

Characterization of AlF_3 -passivated aluminum mirrors using non-contact thermal metrology

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ABSTRACT

We demonstrate the use of steady-state thermorefectance (SSTR) as a technique for characterizing mirror surfaces. Due to the enhanced sensitivity of thermorefectance compared to reflectance, SSTR provides the ability to assess the physical and chemical characteristics as well as the uniformity of thin films and coatings much more rapidly than common metrological methods such as x-ray photoelectron spectroscopy. The use of this technique is demonstrated on AlF_3 -passivated Al surfaces produced using a process developed for the fabrication of far ultraviolet reflectors. However, since SSTR is thermal in nature, this technique negates the need for *a priori* knowledge of the optical properties of the material. This is emphasized by interrogating both homogeneous and non-uniform AlF_3 films.

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I. INTRODUCTION

Identification of surface and near-surface defects is critical in the manufacturing of optics and optical components for x-ray,^{1,2} ultraviolet (UV),^{3,4} visible,^{5–7} and infrared^{8,9} applications. With the proliferation of thin film coatings and surface treatments comes a need for a wide variety of diagnostics for identifying and subsequently understanding the formation of these defects.^{10,11} Many factors must be considered in these techniques, including spatial resolution, measurement duration, and sensitivity to application-specific materials. In manufacturing settings, the ability to rapidly assess large-area reflectors^{12–15} is critical for quality control, particularly in highly sensitive astronomic applications.

Aluminum is a commonly employed material for optical mirrors due to its broadband reflectance, specifically at wavelengths below 380 nm.¹⁶ However, the natural oxidation of Al significantly reduces that reflection below 200 nm. Significant effort has been made to further increase the reflectance of Al mirrors below 200 nm for far UV (FUV) applications in space-based optics by adding thin (≈ 20 – 25 nm), visually transparent metal fluoride layers that prevent oxidation and thus preserves the high reflection of Al.^{17–20} Plasma-based AlF_3 passivation has emerged as a robust method for FUV reflectivity enhancement of Al mirrors.²¹ This process has been shown to significantly enhance the reflectance of Al mirrors in the FUV spectrum with improved durability in comparison with other reflectance enhancement methods.^{22–24} In this work, we investigate

the use of a novel thermorefectance-based technique as a well-suited tool to meet diagnostic needs for these advanced reflectors.

Thermorefectance spectroscopy has emerged as a powerful tool for measuring changes in optical properties of materials and concomitantly relating these changes in optical properties to physical and chemical properties and the associated changes in electronic and thermal transport processes in solids.^{25–36} The principle of thermorefectance relies on measuring the changes in reflectivity of a sample due to a small perturbation in temperature and/or carrier density induced from an external stimulus.^{26,37,38} The most common implementation of thermorefectance measurements employs a laser-based pump–probe geometry, in which a modulated pump laser induces a small oscillating temperature rise while a continuous-wave (CW) probe laser monitors the reflectivity. Lock-in detection at the modulated pump frequency enables sensitivity to changes in probe reflectivity as small as $\Delta R = 10^{-6}$ – 10^{-4} .^{39–42} This ability to detect small fractional changes in surface reflectivity render thermorefectance metrologies viable routes to detect small changes in surface chemistry, defects, and structure that may not be as easily resolvable by more traditionally employed surface characterization methods.^{43,44} In this study, we compare ellipsometry, x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and Fourier transform infrared (FTIR) spectroscopy, as discussed in the following. Furthermore, as laser-based pump–probe thermorefectance spectroscopies rely on focused laser sources (typically on the order of single digit microns in $1/e^2$ spot sizes), this class of measurement also offers exceptional spatial resolution of changes in reflectivity,^{45–49} which, as we demonstrate in this work, can result in a powerful tool for spatially resolving changes in properties of reflecting surfaces.

As a result of its high spatial resolution and signal sensitivity compared to traditional optical imaging techniques, thermorefectance approaches have been undertaken in many applications for quality control and assessment. Transient thermorefectance techniques have been used for defect detection in solar cells,^{43,50} integrated circuits,⁵¹ and bonds used for heterogeneous integration,⁵² and device-specific applications, such as the identification of hot spots and temperature profiles in photodiode,⁵³ laser diode,⁵⁴ and Schottky diode⁵⁵ structures. Thermorefectance techniques such as time-domain thermorefectance (TDTR)³⁰ and frequency-domain thermorefectance (FDTR)³¹ have been used to quantify and image defects in materials and microstructures.^{56–59} More recently, steady-state thermorefectance (SSTR)⁶⁰ has emerged as a strong competitor to other thermorefectance techniques as a result of its high throughput, enhanced thermal penetration depth, and sensitivity to both in-plane and through-plane thermal conductivity over a wide range of values.^{45,61} SSTR has been used to investigate thin films,^{62–64} buried interfaces and substrates,^{65,66} and to quantify thermal conductivity from nanoscale films to bulk materials.^{45,67}

SSTR utilizes an optical pump–probe technique to induce a steady-state temperature rise in a sample, thus realizing several benefits compared to other thermorefectance techniques. Due to its low modulation frequency, the thermorefectance response in SSTR is dominated by material thermal conductivity, independent of heat capacity.⁴⁵ SSTR boasts an increased thermal penetration depth and is sensitive to buried interfaces and substrates several microns below the sample surface, since in the low-frequency steady-state limit, the thermal penetration depth is approximately the same as the laser

spot size.^{45,62,65} Finally, SSTR measures the geometric mean of both in-plane and cross-plane thermal conductivity, resulting in a technique that can resolve both these components by leveraging sample geometries and material stacks.^{60,68}

In this study, we use SSTR to evaluate the spatial homogeneity of plasma-treated Al surfaces designed for enhanced UV reflectors. We investigate specially designed samples in order to further demonstrate the sensitivity and resolution offered by SSTR as an effective diagnostic technique. As a result of the chemical change imparted to the Al surface by this plasma treatment,²⁴ SSTR is able to detect the subsequent changes in reflectivity and further changes in thermal properties. These indicators offer unique sensitivity to both surface chemistry and quality. Combined with automated measurement control, this approach offers a highly sensitive, rapid solution for the assessment of reflective optic quality. In the following, we discuss the process of creating Al mirrors, which have been AlF₃-passivated and demonstrate the application of SSTR measurements and analysis for their surface evaluation.

II. EXPERIMENTAL

Laser thermal's SSTR in fiber (SSTR-F) system^{60,69,70} was used to rapidly measure the thermorefectance and concomitantly spatially resolve changes in surface quality of the samples. The fiber-based platform, coupled with a fully automated optical alignment system and sample motion stage, allows for rapid acquisition and precisely controlled measurements of reflective samples. A low-frequency (1 kHz) modulated 635 nm pump laser is used to thermally excite the sample, and a CW 785 nm probe laser is used to interrogate the surface ΔR . The measured thermorefectance signal is proportional to the magnitude of the thermal resistance of the sample, which is directly related to its physico-chemical properties. Because this measurement results from a thermal excitation of the sample, SSTR analysis is fundamentally different from common optical spectroscopic techniques. This key difference allows for the use of SSTR as a diagnostic for a broad range of reflective samples. Here, we show both single-point SSTR analysis as well as high-resolution raster scans of mm² areas on several optimally designed AlF₃-passivated mirror samples, detailed in the following.

A. Sample creation

The production of thin, uniform AlF₃ films on Al mirror substrates has been described previously (see the references in the following). The samples analyzed in the present work were fabricated using the same general protocol with the addition of physical masking techniques that allowed for the growth of non-uniform (graded) and patterned AlF₃ films on Al mirrors. These nonhomogeneous surfaces provide ideal samples by which to demonstrate the capabilities of the SSTR diagnostic technique.

The fabrication of bare Al mirrors was carried out in a 1 m diameter coating chamber described elsewhere.⁷¹ All bare Al mirrors were deposited on soda-lime glass slides of 50 × 50 mm² area with the conditions stated previously.⁷² For the present investigation, the chamber bake-out prior to the Al coating deposition was omitted. All the samples were produced during the same coating run, with samples distributed over an area of 200 × 160 mm². Based upon

prior characterization of the chamber, the Al composition and film thickness are anticipated to be consistent between samples within a deposition run.

The plasma passivation process employs electron beam generated plasma⁷¹ produced in a mixture of Ar and SF₆. The system generates sheet-like electron beams with typical current densities of 1–5 mA/cm² and beam energies between 1 and 5 keV to drive plasma production.^{73,74} The system consists of a linear hollow cathode (length = 16.2 cm), an entrance aperture through which the electron beam is injected, a termination anode, and magnetic field coils. Materials are introduced on a processing stage that is oriented parallel to the direction of beam propagation and below the beam volume. In this work, the standoff distance between the beam axis and substrate is 2.5 cm. A co-axial magnetic field of 150 G is used to collimate the e-beam and thus ensure uniformity along its length.⁷⁵ The chosen magnetic field strength leaves the plasma ions un-magnetized while aiding in electron confinement. These parameters are sufficient to produce uniform plasma sheets compatible with a processing stage that accepts 150 mm diameter substrates. The processing stage can either be left at ground (unbiased) resulting in substrate bombardment by very-low-energy ions (<5 eV) or biased using either conventional DC or RF voltage to raise the ion energy.

Importantly, in highly electronegative gases such as SF₆ used in this work, electron beam generated plasmas enable the production of plasmas where the dominant negative charge carriers are negative ions rather than electrons. These, so-called ion–ion plasmas allow for the extraction of either positive or negative ion species from the plasma. Early work in Ar/SF₆ plasmas show that for 50:50 mixtures (by pressure), both positive and negative ions can be delivered to the surface in equal amounts and with energies that are commensurate with the extraction bias.⁷⁶ For the present work, a positive DC bias was used to preferentially extract negative species from the plasma. This was found to be critical to the effective growth of thin, stoichiometric AlF₃ layers on Al films.

The production of non-homogeneous films relied on the use of physical masks placed over the Al mirror substrates, as shown in Fig. 1. All the samples were simultaneously exposed to an electron beam generated plasma produced in ≈ 35 mTorr of Ar/SF₆ for ≈ 20 min. The flow rate was 25 SCCM for each gas and the stage bias

was +20 V. The physical masks included a solid Al mask to produce a “binary” sample, i.e., a single sample with exposed and unexposed areas; a perforated stainless steel mask with a circular mesh (diameter ≈ 230 μ m; center-to-center distance ≈ 395 μ m) to produce a patterned sample; and a cantilevered canopy mask to produce a gradient sample. For the latter, an Al plate is cantilevered over the sample using a 1 mm tall Al plate. The plasma is able to penetrate into the gap created by the plates, but that penetration leads to a decreasing exposure along the length and width of the cantilevered plate.⁷⁷ All masks and underlying Al mirrors were electrically connected to the stage. In addition, a control sample without any mask was used to measure the *in situ* growth rate. That measurement indicated a final AlF₃ film thickness of ≈ 16 nm.

III. AlF₃-PASSIVATED MIRROR ANALYSIS

We compare SSTR analysis of three AlF₃-passivated mirror samples to other commonly employed diagnostic techniques, including ellipsometry FTIR spectroscopy, Raman spectroscopy, and XPS. Each of these methods has advantages and disadvantages involving acquisition and prep time, spot size, and sensitivity, as further discussed in the following. As a particularly time-consuming and low-resolution technique, infrared variable-angle spectroscopic ellipsometry (IR-VASE) is not considered suitable as a rapid diagnostic tool and was, therefore, not included in this investigation. However, the use of IR-VASE to further examine the properties of AlF₃-passivated samples is planned for future investigation.

A. Binary sample

Covering part of the mirror during processing provides a comparison of an AlF₃-passivated mirror with an unpassivated Al mirror on a single sample. Initial measurements of this binary sample involved ten SSTR scans on each region of the sample, as shown in Fig. 2(a). The probe signal on the AlF₃-passivated (uncovered) region is higher than the covered region, consistent with previous work reporting decreased thermal conductance (thus high temperature rises and subsequent higher ΔR) in the passivated material.⁷⁸ Figure 2(b) shows vibrational-mode Raman spectroscopy of the

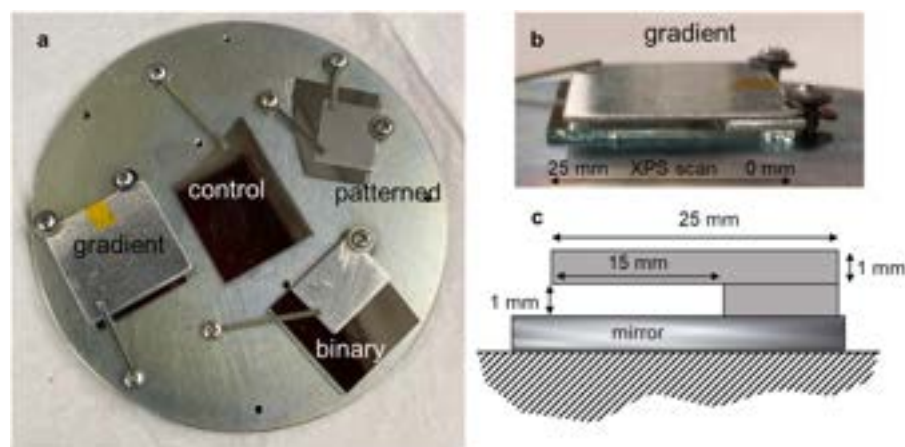


FIG. 1. (a) Setup for processing samples in this study. The control sample was used for monitoring film growth via *in situ* ellipsometry during the AlF₃ passivation process. It should be noted that all mirror surfaces and masks are electrically connected to the underlying platen. (b) Side image of the cantilevered canopy mask used to make the gradient sample and (c) the dimensions of the canopy structure on the gradient sample.

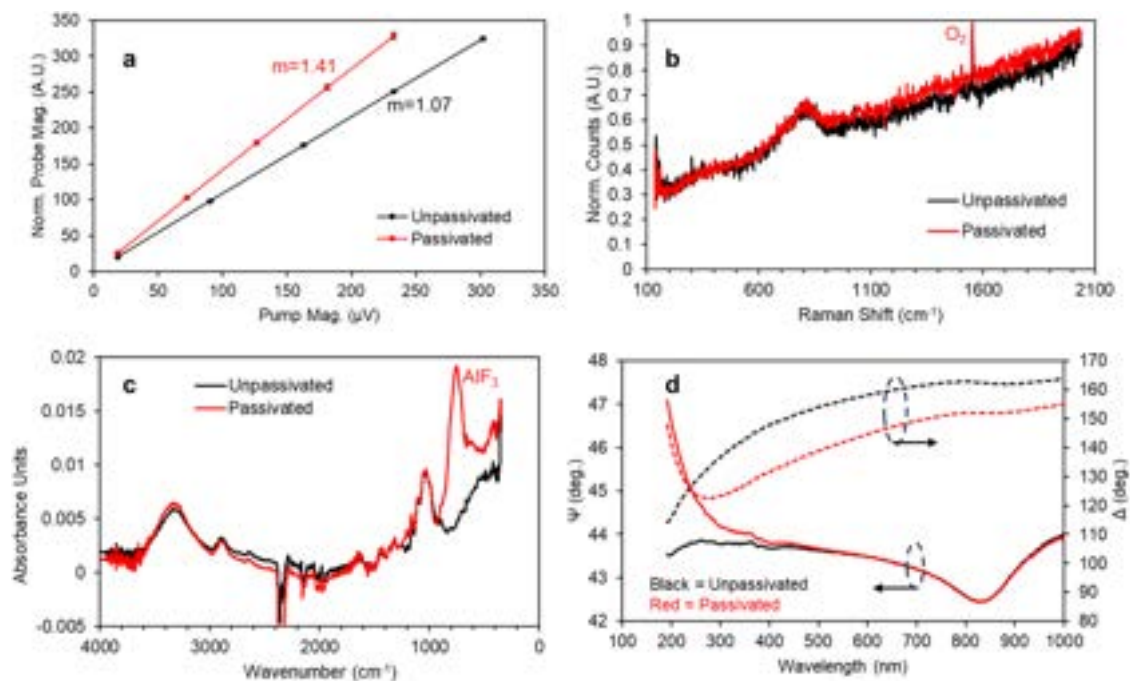


FIG. 2. Analysis of the binary sample via (a) SSTR, (b) Raman spectroscopy, (c) ATR-FTIR, and (d) ellipsometry. The unpassivated region of the sample is indicated by the black curves, and the AlF₃-passivated region of the sample is indicated by the red curves. Slopes (m) of the SSTR measurements are labeled in panel (a). The x axis of panel (a) is the voltage signal of a monitoring pickoff detector of the pump laser, and the y axis is the magnitude of the locked-in probe laser signal divided by its DC magnitude.⁶⁰ Negative values in panel (c) result from FTIR background calibration in the atmosphere prior to the surface-contact ATR-FTIR measurement and are inconsequential for the purpose of this study.

sample, normalized to the small $\approx 1550\text{ cm}^{-1}$ (oxygen) peak, which is a signature of the ambient background and not the samples. No significant difference is seen between the two regions, signifying that this technique is a poor indicator of the AlF₃ passivated surface. Figure 2(c) shows attenuated total reflectance (ATR) FTIR spectroscopy, where the strong AlF₃ peak near 750 cm^{-1} is clear.⁷⁹ ATR-FTIR is a large-area surface-contact analysis technique and is not ideal for delicate optical-quality coatings. Traditional transmission-mode FTIR spectroscopy was attempted; however, no transmission signal was detectable. Finally, Fig. 2(d) shows raw ellipsometry scans of the two regions at 55° incidence. The differences between the two regions become more apparent at shorter wavelengths as a result of the enhanced UV reflectance due to the AlF₃-passivation, particularly in the Ψ parameter (ratio of the r_p and r_s components). There is some broadband, wavelength-dependent distinction between the two regions, specifically in the phase delay/retardance component (Δ). These differences result from the presence or absence of the AlF₃ layer since Δ is very sensitive to thickness variations of the dielectric film. Importantly, the relatively low spatial resolution of ellipsometry (tens of microns at best) compared to other techniques limits its sensitivity to small surface defects.

B. Patterned sample

To investigate the ability of SSTR to sense spatially varying defects and irregularities on mirror surfaces, an Al mirror sample

was covered with a perforated mask that included a mesh pattern of holes roughly $230\text{ }\mu\text{m}$ in diameter. The resultant patterning is invisible to the naked eye; however, the AlF₃-passivated regions have an increased height compared to the surrounding Al by a few tens of nanometers, as indicated by profilometric measurements. While topography is informative for such an intentionally patterned sample, profilometry alone is only sensitive to localized height differences and, therefore, cannot be used to fully characterize smooth surfaces or chemical defects, as in the gradient sample in the following.

XPS is commonly used for analysis of surface materials as it provides chemical composition and bonding information. This technique has been widely employed for the assessment of mirror surfaces.^{24,72,80–84} For this reason, XPS was initially used to assess the patterned sample, as shown in Fig. 3(a). Here, the image is centered at the F1s peak ($\approx 688\text{ eV}$) and was created from ten scans averaged together with $10\text{ }\mu\text{m}/\text{pixel}$ resolution. The potential for overlap of photoelectron peaks could further hamper the spatial resolution. It should be noted that by nature of the technique, XPS is insensitive to features more than $\approx 10\text{ nm}$ from the surface.

In comparison, Fig. 3(b) shows an SSTR map of the patterned sample. This image has $5\text{ }\mu\text{m}/\text{pixel}$ resolution and was created from a single continuous raster scan of the sample. Not only are defects and surface features highly visible in this map but also the AlF₃-passivated regions on the sample are much clearer compared to the XPS map. With the SSTR map, the irregular and noncircular nature

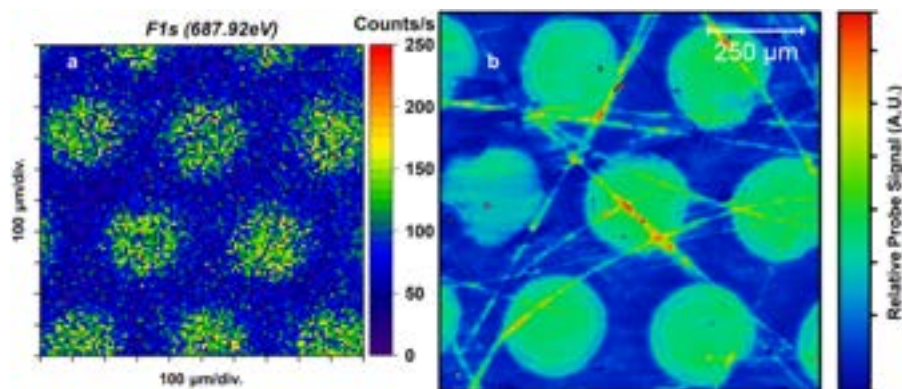


FIG. 3. Analysis of the patterned sample via (a) XPS and (b) SSTR. Each map is produced by scanning over a 1 mm² region of the sample. The XPS map is centered on the F1s peak and was created by averaging together ten maps with 10 μm/pixel resolution. The SSTR map was created with a single continuous scan with 5 μm/pixel resolution.

of the patterned features (as well as scratches in the surface likely due to prior substrate polishing or the physical mask contact) becomes clear, highlighting the importance of the superior resolution and sensitivity offered by SSTR interrogation. SSTR is sensitive to both compositional and topographical changes in the sample with high spatial resolution.

C. Gradient sample

Finally, a sample was created using a cantilevered canopy mask to produce a gradient in the AlF₃ passivation layer. The small (1 mm) gap between the plate and the sample surface serves to reduce density of the plasma and thus the flux of negative ions to the mirror substrate as the plasma diffuses into the volume under the canopy.⁷⁷ This sample allowed for further assessment of the sensitivity of SSTR for surface uniformity analysis.

The sample was initially analyzed via XPS. Spatial surface chemical profiles were generated using Al 2p line profile scans. The Al 2p high resolution spectra were collected using a 400 μm x-ray spot on the sample and stepped 2 mm across the long-axis of the canopied gradient sample, as indicated in Fig. 1(b). A pass energy of 30 eV was used and three scans were averaged for each position, with an average single spectrum collection time of 30 s. Not including stage movement time, a total measurement time of 21 min was necessary to generate the contour profile plot seen in Fig. 4(a). In the contour plot, the support of the cantilevered plate is located at the bottom of the image and extends from 0 to 10 mm. The cantilevered plate extends to 25 mm, thus creating a gap above the sample that extends from 10 to 25 mm. At the bottom of the plot (<10 mm), where the substrate is covered by the support, only Al and Al₂O₃ peaks are seen. An exemplary spectrum from this region is shown in Fig. 4(b) and is characteristic of a typical native oxide layer on

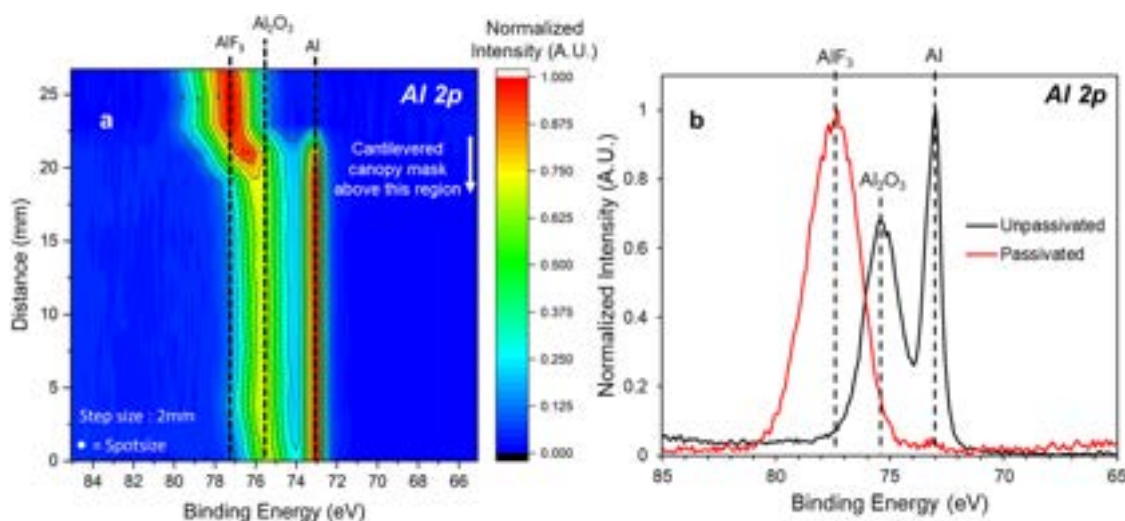


FIG. 4. (a) Contour profile of the gradient surface generated from high-resolution Al 2p XPS spectra, showing the mask produced a chemically graded surface extending 5 mm from the end of cantilevered plate. A strong Al₂O₃ and Al signal is seen in the remaining unpassivated (covered) region, commensurate with a native oxide. The metallic Al peak in the Al 2p spectral region is not present in the exposed portion of the film and is consistent with the increase in probe signal seen in the SSTR data. The y-axis scan distance is indicated in Fig. 1(b). (b) The spectral peaks of both the covered ($d = 0$ mm) and exposed ($d = 25$ mm) regions.

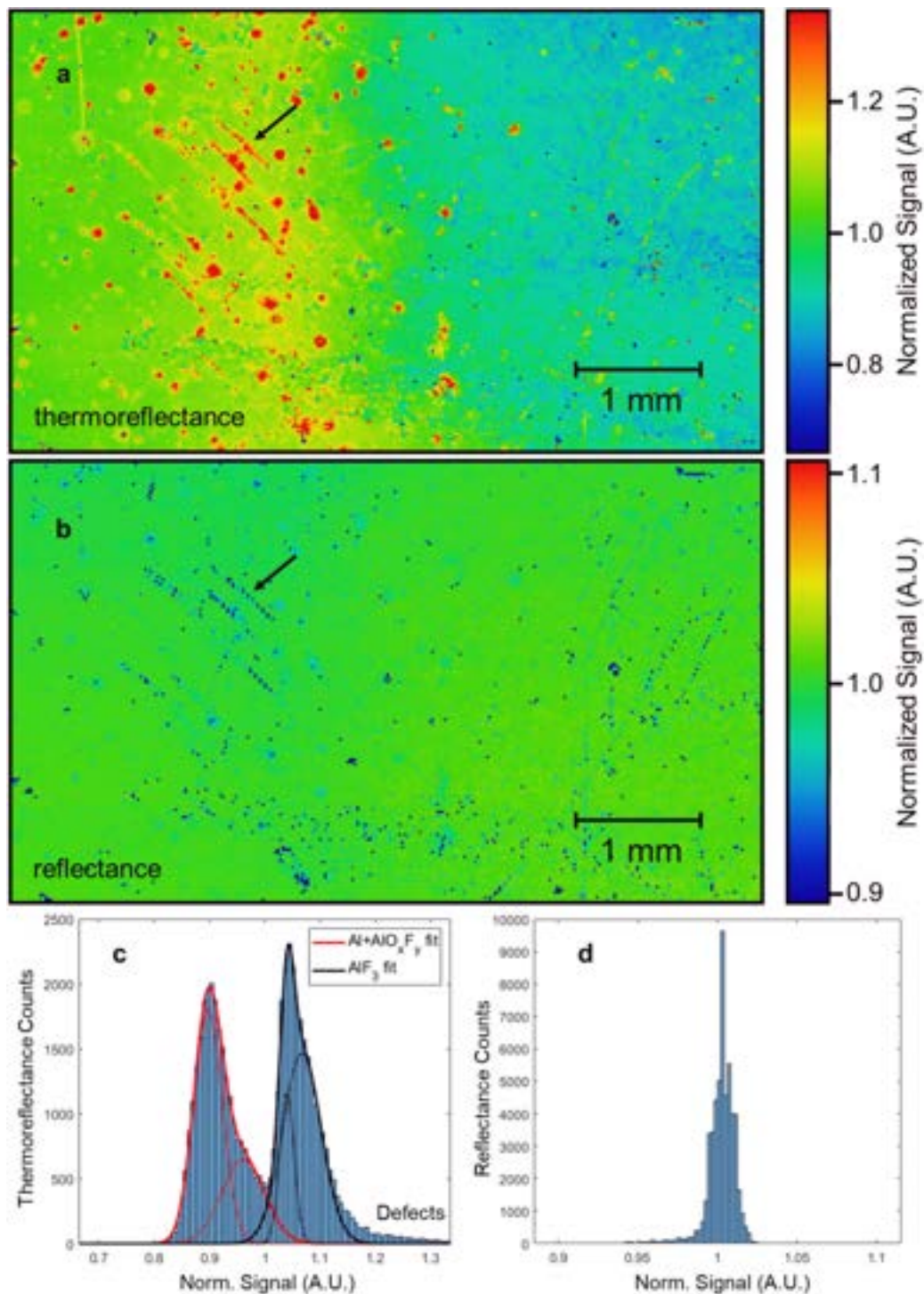


FIG. 5. Gradient sample imaged via (a) the thermoreflectance signal and (b) the reflectance signal. The open end of the cantilevered plate is on the left side. The maps are obtained simultaneously scanning over the exact same $6 \times 3.5 \text{ mm}^2$ region of the sample with $20 \text{ }\mu\text{m}/\text{pixel}$ resolution. Each image is normalized by the mean signal, and the color scale set to $\pm 3\sigma$, allowing for direct comparison. The arrows highlight the differences in clarity for a specific defect. (c) A histogram of the thermoreflectance image in (a) fit with second-order Gaussian functions. The components of these curves are represented by the dashed lines. The tail to the right is the contribution from physical defects. (d) A histogram of the reflectance image in panel (b). Differences between the histograms in panels (c) and (d) illustrate the improved sensitivity to chemical changes and defects obtained using thermoreflectance via SSTR.

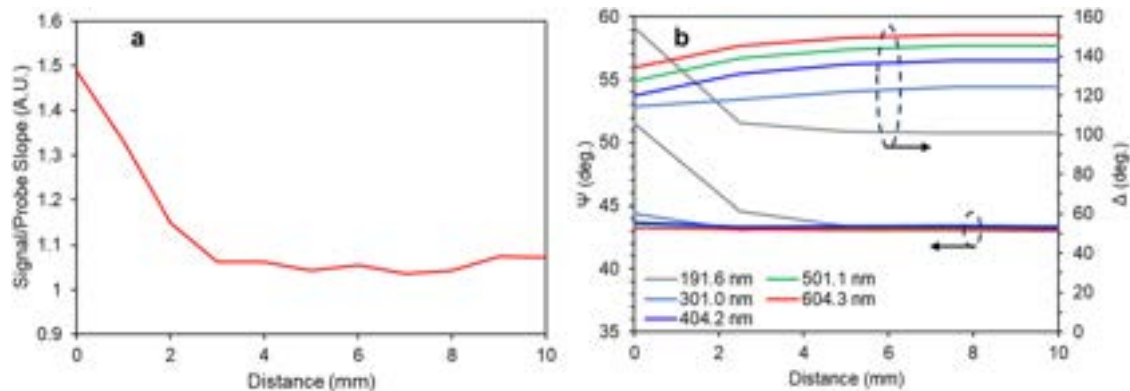


FIG. 6. Gradient sample measured via (a) SSTR and (b) ellipsometry from the open end of the non-contact mask (left side) to beneath it. The magnitude in panel (a) is the point-by-point slope of the thermoreflectance signal, comparable with the color map magnitude in Fig. 5(a). The ellipsometry parameter Ψ shown in panel (b) is only sensitive to the passivation gradient at shorter wavelengths as a result of a polarization inversion. In addition, the SSTR spot size is roughly two orders of magnitude smaller than that of the ellipsometer.

Al. At the top of the plot (>25 mm), which corresponds to the fully exposed region of the sample, neither peak is present. The exemplary spectrum of this region, also shown in Fig. 4(b), clearly indicates that only AlF_3 is present. The distinct AlF_3 signal and absence of an unbound Al signal in the exposed region are compatible with a 16 nm thick AlF_3 passivation layer determined using the *in situ* ellipsometry measurements discussed above. Beginning at ~ 20 mm, the peak intensity shifts toward higher energies indicating the start of the chemical gradient. The full transition from oxide to fluoride is largely complete in a few mm.

The gradient sample was mapped using SSTR similarly to the patterned sample in Fig. 2(b). DC reflectance of the 785 nm probe laser was captured simultaneously during this measurement, allowing for a direct comparison to the SSTR signal. Figure 5 shows the SSTR map (a) and reflectance map (b), emphasizing the enhanced sensitivity of thermoreflectance relative to reflectance in detecting changes in surface features, defects, and chemical changes. Each image is normalized by the mean signal, and the color scale set to $\pm 3\sigma$, allowing for direct comparison of the two. In the thermoreflectance image [Fig. 5(a)], the AlF_3 -passivated region on the left is clear and indicates significant detail, whereas little more than surface physical defects (scratches, pits, debris, etc.) can be discerned within measurement resolution in the reflectance map shown in Fig. 5(b). That is, in addition to the same surface chemistry information obtained by XPS in Fig. 4, thermoreflectance measurements via SSTR capture topographic defect information in Fig. 5(a) with even greater sensitivity than the reflectance map shown in Fig. 5(b).

To better illustrate this, histograms of the thermoreflectance and reflectance maps are shown in Figs. 5(c) and 5(d), respectively. Figure 5(c) indicates two distinct peaks within the image in Fig. 5(a), corresponding to the passivated (AlF_3) and unpassivated (Al) regions. Curve fitting reveals two distinct Gaussian components of each peak. The left peak captures the unpassivated Al region as well as the chemical gradient corresponding to AlO_xF_y . The right peak captures the passivated AlF_3 as well as the higher signal

(yellowish) region near the physical defects. While outside the scope of this study, we suspect this component is due to chemical changes from plasma interactions with this defect-dense region near the edge of the canopy mask. Physical defects are captured in the right-side tail of the histogram. Compared to Fig. 5(c), Fig. 5(d) shows a solitary peak, indicating the insensitivity of reflectance to the varying surface chemistry of the sample.

Figure 6 again compares the SSTR-measured thermoreflectance to ellipsometry. In Fig. 6(a), the slope of periodic SSTR measurements similar to Fig. 2(a) are plotted as a function of distance along the gradient sample, beginning on the open end of the cantilevered plate. Figure 6(b) shows a similar investigation comparing the ellipsometry parameters Ψ and Δ in a scan across the sample with 2.5 mm steps. It should be noted that the ellipsometry parameter Ψ is insensitive to the difference between the AlF_3 -passivated and unpassivated regions except at shorter wavelengths (191.6 nm) corresponding to a polarization inversion effect where r_p becomes higher than r_s ,^{24,72} whereas differences in Δ over the whole range are due to the fact that Δ is very sensitive to thickness variations of the dielectric film. As demonstrated in Figs. 3 and 5, it should be noted again that SSTR analysis is capable of much higher spatial resolution than ellipsometry as a result of the focused laser optics used for sensing (<10 μm -diameter spot size).

IV. SUMMARY

In this study, we highlight the use of SSTR for the physico-chemical assessment of optical surfaces. Here, we focus on the development of AlF_3 -passivated Al surfaces for FUV reflector applications and compare the effectiveness of SSTR with other commonly employed diagnostic techniques. Table I summarizes these measurement characteristics and their advantages and disadvantages.

SSTR has a clear advantage over other techniques in resolution, measurement duration, and AlF_3 sensitivity. Analysis of the binary sample served as a simple demonstration of the sensitivity of these techniques to chemical composition. While spectroscopic

TABLE I. Comparison of techniques used in this study and their relevant attributes.

Measurement technique	Spot size	Single-point acquisition time	Sensitive to AlF ₃
SSTR	1–10 μm $\varnothing$	~ 1 s	Yes
Ellipsometry	0.3×1.2 mm ^{2a}	~ 5 s ^b	Yes
XPS	~ 200 μm $\varnothing$ ^c	> 1 min ^d	Yes
ATR-FTIR ^e	~ 0.5 mm $\varnothing$ ^f	~ 30 s	Yes
Raman spectroscopy	Diffraction limited	> 10 s ^g	No

^aSpecialized high-resolution ellipsometers can achieve roughly 25×60 μm^2 resolution (J. A. Woollam).
^bUnlike other techniques, duration cannot be significantly changed at the expense of signal-to-noise ratio.
^cOther XPS techniques can achieve spots roughly an order of magnitude less than this.
^dSignificant time is required for chamber pump down and optional surface prep.
^eTechnique requires surface contact with the sample and is not suitable for this application.
^fOptical mapping techniques can be used to improve the spectroscopy resolution to much less than the contact area.⁸⁵
^g40 s scans were used in this study.

techniques such as XPS can offer quantitative compositional analysis of materials, the benefit of these factors must be weighed in accordance with their application-specific necessity the additional acquisition time required, as noted in Table I. Analysis of the patterned and gradient samples served to further demonstrate the spatial resolution of SSTR as well as its sensitivity to very slight chemical changes. Figures 3 and 5 further illustrate the sensitivity of SSTR to surface features and defects. For optical applications in particular, surface quality is critical, a characteristic which is more pronounced at shorter wavelengths.^{80,86}

Because SSTR is intrinsically a thermal interrogation method rather than optical, this technique can be used on a multitude of reflective objects, regardless of the optical application. As a result of the enhanced sensitivity offered by thermoreflectance in comparison with other analysis techniques, SSTR provides an exciting platform for high-resolution uniformity and quality assessment of mirrors and other reflective surfaces without the need for *a priori* knowledge of the sample and its optical properties. This was illustrated by interrogating both homogeneous and non-uniform AlF₃ films using SSTR and other common surface characterization techniques.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Andrew H. Jones: Conceptualization (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Writing – original draft (lead). **John T. Gaskins:** Conceptualization (equal); Investigation (equal); Methodology (equal). **Patrick E. Hopkins:** Conceptualization (supporting); Writing – original draft (supporting). **Scott G. Walton:** Conceptualization (supporting); Investigation (supporting); Methodology (supporting); Writing – original draft (supporting). **David R. Boris:** Investigation (supporting); Methodology (supporting). **John. P. Murphy:** Investigation (supporting). **Luis V. Rodriguez de Marcos:** Investigation (supporting). **Javier del Hoyo:** Investigation (supporting). **Manuel A. Quijada:** Investigation (supporting).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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