td>
<td>3</td>
<td>1-20</td>
<td>Nickel-coated LiTaO₃, LiNbO₃ plate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>and 1.95</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Qian et al. [37]</td>
<td>1.50012</td>
<td>3.3</td>
<td></td>
<td></td>
<td>5</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Wang et al. [36]</td>
<td>0.825068, 1.350011, 2.32519</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2 Evolution of Our Gold-Black Manufacturing Cell

In the absence of a suitable off-the-shelf gold-black manufacturing cell, we purchased and modified a commercially available apparatus (MTI Model GDL-1700X-SPC-2) intended for vacuum depositing noble metals such as gold and silver onto suitable substrates to create mirror-
like coatings. However, a long and torturous evolutionary path had to be followed to convert this ordinary metal coater into an optimized gold-black manufacturing cell. In this section we describe in detail this evolutionary process.

3.2.1 Preliminary Evolutionary Stage

The original apparatus consisted of a thick-walled 6-in. (152.4 mm)-ID quartz vacuum chamber. To evacuate the chamber, a 156 L/m double-stage rotary-vane vacuum pump was provided with the original coater. The vacuum chamber is mounted on a chassis which houses, among other functions, a nitrogen flow control valve and a programmable filament-current controller. Figure 3.1 shows the original configuration of the MTI GSL-1700 X-SPC-2 coater as presented in their users’ manual [42].

![Figure 3.1 The original MTI GSL-1700 X-SPC-2 evaporative coater as presented in the users’ manual [42].](image)

Some features were available in the original apparatus which were extraneous for gold-black production; a rotation motor was attached to the specimen holder and a shutter was provided
between the crucible and the specimen holder. Moreover, in the original design, the specimen holder was nearer the crucible than the distance criterion specified in the literature. While providing unneeded features, the cell lacked some essential capability such as substrate temperature control. Considering these differences between the needed and provided features, a modification of the cell, particularly its lid, was required. First, the rotation drive motor and the shutter were removed, and the specimen holder assembly was replaced with a cooled copper plate (the cold finger). The cold finger was designed to maintain the substrate at the required temperature. These modifications are illustrated in Fig. 3.2, and the associated engineering drawings appear in the Appendix A.

Figure 3.2 Cold finger assembly showing the internal coolant passage. (All dimensions in inches.)
As depicted in Figs. 3.2 and 3.3, two extra holes were drilled through the existing lid in order to insert copper tubes carrying coolant to and from the cold finger while also acting to support it. The cold finger was designed to ensure that it could provide adequate cooling while at the same time interfering as little as possible with the circulation of gold molecules from the melt to the upper surface of the cold finger. We later determined through experience that the substrate upon which the gold-black coatings were formed must be mounted on the lower surface of the cold finger. The cold finger was originally designed to be insulated at the lower and side surfaces with a Bakelite shoe, but this was subsequently removed. Detailed engineering drawings of the cold finger, the insulating shoe, and the lid are provided in the Appendix A.

The next step was to choose an appropriate chiller to supply coolant to the cold finger. The external circulating chiller (Across International C15-3-2L) capable of supplying coolant at temperatures as low as −15°C at a flow rate of up to 17 L/min, shown in Fig. 3.4, was selected for
this purpose. The required inert atmosphere within the vacuum chamber was to be created by first purging and then back filling it with ultra-pure nitrogen. We also planned on using Kurt J. Lesker 99.999-percent pure 1/8-in. gold pellets of as the gold source.

![Figure 3. 4 Across International recirculating chiller.](image)

Table 1 reveals wide variation in the literature on choice of a substrate. We eventually investigated a variety of substrate materials including cellophane tape, glass microscope slides and slide covers, aluminum foil, gold foil, copper and silicon wafer.

Figure 3.5 shows the preliminary modification of the apparatus for gold-black production. As the figure shows, the apparatus consists of the vacuum chamber and attendant vacuum gauge, a regulated supply of high-purity nitrogen, an electrically heated crucible for evaporating the gold pellets, the cold finger for sublimating gold vapor to a solid crystalline form, and a coolant refrigerator. A programmable controller is also provided to regulate the nitrogen bleed and the
crucible heating cycle. In this preliminary design the distance between the substrate and the melt is 11 cm.

Figure 3.5 The preliminarily modification of the gold-black manufacturing cell.

Several attempts were required before eventually settling on a well-defined process for manufacturing gold-black. Each attempt provided useful information and acted as a step on the path to develop a successful production process. During the first attempt to make gold-black, it was discovered that the rotary-vane vacuum pump supplied with the commercial cell could not attain a vacuum below $10^{-2}$ torr. The temperature at which gold can reach the evaporation point at this pressure is 1465 °C. Before each operation the vacuum chamber, lid, and cold finger assembly were carefully cleaned using denatured alcohol. Gold pellets were then placed in the crucible. A commercially available mirror (silver-plated glass) was used as our first substrate. The vacuum chamber was maintained at a vacuum of $10^{-2}$ torr overnight with the chiller running. The vacuum
chamber was then flushed with ultrapure nitrogen to create an inert atmosphere. An automatic program for the evaporation cycle was selected. This required defining the evaporation temperature—1465 °C—and designating one of the PID heating programs following instructions provided with the commercial coater. However, it was discovered that the temperature would not increase beyond 700 °C. In fact, beyond this temperature it began to decrease. It is emphasized that an automatic mode was chosen based on instructions the coater operation manual; i.e., the evaporator was operated in automatic rather than manual mode. Several attempts undertaken to solve these problems failed, leading to the following conclusions:

1. The PID controller might not be working properly due to our modification of the evaporator cell. This suggested that it might be preferable to shift to manual mode.

2. According to the operation manual, the S-type thermocouple provided with the evaporator should have been able to span a temperature range of 200-1500°C. It was suspected, however, that the thermocouple could not operate at its upper limit, and therefore that it was not providing a correct signal to the PID controller.

3. To use the existing thermocouple, a stronger vacuum would be required.

We concluded that it would be preferable to use the manual operating option and to replace the existing pump with one providing a harder vacuum.

In the end we replaced the original pump an MTI Compact Turbomolecular Vacuum Pump at the suggestion of the manufacturer. The turbomolecular pump is capable of reaching a vacuum of
10^{-4} \text{ torr}, lowering the evaporation temperature of gold to 1190 °C, which fell within the range of the control thermocouple.

Even with the new vacuum pump, we found that we could not pump below 10^{-3} \text{ torr}, at which the evaporation temperature of gold is 1316 °C. Therefore, we decided to control the evaporator temperature manually. This time the experiment seemed to run as expected; however, no trace of gold-black could be discerned on the mirror substrate.

After several unsuccessful attempts, based on our understanding at the time, we determined that we could not achieve the desired temperature of -15°C on the mirror surface because of its thickness and related thermal resistance. To achieve a temperature near -15°C, we decided to choose a substrate having a higher thermal conductivity and so achieve a more intimate thermal contact with the cold finger. This led us to try thin cellophane tape as a substrate. We removed the insulating shoe from the underside and sides of the cold finger because we could not justify its role. The first successful production of gold-black was then obtained when cellophane tape was used as a substrate. Cellophane was applied to the upper and side surfaces of the bare cold finger. Figure 3.6(a) reveals light film of gold-black on the interior wall of the quartz cell in the vicinity of the cold finger, and Fig. 3.6(b) shows our historic first batch of gold-black. The greyish region of Fig. 3.6(b) is the gold-black layer formed on the upper surface of the cold finger, and the black regions on the left and right sides of the image are gold-black layers formed on the sides of the cold finger.
Figure 3. 6 (a) A thin gold-black film on the interior wall of the vacuum chamber, and (b) on cellophane tape affixed to the top and lateral surfaces of the cold finger.

After successful formation of gold-black on cellophane tape, we become confident that an appropriate environment of creating gold-black had been attained. There remained the not inconsiderable task of optimizing the manufacturing cell and establishing a well-defined process for yielding a thicker layer. Various materials were considered in the search for a candidate substrate that would be appropriate for subsequent measurement of gold-black optical properties. Cellophane tape offers both advantages and disadvantages. While the adhesive side of the tape ensures good thermal contact with the cold finger, it is difficult to remove without damaging the gold-black coating.

3.2.1.1 Exploring Various Substrate Candidates

A literature search shows that gold-black can be deposited on a wide range of substrates. In searching for a suitable substrate, we explored a variety of options such as microscope glass slides, gold foil, and aluminum foil. Figure 3.7 shows results obtained using various substrates.
Figure 3. 7 (a) Microscope glass slide taped in place, (b) gold foil and aluminum foil taped in place, and (c) cold finger covered with gold and aluminum foil placed in the vacuum chamber.

A very thin layer of gold-black is formed on each of these substrates; however, cellophane tape provided the thickest gold-black layer among these candidate substrates. Figure 3.8 shows the gold-black formation on various substrates.

Figure 3. 8 Gold-black formation on (a) a microscope glass slide, (b) gold foil, (c) aluminum foil, and (d) cellophane tape.

A scanning electron microscope (SEM) study was performed on the gold-black sample formed on cellophane tape. Figure 3.9 shows SEM images of three regions of the gold-black sample.
However, we concluded that, although we have established an environment propice for creating gold-black, we have not yet fully achieved the required ability of creating a sufficiently thick layer to use as a coating on a thermal detector. We decided to return to the extant literature for guidance in overcoming this deficiency.

3.2.2 Final Evolutionary Stage

While revisiting the literature, we finally realized the significance of previously read passages that did not make sense at the time. From Table 3.1, we observe that most of the literature cited the vacuum pressure during evaporation; however, nearly all failed to point out a different preliminary vacuum pressure which had to be maintained to purge the chamber of oxygen and other gaseous impurities before the insertion of nitrogen. We found this valuable information only
in two references [24, 39], both of which indicate that it is necessary to initially evacuate the chamber to a range of from $10^{-5}$ to $10^{-6}$ torr, which in fact is a hard vacuum. In fact, success requires that the vacuum chamber be initially evacuated to the range of from $10^{-5}$ to $10^{-6}$ torr and maintained in this range overnight. Only then can the vacuum pressure be increased to a value in the range of 0.10 torr. We observed in Table 3.1 that the recommended value of this final pressure varies in a wide range from 0.1 torr to 20 torr. We concluded that a combination of a very low leakage rate and high pumping rate is required to maintain a vacuum of at least $10^{-5}$ torr. Also, it is essential that the chamber be raised to 0.1 torr by back filling with pure nitrogen without any backflow through the pump. We found that we were unable to attain a sufficiently hard vacuum to meet these requirements.

![Image](image.png)

Figure 3. 10 The modified chamber lid.

To address the inadequate vacuum problem, we performed an acetone leak test to identify the probable leak sources. We discovered that most of the leaks were around the various passthroughs in the lid. This led to the decision to replace the original lid with a new lid design, shown in Fig.
3.10. A more detailed shop drawing is provided in the Appendix B. We took advantage of the lid modification to also extend the length of the copper coolant tubes, allowing the distance between the cold finger and the crucible to be reduced to 5 cm.

We also observed in Table 3.1 that the recommended substrate temperature varied over a wide range from -10°C to -55°C. Our cold finger can attain -15°C, which is adequate according to Table 3.1. However, since we were designing a new lid, we took advantage of the opportunity to include an electrical feedthrough to power an eventual Peltier refrigerator to provide augmented cooling of the cold finger if required. Figure 3.11(a) shows frost forming on the Peltier refrigerator during testing, and Fig. 3.11(b) shows its placement in the vacuum chamber. However, for our final gold-black production process we abandoned the Peltier refrigerator as unnecessary.

Figure 3.11 (a) Frost layer forming on the Peltier refrigerator during testing, and (b) the Peltier refrigerator and cold finger assembly installed in the vacuum chamber.

Another very significant difference noted in Table 3.1 is the amount of gold needed and the method for heating the gold. In our preliminary design, pure gold pellets were melted and evaporated in a small alumina crucible wrapped with a tungsten filament and mounted within a miniature ceramic oven. As a result, a large amount of gold had to be placed in the crucible, and
the evaporation rate produced by this arrangement proved to be inadequate for gold-black production. Only a few citations [17-19, 21] specified the amount of gold used and the process for heating it. The cited efforts used a free-standing “V”-shaped tungsten filament wrapped with a pure gold wire whose length determined the thickness of the deposit. Figure 3.12 compares the original heating arrangement with the method used by the cited investigators.

![Figure 3.12](image)

Figure 3. 12 (a) Heating arrangement in our preliminary design where gold pellets were placed in a crucible wrapped with a tungsten filament, and (b) heating arrangement cited in the literature [17-19, 21] where gold wire is wrapped on a free standing “V”-shaped tungsten coil.

We replaced our heating arrangement with a Kurt J. Lesker tungsten point source (part number EVSP5040W). Figure 3.13 shows the final version of the vacuum chamber, and Fig. 3.14 shows the final evolution of our gold-black manufacturing cell.
Figure 3.13 Final version of the vacuum chamber with its modified lid and heating source.

Figure 3.14 Final evolution of our gold-black manufacturing cell, including the turbo-molecular vacuum pump and the revised heating scheme.
3.3 Gold-Black Manufacturing Process

In this section we describe the gold-black manufacturing process in sufficient detail to allow reproduction of the results presented here. The process may be divided into two parts: substrate preparation and sample preparation.

3.3.1 Gold-Black Sample Preparation

Once confident of the modification to our gold-black manufacturing cell, we carried out a series of trial runs to establish a well-defined manufacturing protocol. Gold-black samples are produced in the vacuum chamber depicted in Fig. 3.13(a). The chamber must be carefully cleaned using denatured alcohol before each coating operation. Substrates are then taped on the downward-facing surface of the cold finger, and a 5-cm length of 0.5-mm diameter gold wire is wound around one of the “V”s of the “W”-shaped tungsten filament. The vacuum chamber is then sealed and evacuated to a pressure of $2.25 \times 10^{-5}$ torr. This hard vacuum is maintained for twelve hours to ensure the complete outgassing of oxygen, water vapor, and any other gaseous impurities. Circulation of coolant (ethylene-glycol) through the cold finger is initiated at the beginning of the evacuation process. The cold finger as well as the attached substrate segments eventually attain a temperature of -12°C.

After twelve hours of continuous pumping, ultra-pure nitrogen is slowly bled into the vacuum chamber until a pressure of $1.65 \times 10^{-2}$ torr is reached. The gate valve between the vacuum pump and the vacuum chamber is then closed to prevent backflow through the vacuum pump, and the
nitrogen flow into the chamber is then carefully metered until a final pressure of 0.645 torr is attained.

Figure 3.15 (a) Gold wire is wrapped on the tungsten filament and substrates are attached to the lower surface of the cold finger, (b) gold has melted to form a bead, (c) the onset of evaporation and gold-black formation, (d) the apparatus at the end of a gold-black manufacturing run, and (e) gold-black deposit formed on the left side of the lower surface of the cold finger and a crescent-shaped sample (a second sample originally taped on the right-hand side has been removed).

Once the desired pressure has been attained, the current flow through the tungsten filament is gradually increased at an average rate of 0.118 A/min until the gold melts and forms a bead at the bottom of the “V”, as illustrated in Fig. 3.13 (b). The maximum heating rate is set by the controller.
provided with the commercial coater to protect the tungsten filament from fusing. The maximum current capacity of the tungsten filament is about 30 A. At this heating rate a little over two hours is required to reach the melting point of gold, which occurs at a filament current of about 24 A. Once the molten bead has formed, the filament current is increased to 26 A. At this point gold evaporation and the formation of gold-black begin, as illustrated in Fig. 3.13 (c).

A period of approximately five minutes is required to completely consume the gold bead. Figure 3.13(d) shows the apparatus at the end of a production run, and Fig. 3.13(e) shows the lower surface of the cold finger with one of the samples still in place on the left-hand side. Once the production run has been completed, the tungsten filament is allowed to cool gradually by slowly reducing the current. The chiller circulating pump is turned off to allow the cold finger and gold-black to return to room temperature. Once room temperature is attained, a vacuum bleed valve is slowly opened, allowing atmospheric air to enter the chamber, after which the chamber is opened, and the gold-black samples carefully extracted and stored for later analysis.

3.3.2 Gold-Black Deposition on Various Substrates

We eventually succeeded in depositing a sufficiently thick gold-black coating on various substrates. Once the protocol for gold-black production was established, we discovered that gold-black can be deposited on any surface offering an adequate heat conduction path to the cold finger. Figure 3.14 shows successful gold-black coatings on the bare copper cold finger, cellophane tape, a microscope glass slide, and a microscope cover slide.
Figure 3. 16 Gold-black deposition on (a) the bare copper cold finger, (b) cellophane tape, (c) a microscope glass slide, and (d) a microscope cover slip.

Figure 3. 17 Gold-black deposit on (a) a microscope glass slide, and (b) SEM images at two different magnifications.

Scanning electron microscope (SEM) observations were performed to investigate the microstructure of the sample. Figure 3.15 shows two SEM images of the gold-black coating on a microscope glass slide. However, our ultimate goal is to measure the BRDF of the gold-black samples in order to determine their directional absorptivity in the visible and near-infrared. In order
to measure the BRDF, a mirror-like substrate is required that maintains its specular behavior across both wavelength ranges.

3.3.3 Substrate Preparation

Gold-black can be deposited on virtually any surface offering an adequate heat conduction path to the cold finger. Our samples were created by evaporative deposition of gold-black on a gold coated 625-µm-thick, single-side-polished, n-doped, silicon wafer (University Wafer, ID #1025). Pure silicon is an excellent conductor of heat but is partially transparent in the near-IR. Because the BRDF measurement process requires that the gold-black coating be deposited on a mirror-like surface at all wavelengths, a Plasma Vapor Depositor (Kurt J Lesker PVD Model 250) was used to lay down a uniform thin layer of pure gold on the silicon wafer. Before applying a 100-nm-thick pure gold finish layer, the wafer was first coated with a 50-nm-thick chromium layer to enhance the adherence of the gold layer. The gold-plated silicon wafer was then carefully excised into small segments using a diamond stylus. The individual segments were then cleaned using a nitrogen jet to remove dust and any chip particles that may have been created during the excising process. Once thoroughly cleaned, the substrate segments were carefully stored in a sealed container. Figure 3.16(a) exhibits the PVD facility used to deposit thin gold layer on silicon wafer, Fig. 3.16(b) shows a gold coated wafer, and Fig. 3.16(c) shows ready-to-use substrates stored in a sealed container.
Figure 3. 18 (a) PVD facility available in the Virginia Tech clean room, (b) a gold coated silicon wafer, and (c) gold coated substrates stored in a sealed container.

3.4. Chapter Summary

In the absence of a suitable off-the-shelf gold-black manufacturing cell, we successfully modified a commercially available gold-mirror coater for use as a gold-black manufacturing cell. We established a standard protocol in sufficient detail to allow production of gold-black using our cell, and demonstrated that gold-black can be deposited on any suitable substrate.
Chapter 4: First-Principle Model for the Directional Spectral Absorptivity of Gold-Black in the Near Infrared

In this chapter, we present an original lossy antenna theory for predicting the directional spectral absorptivity of gold-black. This chapter is adapted with minor changes from the article “First-principle Model for the Directional Spectral Absorptivity of Gold-Black in the Near Infrared” by the author and her co-advisors published in the Journal of the Optical Society of America (Vol. 36, No. 10, pp. 1675-1689, October 2019).

4.1 Manufacture and Micro-Morphology of Gold-Black Coatings

Figure 4.1 shows a putative gold-black manufacturing cell. Pure gold pellets are melted and evaporated in a vacuum chamber back filled with low-pressure pure nitrogen. Gold atoms are ejected from the crucible with an upward momentum depending on the evaporation rate. Their upward motion is moderated by collisions with nitrogen atoms until they are decelerated to the point that their further motion is diffusion dominated. In a well-conceived gold-black
manufacturing cell, the transition from momentum-dominated flow to diffusion-dominated flow occurs as the gold atoms cross the imaginary surface represented by the uppermost dashed line in Fig. 4.1(a). This paradigm emphasizes the importance of the nitrogen fill gas, without which the gold atoms could follow straight-line paths to the walls of the vacuum chamber where they would condense to form a mirror-like coating. In our experience fabricating gold-black layers using the cell in Fig. 4.1(b), we observe the formation of mirror-like coatings on the downward-facing surface of the cold finger while gold-black coatings form on the upward facing surface. Our subsequent experience, described in detail in Chapter 3, confirms that it is an extremely delicate operation to identify the combination of evaporation rate, nitrogen back pressure, and crucible-to-cold-finger spacing required to place this transition surface exactly where it needs to be to produce a gold-black coating having the desired spectral absorptivity.

![Schematic representation and photo of a gold-black manufacturing cell.](image)

Figure 4.1 (a) Schematic representation and (b) photo of a gold-black manufacturing cell.

Previous attempts to predict the spectral absorptivity of gold-black have been informed by the various investigators’ perception of the layer microstructure [17, 18, 20, 22, 30, 31, 32, 33, 41, 43]. Extant models can be divided into two categories: (1) those for which the microstructure
features are assumed to be small compared to the wavelength of incident radiation [17, 18, 22, 33], and (2) those for which the microstructure dimensions are assumed to be on the order of the wavelength considered [20, 30, 32]. In the former case the detailed geometry of the microstructure is deemed unimportant and gold-black is treated as a homogeneous material possessing effective bulk optical properties, while in the latter case the observed microstructure plays an essential role. Recently it has become possible to micro- and even nano-engineer the surface structure of gold-black layers to achieve a desired spectral absorptivity [41, 43]; however, the current contribution deals only with traditional diffusion-deposited gold-black layers.

The micro-morphology of a gold-black layer depends on many factors including the species and partial pressure of the back-fill gas, gold purity and evaporation rate, the temperature and chemistry of the substrate upon which it is deposited, and the geometry of the vacuum chamber in which it is manufactured. Gold-black layers have been variously described as consisting of isolated spheres of various diameters suspended in a non-participating medium [32], as loosely connected strings or aggregations of spheres with gaps and having a “wad-like” appearance [32], and as a collection of cauliflower-like structures [44]. The variability in these descriptions may be a consequence of the spatial resolution of available images, as suggested by the sequence in Fig. 4.2 [35]. While Fig. 4.2(a) resembles an aerial photograph of a forest canopy, Figs. 4.2(b) and 4.2(c) resemble close-up photographs of moss, even though all three images are scanning electron microscope (SEM) images of the same sample obtained at different magnifications. The images in Figs. 4.3(a) – (c) were obtained at the same magnification but for different gold evaporation rates. Many micrographs of gold-black layers may be found in the literature, of which the images in Fig. 4.2 [35] and 4.3 [23] are typical examples.
Figure 4. 2 Scanning electron microscope (SEM) images of the same gold-black layer obtained at three different magnifications; (a) ×500, (b) ×2000, and (c) ×5000 [35]

Figure 4. 3 SEM images obtained at the same magnification of three different gold-black layers created using different gold evaporation rates; (a) 25 µg/s, (b) 0.5 µg/s, and (c) 0.4 µg/s [23].

During the formation of gold-black, gold atoms migrate by diffusion until they come into contact with a sufficiently cold surface, at which point they sublimate from the vapor phase to the solid phase, forming the wispy filament-like structures shown in Figs. 4.2 and 4.3. In order for this to happen, cooling must occur at a vapor pressure below the triple point of gold; otherwise, condensation to the liquid phase forms a smooth mirror-like surface. It is possible—perhaps even probable—that gold atoms will collide with each other as they approach a cooled surface. When this happens at a sufficiently low temperature, the atoms will coalesce to form small gluey gold
globs which build up on the surface as a kind of “gold sleet.” We may hypothesize that this produces the form of gold-black referred to by some authors as consisting of isolated spheres of various diameters suspended in a non-participating medium [32], as loosely connected strings or aggregations of spheres with gaps and having a “wad-like” appearance [33], or as a collection of cauliflower-like structures [44]. In our gold-black manufacturing experiments we strive to attain conditions that produce the moss-like layers depicted in Figs 4.2 and 4.3, because we believe that, for a given layer thickness, they will produce a higher absorptivity at a given wavelength.

Images such as those appearing in Figs. 4.2 and 4.3 suggest that gold-black consists of a wispy, fractal-like aggregation of individual gold filaments reminiscent of hoarfrost or moss. In a previous contribution [45], we present a finite-difference time-domain (FDTD) lossy dipole antenna model for the conversion of incident electromagnetic (EM) radiation to sensible heat within a single gold filament. Here we hypothesize that the aggregate absorptivity of a gold-black layer can be interpreted as the appropriately combined effect of the individual absorptivities of a statistically representative population of these filaments. Examples of a similar approach may be found in two recent contributions [46, 47] in which millimeter-scale metallic thin-film antennas were created by electrodepositing metal ions on dielectric substrates, resulting in tree-like random fractal structures. In the cited articles the reflection coefficient spectra of these millimeter-wave antennas were subsequently measured in an anechoic chamber and shown to be in good agreement with predicted spectra. Such direct confirmation of the model proposed here for gold-black is, of course, not possible because of the microscopic size of the antenna elements. However, indirect confirmation should be possible by comparing predicted and measured overall gold-black layer directional spectral absorptivity spectra.
4.2 Model for the Absorption of EM Radiation by a Single Gold-Black Filament

Figure 4.4 illustrates the physical models which form the basis for the FDTD lossy dipole antenna model previously reported in Ref. 45. Figure 4.4(a) represents a cylindrical strand of gold filament of length $L = \Delta x(K - 1)$ and effective cross-sectional area $A_e$ consisting of $K$ discrete volume elements of individual length $\Delta x$, and Fig. 4.4(b) represents a nodal network consisting of a linear array of low-pass filters consisting of series resistors and shunt capacitors. This latter network is based on standard lossy transmission line theory in which inductance has been neglected. The FDTD form of the Helmholtz wave equation based on Fig. 4.4(a) is [18]

$$E_k^{p+1} = \frac{\Delta t^2}{n_1^2} \left[ \frac{E_{k+1}^p + 2E_k^p + E_{k-1}^p}{\Delta x^2} \right] + 2E_k^p - E_k^{p-1}, \tag{4.1}$$

where $E$ is the electric field strength, $T \equiv c_0 t/L$ is dimensionless time, $X \equiv x/L$ is dimensionless position, $n_1$ is the real part of the complex refractive index, the subscript $k$ is the node number, and the superscript $p$ represents the time step of size $\Delta t$. When using the explicit formulation, we must impose a stability condition. In general, the stability condition (Courant condition) for the wave equation is [48]

$$\Delta t \leq \frac{\Delta}{c\sqrt{d}}, \tag{4.2}$$

where $d = 1, 2$ or $3$, respectively, for one-, two- or three-dimensional problems, and $\Delta$ is the smallest cell size. So, for the one-dimensional case considered here, the stability condition becomes

$$\Delta t \leq \frac{n_1 \Delta x}{c_0}, \tag{4.3}$$
or, in terms of the dimensionless parameters,

\[
\frac{\Delta T \ell}{c_0} \leq \frac{n_1 \Delta X \ell}{c_0}, \quad (4.4)
\]

or, finally

\[
\Delta T \leq \Delta X n_1. \quad (4.5)
\]

Substituting Eq. (4.5) into Eq. (4.1) and rearranging yields

\[
E_{k}^{p+1} = E_{k+1}^{p} + E_{k-1}^{p} - E_{k}^{p-1}. \quad (4.6)
\]

Figure 4. 4 Physical models for a single strand of gold filament forming the basis for (a) the finite-difference time-dependent (FDTD) solution of the one-dimensional lossless wave equation, and (b) the corresponding lossy transmission line model.

We next consider the case in which some of the energy associated with the initial electric field is converted into sensible heat according to Joule’s law, while the remaining energy is temporarily stored in the capacitance of the strand. Equation (4.6) is not applicable in such a “lossy” medium,
and so an FDTD formulation based on the physical model in Fig. 4.4(b) must be used instead. Applying Kirchhoff’s current law at node \( k \) for time step \( p \), we have

\[
i_{k-1\rightarrow k}^p + i_{c}^p = i_{k\rightarrow k+1}^p \quad \text{(C/s)}, \tag{4.7}
\]

where \( i_{k-1\rightarrow k}^p \) is the current from node \( k - 1 \) to node \( k \), \( i_{c}^p \) is the current from the capacitor, and \( i_{k\rightarrow k+1}^p \) is the current from node \( k \) to node \( k + 1 \). Equation (4.7) can be expressed in terms of electrical potential \( V \) (V) as

\[
\frac{V_{k-1}^p - V_k^p}{R} + C \frac{\Delta V_C}{\Delta t} = \frac{V_k^p - V_{k+1}^p}{R}, \tag{4.8}
\]

where \( R \) (V·s/C) is the electrical resistance of the strand segment, \( \frac{\Delta V_C}{\Delta t} \) (V/s) is the average rate of change of electrical potential difference across the capacitor during time step \( p \), \( C \) (C/V) is the capacitance of the shunt capacitor, and \( V_{k-1}^p, V_k^p, \) and \( V_{k+1}^p \) are the instantaneous electrical potential differences, with respect to ground, at nodes \( k - 1, k \) and \( k + 1 \), respectively. Then in terms of the electric field strength \( E \) (V/m), Eq. (4.8) can be written

\[
\frac{\Delta x(E_{k-1}^p - E_k^p)}{R} + C \frac{\Delta x(\Delta E_C)}{\Delta t} = \frac{\Delta x(E_k^p - E_{k+1}^p)}{R}, \tag{4.9}
\]

Or

\[
\frac{(E_{k-1}^p - E_k^p)}{R} + C \frac{(E_k^p - E_{k+1}^p)}{\Delta t} = \frac{(E_k^p - E_{k+1}^p)}{R}, \tag{4.10}
\]

where the superscript “\( p + 1 \)” indicates the electric field at the end of the time step \( p \). Multiplying both sides of the equation by \( R \) yields

\[
(E_{k-1}^p - E_k^p) + R C \frac{(E_k^p - E_{k+1}^p)}{\Delta t} = (E_k^p - E_{k+1}^p), \tag{4.11}
\]
or, upon rearranging,

\[ E_k^{p+1} = \left( 1 - 2 \frac{\Delta t}{RC} \right) E_k^p + \frac{\Delta t}{RC} \left( E_{k-1}^p + E_{k+1}^p \right). \] (4.12)

If the real part of the complex electrical conductivity of the gold is \( \sigma_1 \) (C/V·m·s) and the real part of the complex dielectric function of gold is \( \varepsilon_1 = \varepsilon_0 |\varepsilon_{r_1}| \) (C/V·m), where \( |\varepsilon_{r_1}| \) is the modulus of the real part of the complex relative dielectric function and \( \varepsilon_0 = 8.854 \times 10^{-12} \) C/V·m, the dielectric function of free space, then for an electrical element of effective cross-sectional area \( A_e \) and length \( \Delta x \), we have

\[ R = \frac{\Delta x}{\sigma_1 A_e} \] (4.13)

and

\[ C = \frac{|\varepsilon_1| A_e}{\Delta x}, \] (4.14)

or

\[ RC = \left( \frac{\Delta x}{\sigma_1 A_e} \right) \left( \frac{|\varepsilon_1| A_e}{\Delta x} \right) = \frac{|\varepsilon_1|}{\sigma_1}. \] (4.15)

Note that the effective cross-sectional area divides out; that is, the filament diameter apparently plays no explicit role in the model. The justification for this subtle step lies at the heart of the Drude-Sommerfeld free-electron theory, according to which the interaction between an electrically conducting medium submerged in an electromagnetic (EM) field is limited to a thin layer of “free” electrons near the surface. We consider two possibilities in the case of our cylindrical filament: either (a) the radius is sufficiently small that the surrounding EM field penetrates all the way to the center, or (b) the filament can be divided radially into two regions; the “skin” in which interaction occurs, and the “core” in which no interaction occurs. In either case an effective cross-sectional area can be defined as the cross-sectional area in which free electrons are accelerated by
the EM field, and in both cases the effective cross-sectional area divides out. We return to this question and its possible ramifications later in the article; however, for now let us assume that the filament radius is sufficiently small to assure that all electrons in a given cross-section are accelerated equally by the local electric field. Substitution of Eq. (4.15) into Eq. (4.12) yields

\[ E_{k}^{p+1} = \left(1 - 2 \frac{\sigma_1 \Delta t}{|\varepsilon_1|}\right)E_{k}^p + \frac{\sigma_1 \Delta t}{|\varepsilon_1|} \left(\frac{E_{k-1}^p + E_{k+1}^p}{\varepsilon} \right) . \]  

(4.16)

We find that the value of \( \Delta t \) in Eq. (4.16) is limited by the stability condition, represented by Eq. (4.5), and already imposed when formulating the lossless wave equation. This is required by our unique time-splitting approach to including loss in the wave equation. Then replacing \( \Delta t \) with \( \Delta x \frac{n_1}{c_0} \), we have

\[ E_{k}^{p+1} = \left(1 - 2 \frac{\sigma_1 \Delta x n_1}{|\varepsilon_1|c_0}\right)E_{k}^p + \frac{\sigma_1 \Delta x n_1}{|\varepsilon_1|c_0} \left(\frac{E_{k-1}^p + E_{k+1}^p}{\varepsilon} \right) . \]

(4.17)

In order to assure stability, the factor \( 2 \frac{\sigma_1 \Delta x n_1}{|\varepsilon_1|c_0} \) must be less than or equal to unity. The value of \( \frac{\sigma_1 n_1}{|\varepsilon_1|c_0} \) is fixed for a particular metal at a given wavelength. Therefore, the only parameter that can be varied to obtain a stable solution is \( \Delta x \), whose value determines the number of spatial nodes in a given filament of length \( L \).

Our strategy for including loss in the wave equation is to solve Eqs. (4.6) and (4.17) simultaneously, while alternating between the two equations. This explains why the time step \( \Delta t \) in Eq. (4.17) is limited by the same value as in Eq. (4.6). When modeling a lossy medium corresponding to a certain time step \( p \), the first half of the time step uses Eq. (4.6), while in the second half of the time step Eq. (4.17) is used, with the output of the first time half-step introduced
as the input to the second time half-step. In summary, for a given time step $p$ and a given node position $k$

$$E_k^{p+\frac{1}{2}} = E_k^p + E_k^{p-\frac{1}{2}}$$

(4.18)

and

$$E_k^{p+1} = (1 - 2M)E_k^{p+\frac{1}{2}} + M\left(E_k^{p+\frac{1}{2}} + E_k^{p+\frac{1}{2}}\right),$$

(4.19)

where

$$M = \frac{\sigma_1 \Delta \nu n_1}{|\epsilon_1| \epsilon_0}.$$  

(4.20)

We believe this time-splitting approach to solving the lossy wave equation to be novel.

The Drude-Sommerfeld free-electron theory, which assumes that photons interact with free electrons in a thin layer at the surface of a conducting medium, causing them to accelerate independently with an effective mass $m_e$, leads to the following approximations for, respectively, the complex relative dielectric function, the complex refractive index, and the complex electrical conductivity [49]:

$$\epsilon_r(\omega) = \epsilon_{r_1}(\omega) + i\epsilon_{r_2}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega/\tau_D},$$

(4.21)

$$n(\omega) = n_1(\omega) + in_2(\omega) = \sqrt{\epsilon_r(\omega)},$$

(4.22)

and

$$\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega) = -i\epsilon_0 \omega[\epsilon_r(\omega) - 1];$$

(4.23)

where $\omega = 2\pi c_0/\lambda_0$ ($\text{r/s}$) is the angular frequency and $i \equiv \sqrt{-1}$. The speed of light in a vacuum $c_0$ is taken to be $2.9979 \times 10^8 \text{ m/s}$ and $\lambda_0$ (m) is the wavelength in a vacuum. In Eq. (4.21), $\omega_p = \sqrt{N_e e^2/m_e \epsilon_0}$ ($\text{r/s}$) is the plasma frequency and $\tau_D = \sigma_0 m_e/N_e e^2$ (s) is the electron
Figure 4. Real parts of (a) the dielectric function, (b) the refractive index, and (c) the electrical conductivity of single-crystal pure gold (Experimental results replotted from Ref. 49).
relaxation time, where \( N_e \) is the electron number density, \( e = 1.602 \times 10^{-19} \) C is the electron charge, and \( \sigma_0 = 4.10 \times 10^7 \) C\( \cdot \)V\(^{-1}\)\( \cdot \)m\(^{-1}\)\( \cdot \)s\(^{-1}\) is the direct-current (\( \lambda \to \infty \)) electrical conductivity.

According to Olmon et al. [49, Fig. 9] the skin depth of pure gold is on the order of 25-30 nm in the near infrared. Inspection of Figs. 4.2 and 4.3 suggests that the radius of the gold filaments in our study might well lie in this range. Absent the availability of more precise SEM images, uncertainty must necessarily remain in the value of \( m_e \) to be used in the expressions for the plasma frequency and relaxation time. However, in the cited contribution the authors found that values of \( \omega_p = 1.2914 \times 10^{16} \) rs\(^{-1}\) (converted from units of eV) and \( \tau_D = 14 \times 10^{-15} \) s provide a reasonably good fit of Eqs. (4.21) – (4.23) to their experimental results, as demonstrated in Fig. 4.5. Therefore, we use these values of \( \omega_p \) and \( \tau_D \) to compute \( \varepsilon_1(\omega) \), \( n_1(\omega) \), and \( \sigma_1(\omega) \) for use in our model. Figures 4.5(b) and 4.5(c) make it clear that Drude theory cannot be used with acceptable accuracy in the visible part of the EM spectrum for single-crystal gold, but that it is adequate in the near infrared, at least out to about 7 \( \mu m \). It is likely that the model elaborated in the current contribution can be extended into the visible and further into the infrared using experimental values of the optical and electrical properties rather than those based on Drude theory.

### 4.3 Spectral Absorptivity of a Single Gold-Black Filament

The lossy antenna theory developed in Section 4.2 may now be used to compute the spectral absorptivity of individual gold-black filaments in the near infrared (0.7 to 7.0 \( \mu m \)). We seek a general expression for the linearly polarized spectral absorptivity \( \alpha_L(\lambda) \) at wavelength \( \lambda \) of a single
filament of length $L$. In other words, we assume for the moment that the filament is aligned with the incident electric field. If this is not the case, for example, if the electric field vector and the axis of the filament intersect at an angle $\theta$, then the effective length of the filament is $L \cos \theta$. Our approach is to solve Eqs. (4.18) and (4.19) simultaneously for a range of gold-black filament effective lengths $L$ and wavelengths $\lambda$ and then tease a suitable correlation out of the results obtained. The filament effective lengths and wavelengths investigated and the corresponding material properties are summarized in Table 4.1. In each case the value of the real part of the electrical conductivity, the refractive index, and the relative permittivity of pure gold is based on the Drude-Sommerfeld free-electron theory, with the speed of light in a vacuum taken to be $c_0 = 2.9979 \times 10^8$ m/s and the permittivity of free space taken to be $\varepsilon_0 = 8.854 \times 10^{-12}$ C/V\cdot m. One thousand length-wise nodes are used to represent each filament. The initial condition for the solution of Eqs. (18) and (19) in each case is

$$E(x, t = 0)/E_{\text{max}} = \sin \left( \frac{2\pi x}{L} \right) + \sin \left( \frac{2\pi x}{2L} \right) + \sin \left( \frac{2\pi x}{4L} \right).$$

(4.24)

Figure 4.6 The initial condition for all cases.
The form of the initial condition, illustrated in Fig. 4.6, is chosen to demonstrate the ability of the model to describe the system response to complex waveforms. In principle, we can construct any initial condition waveform using a truncated Fourier series representation with a sufficient number of terms. When considered in its component parts, the initial condition in Eq. (4.24) and Fig. 4.6 consists of the sum of quarter-wave, half-wave, and full-wave excitations of the gold filament. This facilitates numerical solution of the model because the boundary conditions at each end of the filament at each wavelength are then either the Dirichlet (both boundaries for the half-wave and full-wave components and the left-hand boundary for the quarter-wave component) or Neumann (for the right-hand boundary of the quarter-wave component) type. The filament lengths considered fall within the range of observed gold-black micro-morphology and the wavelengths correspond to those for which monopole and dipole antennas are known to be the most efficient.

Figure 4.7 shows the evolution of the electric field in the filament with time for $L = 1.0 \, \mu m$, which is a representative filament length in gold-black structures. With the passage of time the waveform is seen to evolve from that of the initial condition shown in Fig. 4.6, which is composed of all three components, to a nearly flat horizontal line as the higher frequency (shorter wavelength) components are successively damped out by absorption within the filament. Damping is observed to occur very rapidly, with complete damping being achieved in this case after only about one-third of a nanosecond, corresponding to about 10,000 cycles of 1.0-\mu m light. Figure 4.7 was constructed by first solving Eqs. (4.18) and (4.19) for each of the three wavelength components of the initial condition and then summing the electric fields at each node after each time step.
Figure 4.7 Decay of the initial EM wave within the gold-black filament ($L = 1.0 \, \mu m$).

Figure 4.8 features plots of the positive peak value of the relative electric field as a function of time corresponding to the decay of the three wavelength components within filaments of six different lengths. The symbols in each plot are values obtained from the solution of Eqs. (4.18) and (4.19) subject to quarter-wave, half-wave, and full-wave excitation, and the curves correspond to the exponential expressions appearing next to each curve. The excellent fit of these curves to the symbols establishes that absorption is a first-order phenomenon. The corresponding relaxation times $\tau_R$, which are the reciprocal of the numbers multiplying the symbol $t$ in these relations; i.e.,

$$\frac{E}{E_{max}} = e^{-t/\tau_R},$$

where $\tau_R$ is the relaxation time.

Inspection of Fig. 4.8 and Table 4.1 reveals that the relaxation time essentially depends only on wavelength, with very slight variation with filament length.
Figure 4. Exponential decay of quarter-wave, half-wave, and full-wave excitation of gold-black nanofibers for filament effective lengths (a) 0.7, (b) 0.9, (c) 1.1, (d) 1.4, (e) 1.6, and (f) 1.7 μm. The symbols correspond to solution of Eqs. (18) and (19), and the curves are exponential fits to the symbols.
Table 4.1 Results for relaxation time $\tau_R$ and single-filament spectral absorptivity $\alpha_f(\lambda)$ based on solution of Eqs. (4.18) and (4.19).

<table>
<thead>
<tr>
<th>Wavelength $\lambda$ (µm)</th>
<th>Real Part of Refractive Index $n_1$ (Drude Theory)</th>
<th>Negative Real Part of Relative Permittivity $\varepsilon_r,1$ (Drude Theory)</th>
<th>Real part of Electrical Conductivity $\alpha_1$ (Drude Theory)</th>
<th>$M = \frac{\varepsilon_1 \Delta n_1}{\varepsilon_1 - \varepsilon_0}$</th>
<th>Calculation Time Step (10$^{-8}$ s)</th>
<th>Relaxation Time, $\tau_R$ (ns)</th>
<th>Single-Filament Spectral Absorptivity, $\alpha_f(\lambda)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>0.065095</td>
<td>22.0146</td>
<td>14555.1</td>
<td>0.00011342</td>
<td>1.518</td>
<td>0.006784</td>
<td>0.000688</td>
</tr>
<tr>
<td>1.4</td>
<td>0.255721</td>
<td>90.8645</td>
<td>58097.7</td>
<td>0.00043089</td>
<td>5.966</td>
<td>0.028066</td>
<td>0.000333</td>
</tr>
<tr>
<td>2.8</td>
<td>1.013369</td>
<td>363.385</td>
<td>230447.9</td>
<td>0.00169359</td>
<td>23.64</td>
<td>0.111756</td>
<td>0.000167</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filament Length = 0.70 µm (Δx = 0.70 × 10$^{-8}$ m)</td>
<td>0.8</td>
<td>0.084562</td>
<td>29.0534</td>
<td>19006.6</td>
<td>2.255</td>
<td>0.006858</td>
<td>0.000778</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filament Length = 0.80 µm (Δx = 0.80 × 10$^{-8}$ m)</td>
<td>0.8</td>
<td>0.084562</td>
<td>29.0534</td>
<td>19006.6</td>
<td>2.255</td>
<td>0.006858</td>
<td>0.000778</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filament Length = 1.00 µm (Δx = 1.00 × 10$^{-8}$ m)</td>
<td>1.1</td>
<td>0.158515</td>
<td>55.7733</td>
<td>35905.0</td>
<td>5.812</td>
<td>0.006973</td>
<td>0.001052</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filament Length = 1.10 µm (Δx = 1.10 × 10$^{-8}$ m)</td>
<td>1.2</td>
<td>0.188338</td>
<td>66.5426</td>
<td>42715.9</td>
<td>7.5353</td>
<td>0.006998</td>
<td>0.001146</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filament Length = 1.20 µm (Δx = 1.20 × 10$^{-8}$ m)</td>
<td>1.2</td>
<td>0.188338</td>
<td>66.5426</td>
<td>42715.9</td>
<td>7.5353</td>
<td>0.006998</td>
<td>0.001146</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filament Length = 1.30 µm (Δx = 1.30 × 10$^{-8}$ m)</td>
<td>1.3</td>
<td>0.220741</td>
<td>78.2404</td>
<td>50113.8</td>
<td>9.56547</td>
<td>0.007007</td>
<td>0.001238</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filament Length = 1.40 µm (Δx = 1.40 × 10$^{-8}$ m)</td>
<td>1.4</td>
<td>0.255721</td>
<td>90.8645</td>
<td>58097.7</td>
<td>11.9337</td>
<td>0.007017</td>
<td>0.001331</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filament Length = 1.50 µm (Δx = 1.50 × 10$^{-8}$ m)</td>
<td>1.5</td>
<td>0.293274</td>
<td>104.4128</td>
<td>66666.1</td>
<td>14.6637</td>
<td>0.007027</td>
<td>0.001424</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filament Length = 1.60 µm (Δx = 1.60 × 10$^{-8}$ m)</td>
<td>1.6</td>
<td>0.333395</td>
<td>118.8831</td>
<td>75817.5</td>
<td>17.7811</td>
<td>0.007032</td>
<td>0.001518</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filament Length = 1.70 µm (Δx = 1.70 × 10$^{-8}$ m)</td>
<td>1.7</td>
<td>0.376081</td>
<td>134.2729</td>
<td>85550.4</td>
<td>21.3113</td>
<td>0.007042</td>
<td>0.001610</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filament Length = 1.80 µm (Δx = 1.80 × 10$^{-8}$ m)</td>
<td>1.8</td>
<td>0.418628</td>
<td>152.456</td>
<td>1047.909</td>
<td>26.772</td>
<td>0.007052</td>
<td>0.001706</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filament Length = 1.90 µm (Δx = 1.90 × 10$^{-8}$ m)</td>
<td>1.9</td>
<td>0.462499</td>
<td>170.8645</td>
<td>1248.75</td>
<td>32.225</td>
<td>0.007062</td>
<td>0.001798</td>
</tr>
</tbody>
</table>
We seek a correlation for the relaxation time $\tau_R$ in terms of the governing parameters. The availability of such a correlation would obviate the need to solve Eqs. (4.18) and (4.19) for every combination of filament length and wavelength of interest. The data in Table 1 yield the correlation

$$\frac{\sigma_1 \tau_R}{|\varepsilon_1|} \left( \frac{L}{\lambda} \right)^2 = 504.88,$$

with a standard deviation of 2.51, or 0.5 percent. The ratio $|\varepsilon_1|/\sigma_1$ is essentially constant in the near infrared, and so for all practical purposes the relaxation time depends only on the ratio of wavelength to filament length. The relaxation time is independent of $n_1$, the real part of the refractive index. We conclude that, because the real part of the complex electrical conductivity $\sigma_1$ and the magnitude of the real part of the dielectric function $\varepsilon_1$ are known functions of wavelength from Drude theory, Eq. (4.25) can be used to compute the relaxation time for any combination of filament length and wavelength in the near infrared.

We are now ready to determine the absorptivity $\alpha_L(\lambda)$ of a single filament of effective length $L$ at wavelength $\lambda$. The initial condition in the lossy antenna model of Section 3 represents the part of the incident wave that is not scattered; i.e., the part that is “captured” by the filament and ultimately converted to sensible heat. It is convenient to treat the constant rate of EM energy captured by the filament as if it is due to a sequence of individual waves, each with wavelength $\lambda$, imposed at intervals of time equal to the wave period $T = \lambda/c_0$. The power associated with each of these captured waves is then $\overline{E_0^2}/T$, where the overbar indicates an average over the filament length.
Figure 4.9 Evolution with time of the EM energy remaining in a filament of length $L = 0.75 \, \mu m$ for wavelength $\lambda = 1.5 \, \mu m$.

Figure 4.9, which is based on the EM energy conversion model presented in Section 3, shows the evolution with time of the EM energy remaining in the filament of length $L = 0.75 \, \mu m$ for wavelength $\lambda = 1.5 \, \mu m$. The difference between the EM energy captured due to one wave and the associated EM energy remaining in the filament at time $t$ is the energy that has been converted to sensible heat during the time interval $0 \rightarrow t$. Note that re-radiation, or scattering, has already been accounted for in the initial condition. We see from the plot, which is typical of all the cases considered, that the rate of conversion of EM energy to heat decreases exponentially with time; i.e.,

$$
\frac{d}{dt} \left[ \frac{E_0^2}{\tau_A} (1 - e^{-t/\tau_A}) \right] = \frac{1}{\tau_A} E_0^2 e^{-t/\tau_A}.
$$

(4.27)
We know that all of the captured EM energy associated with each wave must ultimately be absorbed, but this does not mean that the single-filament absorptivity is unity. At time $t = 0$, the instantaneous rate of capturing EM energy is $E_0^2 / T$, and the instantaneous rate of conversion of EM energy into sensible heat is $E_0^2 / \tau_A$. The fraction of the initial energy converted to heat during the period $0 \leq t \leq \tau_A$ is $T(1 - b) / \tau_A$, where $b = e^{-1} \approx 0.3679$, the fraction captured during the period $\tau_A \leq t \leq 2\tau_A$ is $T(b - b^2) / \tau_A = T(1 - b) b / \tau_A$, and so forth. Then by inductive reasoning we have

$$\alpha_L(\lambda) = T \left[ (1 - b) + (1 - b) b + \cdots + (1 - b) b^i + \cdots \right] / \tau_A = \left( \frac{T}{\tau_A} \right) \left( 1 - b \right) \sum_{i=0}^{\infty} b^n$$

$$= T / \tau_A.$$  \hfill (4.28)

Finally, noting that $\tau_R = 2 \tau_A$, Eqs. (4.25) and (4.27) can be combined to yield

$$\alpha_L(\lambda) = 0.00396 \left( \frac{\sigma_1}{c_0 |\varepsilon_1|} \right) L^2 / \lambda,$$  \hfill (4.29)

or, upon introduction of the constant values $c_0$ and $\sigma_1 / |\varepsilon_1|$,

$$\alpha_L(\lambda) = 0.0009513 L^2 / \lambda.$$  \hfill (4.30)
Figure 4. 10 Variation of the single-filament spectral absorptivity with filament length and wavelength predicted using Eq. (4.29).

Figure 4.10 shows typical results obtained using Eq. (4.29) when the incident electric field vector is aligned with the filament axis.

4.4 Conversion of Single-Filament Spectral Absorptivity into Gold-Black Layer Directional Spectral Absorptivity

We now seek a model for converting gold-black single-filament spectral absorptivity into directional spectral absorptivity for a gold-black layer. This requires a realistic statistical description of the gold-black fractal tree structure. The diffusion of gold atoms through nitrogen is governed by the Laplace equation, \( \nabla^2 D_{Au} = 0 \), where \( D_{Au} \) is the local number density of gold atoms in the diffusion-dominated region of Fig. 4.1(a). Note that the Laplace equation does not involve a diffusion coefficient; it holds for the diffusion of any chemical species. Assuming that
the concentration of the species of interest is known at the region boundaries, solution of the Laplace equation by any means provides the concentration distribution within the region. Furthermore, any process governed by the Laplace equation may be simulated using a random walk on an appropriate grid [50]. Diffusion-limited aggregation (DLA) is the name given to a numerical process in which particles undergo a random walk, usually on a rectangular grid, and eventually aggregate to form random fractal-like structures [51, 52]. The widespread success of models based on DLA may be attributed to the fact that it correctly describes the underlying physics governing diffusion. We hypothesize that a morphologically correct model for gold-black layer micro-structure can be formulated based on DLA. While DLA has been mentioned elsewhere as a possible approach for simulating the formation of gold-black [52], the authors can find no reference in the literature to this actually having been done.

Figure 4. 11 DLA simulation of gold-black dendrite growth generated by five million walkers on a two-dimensional rectangular grid using six different random number sequences.
Consider a 1000-by-100 two-dimensional rectangular grid with the bottom row of grid points initially fully populated with nucleation sites. A walker released at a random grid point along the top edge is allowed to wander aimlessly from grid point to grid point, randomly turning north, south, east or west at each successive intersection until it eventually reaches a grid point occupied by either a nucleation site or a previous walker that has come to rest there. At this point the walker takes one step backward along its path and itself comes to rest. This is the aggregation rule. The six panels in Fig. 4.11 display the results obtained by tracing 5 million gold atoms per panel using six different random number sequences. The size scale in the figure is arbitrary, but comparison with Fig. 4.2 suggests that the horizontal spacing between the individual “trees” making up the “forest” is on the order of a few micrometers.

Figure 4.11 can be interpreted as six views from different directions of the same three-dimensional forest. It is then natural to refer to the larger composite structures making up the trees as “branches” and the straight horizontal and vertical segments making up the branches as “twigs.” While the twigs on the branches of real trees can be oriented in any direction, those formed by the DLA algorithm are constrained to form on a Cartesian grid. In spite of this limitation on twig growth, the direction of growth of the branches is somewhat random. While recognizing that a real gold-black layer would be more densely populated, we may conclude that the images in Fig. 4.11 correctly represent the statistics of a gold-black layer formed by the diffusion and subsequent sublimation processes described in Section 4.2.
Figure 4.12 is a plot of the frequency of occurrence of a given filament length for each filament in Fig. 4.11. Each symbol plotted in Fig. 4.12 corresponds to one of the six viewing directions in Fig. 4.11. The “filament length” label on the horizontal axes in Fig. 4.12 refers to the number of horizontal or vertical spaces between the grid points at which a change in direction of a walker occurs. This distance is the “effective length” of the various dipole antenna elements represented by the twigs making up the branches of the trees composing the gold-black layer. At this point the units of the filament lengths are arbitrary because there remains some uncertainty about the appropriate size scale of Fig. 4.11. The tight grouping of the symbols at each filament length in Fig. 4.12 indicates that the forest of gold filaments created by the DLA algorithm is statistically stationary with respect to viewing azimuth angle \( \phi \). It follows that the directional absorptivity of the layer must be independent of azimuth angle. However, because the statistical length distributions of the horizontal and vertical antenna elements are different, the layer directional absorptivity is expected to be a function of the zenith angle \( \theta \).

![Figure 4.12 Frequency of occurrence of (a) horizontal and (b) vertical filament lengths as a function of filament length for the six views of the simulated gold-black dendrite growth fields illustrated in Fig. 4.11.](image)
The single-filament spectral absorption theory developed in Section 4 permits calculation of the rate of absorption of EM energy by a single filament of effective length $L$ and at a given wavelength $\lambda$. The single-filament absorptivity $\alpha_L(\lambda)$ has been shown to be a material property depending only on wavelength for a given length. Armed with knowledge of the single-filament spectral absorptivity and the filament length distributions $n(L)$ in the horizontal and vertical directions, it is possible to compute the directional spectral absorptivity of a coating layer.

Figure 4.13 Resolution into vertical and horizontal components of the electric field $\vec{E}$ of a p-polarized EM wave carrying power $\vec{P}$ incident to the gold-black layer with zenith angle $\vartheta$.

Figure 4.13 illustrates the resolution into vertical and horizontal components of the electric field vector $\vec{E}$ associated with a p-polarized EM wave carrying power $\vec{P}$ incident to the gold-black layer at zenith angle $\vartheta$, such that

$$\vec{E}_V(\lambda) = |\vec{E}(\lambda)| \sin \vartheta \, \vec{j} \quad (4.31)$$

And

$$\vec{E}_H(\lambda) = |\vec{E}(\lambda)| \cos \vartheta \, \vec{i} \quad (4.32)$$
The spectral power carried by the vertical component is proportional to

\[ |\vec{E}_V(\lambda)|^2 = |\vec{E}(\lambda)|^2 \sin^2 \theta, \]  

Equation (4.33)

and the spectral power carried by the horizontal component is proportional to

\[ |\vec{E}_H(\lambda)|^2 = |\vec{E}(\lambda)|^2 \cos^2 \theta. \]  

Equation (4.34)

Equations (4.32) and (4.33) represent the spectral power incident to the initial vertical and horizontal filaments encountered by the incident radiation. Upon initial incidence the first vertical filament absorbs spectral power

\[ \alpha_{Lv}(\lambda)|\vec{E}(\lambda)|^2 \sin^2 \theta \]  

Equation (4.35)

and the first horizontal filament absorbs power

\[ \alpha_{LH}(\lambda)|\vec{E}(\lambda)|^2 \cos^2 \theta. \]  

Equation (4.36)

The spectral power scattered by these two filaments is

\[ [1 - \alpha_{Lv}(\lambda)]|\vec{E}(\lambda)|^2 \sin^2 \theta \]  

Equation (4.37)

And

\[ [1 - \alpha_{LH}(\lambda)]|\vec{E}(\lambda)|^2 \cos^2 \theta. \]  

Equation (4.38)
Spectral power scattered by vertical filaments is sensed only by other vertical filaments, and spectral power scattered by horizontal filament is sensed only by other horizontal filaments. This leads to two independent absorption mechanisms for p-polarized radiation; i.e., for linearly polarized radiation whose electric field vector lies in the plane of incidence, as illustrated in Fig. 4.13. First, considering absorption by the vertical filaments, the spectral power incident to the second filament of the same length is given by Eq. (4.36) and the spectral power scattered by that filament is

\[
[1 - \alpha_{LV}(\lambda)] |\vec{E}(\lambda)|^2 \sin^2 \vartheta [1 - \alpha_{LV}(\lambda)].
\] (4.39)

Then by inductive reasoning the spectral power scattered by the \(n_{LV}\)th vertical filament of length \(L_V\) is

\[
[1 - \alpha_{LV}(\lambda)]^{n_{LV}} |\vec{E}(\lambda)|^2 \sin^2 \vartheta.
\] (4.40)

Similarly, the spectral power scattered by the \(n_{LH}\)th horizontal filament of length \(L_H\) is

\[
[1 - \alpha_{LH}(\lambda)]^{n_{LH}} |\vec{E}(\lambda)|^2 \cos^2 \vartheta.
\] (4.41)

When all of the vertical and horizontal filament lengths are taken into consideration the cumulative scattered (i.e., non-absorbed) spectral power is

\[
|\vec{E}(\lambda)|^2 \sin^2 \vartheta \prod_{n_{LV} = 1}^{N_{LV}} [1 - \alpha_{LV}(\lambda)]^{n_{LV}} + |\vec{E}(\lambda)|^2 \cos^2 \vartheta \prod_{n_{LH} = 1}^{N_{LH}} [1 - \alpha_{LH}(\lambda)]^{n_{LH}}
\] (4.42)
The absorbed spectral power is the difference between the incident and scattered spectral power; that is,

\[ \alpha(\lambda, \vartheta) |\vec{E}(\lambda)|^2 = |\vec{E}(\lambda)|^2 - |\vec{E}(\lambda)|^2 \sin^2 \vartheta \prod_{n_{LV}=1}^{N_{LV}} [1 - \alpha_{LV}(\lambda)]^{n_{LV}} \]

\[ - |\vec{E}(\lambda)|^2 \cos^2 \vartheta \prod_{n_{LH}=1}^{N_{LH}} [1 - \alpha_{LH}(\lambda)]^{n_{LH}} \]

Or

\[ \alpha(\lambda, \vartheta) = 1 - \sin^2 \vartheta \prod_{n_{LV}=1}^{N_{LV}} [1 - \alpha_{LV}(\lambda)]^{n_{LV}} - \cos^2 \vartheta \prod_{n_{LH}=1}^{N_{LH}} [1 - \alpha_{LH}(\lambda)]^{n_{LH}}. \] (4.44)

Equation (4.43) is based on three interrelated assumptions: (1) the individual dipole antenna elements are mutually independent, (2) the electric field strength initially incident to an element is independent of the embedded depth of the element within the layer, and (3) radiation scattering by re-radiation from individual elements greatly exceeds the conversion of EM energy into sensible heat (i.e., absorption). These assumptions are justified in the following paragraphs.

Wireless communication would not be possible if individual dipole antenna elements were not mutually independent. The assumption of independence among elements is valid, at least to an acceptable approximation, if the various elements (a) lie in the far fields of their neighbors, (b) are misaligned, or (c) are sensitive to a narrow wavelength band determined by their physical lengths. These, in fact, are the necessary conditions for wireless communication and explain why the
Federal Communications Commission (FCC) assigns broadcast powers and hours of operation to commercial broadcasters depending on their geographic locations, the size and directionality of their antennas, and their carrier frequencies. When considering spectral absorption in our gold-black model, we recognize that antenna elements of significantly different lengths tend not to interfere with each other even if they are near-field neighbors and well aligned. The first assumption may then be restated as follows: filaments having approximately the same length are, on the average, assumed to be sufficiently misaligned or widely spaced to be mutually independent. In principle this hypothesis could be confirmed through examination of SEM images such as those appearing in Figs. 4.2 and 4.3. However, we find ourselves in total agreement with Wang and Zhao [36], who also assume independent scattering in a similar situation because “[i]t is prohibitively complicated to calculate the dependent scattering effects for a system containing non-spherical scatters”.

The validity of the second assumption, that the incident electric field strength is uniform within a layer, can in principle be assured to any desirable degree of accuracy by subdividing the actual layer into parallel strata such that the assumption can be considered true in each stratum. This is not unlike the common practice of assuming incompressible flow in each stage when modeling the performance of a multistage compressor. Stated another way, this assumption is equivalent to replacing the local incident electric field by the average electric field in the stratum and recognizing that the resulting over-evaluation of local absorption in the lower part of the stratum is balanced by its under-evaluation in the upper half, in keeping with the mean value theorem of calculus. Then the accuracy of the resulting analysis increases as the thickness of the strata is reduced and the variation of the electric field through them becomes more linear. Finally, the second and third
assumptions together are favored by the relatively large ratio of re-radiated to absorbed power in a given filament. For example, for a wavelength of twice the filament length (corresponding to a half-wave antenna) the ratio of re-radiated power to absorbed power is about 235.5 [45]. This means that many filaments of a given length are required to obtain a significant reduction in the locally ambient electric field at a specified wavelength, a situation favoring the assumption of a uniform electric field within the layer.

Figure 4.14 (a) DLA model of a gold-black layer and distribution of (b) horizontal and (c) vertical branches in each of four equal-thickness sublayers numbered 1, 2, 3, and 4.

Figure 4.14 consists of histograms showing the distribution of horizontal and vertical branches in each of four equal-thickness strata of the DLA layer shown at the top of the figure. Equation (4.43) could in principle be applied within each stratum and the results combined to obtain the overall layer spectral absorptivity; however, the authors deem this to be an unwarranted complication in view of the adequate agreement between results obtained using the single-laminate theory presented here and measurements reported in the literature and cited in Section 4.6.
Finally, the theory developed in the current contribution does not directly include the effect of layer thickness. However, a thickness effect is implied by the number of antenna elements entering into the calculations through the length frequency data from Fig. 4.12. Presumably, the layer thickness can be related to the antenna element number density determined, for example, from SEM images of the gold-black layer or by fitting measured spectral absorptivity data to the theory.

4.5 Results and Discussion

We first consider normally incident radiation (\( \theta = 0 \)). Due to the azimuthal isotropy noted in Section 4.5, the normal spectral absorptivity is the same for both s- and p-polarization, and thus for natural radiation. Figure 4.15(a) exhibits the variation with wavelength of the normal spectral absorptivity predicted using Eqs. (4.29) and (4.43) with the values of horizontal effective filament length frequency from Fig. 4.12(a). The three curves in Fig. 4.15(a) correspond to three values of a scaling factor applied to the arbitrary filament length scale in Fig. 4.12(a) in order to convert it to micrometers. Measurements of spectral absorptivity [22, 24, 35, 36, 37, 40] and reflectivity [22, 30, 23, 24, 37, 40] of gold-black reported in the literature exhibit wavelength trends and general levels similar to the behavior exhibited in Fig. 4.15(a). Figure 4.15(b) from Nelms and Dowson [23] shows the measured normal spectral absorptivity of three different batches of gold-black whose microstructure is of the type featured in Fig. 4.2 by the same authors. The obvious similarity between Figs. 4.15(a) and 4.15(b) in the near infrared invites speculation that extant published results can be fitted to the theory developed in the current contribution by appropriate adjustment of the filament length scaling factor. The observed differences among the various published results,
including the three curves in Fig. 4.15(b), are attributable to differences in layer thickness and the details of coating preparation.

Figure 4.15 (a) Normal ($\theta = 0$) spectral absorptivity of gold-black as predicted using Eqs. (4.29) and (4.43) with the horizontal effective length frequency data from Fig. 4.12(a), and (b) experimental results obtained by Nelms and Dowson [23].

Confidence in the theory presented here is further enhanced by Fig. 4.16, which compares the predicted normal spectral absorptivity of gold-black and the relative response of a gold-black-coated pyroelectric detector as measured by Lehman et al. [24]. In this case a filament length multiplier of 1.2 $\mu$m has been applied to the horizontal axis in Fig. 4.12(a) to obtain excellent agreement between theoretical and measured results.
Figure 4. 16 Relative response of a gold-black-coated pyroelectric detector as measured by Lehman et al. [24] (symbols) compared with the theoretical response (curve) predicted using the current theory.

Finally, Fig. 4.17(a) is a plot of predicted directional spectral absorptivity for gold-black as a function of wavelength for a range of incident zenith angles for the case of p-polarized incident radiation, and Fig. 4.17(b) is a cross-plot of these same results. Figure 4.17(c) is a plot of predicted directional spectral absorptivity for gold-black as a function of wavelength for a range of incident zenith angles for the case of non-polarized incident radiation, and Fig. 4.17(d) is a cross-plot of these same results. According to the theory developed in this contribution, the directional spectral absorptivity for s-polarized radiation is independent of incident zenith angle because the electric field is always normal to the vertical filaments. Therefore, its variation with wavelength corresponds to that of both p-polarized and non-polarized directional spectral absorptivity at normal incidence ($\vartheta = 0$). The authors know of no published theory or measurements for the directional absorptivity of gold-black. However, the theory developed in this contribution agrees
very well in level and trend with published spectral results, as already stated in the first paragraph of this section.

Figures 4.17(a) and 4.17(c) show a trend with wavelength that is independent of layer thickness. Conventional wisdom attributes the observed fall-off of absorptivity with wavelength to the fact that longer wavelength radiation penetrates more deeply to the underlying substrate from which it can then be reflected [31, Fig. 2.18]. However, the theory presented here does not make any direct reference to layer thickness other than the implied assumption of a “thick” layer. An alternative explanation that must be considered is the well-known fact that longer wavelengths couple less efficiently with shorter antennas.

Figures 4.17(b) and 4.17(d) are particularly interesting because they show that as the incident zenith angle increases, the directional spectral absorptivity gradually transitions from being dominated by the horizontal filaments to being dominated by the vertical filaments. The generally rising trend with increasing incident zenith angle reflects the fact that the number density of the vertical filaments exceeds that of the horizontal filaments, as shown in Fig. 4.12. This suggests that the model presented here might be a useful tool for engineering gold-black layers for directionality by controlling the number density distributions of the horizontal and vertical filaments during the manufacturing process.
Figure 4. 17 Directional spectral absorptivity of gold-black for p-polarized radiation (a) as a function of wavelength for incident zenith angles of 0, 20, 40, 60, and 80 deg, and (b) as a function of incident zenith angle for wavelengths of 2, 3, 4, 5, 6, and 7 μm; and for non-polarized radiation (c) as a function of wavelength for incident zenith angles of 0, 20, 40, 60, and 80 deg, and (d) as a function of incident zenith angle for wavelengths of 2, 3, 4, 5, 6, and 7 μm.

4.6 Conclusions and Recommendations

An explicit finite-difference time-domain formulation is presented for describing the evolution with time of the electric field within individual gold filaments constituting a gold-black layer. Based on a novel time-splitting scheme, the formulation alternates between a lossless Helmholtz model and a lossy transmission line model to describe the conversion of EM energy into sensible
heat within individual filaments treated as lossy antennas. The required optical and electrical properties of pure gold are based on the Drude-Sommerfeld free-electron theory. The results obtained using the model are correlated to obtain an expression for the single-strand absorptivity as a function of wavelength and filament length. A diffusion-limited aggregation algorithm is then used to define the strand-length statistical distribution within the gold-black layer. Finally, the single-strand absorptivity expression is combined with the strand-length statistical distribution to predict the directional spectral absorptivity of the gold-black layer.

Theoretical results for the normal spectral absorptivity of gold-black exhibit the same levels and spectral trends as measurements reported in the literature. Evidence is presented that the theory can be fitted to experimental results by judicious adjustment of a single parameter, the filament length multiplier, whose value is related to the parameters governing the coating process. While the contemporary literature is reticent on the subject of directional absorptivity of gold-black, the new first-principle theory reported here represents a promising first step in that direction. An experimental campaign is currently underway in our laboratory to characterize the directional spectral behavior of gold-black as a function of the chamber pressure, fill gas, gold evaporation rate, and crucible-cold finger spacing. The goal of the ongoing experimental effort is to correlate measured directional spectral absorptivity with the theory reported in the current contribution using the filament length multiplier as the single adjustable parameter.
Chapter 5: Gold-Black Directional Absorptivity in the Visible and Near Infrared

This chapter is adapted with minor changes from a manuscript currently under review at the Journal of Optical Society of America entitled “Gold-black directional absorptivity in the visible and near Infrared,” by the author and her co-advisors and Luan Doan and N. Q. Vinh (Vinh Q. Nguyen).

5.1 Follow-Up of the First-Principle Theory Presented in Chapter 4

As described in the previous chapter, our first-principle model predicts a polarization-sensitive directional absorptivity of gold-black in the visible and near infrared. The predictions are in good agreement with the measurements available in the literature for normal spectral absorptivity. However, suitable experimental data were not available to validate the theory for directional spectral absorptivity, nor for polarization sensitivity. In this chapter we present new measurements of the in-plane bidirectional reflectance distribution function (BRDF) for gold-black for linearly polarized radiation in the visible (λ = 532 nm) and near infrared (λ = 800 and 850 nm) as a function
of thickness, wavelength, and polarization state. A novel method for retrieving the directional absorptivity from in-plane BRDF measurements is established.

The gold-black samples were manufactured following the process described in the Chapter 3. In order to explore the effect of thickness we decided to produce two samples, one having a thickness of approximately the 8 µm and the other having a thickness of approximately 4 µm. The choice of thickness was not arbitrary. As described earlier, in our established protocol we used a 5-cm length of 0.5 mm diameter gold wire to produce a gold-black coating. From SEM measurements we confirmed that using that amount of gold produces a gold-black layer of 8-µm thickness. In order to create a layer of approximately 4-µm thickness, the length of 0.5-mm diameter gold wire used was 2.5-cm. Figure 5.1(a) shows the 8-µm-thick gold-black sample, and 5.1(b) shows 4-µm-thick gold black sample. Although it is impossible to discern a difference visually, the sample thickness is confirmed in the SEM images provided elsewhere in this section. Both samples were deposited on a gold-plated silicon substrate, as described in Chapter 3.

Figure 5. 1 Gold-black samples of (a) 8-µm thickness and (b) 4-µm thickness.
5.1 Measurement of Gold-Black BRDF

5.1.1 Definition of the bidirectional reflectance distribution function (BRDF)

The experimental results are presented in terms of the bidirectional reflectance distribution function (BRDF),

\[ BRDF \equiv \frac{d\lambda_i(\lambda, \theta_i, \varphi_i) \cos \theta_i d\Omega_i}{i_{\lambda,i}(\lambda, \theta_i, \varphi_i) \cos \theta_i d\Omega_i}, \]  

also commonly referred to as the bidirectional spectral reflectivity, \( \rho(\lambda, \theta_i, \varphi_i, \theta_r, \varphi_r) \) [53]. In Eq. (5.1), \( i_{\lambda,i}(\lambda, \theta_i, \varphi_i) \) is the intensity in wavelength interval \( d\lambda \) about wavelength \( \lambda \) incident to the sample from direction \((\theta_i, \varphi_i)\), where \( \theta_i \) is the incident zenith angle measured with respect to the normal to the sample and \( \varphi_i \) is the azimuth angle; \( d\Omega_i = dA_i/r^2 \), where \( dA_i \) is the area of the illuminated spot on the coupon and \( r \) is the distance from the light source to the illuminated spot, \( d\Omega_i \) is the solid angle surrounding direction \((\theta_i, \varphi_i)\); and \( di_{\lambda,r}(\lambda, \theta_i, \varphi_i, \theta_r, \varphi_r) \) is the intensity of the reflected beam in direction \((\theta_r, \varphi_r)\). The geometry and nomenclature corresponding to Eq. (5.1) appear in Fig. 5.2.

Figure 5.2 Geometry and nomenclature corresponding to Eq. (5.1).
The BRDF has the dimensions of inverse solid angle and the units of inverse steradians (sr\(^{-1}\)). The experimental apparatus and procedure for measuring the quantity defined by Eq. (5.1) are described in Sections 5.1.2 and 5.1.3. The significance of the BRDF is that, once obtained for a given surface at a given wavelength and state of polarization, it can be used to compute all other surface optical properties at that wavelength and for that polarization. For example, for a given polarization, the directional spectral absorptivity is

\[ \alpha_\lambda(\lambda, \vartheta_i) = 1 - \rho_\lambda(\lambda, \vartheta_i), \]  

(5.2a)

where

\[ \rho_\lambda(\lambda, \vartheta_i) = \int_0^{2\pi} \int_0^{\pi/2} \rho_\lambda(\lambda, \vartheta_i, \vartheta_r, \varphi_r) \cos \vartheta_r \sin \vartheta_r d \vartheta_r d \varphi_r \]  

(5.2b)

is the directional-hemispherical reflectivity. In Eq. (5.2b), \( \rho_\lambda(\lambda, \vartheta_i, \vartheta_r, \varphi_r) = BRDF(\lambda, \vartheta_i, \vartheta_v, \varphi_v) \) where \((\vartheta_v, \varphi_v)\) is the viewing direction.

The absence of the incident azimuth angle \( \varphi_i \) in the argument lists in Eqs. (5.2) reflects the fact that gold-black, like many surfaces of usual engineering interest, is isotropic. Because our apparatus only measures the variation of BRDF with reflected zenith angle \( \vartheta_r \) for a given value of \( \vartheta_i \), a model for its variation with \( \varphi_r \) is required to use Eq. (5.2) to compute the directional spectral absorptivity. The required model is developed in Section 5.3.
5.1.2 Apparatus for Measuring In-Plane BRDF

An automated BRDF gonio-reflectometer available in the Optic Lab C of the Department of Physics at Virginia Tech, directed by Prof. Vinh Nguyen, was used to measure the in-plane BRDF of our gold-black samples. A detailed description of the reflectometer is available elsewhere [54-56]. The apparatus, shown in Fig. 5.3(a), is a simplified gonio-reflectometer capable of measuring BRDF in the plane of incidence. Two precision stages are assembled coaxially and are controlled by high-precision stepper motors commanded by LabView software. The first rotational stage motor rotates the sample holder while the second stage motor rotates the arm carrying a photodetector. Stationary laser sources illuminate the sample through the optical train illustrated schematically in Fig. 5.3(b). Rotating the sample varies the angle of incidence of the laser beam. Once the sample is illuminated by the laser source, the first stage is commanded via LabView to rotate the sample to a specified incidence angle. Then, the second stage is commanded to rotate the photodetector to a set of specified discrete viewing angles in the plane of incidence. The photodetector then orbits the sample in the plane of incidence and senses the reflected intensity in that plane. LabView simultaneously logs the angular position of both the sample and the detector and the output of the photodetector. Additional details are available in the cited references [54-56].
Figure 5.3 (a) Photo of the automated gonio-reflectometer used to measure the BRDF of our gold-black samples, and (b) the corresponding schematic layout [55].

The intensity and polarization of the incident laser beam are controlled by a half-wave plate and a polarizing beam splitter. The polarizing beam splitters were selected according to wavelength. A THORLABS CCM-PBS252 polarizing beam-splitter cube is used in the visible spectrum ($\lambda = 532$ nm), while in the near infrared ($\lambda = 800$ and 850 nm) a THORLAB PBS102 polarizing beam-splitter cube was used. Figure 5.4 shows the half-wave plate mounted on the laser source and the polarizing beam-splitter cubes in the visible and near infrared.
Figure 5. 4 (a) Half-wave plate mounted on the laser source, (b) polarizing beam splitter in the visible and (c) the near infrared.

A 200-µm slit is mounted as a field-stop on the entrance aperture of a Newport 918-UV photodetector. The area of the slit and the length of the arm carrying the detector determine the solid angle of the reflected beam for the measurements. A rotating-disc optical chopper is synced with a lock-in amplifier to modulate the intensity of the beam and to minimize the effects of ambient light fluctuations. The chopping frequency is sufficiently high to compensate for drift in the signal-conditioning electronics. Figure 5.5(a) exhibits the sample mounted on the sample holder, while the photodetector is placed on the rotating arm. Figure 5.5(b) shows the field stop slit, and Fig. 5.5(c) shows the rotating disc chopper.
Figure 5.5 (a) Sample and photodetector mounted on the reflectometer, (b) field-stop used as an entrance aperture on the detector, and (c) rotating-disc chopper synced with lock-in amplifier to modulate the signal intensity.

Figure 5.6 shows the beam-steering mirrors, the iris diaphragm, and the periscope used to guide a collimated and linearly polarized circular laser beam to the sample.

Figure 5.6 (a) Beam steering mirrors, (b) iris diaphragms, (c) periscope.
5.1.3 Procedure for Measuring and Computing the BRDF

The BRDF of our gold-black samples was measured in the visible (532-nm) and near infrared (800, 850 nm). A power-stabilized 532 nm (green) diode laser was the visible light source, and a tunable Ti-Sapphire laser with a wavelength range of 750 nm to 850 nm was the source of near infrared light. After securing the gold-black sample in place, it was illuminated with the laser and proper alignment was achieved by auxiliary components. Extreme caution was maintained while handling the gold-black sample due to its very fragile nature. The power of the beam, which was controlled by a half-wave plate and neutral-density filter, was maintained at a level sufficiently low to avoid damaging the sample. This range was established experimentally by exposing a sample to the laser beam for several hours and comparing microscopic images before and after exposure. The beam power was measured by a power meter after installation of each component of the optical train to verify that it remained constant during build-up and alignment. As a calibration, the beam was allowed to directly illuminate the photodetector to verify that it produced the same reading as the power meter. The polarization state of the laser was controlled by appropriate orientation of the polarizing beam-splitter cube for each wavelength range.

Our gonio-reflectometer allows the incident zenith angle for BRDF measurement to be varied from 10 to 80 deg. Once the sample has been positioned and illuminated at its center, the first stage is commanded via LabView to rotate the sample to a specified incident zenith angle. The second stage is then commanded to orbit the sample in order to detect the reflected beam over a specified range of viewing zenith angles in the plane of incidence. At each combination of incident zenith angle and viewing zenith angle, LabView logs the sample and the detector positions and the power incident to the photodetector. The beam reflected from the sample is expected to be more powerful
at viewing zenith angles near the specular peaks. Therefore, data were first collected to locate the specular peak, and then data were collected for viewing zenith angles within a limited range surrounding the specular peak. As explained in Section 5.2, specular peaks are observed only when coating samples are thin and/or for incidence angles beyond about 50 deg. Figure 5.7 shows that the gold-black sample in place in the sample holder and ready for BRDF measurement.

The design of the reflectometer is such that the BRDF is related to the measurements according to [53]

\[
BRDF = \frac{P_d/P_s}{\Omega \cos \theta},
\]

where, \(P_d\) is the power of the reflected beam detected by the photodetector, \(P_s\) is the power incident to the sample, and \(\Omega\) is the solid angle established by the area of the slit mounted on the entrance aperture of the photodetector and the sample-detector distance. The same procedure was followed in order to obtain the BRDF measurement of both the gold-plated substrate and the gold-black coating samples.
5.2 Results and Interpretation

5.2.1 Results

Figure 5.8 shows the measured in-plane BRDF\(^1\) of the gold-plated silicon substrate in the visible (\(\lambda = 532\) nm) for both polarizations over the full range of incidence angles. These results are used to interpret the specular component of reflectivity of the gold-black coatings, as described in Section 5.2.2. Both the angular distribution of the peak values of BRDF for the bare gold-plated silicon and the noise-equivalent BRDF measurements, shown in Fig. 5.9 for the same experimental set-up at the same wavelength, exhibit an increasing trend with viewing zenith angle, with the noise floor for the apparatus at this wavelength observed to be more than six orders-of-magnitude below the peak values of BRDF for the substrate.

Figure 5. 8 BRDF of the gold-plated silicon substrate at \(\lambda = 532\) nm for (a) p-polarization and (b) s-polarization.

---

\(^1\) All BRDF measurements reported here were obtained in the plane of incidence. The adjective “in-plane” is suppressed from this point forward except where emphasis is appropriate.
Figure 5.9 Measured noise-equivalent BRDF of the 532-nm (p-polarization) substrate set-up.

Figure 5.10 shows scanning electron microscope (SEM) images at two magnifications of an approximately 8-μm thick sample of gold-black created as described in the Chapter 3. Figure 5.10(a) could be an aerial photograph of a dense deciduous forest, while Fig. 5.10(b) reveals the structure of each “tree,” which is somewhat reminiscent of cotton candy. Figure 5.10(c) is an elevation view of the same sample showing the variability in layer thickness. Inspection of Fig. 5.10(b) reveals the existence of structural features down to the nanometer size scale. In our previous article [57] we show images of numerically grown diffusion-limited aggregation (DLA) “forests” whose structure closely resembles that shown in Fig. 5.10(b), and in the same communication we use the statistics of the DLA images as the point of departure for the development of a gold-black directional spectral absorptivity model based on interpretation of the coating microstructure as a dense lossy dipole antenna farm. The BRDF measurements presented in the present communication provide an opportunity to test that theory.
Figure 5.10 (a) Plan SEM image with 10,000× and (b) 50,000× and (c) elevation SEM image with 10,000× of an approximately 8-μm-thick sample of gold-black.

Figure 5.11 shows the BRDF for the ~8-μm-thick gold-black sample in the visible (λ = 532 nm) for both p- and s-polarization. For p-polarization and for incidence angles between zero and 50 deg, the BRDF is independent of viewing angle and is about one order-of-magnitude above the noise floor. The same can be said for s-polarization in that range of incidence angles, except that now the BRDF is about two orders-of-magnitude above the noise floor. We conclude that, for both polarizations in the visible and in that range of incidence angles, the reflection is diffuse. Furthermore, the absorptivity of the ~8-μm-thick gold-black sample is an order-of-magnitude higher for p-polarized radiation than for s-polarized radiation. This agrees with our previously published theory [57]. The somewhat surprising explanation for the non-diffuse behavior corresponding to incidence angles of 60, 70, and 80 deg for both polarizations is deferred to Section 5.2.2.
Figure 5.11 BRDF of the approximately 8-μm-thick gold-black sample at $\lambda = 532$ nm for (a) p- and (b) s-polarization.

Figure 5.12 shows the SEM images of gold-black sample approximately 4-μm-thick at different magnifications. BRDF measurements for the sample in the visible ($\lambda = 532$ nm) for both p- and s-polarization are presented in Fig. 5.13. The specular peaks at viewing angles of 10, 20, 30, 40, and 50 deg for both polarizations are due to transmission though the thin layer combined with reflection from the gold-plated silicon substrate. However, the specular peaks at 60, 70 and 80 deg are not due to reflection from the substrate, as explained in Section 5.2.2. As in the case of the 8-μm-thick gold-black sample, gold-black in the visible is shown to be a better absorber of p-polarized light than s-polarized light. The diffuse component (off-specular background) of BRDF is once again observed to be about one order-of-magnitude larger for s-polarized light than for p-polarized light.
Figure 5. 12 (a) Plan SEM image with 10,000× and (b) 50,000× and (c) elevation SEM image with 10,000× of an approximately 4-μm-thick sample of gold-black.

Figure 5. 13 BRDF of the approximately 4-μm-thick gold-black sample at \( \lambda = 532 \) nm for (a) p- and (b) s-polarization.

Figure 5.14 shows the measured BRDF of the gold-plated silicon substrate in the near-IR (\( \lambda = 800 \) nm) for (a) p-polarization and (b) s-polarization. Comparison of Figs. 5.8 and 5.14 reveals that the substrate is slightly more reflective in the near-IR than in the visible, as expected. As in the case of the substrate measurements obtained in the visible, these results are used in Section 5.2.2 to imply the transparency of the gold-black coatings. Once again, the BRDF measurements in Fig.
5.14 should be considered in comparison with the noise-equivalent BRDF measurements shown in Fig. 5.15 for the same experimental set-up. As noted in the discussion of Figs. 5.8 and 5.9, Fig. 5.14 shows that the peak values of BRDF for the bare gold-plated silicon, measured at viewing zenith angles equal to the incident zenith angles, gradually increase with incidence angle over a range of about one order-of-magnitude, as does the noise-equivalent BRDF in Fig. 5.15. Figures 5.9 and 5.15 are essentially identical. As in the case of the visible light measurements, the noise floor is almost seven orders-of-magnitude below the peak values of BRDF for the substrate.

Figure 5.14 BRDF of the gold-plated silicon substrate at $\lambda = 800$ nm for (a) p- and (b) s-polarization.
Figure 5.15 Measured noise-equivalent BRDF of the 800-nm, s-polarization, substrate set-up.

Figure 5.16 shows the BRDF for the approximately 8-μm-thick gold-black coating in the near-IR (λ = 800 nm) for both p- and s-polarization. For p-polarization the BRDF rises only slightly above the noise level for incidence angles of less than about 50 deg, indicating a marginal ability to accurately measure the BRDF of this sample at this wavelength for small-to-intermediate incident zenith angles. Comparison of Figs. 5.16(a) and (b) reveals that gold-black is a somewhat better absorber of p-polarized light than s-polarized light in the near-IR. A dramatic difference between the optical behavior of the 8-μm-thick sample in the visible and near-IR is the presence of specular peaks at incidence angles of less than 60 deg for s-polarized radiation. This behavior is fully explainable in terms of our published theory [57], which predicts more efficient absorption of p-polarized radiation. The somewhat surprising explanation for the specular peaks at incidence angles of 60, 70, and 80 deg for both polarizations is once again deferred to Section 5.2.2.
Figure 5. 16 BRDF of the approximately 8-μm-thick gold-black sample at $\lambda = 800$ nm for (a) p- and (b) s-polarization.

Figure 5.17 shows the BRDF for the 4-μm-thick gold-black sample in the near-IR ($\lambda = 800$ nm) for both p- and s-polarization. As in the case of visible light, the specular peaks at viewing angles of 10, 20, 30, 40, and 50 deg for both polarizations are due to transmission though the ~4-μm-thick sample combined with reflection from the gold-plated silicon substrate. However, the specular peaks at 60, 70 and 80 deg are once again not attributable to reflection from the substrate, as explained in Section 5.2.2. As in the case of the ~8-μm-thick sample, gold-black in the near-IR is shown to be a better absorber of p-polarized light than s-polarized light.
Figure 5.17 BRDF of the approximately 4-μm-thick gold-black sample at λ = 800 nm for (a) p- and (b) s-polarization.

Figure 5.18 shows the measured BRDF of the gold-plated silicon substrate at a second wavelength in the near-IR, λ = 850 nm, for p-polarization and s-polarization; Fig. 5.19 shows the noise-equivalent BRDF for the set-up; and Figs 5.20 and 5.21 show the corresponding BRDF data for the ~8-μm-thick and ~4-μm-thick samples, respectively. The descriptions of Figs. 5.18 through 5.21 closely follow those of Figs. 5.14 through 5.17 with two exceptions: (1) the peaks in the s-polarization data in Fig. 5.20(b) for the ~8-μm-thick sample in the 10- to 50-deg incidence angle range are not as well defined as they are in Fig. 5.16(b), and (2) the BRDF corresponding to the 80-deg incidence angle in Fig. 5.21(a) for the ~4-μm-thick sample is much lower than expected. This latter anomaly is almost certainly attributable to experimental error that went unnoticed until the data were actually plotted; it is unreasonable to accept that such a relatively minor change in wavelength could produce such a radical difference between the 80-deg incidence angle BRDFs in Figs. 5.17(a) and 5.21(a). A possible explanation of the former anomaly—the ill-defined specular peaks in Fig. 5.21(b)—is that the shape of the laser spot on the sample may be
distorted: because the spot is not visible to the human eye at this wavelength, any distortion that may have been present would not have been apparent.

Figure 5. 18 BRDF of the gold-plated silicon substrate at $\lambda = 850$ nm for (a) p- and (b) s-polarization.

Figure 5. 19 Measured noise-equivalent BRDF of the 850-nm (s-polarized) substrate set-up.
Figure 5. 20 BRDF of the approximately 8-μm-thick gold-black sample at λ = 850 nm for (a) p- and (b) s-polarization.

Figure 5. 21 BRDF of the approximately 4-μm-thick gold-black sample at λ = 850 nm for (a) p- and (b) s-polarization. The unexpectedly low peak in (a) corresponding to an incident zenith angle of 80 deg is thought to be erroneous.
5.2.2 Interpretation of Results

Even though Figs. 5.9, 5.15 and 5.19, showing the noise-equivalent BRDF of the experimental apparatus, are based on measurements made on three occasions widely separated in time, they are essentially identical, thus establishing the stability of the apparatus. The scatter in these observations is a measure of the experimental uncertainty, and the maximum value of the observations in a given range of viewing zenith angles establishes the noise floor. Both the BRDF uncertainty and noise floor for a given range of viewing angles are observed to increase with viewing angle, with the BRDF noise floor increasing from about 0.01 sr\(^{-1}\) at a viewing zenith angle of 0 deg to about 0.5 sr\(^{-1}\) at 90 deg.

Figures 5.22 and 5.23 represent an initial attempt to interpret the BRDF results presented in Section 5.2.1. Figure 5.22 is a plot of the variation with viewing zenith angle of the ratio of the peak values of gold-black BRDF in Figs. 5.11(a) and 5.13(a) to the corresponding peak values of substrate BRDF in Fig. 5.8(a) for p-polarization, and Fig. 5.23 is a plot of the variation with viewing zenith angle of the ratio of the peak values of gold-black BRDF in Figs. 5.11(b) and 5.13(b) to the corresponding peak values of substrate BRDF in Fig. 5.8(b) for s-polarization. In both figures the circles, representing the \(\sim4\)-\(\mu\)m-thick sample, indicate a decreasing peak reflectivity with incidence angle up to an angle of 60 deg. The peak BRDF for both polarizations in this range of incidence angles is due to reflection from the gold-plated silicon substrate of radiation which has passed through the gold-black layer twice, as illustrated in Fig. 5.24(a). It is clear that the path length of a ray in the gold-black layer increases with increasing incident zenith angle; i.e., the path length of Ray 1 in Fig. 5.24(a) exceeds the path length of Ray 2. While the physical path lengths may be small, the optical path lengths are quite large due to the large effective
absorption index of gold-black. The normalized BRDF therefore decreases with incidence angle in this range of viewing angles.

Figure 5. 22 Ratio of gold-black peak BRDF to gold substrate peak BRDF as a function of incident zenith angle for 4-μm-thick (circles) and 8-μm-thick (squares) gold-black coatings for p-polarized radiation at \( \lambda = 532 \) nm (visible).

Figure 5. 23 Ratio of gold-black peak BRDF to gold substrate peak BRDF as a function of incident zenith angle for 4-μm-thick (circles) and 8-μm-thick (squares) gold-black coatings for s-polarized radiation at \( \lambda = 532 \) nm (visible).

At an incidence angle of 60 deg in both Figs. 5.22 and 5.23 the downward trend of the circle symbols, representing the \( \sim 4 \) μm-thick sample, reverses and begins to rise. Why? The answer to
this question may be found by observing the behavior of the square symbols, which represent the relative BRDF for the \( \sim 8\)-\( \mu \)m-thick sample. We note the complete lack of specular peaks below an incidence angle of 60 deg for both polarizations. More telling is that for incidence angles of 60 deg or greater, the relative BRDFs for both the \( \sim 4\)-\( \mu \)m-thick sample and \( \sim 8\)-\( \mu \)m-thick sample converge to the same values with increasing incidence angle. We hypothesize that this is due the mirage effect illustrated in Fig. 5.24(b). The strong evidence supporting this hypothesis is (1) the increasing strength of the relative BRDFs with increasing incidence angle beyond 50 deg, and (2) the observation that both polarizations produce essentially the same BRDF in the “mirage” range of incidence angles, where the overall sample thickness would no longer matter. This explanation is consistent with Snell’s law for the case where radiation passes from a medium with a relative refractive index of unity into a medium with a relative refractive index less than unity. Assuming an index of refraction of unity for the medium (air or vacuum) above the gold-black layer, the equivalent index for the gold-black layer would have to be less than unity for this explanation to hold. In fact, the real part of the refractive index of gold is less than unity in the visible and near-IR [57, Fig. 5]. The authors completely overlooked this possibility in their previous theoretical development [57].
Figure 5.24 Ray paths through gold-black follow one of two regimes depending on the angle of incidence. In (a) radiation incident at small-to-intermediate zenith angles penetrate to the substrate surface and are specularly reflected back out of the gold-black layer with attenuation which increases with optical path length, while in (b) radiation incident at large incident zenith angles follows a curved path that never intersects the substrate, as in the case of classical road “mirage.”

Figures 5.25 and 5.26, corresponding to a wavelength of $\lambda = 800$ nm (near-IR), are similar to Figures 5.22 and 5.23, except for one remarkable and important difference: while the $\sim 8$-μm-thick sample in Fig. 5.25 exhibits no discernable specular peaks in relative BRDF for p-polarized radiation for incident zenith angles of less than 50 deg, it does exhibit peaks in relative BRDF for s-polarized radiation in this incident zenith angle range. In other words, the $\sim 8$-μm-thick sample is relatively optically thick for p-polarized light and relatively optically thin for s-polarized light in the near-IR.
Figure 5. 25 Ratio of gold-black peak BRDF to gold-plated silicon substrate peak BRDF as a function of incident zenith angle for ~4-μm-thick (circles) and ~8-μm-thick (squares) gold-black coatings for p-polarized radiation at $\lambda = 800$ nm (near-IR).

Figure 5. 26 Ratio of gold-black peak BRDF to gold-plated silicon substrate peak BRDF as a function of incident zenith angle for ~4-μm-thick (circles) and ~8-μm-thick (squares) gold-black coatings for s-polarized radiation at $\lambda = 800$ nm (near-IR).

Figures 5.27 and 5.28, corresponding to a wavelength of $\lambda = 850$ nm, reinforce the 800-nm results given in Figs. 5.25 and 5.26. The near-IR wavelength for Figs. 5.27 and 5.28 is not significantly different from that for Figs. 5.25 and 5.26; therefore, the results in Figs. 5.27 and 5.28 are expected to be similar to those in 5.25 and 5.26. In fact, except for the filled symbol in Fig.
5.27, corresponding to the undoubtedly erroneous BRDF data at an incidence angle of 80 deg in Fig. 5.21(a), Figs. 5.25 and 5.27 are almost identical. The universal convergence of the thin-layer and thick-layer relative BRDF peaks at incident zenith angles of 70 and 80 deg for all three wavelengths and both polarizations in Figs. 5.22, 5.23, and 5.25-5.28 constitutes a strong argument in favor of the “mirage” explanation for the BRDF peaks at large incident zenith angles. Comparison of Figs. 5.26 and 5.28, for s-polarized radiation at 800 and 850 nm, respectively, reveals consistently lower relative BRDF peak values in the latter in the 10- to 50-deg incidence angle range for the ~8-μm-thick sample. This is due to the poorly defined peaks in that incidence angle range for the 850-nm s-polarized radiation, already pointed out in the discussion of Fig. 5.20(b), which spread the specular component of the BRDF over a wider viewing angle range, thereby reducing the peak values. Otherwise, these two figures are identical.

Figure 5. 27 Ratio of gold-black peak BRDF to gold-plated silicon substrate peak BRDF as a function of incident zenith angle for ~4-μm-thick (circles) and ~8-μm-thick (squares) gold-black coatings for p-polarized radiation at $\lambda = 850$ nm (near-IR). The solid symbol is thought to be erroneous.
Figure 5. 28 Ratio of gold-black peak BRDF to gold-plated silicon substrate peak BRDF as a function of incident zenith angle for ~4-μm-thick (circles) and ~8-μm-thick (squares) gold-black coatings for s-polarized radiation at λ = 850 nm (near-IR).

Figures 5.22, 5.23, and 5.25-5.28 convey important information about the directional absorptivity of gold-black in the visible and near-IR. For example, the fact that in the mirage regime the bidirectional reflectivity for the two coating thicknesses converges to the same values for both polarizations reveals that, because the incident radiation does not penetrate to the substrate, the thickness of the coating does not matter at large incident zenith angles. This largely confirms the mirage hypothesis as an explanation for the unexpectedly high specular reflectivity at glancing incident zenith angles.

5.3 Directional Absorptivity of Gold-Black

The directional absorptivity is related to the directional-hemispherical reflectivity as given in Eq. (5.2a). Because the gold-black samples are isotropic, the BRDF does not vary with incident azimuth angle φ_i; however, it is a function of viewing azimuth angle φ_v. It has already been
emphasized that the BRDF measurements reported in Section 5.2.1 were obtained only in the plane of incidence; i.e., at a single viewing azimuth angle $\varphi_{v0}$. Therefore, calculation of the directional-hemispherical reflectivity using Eq. (5.2b) requires a model that relates the complete BRDF, \( BRDF(\theta_{i}, \theta_{v}, \varphi_{v}) \), to the in-plane BRDF, \( BRDF(\theta_{i}, \theta_{v}, \varphi_{v0}) \).

Based on examination of the in-plane BRDF measurements of the gold-black samples reported here, it seems reasonable to consider the gold-black directional-hemispherical reflectivity as consisting of three components:

\[
\rho(\theta_{i}) = \rho_{\text{diff}}(\theta_{i}) + \rho_{\text{aureole}}(\theta_{i}) + \rho_{\text{spec}}(\theta_{i}),
\]

where $\rho_{\text{diff}}(\theta_{i})$ is the diffuse component, $\rho_{\text{aureole}}(\theta_{i})$ is the aureole component, and $\rho_{\text{spec}}(\theta_{i})$ is the specular component. When a light beam is reflected from the substrate (or deflected in the mirage regime), as illustrated in Fig. 5.24, it is surrounded by an accumulating sheath of forward-scattered radiation, as illustrated schematically in Fig. 5.29(a). When viewed from the perspective of the detector, this sheath appears as an aureole surrounding the transmitted peak, as illustrated in Fig. 5.29(b). This aureole corresponds to the second term on the right-hand side of Eq. (5.4). The relationship between the specular peak and the aureole is illustrated in Fig. 5.29(c).
Figure 5. 29 Illustration of the aureole surrounding a narrow beam; (a) its development by forward scattering as the beam transits the gold-black layer, (b) its radial power distribution viewed from the perspective of the detector, and (c) its BRDF profile.

From Eq. (5.2b), the diffuse component of spectral directional-hemispherical reflectivity is

$$
\rho_{diff}(\theta_i) = \int_0^{2\pi} \int_0^{\frac{\pi}{2}} \rho_\lambda(\lambda, \theta_i, \theta_r, \varphi_r) \cos \theta_r \sin \theta_r d\theta_r d\varphi_r = \pi BRDF_{diff}(\theta_i),
$$

(5.5)

where $BRDF_{diff}(\theta_i)$ is the diffuse component of the measured BRDF. For the ~8-μm-thick sample at incidence angles of less than about 50 deg (where the mirage effect is absent), this component accounts for essentially all of the reflectivity for both polarizations in the visible, and for p-polarization in the near-IR.

Formerly BRDF models were said to fall into two broad categories [58]: empirical models primarily intended to meet the needs of computer graphics applications, and theoretical models intended to meet the needs of engineering and science. While both describe reflection from illuminated surfaces, the former were only expected to suggest photo-realistic features such as highlights and shading, while the latter were held to the higher standard of producing
radiometrically verifiable results. While empirical models intended for use in computer graphics and film animation had to be fast and efficient [58-60], theoretical models intended for radiative exchange calculations typically sacrificed speed and efficiency for increased accuracy [54, 57, 61-67]. Increases in computing power over the past 30 years have gradually erased the boundary between empiricism and theory, with the result that high-accuracy semi-empirical BRDF models have emerged that are capable of filling in measurement gaps in BRDF datasets. Contributions by Church et al. [61], Stover [62], and Dittman [63] have led to a family of K-correlation models that, while primarily intended for predicting the BRDF based on independently measured surface roughness, are also useful for extending BRDF datasets [54, 55, 64-66]. Sought here is a model capable of converting measurements obtained only in the plane of incidence to datasets involving fully bidirectional reflectivity. To be deemed successful, the BRDF model, when introduced as $\rho_\lambda(\lambda, \vartheta_i, \vartheta_r, \varphi_r)$ into Eq. (5.2b), must return the actual directional-hemispherical reflectivity $\rho_\lambda(\lambda, \vartheta_i)$ with acceptable accuracy.

Figure 5. 30 Schematic cross-section of the gold-black in-plane BRDF showing its three components for the case of incident zenith angles producing a strong specular peak. The noise-equivalent BRDF is represented by the broken line.
We introduce a novel approach for retrieving the aureole component of the directional-hemispherical reflectivity from in-plane BRDF measurements; that is, from measurements obtained at only a single viewing azimuth angle, $\varphi_{v0}$. The in-plane BRDF, $BRDF(\vartheta_i, \vartheta_v, \varphi_{v0})$, is assumed to be the cross-section of the complete BRDF, $BRDF(\vartheta_i, \vartheta_v, \varphi_v)$, which is symmetrical about the $\vartheta_v, \varphi_{v0}$-plane. The aureole component is modeled as a stack-up of BRDF slabs of “thickness” $\Delta BRDF(\vartheta_i, \vartheta_v, \varphi_v)$ each defined in $\vartheta_v, \varphi_v$-space, as illustrated in Fig. 5.30. This model, expressed symbolically by Eqs. (5.6) and (5.7), emerges from the generalization of Eq. (5.5) for the case where the limits of integration are determined by the intersection of a cone with a sphere, as illustrated in Fig. (5.31). Because the BRDF associated with a given slab is considered uniform, it can be removed from the integral, and the value of the remaining integral is the area of the projection in the $x', y'$-plane of the cap area shown in Fig. 5.31. For example, in the special case of $\theta = 0$ and $\alpha = \pi/4$, the integral becomes $\pi$, as in Eq. (5.5). In this model the cone represents a diffuse beam whose BRDF is $\Delta BRDF(\vartheta_i, \vartheta_v, \varphi_v)$.

![Figure 5.31](image_url) Interception between a unit sphere centered at $(x_0, 0, z_0)$ and a cone whose vertex is at $(0, 0, 0)$. The cone has an opening angle $2\alpha$, and is coaxial with the z-axis. The y- and y'-axes are into the page (i.e., both coordinate systems are right-handed).
Treating the \( j \)th BRDF slab of thickness \( \Delta BRDF_j = BRDF_j - BRDF_{j-1} \) as a “local” diffuse contribution to the directional-hemispherical reflectivity, we then have

\[
\rho_j(\theta_i) = \Delta BRDF_j \int_0^\pi \int_0^{2\pi} \cos(\theta)\sin(\theta) d\theta d\phi = \Delta BRDF_j \Omega_j,
\]

(5.6)

where \( \Omega_j \) is the value of the \( j \)th integral. The cone half-angle \( \alpha \) determines the \( x',y' \)-range over which the double integral in Eq. (5.6) is to be evaluated for a given value of \( j \); i.e., it determines the specific contour defining the cap on the sphere in Fig. 5.31. Note that the angle defined by the intersection of the cone axis with the sphere in the \( x',y',z' \)-coordinate system is twice the negative of the angle \( \theta \) in the \( x,y,z \)-coordinate system. Following convention, we call this angle \( \theta_p \), the viewing angle at which the peak in the BRDF occurs. In the absence of off-specular peaking, \( \theta_p = \theta_i \). It follows that the components of the directional-hemispherical reflectivity due to the aureole are given by

\[
\rho_{\text{aureole}}(\theta_i) = \sum_{j=1}^{J} \rho_j(\theta_i),
\]

(5.7)

where \( J \) is the number of diffuse slabs into which the aureole component of the BRDF has been resolved.

In Fig. 5.31, the cone is defined in the right-handed \( x,y,z \)-coordinate system, while the sphere lives in the right-handed \( x',y',z' \)-coordinate system. The two coordinate systems are related by the rotation matrix

\[
R_y(\theta) = \begin{bmatrix}
\cos(\theta) & 0 & -\sin(\theta) \\
0 & 1 & 0 \\
\sin(\theta) & 0 & \cos(\theta)
\end{bmatrix},
\]

(5.8)
where $\theta$ is positive in the counter-clockwise sense, as shown in the figure. Then

\[
\begin{align*}
x' &= x\cos(\theta) - z\sin(\theta) \\
y' &= y \\
z' &= x\sin(\theta) + z\cos(\theta)
\end{align*}
\] (5.9)

In the $x, y, z$-coordinate system, the equation for the cone is

\[
x^2 + y^2 = \tan^2(\alpha)z^2,
\] (5.10)

and the equation for the sphere is

\[
(x - x_0)^2 + y^2 + (z - z_0)^2 = a^2.
\] (5.11)

For a unit sphere we have $x_0 = \sin(\theta)$, $z_0 = \cos(\theta)$, and $a = 1$. Combining Eqs. (5.10) and (5.11) yields the equation for the curve $y = y(x)$ representing the intersection of the cone and the sphere in the $x, y, z$-coordinate system. This result can be expressed in the $x', y', z'$-coordinate system by applying Eqs. (5.9). Figure 5.32 shows a family of such curves for a range of cone half-angles and for $\theta = -25$ deg, corresponding to $\theta_p = 50$ deg. The double integral in Eq. (5.6) yields the projection in the $x', y'$-plane of the cap area, shown in Fig. 27, bounded by curves like those shown in Fig. 5.32.

The double integral in Eq. (5.6) corresponding to a given value of $\Delta BRDF_j$ is evaluated using

\[
\Omega_j = \iiint_{A'_{\Delta}} dx'dy',
\] (5.12)
where $A_j'$ is the area of the spherical cap in Fig. 5.31 projected onto the $x', y'$-plane, as illustrated in Fig. 5.32(b). The units of the quantity defined by Eq. (5.12) are steradians (sr) since the projected area is based on the surface area of a unit circle. The integral has been evaluated numerically on a $10,000 \times 10,000$ mesh for the cone half-angles $\alpha$ used to generate Fig. 5.32, and the results are plotted in Fig. 5.33. Note that the integrand in Eq. (5.12) will be negative when $z' < 1$. This occurs in Fig. 5.32 when $\alpha = 25$ deg and the corresponding contour dips below the “equator” of the sphere for sufficiently large values of $x'$.

Figure 5. 32 Contours on the unit sphere defined by the intersection of the sphere tilted an angle of $\theta = -25$ deg with respect to the cone axis for cone half-angle $\alpha = 1.0, 2.5, 5, 10, 15, 20,$ and $25$ deg. (b) Projection of contours on the $x', y'$-plane.

The viewing zenith angle $\theta_v$ in Fig. 5.30 is related to the cone half-angle $\alpha$ and the reflected peak angle $\theta_p$ according to

$$\theta_v = \theta_p - \alpha. \hspace{1cm} (5.13)$$

The model introduced here for converting BRDF to the aureole component of directional-hemispherical reflectivity has the distinct advantage of requiring neither fitting parameters nor $a$
priori knowledge of surface roughness. Rather it depends only on the reasonable assumption of symmetry about the plane of incidence: the model is fully defined by the in-plane BRDF measurements themselves.

Referring to Fig. 5.30, the three components of directional-hemispherical reflectivity identified in Eq. (5.4) are

\[
\rho(\theta_i)_{\text{diff}} \leq \pi \langle BRDF(\theta_i) \rangle, \tag{5.14}
\]

\[
\rho(\theta_i)_{\text{aureole}} = \sum_{j=1}^{J} \Delta BRDF(\theta_i, \theta_j)_{\text{aureole}} \Omega_j, \tag{5.15}
\]

and

\[
\rho(\theta_i)_{\text{spec}} = \frac{BRDF(\theta_i, \theta_p)_{\text{gold-black}} - BRDF(\theta_i, \theta_p - 1 \, \text{deg})_{\text{gold-black}}}{BRDF(\theta_i, \theta_p)_{\text{substrate}}}. \tag{5.16}
\]

Figure 5.33 The value of the integral \(\Omega_j\) defined by Eq. (5.12) as a function of viewing zenith angle for a reflected peak angle \(\theta_p\) of 50 deg.
In Eq. (5.14),

\[
\langle BRDF(\theta_i) \rangle \equiv \frac{1}{K} \sum_{k=1}^{K} BRDF(\theta_i, \theta_k),
\]

where \( K \) is the number of \( \theta_v \) observations between \( \theta_v = 0 \) and \( \theta_v = \theta_p - \pi/4 \). The inequality in Eq. (5.14) recognizes the uncertainty introduced by the fact that the noise-equivalent BRDF is in some cases within less than one order-of-magnitude of the value of \( \langle BRDF(\theta_i) \rangle \). In the absence of visible peaks, only Eq. (5.14) is used. Note in Eq. (5.16) that the background value of BRDF, represented symbolically by \( BRDF(\theta_i, \theta_p - 1 \ deg) \), is subtracted from the peak value, although this correction is usually negligible. The directional-hemispherical reflectivity and directional absorptivity results obtained as described in Section 5.2.2 from the BRDF measurements reported in Section 5.2.1 for the approximately 8-\( \mu \)m-thick gold-black sample appear in Table 5.1.

The natural polarization results in Table 5.1 were obtained by averaging the directional-hemispherical reflectivity results for \( p \)- and \( s \)-polarization. (Due to an oversight, \( s \)-polarization data were not obtained at 532 nm at 40 deg.) Except for \( p \)-polarization at 800-nm, aureole reflectivity results are not given for viewing incidence angles at 80 deg. This is because the aureole model leads to directional reflectivities somewhat in excess of 1.0, as illustrated in the table for the 800-nm, \( p \)-polarized case. We attribute this failure of the model to the difficulty in obtaining reliable data at large viewing zenith angles as well as the increasingly strong asymmetry of the aureole as the viewing zenith angle approaches 90 deg.
Table 5. Directional-hemispherical reflectivity and directional absorptivity of the approximately 8-µm-thick gold-black sample in the visible (λ = 532 nm) and near-IR (λ = 800 and 850 nm).

<table>
<thead>
<tr>
<th>θ, deg</th>
<th>532 nm</th>
<th>800 nm</th>
<th>850 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>p</td>
<td>s</td>
<td>natural</td>
</tr>
<tr>
<td>10</td>
<td>0.143256</td>
<td>0.238789</td>
<td>0.191023</td>
</tr>
<tr>
<td></td>
<td>0.122298</td>
<td>0.250654</td>
<td>0.186476</td>
</tr>
<tr>
<td>20</td>
<td>0.10344</td>
<td>0.307351</td>
<td>0.205395</td>
</tr>
<tr>
<td></td>
<td>0.136172</td>
<td>No Data</td>
<td>No Data</td>
</tr>
<tr>
<td>30</td>
<td>0.189718</td>
<td>0.246589</td>
<td>0.218153</td>
</tr>
<tr>
<td></td>
<td>7.14E-06</td>
<td>3.71E-05</td>
<td>2.21E-05</td>
</tr>
<tr>
<td>40</td>
<td>0.04871</td>
<td>0.263154</td>
<td>0.155932</td>
</tr>
<tr>
<td></td>
<td>0.011998</td>
<td>0.108564</td>
<td>0.060281</td>
</tr>
<tr>
<td>50</td>
<td>0.060715</td>
<td>0.371755</td>
<td>0.216235</td>
</tr>
<tr>
<td></td>
<td>0.042445</td>
<td>0.327678</td>
<td>0.185062</td>
</tr>
<tr>
<td>60</td>
<td>0.001895</td>
<td>0.00756</td>
<td>0.004728</td>
</tr>
<tr>
<td></td>
<td>0.10489</td>
<td>0.554952</td>
<td>0.329921</td>
</tr>
<tr>
<td>70</td>
<td>0.149231</td>
<td>0.89019</td>
<td>0.51971</td>
</tr>
<tr>
<td></td>
<td>0.850769</td>
<td>0.10981</td>
<td>0.48029</td>
</tr>
<tr>
<td>80</td>
<td>0.055659</td>
<td>0.504376</td>
<td>0.280018</td>
</tr>
<tr>
<td></td>
<td>0.103064</td>
<td>0.346386</td>
<td>0.224725</td>
</tr>
</tbody>
</table>

8-µm-thick gold-black coating on a vapor-deposited gold substrate.
Figure 5.34 shows the diffuse component of directional absorptivity for the ~8-μm-thick gold-black sample for all three wavelengths and both polarization states, and Fig. 5.35 shows the overall directional absorptivity for the same sample for all three wavelengths for both polarization states. The noise ceiling, defined as 1 – noise floor, is shown as a broken line in both figures.

Figure 5.34 Measured diffuse components of directional absorptivity for the ~8-μm-thick gold-black sample in the visible (532-nm) and near infrared (800 and 850 nm).

Figure 5.35 Comparison of overall directional absorptivity for p- and s-polarized light.
In Fig. 5.34 we see that the diffuse component of directional absorptivity is weakly dependent on incident zenith angle in both the visible and infrared, especially at incident zenith angles less than about 60 deg. Furthermore, we see that gold-black is a more efficient absorber of p-polarized radiation than s-polarized radiation, even without considering the specular and aureole components of reflectivity. This is in keeping with our theory [57]. When all three components of directional-hemispherical reflectivity are used to compute the directional absorptivity, Fig. 5.35, it is evident that the mirage effect at grazing incident zenith angles is stronger for p-polarized light than for s-polarized light in both the visible and infrared.

5.4 Conclusions and Recommendations

New in-plane BRDF measurements for two thicknesses (~4 μm and ~8 μm) of gold-black in the visible (532 nm) and near-infrared (800 and 850 nm) are presented for p- and s-polarizations. The equipment and procedure used to create the gold-black samples and to perform the BRDF measurements are described. Compelling evidence is presented of an unanticipated mirage effect at large incident zenith angles, and a rudimentary theory for this phenomenon is proposed. A novel approach is then presented for converting in-plane BRDF measurements to directional absorptivity. Experimental results are found to be in good agreement with those anticipated by our earlier theory [57]. Specifically, measurements verify that gold-black absorbs p-polarized light more efficiently than s-polarized light. Furthermore, because of the mirage effect, the directional absorptivity of gold-black at large incident zenith angles cannot be increased by increasing the coating thickness. For this reason, it is recommended that the operation of thermal radiation detectors coated with gold-black be limited to incident zenith angles of less than about 50 deg.
Results presented here make it clear that the thickness of gold-black coatings on thermal radiation detectors intended for use in the visible and near-IR should significantly exceed the maximum value of approximately 8 μm studied here. Based on our experience, a thickness of at least 20 μm is recommended. It is further recommended that future measurements extend the wavelength range into the mid-IR. Also, any apparatus intended for measuring the BRDF of strong absorbers such as gold-black must have a noise floor below 0.001 sr⁻¹. Finally, operation of the gonio-reflectometer needs to be extended to permit out-of-plane BRDF measurement so that the novel approach presented here for converting in-plane BRDF to out-of-plane BRDF can be validated.
Chapter 6: Off-Specular Reflectance in Multilayer Gold-Black Coatings

In an attempt to increase the thickness of the gold-black coating, we attempted to build up a multilayer coating by laying down successive layers one on top of the other. We found that the “specular” peaks for incident angles of 60 deg or less occurred at off-specular zenith angles. In this chapter we attempt to decipher this enigma.

6.1 Motivation

It is made clear in Chapter 5 that a practical thermal radiation detector absorptive coating must be thicker than eight micrometers. Thicker coatings can be achieved in one of two ways: (1) a single layer can be created using a larger amount of gold in one continuous coating operation, or (2) the same amount of gold can be laid down in successive layers one on top of the other in a series of coating operations. Apparently, this latter approach has not been explored by previous investigators; at least, it has not been reported in the open literature. While it would seem more straight-forward to simply extend our single-layer process using a larger melt mass in a continuous
coating process, experience with our apparatus discourages this approach. In one such attempt, two separate gold wire segments were wound on two adjacent “V”s of the “W”-shaped tungsten filament; and in a second attempt, only one of the two “V”s was used but a steeper heating curve was followed. In the attempt involving two adjacent melts, heating proved to be uneven, with the result that one bead reached the melting point before the other and broke loose from the filament under the force of gravity before the second bead melted. In the attempt involving more rapid melting of only a single gold wire, gravity once again overcame surface tension with the same catastrophic result—the bead broke free. It was clear that an even larger melt mass would most likely suffer the same fate. These experiences led to the investigation of multilayer coatings.

6.2 Manufacture of Multilayer Gold-Black Coatings

The decision was made to create a three-layer gold-black coating following the previously established protocol for creating each of the individual layers. We placed a gold-coated silicon substrate on the lower surface of the cold finger, and wound a 5-cm length, 0.5-mm diameter gold wire around one of the “V”s of the tungsten filament. After 12-hours of chamber evacuation we followed the protocol established in Chapter 3 to create a single coating, except that this time we did not collect the sample. The following day, we broke vacuum to wrap another gold wire of the same length and diameter on the tungsten filament, being careful not to touch anything else in the chamber. After repeating the 12-hr evacuation process, we deposited the second layer on top of the first layer. A third layer was laid down on top of the second layer following the same process. One important consideration is that typically during the 12-hr evacuation process we tried to maintain the vacuum pressure near $2.25 \times 10^{-5}$ torr. Previous experience had confirmed that the
optimum vacuum pressure can vary depending on the laboratory temperature and humidity. We remarked that during pump-down before laying down the first layer, the chamber was unable to attain a vacuum of $2.25 \times 10^{-5}$ torr. In spite of this, the decision was made to continue the run, which proceeded without incident. However, during subsequent SEM examination of the three-layer coating it was discovered that initial layer was thinner than the other two, as illustrated in Fig. 6.1.

![Figure 6.1](image)

Figure 6.1 Elevation SEM image of the three-layered gold-black sample showing that the bottom layer is thinner than the top two.

The SEM image in Fig. 6.1 shows two 8-µm-thick gold-black layers laid down on top of an approximately 5-µm-thick gold-black layer, which itself was formed on a gold-plated polished silicon wafer substrate. The interface between the two 8-µm-thick layers is obvious in the image, but the interface between the lower 8-µm-thick layer and the 5-µm-thick layer is less evident. The three interfaces are indicated in the figure.
6.3 Results and Interpretation

6.3.1 Results

Figures 6.2 through 6.7 are BRDFs for the three-layer sample corresponding to wavelengths of 532, 800, and 850 nm, for both p- and s-polarization, and for incident zenith angles of 10, 20, 30, 40, 50, 60, 70, and 80 deg. Comparison of Figs. 6.2 and 6.3, which show the BRDF of the sample in the visible, reveals that, as in the case of the single-layer samples, the three-layer coating is a somewhat better absorber of p-polarized light than of s-polarized light. The specular peaks are sharper and more salient for s-polarization than for p-polarization, indicating less absorption and scattering of s-polarized light. This is consistent with the theoretical development in Chapter 4.

Figure 6.2 BRDF of the three-layer gold-black sample illuminated with p-polarized light at a wavelength of 532 nm.
Figure 6.3 BRDF of the three-layer gold-black sample illuminated with s-polarized light at a wavelength of 532 nm.

For p-polarization at 532 nm in Fig. 6.2 and for s-polarization at 532 nm in Fig. 6.3, the mirage regime (beyond 50 deg incident zenith angle) reveals essentially the same trend as for the 8-µm-thick sample in Fig. 5.11. The only obvious difference in optical performance between the two samples is that the peaks in the mirage regime for p-polarization for the three-layer sample are somewhat lower. However, for p-polarization at 532 nm, for incident zenith angles between zero and 50 deg, the three-layer BRDF reveals an aureole component surrounding the specular viewing zenith angle which is absent in the single-layer BRDF in Fig. 5.11(a). For s-polarization at 532 nm the three-layer BRDF in Fig. 6.3 exhibits clear specular peaking at the smaller incident zenith angles that is missing in the p-polarization at 532 nm BRDF in Fig. 6.2. Furthermore, the results for both polarizations are different from those produced by the single-layer sample, Fig. 5.11,
which exhibits diffuse behavior at this wavelength. Generally, the reflectivity for incident zenith angles of 60 deg or less appears to be slightly greater for the three-layer sample than for the single-layer sample at this wavelength for both polarizations, which is unexpected. This anomalous behavior is hypothesized to be associated with the layered structure.

![Graph](image.png)

Figure 6.4 BRDF of the three-layer gold-black sample illuminated with p-polarized light at a wavelength of 800 nm.

Figures 6.4 and 6.5 show the BRDF for the multilayered gold-black coating in the near-IR ($\lambda = 800$ nm) for p- and s-polarization, respectively. Comparing Figs. 6.4 and 6.5 with each other and with Fig. 5.16, no significant difference is observed either between the two polarizations for a given coating structure or between the two coating structures for a given polarization in the mirage region.
Figure 6.5 BRDF of the three-layer gold-black sample illuminated with s-polarized light at a wavelength of 800 nm.

This and the remaining paragraphs in this subsection refer to incidence angles of 60 deg or less. For p-polarization at 800 nm, Fig. 6.4, peak BRDF values surrounding viewing zenith angles corresponding to the incident zenith angle are an order of magnitude greater than in the visible, Fig. 6.2. The most interesting observation in Fig. 6.4, however, is the appearance of what might be referred to as off-specular peaks. Having been alerted to this possibility, we can now discern a slight tendency for this off-specular peaking phenomenon at sufficiently small incident zenith angles in the p-polarized, 532-nm BRDF, Fig. 6.2.

The tendency for off-specular peaking is even more apparent for s-polarization at 800 nm, Fig. 6.5. In fact, rather than exhibiting a specular peak, only the off-specular peak is present. The off-
specular peaks are more than one order-of-magnitude higher than those in the visible, Fig. 6.3, but one order-of-magnitude lower than those obtained for 8-μm-thick gold-black sample at this same wavelength and polarization, Fig. 5.16(b).

Figure 6. 6 BRDF of the three-layer gold-black sample illuminated with p-polarized light at a wavelength of 850 nm.

Figures 6.6 and 6.7 show the measured in-plane BRDF of the multilayer gold-black sample at a second wavelength in the near-IR, λ = 850 nm, for p-polarization and s-polarization. Discussion of the s-polarization BRDF at 850 nm, Fig. 6.7, closely follows that for 800 nm, Fig. 6.5, in that both feature prominent off-specular peaking. However, for p-polarization, Fig. 6.6, the peak surrounding a viewing zenith angle corresponding to the incident zenith angle shows a more obvious off-specular peak than for p-polarization at 800 nm, Fig. 6.4.
We are left with three enigmas associated with the three-layer sample:

1. What is the explanation for the observed off-specular peaking apparent in the infrared but less so in the visible?

2. Why is off-specular peaking more pronounced at 850 nm than at 800 nm for p-polarization?

3. For incident zenith angles at 60 deg or less, the three-layer coating exhibits broadened peaks about viewing zenith angles corresponding to the incident zenith angle for both polarizations at 532 nm, and for p-polarization at 800 nm, while the single-layer coating does not. Why is this?

4. When present, why is off-specular peaking in the near-IR more prominent for s-polarization than for p-polarization? (And why is this not true in the visible?)
A fundamental understanding of the off-specular peaking phenomenon is required to answer these questions.

6.3.2 A Theory for Off-Specular Peaking

Figure 6.8, an idealization of the upper two gold-black layers and the intervening air gap, is inspired by the SEM image of the three-layer gold-black coating in Fig. 6.1. The idealization takes the superficial form of an étalon. In the case of a Fabry-Perot filter, the two elements forming the gap would normally be electrical conductors, and the gap itself would be filled with an absorbing dielectric. The essential requirement is that the two materials involved must have different refractive indices.

Radiation entering the air gap becomes trapped at any wavelength for which

\[ n\lambda/2 = \ell / \cos\theta_{peak}, \quad n = 1, 2, 3, \ldots \text{ (resonance)} \]  

(6.1)

where \( \ell \) is the gap width. Equation (6.1) assumes that the gold-black/air interfaces are ideal reflectors with or without a 180-deg phase shift, with \( n \) taking on odd integer values in the presence of a phase reversal and even values in the absence of a phase reversal. In the former case an electric field node will be established at each interface (destructive interference), and in the latter case an antinode will be established (constructive interference). The presence of the \( \cos\theta_{peak} \) factor in Eq. (6.1) is unexpected but necessary in this discussion because the gap \( \ell \) and wavelength \( \lambda \) are fixed. This means that the electric field standing wave associated with resonance must be “tilted” to fit within the space, as illustrated in Fig. 6.1.
To be successful, the off-axis peaking theory postulated here requires resonance within the air gap. The magnitude and sign of the reflection coefficient at the gold-black/air interfaces is unknown. However, it was established in the theoretical development in Chapter 4 that the filaments making up gold-black are highly conductive; therefore, it is natural to hypothesize the presence of odd modes only. Also, because of the strong absorptivity of gold-black we can safely assume that the higher-order resonances \((n > 1)\) associated with larger values of \(\theta_{peak}\) will be significantly damped compared to the fundamental, which corresponds to half-wave resonance.

Radiation energy entering the air gap from either boundary at the critical zenith angle will accumulate until a balance is achieved between energy entering and energy absorbed in the walls. The preponderance of the radiation energy trapped within the air gap will have a wavelength of \(\lambda = 2\ell/\cos\theta_{peak}\). As in the case of a Fabry-Perot filter, radiation incident to the upper gold-black layer at zenith angle \(\theta_{peak}\) will be preferentially reflected while radiation entering at all other angles will pass through the gap and into the lower absorbing layer, where most of its energy will be absorbed.

![Diagram of gold-black layers with air gap](image)

Figure 6.8 Idealization of the upper two gold-black layers with the intervening air gap (thickness exaggerated).
Figure 6.9 is a plot of the observed off-specular peak zenith angles as a function of incident zenith angle for the cases of 800 and 850 nm, with both p- and s-polarization. When interpreted in terms of the theory developed in preceding paragraphs, the figure establishes that the effective gap width $\ell$ is a function of the incident zenith angle $\theta_i$. Otherwise, the slope of the straight line in Fig. 6.9 would be zero. For the special case where the incident zenith angle is zero, extrapolation of the line to its $y$-intercept yields a value of off-specular peaking of about 10 deg, in which case the effective gap width $\ell$ would have to be 0.406 $\mu$m according to Eq. (6.1) with $\cos \theta_{\text{peak}} = 1$. In fact, examination of Fig. 6.8 lends credence to this result.

Figure 6.9 Off-specular peaking zenith angle as a function of incident zenith angle for the three-layer coating at 800 and 850 nm, p- and s-polarization.
There now remains the need to justify the apparent dependence of the effective gap width \( \ell \) on the incident zenith angle. To do that, we turn to a couple of half-century old investigations by Torrence et al. [68,69], who were the first to report measurements of off-specular peaking in the context of roughened surfaces in 1966. The cited authors attempt to explain off-specular peaking in terms of multiple reflections from adjacent peaks and shadowing in valleys when a roughened specimen is illuminated at non-zero incident zenith angles. The validity of their explanation, while open to question, does not invalidate their experiments in which off-specular peaking of semi-polished surfaces is observed. After studying the cited contributions, and in particular the theory they offer, it is easy to imagine that two roughened semi-transparent surfaces mounted parallel and face-to-face to form a narrow gap could lead to angle-dependent off-specular peaking of light entering through the back of one of the surfaces. That is, the effective gap, due to the irregular relief of the surfaces used to form it, might be expected to be angle-dependent.

Armed with this tentative understanding of off-specular peaking, we can now speculate on the answers to the four questions posed at the end of Subsection 6.3.1.

1. As already noted, careful inspection of Fig. 6.2, which shows the in-plane BRDF for the three-layer coating at 532 nm, with p-polarization, reveals the suggestion of off-specular peaking at incident zenith angles of 10, 20, and perhaps even 30 deg. Therefore, while the phenomenon is not necessarily limited to the infrared, it is more prominent there. The explanation for the observed off-specular peaking is incident-zenith-angle-dependent resonance within the air gap between the upper two layers of gold-black.

2. Resonance is by its very nature very sensitive to wavelength, even in a highly absorptive optical environment. Two reflection modes, specular and off-specular, struggle for their
share of the same available energy. It is not surprising to find that, with a relatively small change in wavelength, the shift of dominance between competing modes can be abrupt.

3. In the case of the three-layer coating, the opportunity for development of an aureole surrounding a reflected beam is greater because of the increased path length through a scattering medium. This explanation is based on the description of the aureole surrounding Fig. 5.29.

4. Off-specular peaking in the near-IR is more prominent for s-polarization than for p-polarization for the same reason that reflection in general is stronger for s-polarization than for p-polarization. This may also be true in the visible, but specular reflection from the substrate is so much stronger there that it obscures any off-specular component. This is consistent with the theory developed in Chapter 4, which is based on the fact that gold-black structure statistically favors “vertical” fibers over “horizontal” fibers due to diffusion-limited aggregation (DLA).
Chapter 7: Summary, Conclusions, and Recommendations

The stated motivation for this dissertation is to investigate the optical properties of an increasingly popular absorptive coating—gold-black—frequently applied to thermopile and thermistor bolometers. Several government authorities including the NASA, NOAA, ESA, JAXA, and NICT are using thermopile and thermistor bolometers in instruments for monitoring the Earth radiation budget from low Earth orbit. The performance and accuracy of thermopile and thermistor bolometers depend on the properties of the absorptive coating material. Gold-black has emerged as a popular coating for thermal radiation detectors in aerospace applications. In spite of its suitability for the thermal radiation detector applications, its directionality and polarization sensitivity have not been the subject of previous investigations. Our goal is to understand the directional spectral absorptivity and polarization sensitivity of gold-black.
7.1 Summary

The dissertation can be summarized as follows

1. A successful experimental campaign has been pursued to design and manufacture a gold-black fabrication cell. A protocol has been established in sufficient detail to allow the production of gold-black using the cell. Gold-black samples of different thicknesses and laid down in multiple layers have been manufactured using the cell.

2. A first-principle model based on lossy antenna theory has been posed for predicting the polarization dependent directional spectral absorptivity of gold-black. The principles of diffusion-limited aggregation (DLA) are applied to mimic the observed microstructure of actual gold-black layers consisting of a random-fractal distribution of dendritic gold nanostructures whose individual filaments are postulated to behave as dipole antennas. Absorption of incident electromagnetic radiation by individual filaments is predicted using the unique time-dependent lossy antenna model drawing on the Drude-Sommerfeld free-electron theory. Single-filament spectral absorptivities are combined based on the DLA microstructure model to predict the spectral and, for the first time, directional absorptivity of the gold-black layer. Results from the first-principle model are in good agreement with the measurements reported for normal spectral absorptivity. However, suitable experimental data were not available to validate the predicted polarization sensitive directional absorptivity.

3. New in-plane bidirectional reflectivity distribution function (BRDF) measurements for two thicknesses (~4 μm and ~8 μm) of gold-black in the visible (532 nm) and near-infrared (800 and 850 nm) are performed for p- and s-polarizations in support of the first-principle model. A novel approach is presented for converting in-plane BRDF
measurements to directional absorptivity. Experimental results are found to be in good agreement with those anticipated by our earlier theory. Specifically, measurements verify that gold-black absorbs p-polarized light more efficiently than s-polarized light. Furthermore, compelling evidence is presented of an unanticipated mirage effect at grazing incident angles, and a rudimentary theory for this phenomenon is proposed.

4. A three-layer gold-black sample was fabricated in an attempt to increase the thickness of the gold-black coating. The in-plane BRDF of the three-layer gold-black sample is measured in the visible (532 nm) and near-infrared (800 and 850 nm) for p- and s-polarizations. The three-layer gold-black sample exhibits off-specular peaking in the near-IR. Rudimentary theory is presented to explain the off-specular behavior of multilayer gold-black coatings.

7.2 Conclusions

Several conclusions can be drawn from the investigation which we believe provide valuable information for next-generation thermal radiation detector designers.

1. Previous contributions ignored the detailed geometry of the gold-black microstructure and treated it as a homogeneous material possessing effective bulk optical properties. However, our first-principle theory reveals that prediction of the directional absorptivity of gold-black requires that the microstructure be correctly mimicked. Therefore, we used DLA to correctly describe the random fractal distribution of dendritic gold nanostructures.

2. From our experience gained by fabricating and optimizing a gold-black manufacturing cell, we conclude that the initial vacuum pressure and the vacuum pressure during evaporation
are the two most important parameters among several for successful formation of gold-black.

3. We conclude from our first-principle model and our experimental results that the directional absorptivity of gold-black is a function of polarization and wavelength. Specifically, measurements verify that gold-black absorbs p-polarized light more efficiently than s-polarized light.

4. Furthermore, because of the mirage effect, the directional absorptivity of gold-black at grazing incident zenith angles cannot be increased by increasing the coating thickness. For this reason, it is recommended that the operation of thermal radiation detectors coated with gold-black be limited to incident zenith angles of less than about 50 deg.

5. Results presented here make it clear that the thickness of gold-black coatings on thermal radiation detectors intended for use in the visible and near-IR should significantly exceed the maximum value of approximately 8 μm studied here. Based on our experience, a thickness of at least 20 μm is recommended.

6. In an attempt to increase the thickness of the gold-black coating, we attempted to build up a multilayer coating by repeating the coating operation multiple times. From our initial study we observed polarization-sensitive off-specular peaking for a three-layered gold-black sample. Based on this preliminary investigation we recommend using a solid continuum of gold-black rather than using a multilayered coating, until the enigmas associated with multilayered gold-black coatings are fully understood.
7.3 Recommendation

The following activities should be considered for future work:

1. The in-plane BRDF measurement should be extended to the mid-infrared with both p- and s-polarization.

2. The automated goniometer-reflectometer should be modified to permit out-of-plane BRDF measurement.

3. A layer of approximately 20-µm thickness is recommended for future study. However, any apparatus intended for measuring the BRDF of gold-black with that thickness must have a noise floor below 0.001 sr⁻¹.

4. A detailed investigation is recommended in order to confirm the physics behind the off-specular peaking phenomenon observed in multilayered gold-black samples.

5. Gold-black is very fragile in nature. Research should be extended to overcome the handling difficulty of gold-black.

6. Research should be extended to consider gold-black as a potential absorptive coating for photon detectors.

7. The possibility of differences in the optical behavior of gold-black in air and in vacuum should be studied.
Work Cited


42. User manual of MTI GSL-1700X-SPC-2 provided by MTI corporation.


Appendix A

Cold Finger and Insulator Assembly

Note A: Use Available Brass Hardware

Silver Solder Here Before Inserting Plugs At Other End Of Channels.

Note B:
Mill (or Grind)
1/4-in. Radius
(Must Fit Snugly Into Insulating Shoe)

Plan View

2.00
1/4
1.00

Note B:

Elevation View

1-1/2
3/16-in. Dia Clear
1/4-in. Deep

End View

2.00
1.00

1/4-in. Dia

Detail A:
1/8-in. NPT Plugs

Copper Finger Surface

Notes:
1. Wrap Pipe Threads With Teflon Tape Before Seating.
2. Grind Off Hex Flush With Copper Surface After Seating.

Copper Cold Finger
1/4 R
2 Places
(Note C)

Plan View

Section A-A

End View

Phenolic Insulating Shoe

Note C:
Cut Radius With
1/4-in. End Mill
(See Note B)