RESEARCH ARTICLE | NOVEMBER 15 2023

## In situ monitoring of sapphire nanostructure etching using optical emission spectroscopy ⊘

Special Collection: Papers from the 66th International Conference on Electron, Ion and Photon Beam Technology and Nanofabrication (EIPBN 2023)

Kun-Chieh Chien 💿 ; Noah Graff 💿 ; Dragan Djurdjanovic 💿 ; Chih-Hao Chang 🕿 💿

() Check for updates

J. Vac. Sci. Technol. B 41, 062807 (2023) https://doi.org/10.1116/6.0003023



**CrossMark** 







info@hiden.co.uk

🕲 www.HidenAnalytical.com







# *In situ* monitoring of sapphire nanostructure etching using optical emission spectroscopy

Cite as: J. Vac. Sci. Technol. B **41**, 062807 (2023); doi: 10.1116/6.0003023 Submitted: 31 July 2023 · Accepted: 23 October 2023 · Published Online: 15 November 2023



Kun-Chieh Chien, 💿 Noah Graff, 💿 Dragan Djurdjanovic, 💿 and Chih-Hao Changa) 💿

#### AFFILIATIONS

Walker Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas 78712

**Note:** This paper is part of the Special Topic Collection: Papers from the 66th International Conference on Electron, Ion and Photon Beam Technology and Nanofabrication (EIPBN 2023).

<sup>a)</sup>Author to whom correspondence should be addressed: chichang@utexas.edu

#### ABSTRACT

Fabrication of nanostructures on sapphire surfaces can enable unique applications in nanophotonics, optoelectronics, and functional transparent ceramics. However, the high chemical stability and mechanical hardness of sapphire make the fabrication of high density, high aspect ratio structures in sapphire challenging. In this study, we propose the use of optical emission spectroscopy (OES) to investigate the sapphire etching mechanism and for endpoint detection. The proposed process employs nanopillars composed of polymer and polysilicon as an etch mask, which allows the fabrication of large-area sapphire nanostructures. The results show that one can identify the emission wavelengths of key elements Al, O, Br, Cl, and H using squared loadings of the primary principal component obtained from principal component analysis of OES readings without the need of domain knowledge or user experience. By further examining the OES signal of Al and O at 395.6 nm, an empirical first-order model can be used to find a predicted endpoint at around 170 s, indicating the moment when the mask is completely removed, and the sapphire substrate is fully exposed. The fabrication results show that the highest aspect ratio of sapphire nanostructures that can be achieved is 2.07, with a width of 242 nm and a height of 500 nm. The demonstrated fabrication approach is can create high sapphire nanostructures without using a metal mask to enhance the sapphire etch selectivity.

Published under an exclusive license by the AVS. https://doi.org/10.1116/6.0003023

### I. INTRODUCTION

Sapphire has many applications in photonics,<sup>1–3</sup> optoelectronics,<sup>4,5</sup> and functional transparent ceramics<sup>6,7</sup> due to its attractive characteristics, such as high mechanical hardness, thermal tolerance, chemical stability, and high optical transmittance in the infrared spectrum.<sup>8–10</sup> However, these prominent properties make processing sapphire for features with high density and high aspect ratio (HAR) challenging. This limitation has led to less exploration of the functional sapphire surface enabled by bioinspired nanostructures, such as antiglare<sup>11–15</sup> and self-cleaning,<sup>14,16–19</sup> which can be found in conventional silicon oxide-based materials.

For sapphire processing via dry etching, previous studies demonstrated  $Al_2O_3$  films<sup>20–22</sup> and sapphire<sup>23–26</sup> etching, but they either focused on amorphous  $Al_2O_3$  films or operated at the micrometer scale with a low aspect ratio or random order. Considering scalability, other works utilizing nanoimprint lithography following an inductively coupled plasma reactive-ion etching (ICP-RIE) were used to fabricate patterned sapphire substrates, which can improve light-extraction efficiency of GaN light-emitting diodes.<sup>27,28</sup> At the 100 nm length scale, a recent work using a multilayer etching mask was demonstrated to enhance the total etch selectivity, resulting in the production of antireflection sapphire nanostructures with an HAR of 2.03.<sup>29</sup> However, the above techniques require either a hard mask, multilayer mask, or metal mask to enhance the sapphire etch selectivity, potentially leading to mask removal issues and higher surface roughness. Such processes are also relatively complicated and can limit potential applications.

In this work, we present a simplified technique to fabricate large-area HAR sapphire nanostructures using polysilicon nanopillars as an etch mask. The etch process is monitored using optical emission spectroscopy (OES) sensor readings, which are processed by principal component analysis (PCA) to investigate the sapphire etching mechanism and for endpoint detection. PCA is a multivariate statistical analysis tool commonly used for dimensionality reduction, in which correlated data are projected onto a smaller set



of uncorrelated data to obtain a smaller data size, while preserving as much variation in the reduced-dimensionality data set as possible.<sup>30,31</sup> PCA is suitable for processing OES data for the following reasons. First, each source of optical emissions is distributed across multiple wavelengths in the spectrum. Second, optical emissions from each source have a strong correlation to one another. Lastly, PCA can capture different correlations in different principal components (PCs). Therefore, PCA has been used in previous studies to identify key emission wavelengths without any domain knowledge,<sup>32,33</sup> and to detect the endpoint in the etching process.<sup>34–36</sup> In this study, we will discuss using PCA to identify key element emissions during the sapphire etching process. An empirical first-order etching model will be fitted to the OES signal to find a predicted endpoint in the sapphire etching process, which indicates the moment when the mask is completely removed, and the sapphire substrate is fully exposed. This work improves understanding of the sapphire etching process by using in situ monitoring and demonstrates the fabrication of HAR sapphire nanostructures, which can find applications in nanophotonics, optoelectronics, and functional transparent ceramics.

#### II. METHOD

The proposed processes for the fabrication of HAR sapphire nanostructures are illustrated in Fig. 1. Initially, a thick polysilicon layer with a thickness of around  $1 \,\mu m$  is deposited on the sapphire substrate using low-pressure chemical vapor deposition (LPCVD). An antireflection coating (ARC i-con-7, Brewer Science) is spincoated with a thickness of 100 nm to minimize the amount of light reflected from the polysilicon layer and reduce standing wave and sidewall waviness. A 200 nm PR (PFI-88A2, Sumitomo) is then spin-coated on the ARC layer. The PR is exposed using Lloyd's mirror interference lithography<sup>37</sup> with a 325 nm HeCd laser in the transverse electric (TE) mode. In Lloyd's mirror interference lithography, the spatial period  $\Lambda$  of interference fringes is controlled by the angle of incidence of two laser beams, which is set by rotating the stage that holds the mirror and chuck, as determined by

$$\Lambda = \frac{\lambda}{2\sin\theta},\tag{1}$$

where  $\lambda$  is the wavelength of the laser and  $\theta$  is the half of the angle between the two interfering beams, which also corresponds to the rotating angle of the stage holding the mirror and the chuck. 1D grating patterns are obtained with a single exposure, and 2D periodic pillar arrays are achieved with two orthogonal exposures. Lloyd's mirror interference lithography can fabricate nanostructures over a large area, making potential applications more practical and feasible. After forming 2D pillar arrays with a 300 nm period in the PR, the pattern is transferred to the underlying layers using ICP-RIE (Oxford 100). Oxygen gas is used (145 s etch time, RF power 60 W, pressure 13 mTorr, and flow rate 25 SCCM) to transfer the PR pattern into ARC, and HBr gas (80 min etch time, RF power 20 W, ICP power 200 W, pressure 8 mTorr, and flow rate 20 SCCM) is used to further etch into the polysilicon layer. A low RF power in the HBr etch is used to enhance etch selectivity,<sup>3</sup> allowing the formation of HAR polysilicon nanopillars as an etch allowing the formation of HAR polysilicon nanopillars as an etch mask for the sapphire etching process. Finally, BCl<sub>3</sub>/HBr ICP-RIE (18 min etch time, RF power 400 W, ICP power 1500 W, pressure 8 mTorr, and flow rate 15 SCCM for each gas) is used to further Development Period of 300 nm





FIG. 1. Fabrication processes for HAR sapphire nanostructures in this study. The structures are patterned using Lloyd's mirror interference lithography and transferred to the sapphire substrate using ICP-RIE with various etch chemistry.



etch the pattern into the substrate to create sapphire nanostructures.

To understand the ICP-RIE sapphire etching process, a broadband spectrometer (Ocean Insight HR4Pro) is attached to the viewport of the ICP-RIE system to collect the OES signal during etching. The analysis methodology used in this study involves utilizing loadings obtained from PCA to identify key emission wavelengths during the sapphire etching process.<sup>32</sup> PCA is defined as an orthogonal linear transformation that converts raw data into a new coordinate system, which can then be used to express the original data using fewer dimensions. For an OES data in the form of a  $m \times n$  matrix X, with m being time samples and n wavelengths, the PCA operation results in the OES data X being the product of the score matrix T and the loading matrix W, along with an additional residual matrix E, is given by

$$X = TW^T + E, (2)$$

where

$$T = [t_1, t_2, \cdots, t_l],$$
 (3)

$$W = [w_1, w_2, \cdots, w_l].$$
 (4)

Here, l is the number of principal components, which is normally much less than n. The matrix term  $TW^T$  represents the PCA modeled component of reduced dimensionality, while residual matrix E is the unmodeled component. The loading matrix W consists of a set of eigenvectors obtained by eigen-decomposition of the covariance matrix of the OES data X, which is scaled to have column-wise zero mean. Since both score matrix T and loading matrix W are orthogonal,<sup>39</sup> Eq. (2) can be rewritten as

$$t_k = X \cdot w_k$$
, where  $k \le l$ . (5)

The score vector  $t_k$  is the projection of the original OES data X onto the kth principal component, which implies that the loading vector  $w_k$  shows the contribution of each wavelength to form the score vector  $t_k$ . Since loadings can be positive or negative, squared loadings are used in this paper to identify key emission wavelengths in the OES data, meaning that the higher the squared loading, the more significant the contribution of the corresponding wavelength is deemed to be.

#### **III. RESULTS AND DISCUSSION**

#### A. OES of the sapphire etching process

To investigate the sapphire etching mechanisms, OES data are collected for each timestamp during the BCl<sub>3</sub>/HBr ICP-RIE process. The integration time of the spectrometer is set to 10 s to increase the signal-to-noise ratio. The raw OES data for sapphire etching which lasted for 18 min, as well as a picture of the etching sample, are shown in Figs. 2(a) and 2(b), respectively. In Fig. 2(a), multiple peaks or strong emissions across the spectra can be observed, but it is not possible to directly identify which emission peak contains important process information. In Fig. 2(b), it can be observed that most parts of the mask, which consists of polysilicon





**FIG. 2.** (a) Experimentally collected OES data from HBr/BCl<sub>3</sub> sapphire etching with an etch time of 18 min. Measured OES data from 300 to 900 nm wavelength at 107 timestamps at 10 s intervals. Top ten key wavelengths identified via squared loadings of PC1 and corresponding materials at key emission wavelengths found in the NIST table, including Al and O (393.5–395.6 nm), Br and H (655.4–655.7 nm), Br (826.3 nm), and CI (836.8 nm). The inset shows key emissions of Al and O from 393 to 396 nm. (b) The sapphire sample after etching for 18 min. The polysilicon mask exhibiting a deep-colored appearance is not completely removed at the sides.

nanopillars exhibiting a deep-colored appearance, have been removed. However, due to the nonuniform thickness of the polysilicon layer from the LPCVD process and location-dependent variations in ICP-RIE etch rates, some parts of the polysilicon nanopillars around the sample's edges have not been completely removed. Since the goal of this study is to achieve the tallest possible sapphire nanostructures, the endpoint of this study is defined



FIG. 3. PCA analysis of the OES data from HBr/BCl<sub>3</sub> sapphire etching with an etch time of 18 min. (a) Calculated scores on PC1, PC2, and PC3. (b) Squared loadings of PC1 and corresponding materials at key emission wavelengths, including Al and O (393.5–395.6 nm), Br and H (655.4-655.7 nm), Br (826.3 nm), and Cl (836.8 nm). The inset shows squared loadings of PC2 and corresponding materials at key emission wavelengths, including Br (826.1-826.6, 843.9, 863.2, and 888.6-889.1 nm) and Cl (836.5-837 nm).

as the moment when the polysilicon mask is completely removed during the sapphire etching process. In other words, the endpoint of the sapphire etching process has not been reached within the etch time of 18 min. Therefore, an additional sapphire etching for 5 min is performed, and the result shows that the mask is completely removed, with the sample being fully transparent.

Then, key wavelength analysis via PCA is performed to identify which emissions are critical to the etching process. The calculated scores on the three most significant principal components of the OES data obtained from 18 min of etching are plotted in Fig. 3(a). The scores on the most prominent principal component, labeled as PC1 and denoted with a blue line, show an increasing trend over time, which is reasonable due to more sapphire being exposed during the etching process. However, even though scores on the second most significant principal component, labeled with PC2 and denoted by a red line, show a minimum point at around 10 min, it is not a true endpoint since the mask has not been completely removed after 18 min. Scores on the third most significant component, labeled as PC3 and denoted by a vellow line, appear random and can be attributed to noise due to their stochastic distribution. Therefore, the squared loadings of PC1 should be used for the identification of the key wavelengths. To validate this statement, the squared loadings of PC1 and PC2, as shown in Figs. 3(b) and 3(c), are further discussed. In Fig. 3(b), the wavelengths having the top ten squared loadings are selected and can be categorized into four groups: 393.5-395.6, 655.4-655.7, 826.3, and categorized into rour provided by the National Institute of Standards of spectra database provided by the National Institute of Standards of and Technology to identify corresponding critical materials in the <sup>40</sup> The results are shown in Table I, as well as Figs. 2(a) and 3(b). The range from 393.5 to 395.6 nm represents emissions of Al and O, while the range from 655.4 to 655.7 nm represents emissions of Br and H. The emission at 826.3 nm represents Br, § and 836.8 nm represents emissions of Cl. On the other hand, the results in Fig. 3(c) show that wavelengths with the top squared loadings of PC2 are mainly emissions of Br and Cl, which include 826.1-826.6, 836.5-837, 843.9, 863.2, and 888.6-889.1 nm. From a process perspective, selecting the emission of Br or Cl, which come from the input gases, to monitor the etching process might not be the best way since it cannot directly represent the etching condition on the sample. On the other hand, since Al and O originate from the sapphire sample during the etching process, their emissions can accurately reflect the exposed portions of the sapphire sample. As a

TABLE I. Top ten key wavelengths identified via squared loadings of PC1 vs NIST emission lines.

Key wavelength (nm)	Corresponding element and emission wavelength (nm) found in NIST table
393.5, 393.7, 394.5, 395	Al I (394.4 and 396.2)
395.3, and 395.6	O I (394.7 and 394.8)
655.4 and 655.7	Br I (654.4 and 656)
	H I (656.3)
826.3	Br I (826.5)
836.8	Cl I (837.6)





**FIG. 4.** (a) The emission of Al and O over time at 395.6 nm during the sapphire etching process. (b) The emission of Br over time at 826.3 nm during the sapphire etching process.

result, although the scores on PC2 seem to have an interesting trend, but it is not considered as a candidate for the analysis of the key wavelength selection.

Further investigation of the OES signals at those wavelengths reveals that emissions of Al and O, originating from the sapphire substrate, become stronger over time. On the other hand, emissions of Br, H, and Cl, which come from the input gases, become weaker over time. For example, Fig. 4(a) shows an increasing emission of Al and O at 395.6 nm over time, while Fig. 4(b) demonstrates a decreasing emission of Br at 826.3 nm. The increasing trend in Al and O emissions can be attributed to more areas of the sapphire substrate becoming exposed during etching, while the decreasing trend in Br, H, and Cl emissions is a result of increased reaction due to the expanding sapphire surface. Another interesting observation from the OES data shown in Fig. 2(a) is that emissions of Br, H, and Cl are significantly stronger compared to emissions of Al and O from 393.5 to 395.6 nm, which are shown in the inset of Fig. 2(a). This can be attributed to the relatively smaller size of the sapphire sample in comparison to the volume of input gases distributed throughout the entire chamber. However, PCA enables the identification of Al and O emission peaks, which are of lower intensity but carry important process information and are critical for process development.

Based on the previous discussion, the squared loading of PC1 has the highest value at 395.6 nm, representing an emission of key elements Al and O. Furthermore, the parameters of each sapphire etching process are the same and remain constant throughout. That is, the OES data are collected and analyzed under the same process conditions. Therefore, in this study, the OES data collected during the first 18-min etching process is used to identify key wavelengths, and the one collected during the additional etching process is used to find the endpoint in the process. As a result, the OES signal of an additional etching for 5 min at 395.6 nm is further discussed. As shown by the red line in Fig 5(a), the OES signal increases exponentially and finally reaches a steady state, which is reasonable since the polysilicon mask has been etched away and the sapphire substrate is fully exposed during this etching process. Moreover, it can be observed that the OES signal behaves like a typical first-order system.<sup>4</sup>

To explain this observation, an empirical first-order system for the plasma etching process and the corresponding OES signal is discussed. During the etch, the emission intensities are proportional to the densities of the electronically excited species, and the amount of excited species promoted by electrons is determined by the electron energy distribution function of the plasma.<sup>42</sup> Since process parameters, such as RF and ICP power, gas flow, and chamber pressure, do not change significantly during the etching process, one can assume that the electron energy distribution of the plasma does not vary over time. With this assumption, the optical emission intensity I(t) can be expressed as

$$I(t) \propto n_{\text{excited}}(t) = cQ(t), \tag{6}$$

where  $n_{\text{excited}}$  is the density of the species in a certain exited state, Q(t) is the total amount of the species in the ground state, and *c* is a constant showing the relationship between the density of the excited species and the total amount of the ground state species. Furthermore, as shown in Fig. 5(b), the density of the excited species during the etching process will be affected by the etch rate dy/dt, where *y* is the thickness etched from the substrate, and the amount of the ground state species being pumped out of the chamber dQ/dt. Therefore,  $n_{\text{excited}}(t)$  can be expressed as

$$n_{\text{excited}}(t) = \alpha \frac{dy}{dt} - \beta \frac{dQ}{dt},$$
(7)

where  $\alpha$  and  $\beta$  are experimental constants. Here, we assume that the etch rate does not change dramatically during the 5 min long



pubs.aip.org/avs/jvb

etch and is constant in this process. With this assumption and combining Eqs. (6) and (7), we can find that the optical emission intensity I(t) is proportional to the total amount of the ground state species Q(t). Function Q(t) is the solution of a first-order differential equation with a step response input,

$$\beta \frac{dQ}{dt} + cQ(t) = \gamma, \qquad (8)$$

where  $\gamma$  is a constant which equals to  $\alpha$  times the constant etch rate. Based on this model, the empirical first-order solution is



FIG. 5. (a) OES signal at 395.6 nm (red solid line) in the additional etching for 5 min. A solution of the first-order system (blue dashed line) fitted to the OES signal. (b) Schematic of the simplified etching process approximated by a firstorder system.

found by least squares fitting to the OES signal at 395.6 nm and is found to be

$$I(t) = -317.2e^{\frac{-(t-10)}{42.2}} + 1659.$$
 (9)

This fit is plotted in Fig. 5(a) as a blue dashed line.

Since the settling time in a first-order system is  $4\tau$  and the time constant  $\tau$  in Eq. (9) is 42.2 s, a predicted endpoint in this sapphire etching process should be at 168.8 s. This implies that after etching for around 170s in the additional etch, the HAR nanopillars mask will be completely removed and the sapphire substrate will be fully exposed. Over-etching beyond this point can lead to rounding of the sapphire structures and a reduced aspect ratio.

#### **B.** Fabrication of sapphire nanostructures

With a better understanding and monitoring of the sapphire etch process, the proposed process can be used to demonstrate the fabrication of HAR sapphire nanostructures. Figure 6(a) shows an SEM image where the 2D pillars are successfully transferred into the ARC layer by O<sub>2</sub> ICP-RIE for an etch time of 145 s. It can be observed that, compared to the thickness of the polysilicon layer, the total thickness of the ARC and PR is much thinner at 225 nm,



FIG. 6. SEM images of (a) pattern transferring into the ARC layer by O2 ICP-RIE and (b) HAR nanopillars that are fabricated by HBr ICP-RIE with a 20 W RF power.



yielding an aspect ratio of 0.95. However, using a low RF power setting to enhance etch selectivity by favoring chemical etching, HAR nanostructures can be fabricated even when a very thin polymer mask is used.<sup>38</sup> Figure 6(b) shows that after HBr ICP-RIE with a low RF power of 20 W for an etch time of 80 min, polysilicon nanopillars with an aspect ratio of around 10 can be obtained. These HAR nanopillars will serve as an etching mask for the following sapphire etching process.

As mentioned in Sec. III A, after using BCl<sub>3</sub>/HBr ICP-RIE to etch the sapphire substrate for 18 min, it can be observed that most parts of the HAR polysilicon nanopillars are removed near the center of the substrate. Sapphire nanostructures in that area, as shown in the cross-sectional SEM image in Fig. 7(a), follow a tapered profile with a width of 242 nm and a height of 385 nm, resulting in an aspect ratio of 1.59. However, the HAR polysilicon pillars around the edge of the sample are not completely removed after the 18 min etching due to the nonuniform thickness of the polysilicon layer. After an additional 5 min etch time, which is a bit longer than the predicted endpoint of 170 s, obtained using methods described in Sec. III A, the remaining HAR nanopillars



FIG. 7. SEM images of tapered sapphire nanostructures fabricated by HBr/BCl<sub>3</sub> ICP-RIE with an etch time of (a) 18 and (b) 18 + 5 min.

are completely removed. The additional etching results in the tapered sapphire nanostructures with a height of 500 nm, which leads to a higher aspect ratio of 2.07, as shown in Fig. 7(b). This result indicates that higher sapphire nanostructures can be obtained if a thicker polysilicon mask is used and that the etching time of the sapphire structure is near the endpoint where all the polysilicon nanopillars are completely removed. Further etching beyond the endpoint can result in rounding of the sapphire structures, resulting in a lower aspect ratio.

The use of OES in determining the endpoint of the sapphire etch is critical in this work. However, the current spectrometer limits the temporal resolution due to its low sensitivity. Lower temporal resolution may fail to capture rapid fluctuations or transient phenomena occurring in the plasma, which can be important in certain etching processes. Additionally, the emission intensity is highly sensitive to chamber conditions. For example, the emission intensities at 395.6 nm during the first and the additional etching are not at the same level. The intensity of the OES signal shown in Fig. 4(a) ends at around 1750 arbitrary unit during the first etch, while the intensity of the OES signal shown in Fig. 5(a) starts at around 1350 arbitrary unit and never reaches 1750 arbitrary unit during the additional etch. This phenomenon might be due to uncontrollable changes in the chamber condition between these two noncontinuous etching processes.

During the nanofabrication process, although HAR sapphire nanostructures can be obtained, the nonuniform thickness of polysilicon leads to uneven heights of sapphire nanostructures. This issue needs to be addressed, especially when the sample is applied to large-area applications. For future works, antireflection, antifogging, and antidust experiments will be performed to demonstrate and test the multifunctional ability of these sapphire nanostructures. Additionally, sapphire nanostructures will be fabricated on the other side of the substrate to further enhance multifunctional performance. Furthermore, exploring the application of a thicker polysilicon mask can be considered to increase the aspect ratio of sapphire nanostructures. Also, sapphire nanostructures with a smaller period can be fabricated to reduce the diffraction effect and enhance the transmittance at shorter wavelengths. Last, this empirical first-order model can be applied to various etching processes for endpoint detection and comparison with other approaches to help identify the etching endpoint.

#### IV. CONCLUSION

The proposed approach demonstrates a simple fabrication process to obtain HAR sapphire nanostructures using polysilicon nanopillars as etch masks and *in situ* OES for process development. The analysis of key wavelengths accomplished via PCA of OES signals shows the ability to identify key emissions of Al, O, Br, Cl, and H in the first sapphire etch process based on the squared loadings of PC1. Additionally, emissions with lower intensities, but having important process information, such as Al and O emissions, can be identified via PCA without any domain knowledge. An empirical first-order model with the assumptions of a constant etch rate and time-independent electron energy distribution is pursued and fitted to the OES signal of Al and O at 395.6 nm. Based on the fitted first-order response, a predicted



endpoint at 170 s can be identified in the sapphire etching process. The sapphire etching results show that the highest aspect ratio of sapphire nanostructures achieved is 2.07, with a width of 242 nm and a height of 500 nm.

#### ACKNOWLEDGMENTS

This work was performed at UT Austin Texas Materials Institute (TMI), the Nanomanufacturing System for Mobile Computing and Energy Technologies (NASCENT), and Texas Nanofabrication Facilities, which is supported by the National Science Foundation (NSF) as part of the National Nanotechnology Coordinated Infrastructure (NNCI) (Grant No. NNCI-2025227). This work was funded by the Army Research Office (ARO) under Grant No. W911NF-22-1-0124.

#### AUTHOR DECLARATIONS

#### Conflict of Interest

The authors have no conflicts to disclose.

#### Author Contributions

Kun-Chieh Chien: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). Noah Graff: Conceptualization (equal); Formal analysis (equal); Methodology (equal). Dragan Djurdjanovic: Investigation (equal); Supervision (lead); Validation (equal); Writing – review & editing (equal). Chih-Hao Chang: Funding acquisition (lead); Investigation (equal); Project administration (lead); Resources (lead); Supervision (lead); Validation (equal); Writing – review & editing (equal).

#### DATA AVAILABILITY

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

#### REFERENCES

- <sup>1</sup>G. M. Katyba *et al.*, Adv. Opt. Mater. **6**, 1800573 (2018).
- <sup>2</sup>T. Kudrius, G. Šlekys, and S. Juodkazis, J. Phys. D: Appl. Phys. **43**, 145501 (2010).
- <sup>3</sup>Y. Zou, S. Chakravarty, P. Wray, and R. T. Chen, Opt. Express 23, 6965 (2015).
- <sup>4</sup>A. G. Andreou, Z. K. Kalayjian, A. Apsel, P. O. Pouliquen, R. A. Athale, G. Simonis, and R. Reedy, IEEE Circuits Syst. Mag. 1, 22 (2001).
- <sup>5</sup>M. Umeno, T. Egawa, and H. Ishikawa, Mater. Sci. Semicon. 4, 459 (2001).
- <sup>6</sup>Z.-Q. Lin, G.-G. Wang, J.-L. Tian, L.-Y. Wang, D.-D. Zhao, Z. Liu, and J.-C. Han, Nanotechnology **29**, 055302 (2018).
- <sup>7</sup>X.-Q. Liu, Y.-L. Zhang, Q.-K. Li, J.-X. Zheng, Y.-M. Lu, S. Juodkazis, Q.-D. Chen, and H.-B. Sun, PhotoniX 3, 1 (2022).

- <sup>8</sup>E. R. Dobrovinskaya, L. A. Lytvynov, and V. Pishchik, *Sapphire: Material, Manufacturing, Applications* (Springer Science & Business Media, New York, 2009).
  <sup>9</sup>K. R. Williams, K. Gupta, and M. Wasilik, J. Microelectromech. Syst. **12**, 761 (2003).
- <sup>10</sup>B. S. Patel and Z. H. Zaidi, Meas. Sci. Technol. **10**, 146 (1999).
- <sup>11</sup>P. Vukusic and J. R. Sambles, Nature 424, 852 (2003).
- <sup>12</sup>Y. Kanamori, M. Sasaki, and K. Hane, Opt. Lett. 24, 1422 (1999).
- <sup>13</sup>P. Lalanne and G. M. Morris, Nanotechnology 8, 53 (1997).
- <sup>14</sup>K.-C. Park, H. J. Choi, C.-H. Chang, R. E. Cohen, G. H. McKinley, and G. Barbastathis, ACS Nano 6, 3789 (2012).
- <sup>15</sup>Y.-A. Chen, S. V. Naidu, Z. Luo, and C.-H. Chang, J. Appl. Phys. **126**, 063101 (2019).
- <sup>16</sup>A. Lafuma and D. Quéré, Nat. Mater. 2, 457 (2003).
- <sup>17</sup>A. R. Parker and C. R. Lawrence, Nature 414, 33 (2001).
- <sup>18</sup>S. S. Lee, L. Micklow, A. Tunell, K.-C. Chien, S. Mohanty, N. Cates, S. Furst, and C.-H. Chang, ACS Appl. Mater. Interfaces 15, 13678 (2023).
- <sup>19</sup>A. Pan, H. Lu, and L.-Z. Zhang, Energy 181, 645 (2019).
- <sup>20</sup>D.-P. Kim, J.-W. Yeo, and C.-I. Kim, Thin Solid Films **459**, 122 (2004).
- <sup>21</sup>S.-M. Koo, D.-P. Kim, K.-T. Kim, and C.-I. Kim, Mater. Sci. Eng. B 118, 201 (2005).
- 22 J. D. B. Bradley, F. Ay, K. Wörhoff, and M. Pollnau, Appl. Phys. B 89, 311 (2007).
- <sup>23</sup>C. H. Jeong, D. W. Kim, H. Y. Lee, H. S. Kim, Y. J. Sung, and G. Y. Yeom, Surf. Coat. Technol. **171**, 280 (2003).
- <sup>24</sup>J. W. Leem and J. S. Yu, Opt. Express 20, 26160 (2012).
- <sup>25</sup>Y. P. Hsu, S. J. Chang, Y. K. Su, J. K. Sheu, C. H. Kuo, C. S. Chang, and S. C. Shei, Opt. Mater. 27, 1171 (2005).
- <sup>26</sup>W.-K. Wang *et al.*, IEEE J. Quantum Electron. **41**, 1403 (2005).
- <sup>27</sup>H. Park, K.-J. Byeon, J.-J. Jang, O. Nam, and H. Lee, Microelectron. Eng. 88, 3207 (2011).
- <sup>28</sup>H. Chen, Q. Zhang, and S. Y. Chou, Nanotechnology 26, 085302 (2015).

<sup>29</sup>Y.-A. Chen, K.-C. Chien, I.-T. Chen, and C.-H. Chang, Micro Nano Eng. 14, 2

- 100115 (2022). 30 I. T. Jolliffe and J. Cadima, Philos. Trans. R. Soc. A 374, 20150202
- (2016).
   <sup>31</sup>J. E. Jackson, A User's Guide to Principal Components (Wiley, New York, 2005).
- <sup>32</sup>2. H. Yue, S. J. Qin, J. Wiseman, and A. Toprac, J. Vac. Sci. Technol. A **19**, 66 g
- 33 K.-C. Chien, C.-H. Chang, and D. Djurdjanovic, J. Vac. Sci. Technol. B 39, 064003 (2021).
- <sup>34</sup>D. A. White, B. E. Goodlin, A. E. Gower, D. S. Boning, H. Chen, H. H. Sawin, and T. J. Dalton, IEEE Trans. Semicond. Manuf. 13, 193 (2000).
- and T. J. Dalton, IEEE Trans. Semicond. Manuf. 13, 193 (2000). <sup>35</sup>K. Han, E. S. Yoon, J. Lee, H. Chae, K. H. Han, and K. J. Park, Ind. Eng. Chem. Res. 47, 3907 (2008).
- <sup>36</sup>S.-I. Jeon, S.-G. Kim, Y.-S. Han, S.-H. Shin, and S.-S. Han, ECS Trans. 44, 1087 (2012).
- <sup>37</sup>I. Wathuthanthri, W. Mao, and C.-H. Choi, Opt. Lett. 36, 1593 (2011).
- <sup>38</sup>K.-C. Chien and C.-H. Chang, J. Vac. Sci. Technol. B 40, 062802 (2022).
- <sup>39</sup>R. Bro and A. K. Smilde, Anal. Methods 6, 2812 (2014).
- <sup>40</sup>A. Kramida, Yu. Ralchenko, J. Reader, and NIST ASD Team, *NIST Atomic Spectra Database* (version 5.10) (National Institute of Standards and Technology, Gaithersburg, MD, 2022).
- <sup>41</sup>K. Ogata, System Dynamics (Pearson, London, 2004).
- <sup>42</sup>J. W. Coburn and M. Chen, J. Appl. Phys. **51**, 3134 (1980).