

# Black optical coating for high-power laser measurements from carbon nanotubes and silicate

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We describe a coating based on potassium silicate, commonly known as water glass, and multiwall carbon nanotubes. The coating has a high absorbance (0.96 at 1064 nm in wavelength) and a laser damage threshold that is comparable to that of ceramic coatings presently used for commercial thermopiles for high-power laser measurements. In addition to a potassium silicate-based coating we discuss sodium silicate, lithium silicate, and a commercially available ceramic coating. We document the coating process and experiments that demonstrate that the laser damage threshold at 1064 nm is 15 kW/cm<sup>2</sup>.

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The National Institute of Standards and Technology (NIST) maintains thermal detectors as measurement standards (standard detectors) for measuring optical power from laser sources. Lasers capable of ever-higher irradiance are continually being developed for industrial and military applications. Designing a thermal detector to measure light from such a laser that is intended to significantly alter its target is a challenge, particularly when the intent of the standard detector is to collect and measure all of the laser beam power.

We have shown that carbon nanotubes (CNTs) have desirable properties for thermal detector coatings by spraying CNTs suspended in a volatile organic solvent [1]. The resulting black coating is a mat of CNTs presumed to adhere to the detector's surface by van der Waals forces. We continue to seek a black coating that can be easily applied and is durable, such as enamel paint, yet with the desirable properties of CNTs. The desirable attributes include high damage threshold, high thermal diffusivity, and high optical absorbance. CNT-based coatings are hydrophobic and more stable compared to other percolated metal coatings, such as gold black [2]. Previously, single-walled carbon nanotube (SWCNT)-based films prepared by way of an inorganic sol-gel route using silicic acid were described [3]. A multiwalled carbon nanotube (MWCNT)-based coating, rather than a SWCNT coating, manifests a broad and uniform spectral absorbance from the visible to infrared wavelengths, a high damage threshold on the order of 15 kW/cm<sup>2</sup>, and excellent thermal conductivity [1,4–6]. The ideal coating might consist purely of nanotubes that are free of defects and arranged in a manner that optimizes optical absorbance. This can be achieved more readily with tubes grown on a flat surface, but we also have a requirement to coat complicated cavity structures (for example, cones and tubes) that improve the absorption of the laser beam power by virtue of geometry and surface absorptivity. In the absence of perfect tubes and complete control of the topology, we have pursued MWCNTs forming a percolated matrix along with a binder that is small in proportion to the CNTs.

The solution was prepared from four constituents: distilled water, dodecylbenzensulfonic acid (DBS), MWCNTs, and potassium silicate solution [7]. The proportions were formed from 100 ml of distilled water, 300 mg of DBS, 300 mg of MWCNTs, and 5 ml of potassium silicate. The MWCNTs are described as being greater than a 96% CNT content and approximately 10 to 30 nm in diameter [8]. The distilled water, MWCNTs, and DBS were sonicated with a horn sonicator for 10 min. The potassium silicate was then added, and the complete solution was stirred for 1 min.

The solution was applied by means of an airbrush [9]. The airbrush propellant is nitrogen gas with a pressure of 124 kPa. The solution was sprayed onto copper coupons maintained at a temperature of 95°C. The dimensions of the coupon were nominally 25 mm × 67 mm and 1 mm in thickness. Spraying was done with slow passes over the coupon along the long axis, allowing time between each pass for the water to evaporate and the coating to set. Approximately 40 mL of solution were sprayed onto the coupon, with some overspray landing off the coupon. The coated coupon was further baked at 300°C. The 300°C bake was intended to drive off any remaining water and fully cure the silicate. We measured the thickness of the coating by mechanical means and find that it is approximately 10 μm. This should be considered an estimate, however, and we state this measurement without an uncertainty value.

We duplicated the MWCNT solution with two other silicates: sodium silicate [10] and lithium silicate [11]. A photograph of the representative coupons is shown in Fig. 1. For comparison, we also obtained a coupon coated with ceramic that is typical of commercially available thermopiles. The exact nature of the coating depends on the source. We know that, in general, the coating consists of an aluminum oxide, and there are several types of ceramic coating processes, including flame, plasma, and high-velocity spraying. The ceramic coating that we tested was probably manufactured by means of the flame process. Further details regarding the manufacturer and process pa-

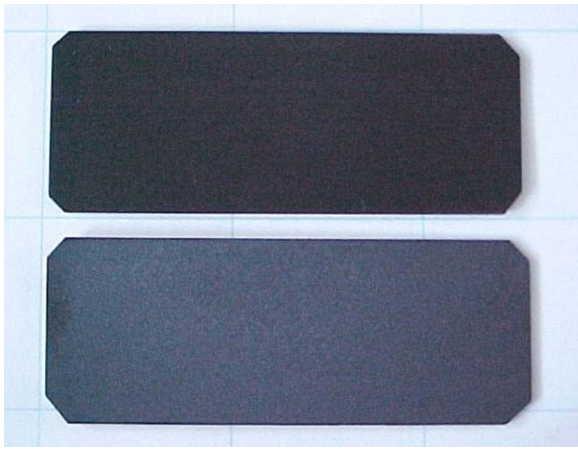


Fig. 1. (Color online) Photograph of copper coupons coated with MWCNT and sodium silicate. The lower coupon has been baked at 300°C and shows efflorescence. The brightness of the image has been modified to enhance the distinction.

rameters are proprietary and not presented here. Our goal was merely to have a sample for comparison rather than to fully evaluate a commercially available product.

In the past we evaluated MWCNT coating properties by exposing the coating to laser light and measuring the coating efficiency and damage threshold by means of a flowing-water optical power meter. The details of this are found elsewhere, and the measurement process is repeated here [1]. Briefly, the optical power absorbed by the coating sample is evaluated by measuring the temperature change of water flowing in contact with the coupon. The temperature change, the mass flow rate of the water, and the specific heat of the water are multiplied to calculate the absorbed power. A calibrated beam splitter and a monitor detector together provide the known incident power used to determine the absorbance of the coating at 1064 nm in wavelength (neodymium-doped yttrium aluminum garnet or Nd:YAG laser). The irradiance at which the absorbance declines is considered the onset of damage. The laser damage threshold will depend on the water flow rate, beam diameter, and other factors. The beam was focused to a spot size of 2 mm and possessed a nearly flat-top profile on the sample. The laser power was increased incrementally until the onset of damage to the coating is evident by a significant drop in the absorption efficiency. Qualitatively, the damage threshold corresponds to oxidation (plume) of the carbon and, eventually, a small melted pool of silicate.

The measurement results are summarized in Table 1. The damage threshold is stated along with the average absorbance. The average absorbance is based on the irradiance values up to, but not including, the onset of damage (where the absorption efficiency decreases by more than 2%). An image of a representative damaged spot is shown in Fig. 2. The uncertainty of the damage measurements has not been fully evaluated. The uncertainty of the measurement in the absorbed power with the cooling water is typically on the order of 1%, based on knowledge of the

Table 1. Absorbance ( $\alpha$ ) and Damage Threshold ( $P_t$ ) at 1064 nm in Wavelength

| Material                 | $\alpha$<br>(average) | $P_t$<br>(kW/cm <sup>2</sup> ) |
|--------------------------|-----------------------|--------------------------------|
| MWCNT-Sodium silicate    | 0.91                  | 10                             |
| MWCNT-Potassium Silicate | 0.96                  | 15                             |
| MWCNT-Lithium Silicate   | —                     | —                              |
| Ceramic                  | 0.91                  | 12                             |

mass flow rate, specific heat, and temperature change of the flowing water. The thermopile is capable of measurements having an uncertainty of approximately 1.2% [8]. In this Letter, the uncertainty of the measurement is likely dominated by the increment size of laser power, the beam nonuniformity, and the variability in the material purity, coating thickness, and topology. In the past, repeated damage experiments on coating preparations that are considered to be nominally the same ranged in magnitude by  $\pm 15\%$  [1]. Laser damage may also depend on beam diameter, rather than merely on irradiance. We did not evaluate the damage threshold as a function of the beam diameter.

We also measured the specular reflectance of the potassium silicate-based coating by means of a commercially available spectrophotometer over the wavelength range of 400 to 2000 nm. Over the entire wavelength range, the reflectance was approximately zero, and the measurement result was dominated by noise. This implies that the specular reflectance is less than 0.01 and that the reflectance is diffuse. The 0.04 absorbance that is not accounted for in the absorbance of potassium silicate at 1064 nm is attributable to diffuse reflectance.

Our goal was to create a coating of MWCNTs that retained the high thermal conductivity of the mat while encapsulating the tubes in a binding material having a melting temperature high enough to prevent oxidation. Desirable properties of a thermal detector coating include high thermal conductivity to

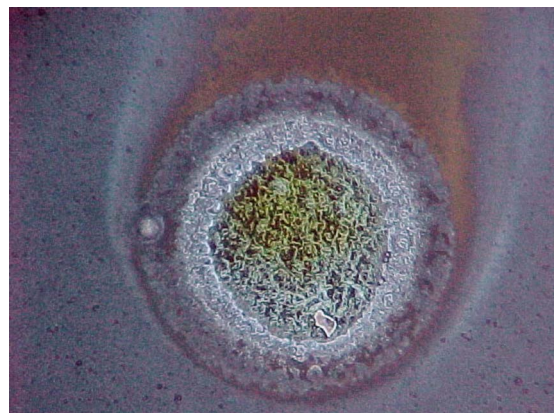


Fig. 2. (Color online) Photographic image of a laser-induced damaged area. The diameter of the damaged area, indicated by the outermost ring, is approximately 2 mm. The translucent nature of the center suggests that the carbon is depleted and the frozen silicate remains. The brightness and contrast are modified to enhance the visibility of the black coating that surrounds the damaged area.



dissipate heat from the site of laser exposure and a high oxidation or melting temperature. We presume that a MWCNT mat fails (is damaged by a laser) because the MWCNTs at the surface get hot enough to oxidize. It is known that MWCNTs burn in the presence of oxygen at 450°C, whereas in vacuum they are potentially stable up to 2800°C [12]. When cured, silicates form a transparent glassy material having very low thermal conductivity and high melting temperature (~760°C according to the manufacturer). With this in mind, our composition strategy is to take advantage of the higher melting temperature of the silicate binder to prevent oxidation of the MWCNTs and yet have a percolated structure of MWCNTs to achieve high thermal conductivity and high optical absorbance. In other words, we want just enough silicate to keep the tubes bound together. Previously, we explored MWCNT coatings in the absence of silicates or other binders [1]. In this Letter, we have found that with less than 2.5 mg of potassium silicate, the cured composite is loosely bound and the MWCNTs dislodge more, as if no binder were present.

Sodium silicate was less favorable because of a lower damage threshold and lower absorbance. We attribute the lower absorbance to efflorescence, which manifests itself by a chalky (less black) appearance. Initially we experimented with sodium silicate in preparing the coatings but found that the coating developed significant efflorescence when baked at 300°C owing to the formation of a white carbonate film (as shown in Fig. 1) on the surface of the coating. These carbonates form either through reaction with carbon dioxide in air or from decomposition of nonnanotube carbons in the coating. By the same process with potassium silicate and lithium silicate, we observed no efflorescence. Lithium silicate is favored in high-temperature environments; therefore we expected lithium silicate to perform favorably. However, the lithium silicate flaked from the copper coupon during the cure at 300°C. This is possibly due to either the brittle nature of lithium silicate or an unfavorable mismatch in thermal conductivity between the copper substrate and the coating.

Preliminary tests with sodium silicate using sodium dodecyl sulfate (SDS) as a surfactant to disperse the MWCNTs were successful. However, SDS used with potassium silicate immediately formed a milky precipitate, and the solution was neither sufficiently stable nor well enough dispersed to prevent clogging the airbrush. The DBS surfactant did not cause the potassium silicate to precipitate. This is likely due to the pH of the DBS being more compatible with that of the silicate, which has a very high pH (~13).

We evaluated three different MWCNT-silicate coatings with respect to laser damage threshold at 1064 nm and compared them to a commercially available ceramic. The composite based on potassium silicate has a higher damage threshold and higher ab-

sorbance compared to that based on either sodium silicate or the commercially available ceramic coating. We attribute the lower absorbance of sodium silicate to efflorescence. Lithium silicate did not manifest efflorescence, but the coating failed to adhere to copper after curing. The damage threshold of approximately 15 kW/cm<sup>2</sup> is comparable to the damage threshold that we had measured previously for a mat of bare tubes. The mere presence of the silicate, however, is favorable, because the cured coating is more physically stable and there is lower risk of individual CNTs being dislodged from physical contact. Future work will include optimizing the proportions of silicate to MWCNTs and the evaluation of the thermal resistance of the composite. Higher-temperature coatings might be obtained by adding metallic powder or clay to the silicate, which could increase the damage threshold. Also it may be possible to reduce efflorescence by employing MWCNTs having higher purity (proportionally less nonnanotube carbon), which may reduce CO<sub>2</sub> generated in the coating during curing and reduce efflorescence. By combining relatively inexpensive MWCNTs with a silicate solution we have established a black absorbing coating that is suitable for large-area thermal detectors and has the convenience of a spray paint.

#### Disclaimer

Trade names are identified only for reference purposes and do not represent or imply an endorsement by NIST.

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