

Increasing etching depth of sapphire nanostructures using multilayer etching mask

Yi-An Chen, I-Te Chen, and Chih-Hao Chang^{a)}

Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, North Carolina 27695

(Received 10 July 2019; accepted 18 September 2019; published 30 October 2019)

In this study, the etching of sapphire nanostructures in inductively coupled plasma reactive ion etching using a multilayer etch mask is studied. The goals are to increase the etching depth and enable the fabrication of higher aspect ratio nanostructures in sapphire, which is traditionally difficult to micromachine. The etching rates and chemistry of different masking materials are examined for better understanding of the etching process. The etching of sapphire nanostructures is then studied using single and multilayer masks with Cl_2 -based chemistry. The fabrication results show that using the multilayer mask is an effective method for sapphire nanostructure fabrication, increasing the maximum etching depth from 25 to 230 nm for a ninefold improvement. To further validate the optical properties of fabricated sapphire nanostructures, the antireflection effects have been characterized. This work indicates that applying the multilayer mask can increase the etching depth of sapphire nanostructures, which can find applications in thin-film optics, optoelectronic devices, and composite windows. *Published by the AVS*. https://doi.org/10.1116/1.5119388

I. INTRODUCTION

Sapphire has many applications in photonics and optoelectronics due to its high mechanical hardness, thermal tolerance, chemical stability, and high optical transmittance. However, due to these properties, sapphire is also difficult to micromachine using physical and chemical means, making the fabrication of nanostructures in sapphire challenging. The ability to define high-resolution features in sapphire can further improve the physical properties of sapphire. For example, Fresnel reflection losses are higher in sapphire than other transparent materials (e.g., fused silica and glass) due to its relatively higher refractive index.^{1–3} Sapphire and other alumina-based materials can also be used in multilayer composites for protective armor.^{4–7} However, in these materials, the multiple interfaces can result in reflection losses and interference effects. These losses may be mitigated using antireflective subwavelength structures inspired from moth eyes.^{8,9} In this manner, the discontinuity in the refractive index can be replaced by an effective medium with a continuously changing index.¹⁰ Nanoscale features can also potentially enhance the toughness of sapphire by reducing brittleness, which has been demonstrated in other materials such as silicon and diamond.^{11,12}

Given its chemical inertness, reactive ion etching (RIE) of sapphire is challenging. Previous works in the literature have demonstrated etching of Al₂O₃ films^{13,14} and sapphire substrates.^{15–17} However, these studies either focus on amorphous Al₂O₃ films or generally have large features at a micrometer scale. Recent works have also studied fabricating sapphire microstructures^{18–20} and sub-micrometer

structures^{21–24} using Cl- and Br-based chemistry. Nevertheless, these structures generally either have a low aspect ratio (AR) or have random order and high line-edge roughness. There are a number of techniques that have demonstrated subwavelength antireflective nanostructures on other material surfaces such as silicon and silica, which can be more readily etched. These patterning methods include an interference lithography (IL),²⁵ a colloidal assembly,²⁶ and a random structure fabrication²⁷ to fabricate nanostructures on the surface. However, it is difficult to etch sapphire due to its chemical inertness, which leads to poor etching selectivity to the etching mask. The fabrication of finer sapphire nanostructures with higher AR is still a challenge that needs to be explored.

In this study, an improved etching depth for sapphire nanostructures by using a multilayer mask is demonstrated. This approach centers on using various hard mask materials that have high selectivity using different etching chemistries. This allows the selectivities between the masking layers to be compounded, effectively increasing the overall etching selectivity. We propose and demonstrate a multilayer mask that consists of SiO₂, poly-silicon, and silicon nitride layers to increase the etch depth of sapphire nanostructures. Various etching chemistries were performed using inductively coupled plasma reactive ion etching (ICP-RIE) for better selectivity at each etching step to achieve taller sapphire nanostructures. The etching result of Cl₂ ICP-RIE shows that the fabricated sapphire nanostructures have 470 nm width and 230 nm height, yielding an AR of 0.49. The optical properties of the nanostructured sapphire surface have been characterized, with a reflectivity measurement showing that the reflection losses can be suppressed from 50% to 25% at 70° incident angle. The proposed multilayer mask approach can potentially achieve finer nanostructures with higher AR by using BCl₃ to etch into sapphire and more optimized layer thicknesses.

Note: This paper is part of the Conference Collection: The 63rd International Conference on Electron, Ion, and Photon Beam Technology and Nanofabrication (EIPBN 2019).

^{a)}Electronic mail: chichang@ncsu.edu

II. CHARACTERIZATION OF ETCHING PROCESS

It is well-known that sapphire is notoriously difficult to dry etch due to its high mechanical hardness and chemical stability. One effective method is to use metal masks such as nickel, which has higher etching selectivity versus sapphire in Cl₂-based chemistry. However, metal masks may lead to higher surface roughness due to mask corrosion during etching, and mask removal remains an issue.^{17,19,20,22} In the literature, it has been demonstrated that silicon nitride is a good mask candidate for amorphous Al₂O₃ film etching in the micrometer scale.²⁰ To examine the etching rate of nitride and selectivity to crystalline sapphire, plasma-enhanced chemical vapor deposition (PECVD) and low pressure chemical vapor deposition (LPCVD) silicon nitride thin films were deposited on Si substrates. The stoichiometry and the silicon content of the nitride film play a significant role in its physical properties; therefore, films using both CVD methods are examined. The etching rates of the films are then compared with sapphire substrates, allowing the etching selectivity to be determined. This enables the selection of materials for the multilayer mask to fabricate nanostructures with higher AR.

The etching properties for both PECVD and LPCVD silicon nitride films are studied by measuring the film thickness before and after ICP-RIE. The etching depth versus time and the standard deviation error bar for both PECVD and LPCVD nitride films on the silicon wafer are determined using spectroscopic ellipsometry and are plotted in Fig. 1. Silicon substrates are used for the etching tests because of a higher optical signal in the ellipsometry measurement and a lower material cost. The etching conditions are BCl_3 : HBr = 1:1, the total flow rate of 100 sccm, pressure of 15 mTorr, ICP power of 400 W, and RF power of 200 W. From the literature review, 20 BCl₃: HBr = 1:1 has higher selectivity when compared with pure Cl₂ or BCl₃. Lower etching pressure is used to increase an ion mean free path to achieve higher etching anisotropy and reduce undercut. A relatively low RF power is used to reduce kinetic energy and reduce sputtering, which increases selectivity, and a high



FIG. 1. Etching depth vs time of PECVD and LPCVD silicon nitride films.

ICP power is used to produce high density plasma for a higher etching rate. The triangular and circular points represent the etched depth for PECVD and LPCVD silicon nitride samples, respectively. Linear fitting equations are calculated and plotted using corresponding dashed lines. These show that the etching rate, as defined by the slope of dashed lines, of LPCVD nitride is lower than that of PECVD nitride. These results indicate that LPCVD nitride has higher etching resistance and can lead to higher selectivity versus sapphire. The different etching rates can be attributed to the difference in the film density and compositions produced by two deposition approaches.

In the sapphire etching process, it is understood that Cl₂ reacts with Al to produce AlCl₃. BCl₃ can serve as a reducing agent that reacts with Al₂O₃ to form Al, facilitating the etch process. The etching rate and selectivity of Cl₂ and BCl3 under different proportions are studied to examine this hypothesis. The samples used in these experiments are LPCVD nitride thin films on the silicon wafer. The nitride thin film thicknesses before and after ICP-RIE were measured by an ellipsometer to determine the etching rate. For comparison, sapphire substrates with the (0001) orientation covered by the silicon mask were used. After ICP-RIE, the depth difference between areas with and without mask protection was measured using a contact profilometer (Dektak 150, Veeco Inc.). The Cl₂ and BCl₃ selectivities of sapphire over LPCVD nitride and etching rate data are plotted in Fig. 2. The processing conditions for these experiments are pressure of 10 mTorr, the total flow rate of 50 sccm, ICP power of 500 W, and RIE power of 300 W. The data indicate that increasing BCl₃ results in better selectivity and a higher etching rate. This agrees with the hypothesis that it acts as a reducing agent, which limits the overall Al₂O₃ etching process.

While Cl_2 has lower etching rate and selectivity, it can be used to investigate the effect of using the multilayer versus single-layer etching mask. This can demonstrate that using the multilayer mask can improve the nanostructure etching depth even under etching conditions that are not optimized.



Fig. 2. Etching rate and selectivity of sapphire over LPCVD silicon nitride vs Cl_2 and BCl_3 concentration.



Fig. 3. Etching by-product from OES during sapphire etching using Cl_2 plasma.

To better understand the etch reactions, optical emission spectrometer (OES) was used to analyse the etch products during sapphire etching. This was performed by connecting a fiber spectrophotometer (Model USB4000, Ocean Optics, Inc.) at the viewing port of the plasma chamber. The processing conditions for this experiment are pressure of 8 mTorr, the total flow rate of 30 sccm, ICP power of 1500 W, and RF power of 200 W. Analyzing etching products by OEM can also serve as a function of etching end point detection to control the etching time.^{28,29} The measured spectrum for Cl₂ ICP-RIE after 5 min of etching is plotted in Fig. 3, where several elements and components can be identified. The critical emission wavelengths of AlCl, Al, and O are detected at 261, 396, and 616 nm, respectively, which indicates that Al_2O_3 is being etched by the Cl_2 plasma. It can be observed that the strong Si signal comes from etching by-products of the multilayer mask that consists of SiO₂, polysilicon, and nitride.

III. FABRICATION OF SAPPHIRE NANOSTRUCTURES USING SINGLE-LAYER MASK

After the etching properties of the silicon nitride mask were examined, its suitability as an etch mask for etching into (0001) sapphire substrates can be tested. The nanostructures are patterned using an IL and transferred using RIE. The fabrication process for the single-layer mask is illustrated in Fig. 4. First, a sapphire substrate is deposited with a 130 nm nitride layer using PECVD as the etching mask. Then, a 130 nm antireflection coating (ARC i-con-7, Brewer Science) and a 250 nm photoresist (PFI-88A2, Sumitomo) were spin-coated. The ARC film is needed to reduce reflection from the substrate during lithography. One-dimensional (1D) periodic grating is then patterned in the photoresist using a Lloyd's mirror interference setup,³⁰ as shown in Fig. 4(b). The period of the nanostructure is 300 nm, which can be controlled by the incident angle. As illustrated in Fig. 4(c), O_2 and CHF₃ RIE are



FIG. 4. Schematic of the fabrication process for sapphire nanostructures using a single-layer mask. (a) Sample preparation includes PECVD deposition of nitride and spin coating ARC and PR layers on the sapphire substrate. (b) 1D nanostructure is patterned in the photoresist using IL. (c) The pattern is transferred into the nitride mask layer using RIE and (d) into the sapphire substrate using ICP-RIE.

used to transfer the pattern to the photoresist and the nitride layer, respectively. Then, ICP-RIE is applied to transfer a nanostructure pattern to the sapphire substrate by using Cl_2 , BCl_3 , and/or HBr, as depicted in Fig. 4(d). Different etching chemistries were examined for sapphire etching to determine the highest etching depth.

The fabricated 1D nanostructures are etched into ARC and nitride layers using O_2 and CHF₃ RIE, respectively, forming a single-layer hard mask consisting of nitride. A mixture of Cl₂, BCl₃, and HBr ICP-RIE is then used to etch into the underlying sapphire substrate. Different gases and ratios were used, including BCl₃: HBr = 1:1, 1:2, and pure Cl₂. The best etching results were obtained using BCl₃: HBr = 1:1, and the SEM images of the cross section after 20 and 40 s etching are depicted in Figs. 5(a) and 5(b), respectively. The etching conditions are the total flow rate of 100 sccm, pressure of 15 mTorr, ICP power of 400 W, and RF power of 200 W. After 20 s of ICP-RIE, some ARC and nitride remained on the surface, which can be observed as the tapered profile. As etching time is increased to 40 s, only the nitride mask and



Fig. 5. Cross section SEM images of an etched nitride mask on top of the sapphire substrate after (a) 20 s and (b) 40 s of ICP-RIE etching.



FIG. 6. Cross section SEM images of sapphire nanostructures with (a) 25 nm height using Cl_2 ICP-RIE and (b) 60 nm height using BCl_3 : HBr = 1:1 ICP-RIE.

sapphire nanostructures remain, but the boundary between the two materials is hard to distinguish. However, a change in slope attributed to the sapphire nanostructures can be observed from the side wall at the bottom of the 1D grating profile, as depicted in Fig. 5(b). The sapphire nanostructures in fairly shallow comparing to the nitride mask etched during ICP-RIE, which implies relatively poor selectivity.

After the ICP-RIE processes, 49% HF is used to remove the remained silicon nitride followed by an RCA clean which is a standard wafer cleaning process. The resulting structures have a similar width of 130 nm but show varying etch depths for different gases used to etch into the sapphire substrate. For pure Cl₂, the sapphire nanostructures have only 25 nm height and AR around 0.19, as shown in Fig. 6(a). The best etching results are obtained using BCl_3 : HBr = 1:1 ICP-RIE, yielding structures with 60 nm height and AR around 0.46, as shown in Fig. 6(b). At higher HBr concentration with BCl_3 : HBr = 1:2, the fabricated nanostructures have 45 nm height, yielding AR around 0.35. While the BCl₃: HBr etch chemistry achieved better results, the etch depth is still shallow given that the nitride mask is 130 nm thick. While a higher thickness mask can be used for larger features, this would result in a collapse of the photoresist pattern for nanostructures. Therefore, these results highlight the fabrication limitation of using a single-layer etching mask for sapphire nanostructure fabrication.

J. Vac. Sci. Technol. B, Vol. 37, No. 6, Nov/Dec 2019

IV. FABRICATION OF SAPPHIRE NANOSTRUCTURES USING MULTILAYER MASK

From previous 1D nanostructure etching results, the etch depth is shallow due to relatively poor selectivity between the etch mask and the sapphire substrate. This is imposed by the chemical inertness of crystalline sapphire and indicates that using a single-layer etching mask has its limitation. To further acquire taller nanostructures, the multilayer etching mask is needed. Therefore, a three-layer mask consisting of silicon nitride, poly-silicon, and SiO₂ is employed to achieve higher two-dimensional (2D) nanostructures. These mask layers were constructed in this order because the corresponding etch selectivity between neighboring layers is high based on literature values. Namely, SiO₂ has high selectivity around 3-5 versus poly-silicon in Cl/Br-based RIE, and poly-silicon has high selectivity versus nitride in CHF₃ RIE with selectivity around 4. Taken into account the less than unity etch selectivity of sapphire, the total selectivity is expected to be around 1 for Cl₂ and up to 5 for BCl₃ ICP-RIE, when the whole stack is used to etch into sapphire. This is a significant improvement over using a single-layer mask consisting of nitride.

The fabrication process of 2D sapphire nanostructures using the multilayer mask is illustrated in Fig. 7. First, a sapphire substrate with the (0001) orientation is deposited with 430 nm nitride and 350 nm poly-silicon using LPCVD, as



Fig. 7. Schematic of the fabrication process for sapphire nanostructures using the multilayer mask. (a) Sample preparation by depositing LPCVD nitride and poly-silicon layers on the sapphire substrate. (b) Pattern 2D nanostructures' mask by using self-assembly of SiO₂ colloidal nanospheres. (c) Etch pattern into poly-silicon and nitride layers using Cl₂ ICP-RIE and CHF₃ RIE, respectively. (d) Etch pattern into the sapphire substrate using Cl₂ ICP-RIE.

depicted in Fig. 7(a). Note LPCVD nitride was used due to its higher etch selectivity. SiO_2 nanospheres with 500 nm diameter are then assembled on the stack, forming a monolayer of 2D hexagonal close-packed nanostructures. The whole multilayer mask stack with silica colloidal particles is shown in Fig. 7(b). The nanostructure pattern is transferred into the underlying poly-silicon layer using Cl₂ ICP-RIE and then into the nitride layer using CHF₃ RIE, forming a thick multilayer mask as illustrated in Fig. 7(c). Finally, ICP-RIE can be applied to transfer the nanostructures to the sapphire substrate by using Cl₂, BCl₃, or HBr etching chemistry, as shown in Fig. 7(d).

The cross section SEM images of the colloidal silica nanoparticles, poly-silicon, and silicon nitride mask after Cl_2 ICP-RIE and CHF₃ RIE are illustrated in Figs. 8(a) and 8(b). Some silica nanospheres remain on the poly-silicon and nitride layers, which are patterned with the 2D nanostructures on the sapphire surface. This results in a multilayer mask consisting of SiO₂, poly-silicon, and nitride. Some defects from the colloidal assembly can be seen. It can be observed



FIG. 8. Cross section (a) high and (b) low-magnification SEM images of poly-Si and silicon nitride mask after Cl_2 ICP-RIE and CHF₃ RIE. Note some silica nanospheres remain, forming a multilayer mask consisting of SiO₂, poly-silicon, and nitride with a total thickness of 950 nm.

that the silica nanospheres are also etched during the RIE processes, forming a disk-like geometry. Also, the gap between nanostructures is mainly determined by the lateral etching rate of silica nanospheres, which are in close-packed geometry initially. It is important to note that the vertical etching rate of silica nanospheres is higher than the lateral etching rate since the etching conditions are anisotropic.

The multilayer mask is then transferred to the underlying sapphire substrate using ICP-RIE. In this work, Cl₂ is used, which has poorer selectivity as observed in the 1D nanostructure etch tests, to demonstrate that a higher etching depth can be achieved using the multilayer mask. The etching conditions for sapphire etching are the Cl₂ flow rate of 30 sccm, pressure of 8 mTorr, ICP power of 1500 W, and RF power of 200 W. High ICP power is used to increase the etching rate. A relatively low RF power is used to reduce surface damage and sputtering, which increases selectivity. Lower pressure is used to reach higher anisotropic etching. The SEM images of sapphire nanostructures after 49% HF and RCA cleaning are shown in Fig. 9. It can be observed that the fabricated 2D sapphire nanostructures have hexagonal lattice with some defects. These defects come from the colloidal assembly, and it can be eliminated by improving the nanosphere assembly process or using the interference lithography. The etching using the multilayer mask results in structures with 470 nm width and 230 nm height, which has



Fig. 9. (a) Cross section and (b) tilted-view SEM images of the sapphire nanostructure after HF and RCA cleaning. The structures are of 470 nm width and 230 nm height.

AR around 0.49. As mentioned previously, the vertical etching rate of silica nanoparticles is higher than the side etching rate due to high RIE and ICP power leading to high DC bias. These mainly dominate the nanostructure shapes that affect AR after transferring the pattern to the sapphire substrate. From previous experiments using a single-layer mask, the sapphire nanostructures are only etched 25 nm under Cl₂ ICP-RIE. However, by applying the multilayer thicker etching mask, the nanostructures' height can be increased to 230 nm, a ninefold improvement. While the AR achieve is similar to the single-layer mask, this is attributed to larger features patterned by the nanosphere assembly. Finer features can be patterned using smaller nanospheres or the interference lithography to increase AR further. Structure with the higher etch depth and AR can also be potentially achieved by employing gas with better selectivity like BCl₃.

V. OPTICAL CHARACTERIZATION

The fabricated 2D sapphire nanostructures can find applications in optical and photonic devices due to its high index and mechanical properties. One example is antireflection where the surface nanostructures function as a gradient-index medium to eliminate Fresnel losses induced by the refractive index mismatch between air and the substrate. The optical properties of the sapphire nanostructures are characterized to demonstrate the antireflection effect, as shown in Fig. 10. Here, the reflectivity



FIG. 10. Measured and simulated reflectivities under different incident angles for the sapphire substrate with and without surface nanostructures.

of the sapphire substrates with and without the nanostructures is measured using a 633 nm HeNe laser (Model 30995, Research Electro-Optics, Inc.) in transverse-electric polarization. A rotation stage is used to rotate the sample and change the incident angles from 0° to 70° with 1° resolution. A photodiode detector (Model 918D-UV-OD3, Newport Co.) is used to measure the reflection light intensity. Here, the reflectivity is reduced from 8% to 5% near normal incidence with the use of the nanostructures. The reflectivity can be further suppressed from 50% to 25% at 70° incident angle. It is important to note that these are specular reflection, and there might be scattering since the structure is not perfectly ordered. Nevertheless, the reflectivity can be further suppressed by applying finer nanostructures with higher AR.

The optical properties of sapphire with nanostructures are modeled using rigorous coupled-wave analysis (RCWA), which can solve the Maxwell's equations for the electromagnetidc diffraction by grating structures. The discrete 2D grating nanostructures are approximated with varying duty cycles. The RCWA simulation model is based on alternating air (n = 1) and sapphire (n = 1.75) periodic layers along both x and y directions in a square lattice with 500 nm period. The top and bottom layer materials are air and sapphire, respectively, and are modeled as semi-infinite media. The nanostructures are approximated into discrete planar slices with different thicknesses and feature widths. The nanostructures' profile is built from the SEM images to simulate the fabricated nanostructures' shape, having a height of 230 nm and a duty-cycle between 0.88 and 0.94. Note only the 0th-order specular reflection is considered. The planar model using the Fresnel equation is also shown. It can be observed that the data agree well with the RCWA and Fresnel models for the samples with and without the nanostructures, respectively.

For further work, a 2D nanostructure with a shorter period can be patterned using IL to improve the antireflection effect and enhance transmission. The thicknesses of each masking layer can also be optimized, and BCl₃ ICP-RIE will be explored to acquire tapered taller nanostructures. This is expected to have better antireflection effects with higher transmission and lower losses. The etch products will also be investigated by OES at each etching step to better understand the reactions, which can also serve as end-point detection to control the etching time better. Different gas proportions such as Cl_2 , BCl_3 , CF_4 , and HBr to improve the etching rate and selectivity versus different mask layers will be evaluated. Lastly, the optical reflectance and transmittance of the fabricated structures will be characterized.

VI. CONCLUSIONS

In this work, a multilayer etching mask to increase the sapphire nanostructures' etching depth is introduced and demonstrated. The goal of this approach is to compound the etch selectivities of neighboring layers to enhance overall etch selectivity of crystalline sapphire. The Cl₂ ICP-RIE etching of 1D sapphire nanostructures using a single PECVD silicon nitride mask is evaluated, and the maximum etch depths of 25 nm was obtained. Using a multilayer etch mask consisting of SiO₂, poly-silicon, and nitride, an etch depth of 230 nm was obtained, a ninefold improvement. The fabricated nanostructure AR was around 0.49, which is expected to further increase using finer pattern features and ICP-RIE chemistry with higher sapphire selectivity such as BCl₃. The antireflection effect of 2D sapphire nanostructures was also examined. Using the nanostructures, the reflectivity is reduced from 8% to 5% near normal incidence and from 50% to 25% at 70° incident angle. This work demonstrates that the multilayer etching mask can enhance the etching depth and enable the fabrication of a higher AR sapphire nanostructure.

ACKNOWLEDGMENTS

This work was performed in part at the NCSU Nanofabrication Facility (NNF) and the Analytical Instrumentation Facility (AIF), members of the North Carolina Research Triangle Nanotechnology Network (RTNN), which is supported by the National Science Foundation (NSF) as part of the National Nanotechnology Coordinated Infrastructure (NNCI). This work was supported by the Army Research Office (ARO) under Grant No. W911NF-17-1-0591 and partially supported by National Science Foundation (NSF) under Grant No. CMMI#1552424.

- ¹P. Lalanne and G. M. Morris, Nanotechnology **8**, 53 (1997).
- ²B. S. Patel and Z. H. Zaidi, Meas. Sci. Technol. **10**, 146 (1999).
- ³Y. Kanamori, M. Sasaki, and K. Hane, Opt. Lett. 24, 1422 (1999).
- ⁴P. J. Patel, G. A. Gilde, P. G. Dehmer, and J. W. McCauley, Proc. SPIE **_4102**, 1 (2000).
- ⁵C. T. Warner, T. M. Hartnett, D. Fisher, and W. Sunne, Proc. SPIE **5786**, 95 (2005).
- ⁶L. M. Goldman, R. Twedt, S. Balasubramanian, and S. Sastri, Proc. SPIE **8016**, 801608 (2011).
- ⁷M. Ramisetty, S. Sastri, U. Kashalikar, L. M. Goldman, and N. Nag, Am. Ceram. Soc. Bull. **92**, 20 (2013).
- ⁸Q. Yang, X. A. Zhang, A. Bagal, W. Guo, and C.-H. Chang, Nanotechnology **24**, 235202 (2013).
- ⁹Y.-A. Chen, S. V. Naidu, Z. Luo, and C.-H. Chang, J. Appl. Phys. **126**, 063101 (2019).
- ¹⁰P. Vukusic and J. R. Sambles, Nature 424, 852 (2003).
- ¹¹A. Banerjee *et al.*, Science **360**, 300 (2018).
- ¹²M. J. Gordon, T. Baron, F. Dhalluin, P. Gentile, and P. Ferret, Nano Lett. 9, 525 (2009).
- ¹³D.-P. Kim, J.-W. Yeo, and C.-I. Kim, Thin Solid Films 459, 122 (2004).
- ¹⁴S.-M. Koo, D.-P. Kim, K.-T. Kim, and C.-I. Kim, Mater. Sci. Eng. B 118, 201 (2005).
- ¹⁵Y. J. Sung, H. S. Kim, Y. H. Lee, J. W. Lee, S. H. Chae, Y. J. Park, and G. Y. Yeom, Mater. Sci. Eng. B 82, 50 (2001).
- ¹⁶C. H. Jeong, D. W. Kim, H. Y. Lee, H. S. Kim, Y. J. Sung, and G. Y. Yeom, Surf. Coat. Technol. **171**, 280 (2003).
- ¹⁷Y. 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).
- ¹⁸S.-H. Park, H. Jeon, Y.-J. Sung, and G.-Y. Yeom, Appl. Opt. 40, 3698 (2001).
- ¹⁹C. H. Jeong, D. W. Kim, J. W. Bae, Y. J. Sung, J. S. Kwak, Y. J. Park, and G. Y. Yeom, Mater. Sci. Eng. B **93**, 60 (2002).
- ²⁰J. D. B. Bradley, F. Ay, K. Wörhoff, and M. Pollnau, Appl. Phys. B 89, 311 (2007).
- ²¹Y.-S. Lin, W.-C. Hsu, K.-C. Huang, and J. A. Yeh, Appl. Surf. Sci. **258**, 2 (2011).
- ²²J. W. Leem and J. S. Yu, Opt. Express **20**, 26160 (2012).
- ²³H. Chen, Q. Zhang, and S. Y. Chou, Nanotechnology 26, 085302 (2015).
- ²⁴Z.-Q. Lin, G.-G. Wang, J.-L. Tian, L.-Y. Wang, D.-D. Zhao, Z. Liu, and J.-C. Han, Nanotechnology **29**, 055302 (2018).
- ²⁵K.-C. Park, H. J. Choi, C.-H. Chang, R. E. Cohen, G. H. McKinley, and G. Barbastathis, ACS Nano 6, 3789 (2012).
- ²⁶W.-L. Min, B. Jiang, and P. Jiang, Adv. Mater. **20**, 3914 (2008).
- ²⁷A. H. Peltier, G. Sapkota, J. R. Case, and M. K. Poutous, Opt. Eng. 57, 037109 (2018).
- ²⁸S. Thomas, H. H. Chen, C. K. Hanish, J. W. Grizzle, and S. W. Pang, J. Vac. Sci. Technol. B 14, 2531 (1996).
- ²⁹X. Li, M. Schaepkens, G. S. Oehrlein, R. E. Ellefson, L. C. Frees, N. Mueller, and N. Korner, J. Vac. Sci. Technol. A **17**, 2438 (1999).
- ³⁰H. I. Smith, Phys. E **11**, 104 (2001).