

Influence of Hafnium Defects on the Optical and Structural Properties of Zirconium Nitride

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Recently, the application of transition metal mononitrides (TMNs) to plasmonics and nonlinear optics has grown at an astounding rate. TiN and ZrN have emerged as the dominating materials in this direction. However, even though ZrN is reported to have lower dielectric losses and enhanced tunability in plasmonic applications when compared with TiN, the body of work regarding TiN is much more mature than that of ZrN. This imbalance of work regarding ZrN may be in part an effect of pollution in precursor materials for the fabrication of ZrN, leading to an increased imaginary part of permittivity and frustration in reproduction of ZrN with literature-like properties. Herein, the effects of Hf defects (a common pollutant in Zr) on the optical properties of nitride films grown with radio frequency (RF) magnetron sputtering are reported. Hf defects are introduced into nitride films with a sputtering target made of the Hf-polluted "grade 702" Zr alloy. Hf defects are found in all analyzed films with concentrations at around $\approx 0.5-1$ at %. Chemical, structural, and optical properties of RF magnetron-sputtered Hf_x:Zr_yN_z films ($x \ll y$,z) are characterized and discussed.

1. Introduction

A need for materials with simultaneously large optical nonlinearities and robustness to extreme environments has been growing in league with the growth of optical technology sectors related to communications, defense, and metrology. Transition metal mononitrides (TMNs) is an exciting platform of emerging alternatives to Au and Ag in the realm of extreme, refractory materials for plasmonics and nonlinear optics^[1–5] because they can have large nonlinearities^[6,7] and Au-like optical properties in the visible range,^[8,9] while simultaneously circumventing many drawbacks of noble metals, which include low melting

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/pssr.202100372.

DOI: 10.1002/pssr.202100372

temperatures, thermally induced recrystallization, high self-diffusion, percolation,^[10,11] and low hardness (as well as oxidation in cases like Ag).

Effective tunability of the optical, electronic, and structural properties of some TMNs may be controlled by exploiting their sensitive dependence on chemistry,^[12–14] enabling a platform of tunable plasmonic materials. Mixing of metal species in TMNs is another means of parameter tuning. These intermediate alloys of transition metal nitrides, known as ternary nitrides,^[15] extend the mononitrides and offer a compelling platform for the optimization of tunable plasmonic conductors,^[16] making them popular in plasmonics applications^[17–20] over a variety of spectral ranges. Ternary nitrides can be grown with cosputtering^[21] and are formed to some extent from sputtering with impure alloy

targets. It is important to note that ternary nitrides have properties distinct from mononitrides, a trait which may be more or less desirable depending on the particular application.

The range of TMNs are broadly applicable in plasmonics^[22] and present a useful platform for the application of metasurfaces.^[23] In addition, some show high bioinertness, which drives interest in nitride biomaterials,^[24,25] and they can withstand the extreme optical fields necessary to excite large nonlinear optical effects.^[6,7] In the range of TMNs, TiN and ZrN have emerged as frontrunners. However, even though ZrN is shown to have lower dielectric losses, higher microhardness,^[26] and higher chemical tunability than TiN, the development of ZrN in experimentally realized devices is evidently less extensive than that of TiN.^[1]

Part of this seemingly paradoxical asymmetry of application is attributed here to the sensitive chemistry dependence of ZrN acting as a double-edged sword as the purity of precursor materials is a deciding factor in the quality of synthesized materials. The isolation of Zr from mixtures of Zr and Hf with a high separation factor is expensive and time-consuming due to the nearly identical chemical properties and similar ionic radii of Zr and Hf.^[27] Most commercially available Zr is separated into grades, governed by ASTM-B495, which allows a maximum Hf content of 4.5%. Of these, the most commonly used is the so-called "grade 702" Zr alloy which is sold frequently as a > 99% metals basis purity. However, the metals basis designation means that this material is a > 99% combination of Zr and Hf, where the Hf content will frequently be $\approx>$ 4.5%; this Hf content is most frequently not advertised. Purity of Zr above the ASTM regulations, in the best cases, is reported with ppm concentrations of Hf and



other impurities. However, standardization is lacking and Zr is widely still reported on a metals basis: even cases advertising 99.95% of pure Zr precursor material frequently have \approx 0.5 at% or more Hf present; extensive searching may be needed to find Zr with few (\approx < 500 ppm) Hf impurities.

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Radio frequency (RF) sputtering is a technique commonly used to grow ZrN because of its convenient ability to control N-fraction in TMN films. Like other growth techniques, an important caveat is that film purity and properties have sensitive dependence on sputter target purity. Experimental studies of ZrN in the literature report fabrication with high-purity (\approx >99% pure) Zr targets^[28,29] but, as discussed, it is not clear the extent to which this purity may be reported on a metals basis and reflect a combination of Zr and Hf.

The role of Hf impurities in sputtered ZrN films has been explored to some extent regarding its hardness and oxidation resistance at high temperature,^[30] but the effects of these Hf defects on permittivity of the Hf_x:Zr_yN_z system are unreported and of large value to reducing the barrier to entry of studies relying on the optical properties of sputtered ZrN and attainment of low-loss plasmonic materials. To explore the effects on permittivity of this nontrivial Hf concentration and determine whether impurities play a significant role in ZrN optical properties, our approach is to measure the structural, chemical, and optical properties of ZrN films grown on Si and c-sapphire substrates with reactive RF magnetron sputtering from a Kurt Lesker-grade 702 Zr target (having Hf impurities) over a broad Zr and N stoichiometry range.

Impurities in Zr sputtering targets used in RF sputtering result in the formation of unintentional ternary nitride products, specifically $Hf_x:Zr_yN_z$ where $x \ll y.z$. As Zr precursor materials can often be mistaken for being of ultrahigh purity by the reported metals basis purity, the attainment of pure, stoichiometric ZrN with attractive properties similar to those reported in the literature can be significantly frustrated. The aim of this work is to remove ambiguity in the relationship between Zr precursor purity and optical and structural properties of ZrN films grown from a known grade 702 sputtering target with RF sputtering and thereby reduce the barrier to entry to which ambiguity in precursor material purity has given rise.

Using Rutherford backscattering spectrometry (RBS), films of ZrN sputtered from the same grade 702 target are found here to have Hf concentrations at the $\approx 0.5-1$ at% level. RBS was selected to determine atomic concentrations in films for their high sensitivity, which can detect heavy elements on the order of 10 ppm^[31–33] in combination with its ability to simultaneously detect light elements like N.

X-ray diffraction (XRD) is used to characterize structural parameters, and X-ray reflectometry (XRR) is used to characterize thickness and roughness of films. Reflection and transmission (RT) spectroscopy is used with in-house developed code (see Experimental Section for details) to extract the real and imaginary parts of the permittivity of these films.^[34] To understand the extent of tunability in this Hf-defected ZrN system (referred to as $Hf_x:Zr_yN_z$ throughout this work) and the effects that growth parameters have on a given film's optical properties, these measurements were carried out over a range of N concentrations for thick (Thick-A–Thick-E) and thin (Thin-A–Thin-E) film regimes

which are, respectively, relevant to industrial decorative and hard coatings for tools and to thin-film optical and electronic devices.

2. Results and Discussion

To explore the thick film regime and develop a recipe for $Hf_x:Zr_yN_z$ (where $y \approx z$) from a grade 702 target, an initial set of five films (a thick film sample set with samples referred to as Thick-A—Thick-E) all having varied N concentrations were grown with reactive RF sputtering (growth recipes given in Experimental Section). Thick-A—Thick-E were grown in the thick-film regime from ≈ 60 to 400 nm (determined from XRR and RBS). Using SIMNRA,^[35] elemental compositions (in at%) of the thick sample set (shown in **Table 1** and **Figure 1**) were determined from the RBS measurements. Hf concentrations increase with decreasing chamber pressure (the pressure controller had a resolution of ≈ 0.24 mTorr).

ZrN without the incorporation of Hf defects has a well-known bright, whitish gold appearance. In the Zr-rich case, films are known to become increasingly silvery, and, in the N-rich case, film colors progress to a pale (reflective) yellow-green as stoichiometries approach Zr₃N₄; in the highly N-rich and amorphous case, a film's appearance becomes bluish.^[2,36] Photographs of the thick Hf_x:Zr_yN_z films sputtered on c-sapphire substrates are included on the right-hand side of Figure 1 (the images were white balanced to the clean room wiper on which they were photographed). Here, the Zr-rich (y > z) films Thick-D-Thick-E are metallic, reflective, and opaque; nearly stoichiometric films like Thick-C ($y \approx z$) are metallic and transmissive in the \approx 450 nm range and, in the N-rich case (y < z), like films Thick-A-Thick-B, films appear dark and absorptive. Hf_x: Zr_vN_z appearances can be understood more intuitively when considering that increasing N-fraction partially depletes the conduction band of electrons, causing semiconducting properties and a blueshift in the bandgap energy.^[1]

XRD was used to characterize structural parameters of the thick-film samples. Results are shown in **Figure 2**a. The degree of ordering in the thick-film sample set increases as N concentration approaches a 1:1 ratio with Zr. Film hardness and texture are correlated in TiN and ZrN with (111) being the hardest preferred orientation^[37] for durable optical films. In this thick-film regime, (111) textures are favorable at lower N fractions, and (200) textures are favorable at higher N fractions. Formation of (220) peaks increases with increasing N-fraction as well.

To determine a defect accommodation mechanism in the lattice, the lattice parameter a_0 as a function of atomic percentage of N was computed from the XRD measurements in Figure 2a

 Table 1. Composition parameters (in atomic percent) of the thick film samples fit from RBS data with the SIMNRA software.

Sample	Hf [at%]	Zr [at%]	N [at%]	
Thick-A	$\textbf{0.436} \pm \textbf{0.001}$	$\textbf{32.682} \pm \textbf{0.066}$	$\textbf{66.882} \pm \textbf{0.136}$	
Thick-B	$\textbf{0.490} \pm \textbf{0.002}$	$\textbf{40.865} \pm \textbf{0.156}$	58.645 ± 0.224	
Thick-C	$\textbf{0.685} \pm \textbf{0.001}$	$\textbf{50.395} \pm \textbf{0.062}$	$\textbf{48.920} \pm \textbf{0.079}$	
Thick-D	$\textbf{0.645} \pm \textbf{0.001}$	$\textbf{57.042} \pm \textbf{0.090}$	$\textbf{42.312} \pm \textbf{0.066}$	
Thick-E	$\textbf{1.064} \pm \textbf{0.021}$	$\textbf{58.819} \pm \textbf{1.143}$	40.117 ± 0.001	





Figure 1. Normalized RBS measurements (counts per channel) and appearance of the thick film samples as well as corresponding SIMNRA fits (black dashed curves) on Si (111) substrates. Films having peaks with wider breadth are thicker than those with peaks of thinner breadth. Approximate channel locations of element signal onset are denoted with vertical dotted and dashed lines. Photographs (reflections can be seen on the surfaces of Thick-B and Thick-E) are included of the as-grown films on c-sapphire substrates. Transparent, triangular bare sections at the bottom-left corners of the thick-film samples (result of a sputter shadow from substrate clips on sample stage) show film opacity relative to sapphire.

using Bragg's law. A monotonic decrease in a_0 was found with increasing N in composition $< \approx 55\%$ (Figure 2b). A modest slope and a lattice parameter maintained in the $\approx 0.456-0.460$ nm range correspond well with the vacancy mechanism of nonstoichiometry accommodation in the lattice.^[38,39]

The thick-film regime demonstrates that $Hf_x:Zr_yN_z$ with a metallic appearance and ZrN-like structure can be attained. Texture in films and the degree of ordering are dependent on the N-fraction, showing a regime shift from (111) to (200) as N concentrates. In addition, a vacancy mechanism (instead of a less energetically favorable antisite or interstitial mechanism) of defect accommodation in the lattices is identified, which agrees with intuition from measurements. Finally, a wide range of $Hf_x:Zr_yN_z$ visual appearances similar to those in stoichiometric ZrN hard, decorative coatings for manufacturing are achievable with lower-cost precursor materials than Zr with very low ppm Hf impurities.

The thin-film regime and its applicability to optics were studied next. A set of thin-film samples (Thin-A–Thin-E) was grown for the measurement of optical properties based on variations of the recipe for Thick-C. Thick-C was chosen as a prototype plasmonic $Hf_x:Zr_yN_z$ chemistry and as a recipe starting point because of its $Hf_{\approx 0.01}:Zr_{\approx 0.49}N_{\approx 0.50}$ stoichiometry, its visual optical properties, and low strain (as determined by calculations from the XRD measurements) to the literature value of stoichiometric ZrN. Sputtering powers were reduced from 200 W (used in the thick-film sample set growth) to 150 W to facilitate smoother films with more controllable and slower growth rates for fabrication of optical quality thin films.



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Figure 2. XRD measurements on the set of thick-film samples for determination of phase. a) XRD 2θ - ω scans for Hf_x: Zr_yN_z Thick-A-Thick-E as grown on c-sapphire substrates, showing a range of structures from ordered to disordered. Vertical dotted lines correspond to ideal ZrN peak positions as labeled, vertical dotted, and dashed lines correspond to substrate peaks. b) Computed lattice parameters from XRD measurements of samples Thick-A-Thick-E show a monotonic decrease with increasing N fraction up to \approx 55% N with error bars. The outlier point at 66.88 at% N corresponds to a different regime and is not included in the linear fitting shown for the ZrN B-type lattice.

The primary properties of interest for measurement in the thin-film regime are the real and imaginary parts of permittivity. Precise knowledge of a film's thickness is a prerequisite for the extraction of permittivity from reflectivity *R* and transmissivity *T* of a thin film. In the range of \approx 5–80 nm, XRR can reliably determine a film's thickness. The set of thin-film samples (thicknesses in the range \approx 10–60 nm) is suited well to XRR and allows facile measurement of *R* and *T* when grown on transparent c-sapphire substrates. Growth recipes, as well as thicknesses measured with XRR for the set of thin-film samples, are given in the Experimental Section.

For confirmation of stoichiometries as compared with that of Thick-C, chemical compositions of the set of thin-film samples were measured using RBS. Just as before with the set of



Table 2. Composition parameters (in at%) of the thin-film samples fit from RBS data with the SIMNRA software.

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Sample	Hf [at%]	Zr [at%]	N [at%]	
Thin-A	$\textbf{0.515} \pm \textbf{0.001}$	45.684 ± 0.087	$\textbf{53.801} \pm \textbf{0.063}$	
Thin-B	$\textbf{1.003} \pm \textbf{0.001}$	$\textbf{48.812} \pm \textbf{0.001}$	$\textbf{50.185} \pm \textbf{0.003}$	
Thin-C	$\textbf{0.546} \pm \textbf{0.001}$	$\textbf{47.921} \pm \textbf{0.076}$	$\textbf{51.533} \pm \textbf{0.082}$	
Thin-D	$\textbf{0.495} \pm \textbf{0.001}$	$\textbf{47.579} \pm \textbf{0.129}$	$\textbf{51.926} \pm \textbf{0.141}$	
Thin-E	$\textbf{0.485} \pm \textbf{0.175}$	$\textbf{43.064} \pm \textbf{15.513}$	$\textbf{56.451} \pm \textbf{0.927}$	

thick-film samples, elemental compositions were determined for Thin-A—Thin-E (see **Table 2**). RBS analysis in the thin-film regime was conducted with greater resolution per channel (advantageous for thinner films at the cost of more specialized hardware) compared with the thick-film sample set (see **Figure 3**a).

Photographs (white balanced in the same way as the thick-film samples) of the thin-film sample set are included on the right side of Figure 3a. In the Hf_x : Zr_vN_z thin-film regime, the Zr-rich (y > z) film Thin-C appears bright and noticeably whitish golden similar to Thick-C with specular reflection and deep blue transmission. In the stoichiometric case ($\gamma \approx z$), Thin-B appears golden but slightly darker and more transmissive with specular reflection and deep blue transmission, a deviation from the stoichiometric cases in the set of thick film samples. Finally, in the N-rich case (y<z), and similar to the N-rich case in the set of thick-film samples, films Thin-A and Thin-E appear darker and more transmissive with Thin-D, looking noticeably golden but still darker than the highly stoichiometric cases. All films from the set of thin-film samples are smooth (roughness fit by GenX^[40] $\sigma = 20.1 \pm 1.1$ Å, 5.1 ± 0.4 Å, 4.3 ± 0.5 Å, 4.6 ± 0.6 Å, and 8.3 ± 0.7 Å from Thin-A to Thin-E, respectively) and continuous, as measured with XRR over a spot size of \approx 4 mm² (see Figure 3b). In comparison with wavelengths used in UV-vis-NIR spectroscopy, these roughness values correspond approximately to $\lambda/40$ for Thin-A and $\lambda/50$ for Thin-B-Thin-E. Films Thin-C-Thin-E are fabricated with decreasing thickness but otherwise identical growth parameters.

Phases present in films from the set of thin-film samples were characterized with XRD, as shown in Figure 4a. For films in this thickness range, (111) orientation is found to be generally favorable for all tested stoichiometries. Unlike the rest, Thin-B shows a (200) peak accompanying the (111) peak, which may be a consequence of its larger Hf concentration relative to the other films. A slightly expanded lattice parameter is measured for films of Ndeficient (y>z) Hf_x:Zr_vN_z, whereas a slightly shrunken lattice parameter is measured for N-rich (y < z) Hf_x:Zr_yN_z. Tilt of crystallites in the first film grown from the set of thin-film samples (Thin-A) is characterized with a series of XRD 2θ - ω scans (see Experimental Section for details of ψ -angle tilt XRD) aligned to the film's (111) peak over a range of ψ -angle tilts with respect to the *c*-axis of its sapphire substrate (Figure 4b). Increasing tilt from 0 to 4° shows a marked cutoff in diffracted beam intensity which approaches 0° at 8° from the normal. Because of the steep intensity cutoff with small increases of ψ -angle, we can conclude that most crystallites are arranged with the (111) direction normal to the *c*-axis of the sapphire substrate.



Figure 3. a) Normalized RBS measurements (counts per channel) and appearance of the set of thin-film samples as well as corresponding SIMNRA fits (black dashed curves) on Si (111) substrates for Thin-A, Thin-C–Thin-E, and c-sapphire for Thin-B. Approximate channel locations of element signal onset denoted with vertical dashed lines. Photographs (reflections can be seen on Thin-C and Thin-E) are included in same order of Thin-A–Thin-E as grown on c-sapphire substrates. b) Normalized XRR measurements of the set of thin-film samples as well as corresponding GenX fits (black dashed curves) where 2θ distance between oscillations is inversely proportional to film thickness *d* and 2θ breadth of oscillations is correlated with roughness σ .

Real and imaginary parts of permittivity, with precise knowledge of film thickness from XRR, were extracted using code developed in-house (see Experimental Section for a description and testing information of the permittivity extraction code) for the determination of the refractive index n and the extinction coefficient k from the reflection coefficient R and the transmission coefficient T measurements. Wavelength-dependent R and T coefficients measured for the set of thin-film samples are shown in **Figure 5**a,b respectively. Real and imaginary parts of the extracted permittivity spectra of the set of thin-film samples are shown in Figure 5c,d, respectively. Permittivity spectra are plotted in comparison with the reported permittivity of www.advancedsciencenews.com

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Figure 4. XRD measurements from the set of thin-film samples. a) Logscale XRD 2θ - ω scans for Hf_x:Zr_yN_z grown on c-sapphire substrates of Thin-A-Thin-E (from bottom to top, respectively, with Thin-A in indigo and Thin-E in green), showing mostly (111) texture. Vertical dotted lines correspond to ideal ZrN peak positions as labeled, vertical dotted, and dashed lines correspond to substrate peaks. b) XRD measurements on sample Thin-A with varying ψ -tilt (from top to bottom, $\psi = 0, 1, 2, 3, 4, 6, 8, 10^{\circ}$) on a Panalytical multipurpose stage to characterize sharpness of crystallite alignment with respect to the surface normal of a c-sapphire substrate in the vicinity of the ideal ZrN (111) peak.

ZrN,^[41] where Thin-C–Thin-D shows the most similar real part but has a larger imaginary part.

Unlike all other samples, which were grown at 300 °C, Thin-A was grown at room temperature (≈ 17 °C to test and see if a plasmonic Hf_x:Zr_yN_z can be grown at low temperature) and shows a small real part of permittivity. Even though Thin-A has approximately stoichiometric composition, the real part of its permittivity is significantly more positive than that of literature ZrN. Sample Thin-B was grown with pressure intermediate between Thin-A and Thin-C—Thin-E at 300 °C; it shows optically intermediate properties between those of Thin-A and Thin-C—Thin-E. Growth temperature has a strong effect on *R* and *T* with their maxima redshifting.



For samples Thin-C and Thin-E, only the film thicknesses were varied, and all other growth conditions (see Table 1 in Experimental Section) were kept identical between the three. The thinnest of these samples, Thin-E, shows a substantially smaller real part of permittivity and larger imaginary part compared with the thicker samples Thin-C-Thin-D. Chemistry of Hfx:ZrvNz films shows thickness dependence, which leads to changes in the dielectric function as films become thin when all other growth conditions are held constant. With the recipe for Thin-C-Thin-E held constant for all parameters other than thickness/growth time, decreasing thickness yields a corresponding decrease in Zr fraction. Correspondingly, the real part of permittivity becomes increasingly positive with decreasing thickness. The same trend follows for the imaginary part of permittivity, and samples become increasingly lossy with decreasing thickness (and increasing N-fraction).

The thin-film regime demonstrates that $Hf_x: Zr_y N_z$ with highly ZrN-like permittivity is difficult to attain, even when $y \approx z$. Second, sputtering growth rate and film thickness are inversely correlated, for example, sputtering rate accelerates as films grow. Chemistry also depends on the thickness, with films usually being N rich for a given recipe when it is in a very thin film compared with a thick film grown with the same recipe. This thickness dependence of film chemistry strongly impacts optical properties and leads to larger dielectric losses in a thin Hf_x: Zr_vN_z film compared with a thick film prepared with the same growth conditions with only the growth time being varied. Hf_x: Zr_vN₂ thin films can be sputtered with low roughness suitable for optical applications. The most favored crystallite orientation is (111) with only a small (200) peak visible in Thin-B. Crystallites are strongly oriented normal to the c-axis of the sapphire substrates. Finally, growth at low temperature redshifts transmission and reflection maxima with respect to high-temperature growth and incurs a substantially larger real part of permittivity.

3. Conclusion

The role of Hf contamination in impure ZrN precursor materials and how it influences the optical properties of ZrN films were explored in thick- and thin-film regimes. Hf contamination is present in most Zr precursor materials to the point of being difficult to avoid. Truly ultrahigh-pure Zr (and not just high metals basis, e.g., Zr + Hf purity) is a much more expensive specialty product than the commonly available ASTM-standardized Zr grades. These Hf impurities are demonstrated to contribute an increased imaginary part of permittivity to the optical properties of ZrN grown with contaminated precursor materials.

Changes in the optical properties of the $Hf_x:Zr_yN_z$ system can be understood intuitively as coming partially from the incorporation of intrinsically more lossy $HfN^{[41]}$ in the ZrN host material as well as the addition of local inhomogeneity (the Hf atoms themselves), which introduces enhanced electron scattering. HfN has a greater absorptivity^[41] and a greater heat capacity^[42] than ZrN. Impurity-induced modifications to the optical and thermal properties of real devices fabricated from ZrN may be made by controlling the concentration of Hf defects. In addition to enhancing the imaginary part of permittivity, the ability for ZrN to generate heat and thermal radiation can be modified with www.advancedsciencenews.com





Figure 5. Optical properties of H_{x} : Zr_yN_z films from the set of thin film samples. a) Reflection coefficient of Thin-A–Thin-E (percent reflectance per nanometer wavelength). b) Transmission coefficient of Thin-A–Thin-E (percent transmission per nanometer wavelength). c) Real part of the permittivity and d) imaginary part of permittivity for Thin-A–Thin-E compared with literature values of ZrN (shown with the black dotted and dashed line).

the incorporation of Hf defects. In addition, changes to the permittivity resulting from Hf incorporation and the sensitive dependence on chemistry of ZrN (especially in cases where precursor materials have been misleadingly labeled or sold) may result in frustration in the attainment of ideal ZrN with literature-like properties and may describe why there is such a greater quantity of TiN development with respect to ZrN in the literature.

Films of $Hf_x:Zr_yN_z$ were grown using RF magnetron sputtering using an impure but ubiquitously available grade 702 Zr target to determine effects of purity on permittivity. Primary controlled parameters were mTorr pressure of N₂ gas in the vacuum chamber, growth temperature, and growth time. N₂ gas pressure in the chamber during reactive sputtering allows for manipulation of final chemistry in sputtered films and correlates positively with increased N-fraction. Hf concentration increases with increasing chamber pressure. Room-temperature growth redshifted RT maxima, resulting in more lossy permittivity than films grown at 300 °C. Texture and composition are strongly thickness dependent, and (111) texture dominates the thin-film regime. For a given recipe, sputtering rates accelerate as films grow thicker, even with all other parameters held constant. Differences in single-recipe N-content at different thicknesses can complicate recipe development.

Large deviations from literature-like ZrN permittivity resulted from Hf contamination, even while films maintained roughly 1:1 Zr:N stoichiometry, high-quality crystallization, and low misalignment of crystallites. We conclude that Hf contamination, as well as differences in single-recipe N-content at different thicknesses, contribute significant frustration in attaining low-loss plasmonic $Hf_x:Zr_vN_z$ (where $x \ll y,z$) and partially account for the overabundance of studies regarding TiN compared with ZrN. Therefore, truly ultrahigh-pure Zr sputter targets (those with <500 ppm of Hf) and ultrahigh-pure precursor materials in general are critical for attainment of ZrN and TMN films with ideal properties, especially in optical and plasmonic applications. Researchers may be inadvertently adding Hf or other defects into their films even when they think they may have an ultrahigh-pure precursor material, complicating optical properties with less expensive but chemically dubious targets. This presents an interesting tradeoff: the incorporation of small quantities of Hf atoms may increase microhardness in ZrN films^[30] (additionally a more

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economical alternative compared with the use of highly pure Zr precursors), which is relevant to industrial applications in hard, durable, and decorative coatings for extreme environments, but this may also lead to a larger imaginary part of permittivity arising from incorporation of the inherently more lossy HfN in the ZrN host material and a decrease in the damage threshold of a ZrN film, limiting its value in extreme environments.

4. Experimental Section

RF Magnetron Sputtering: Thin films of Hf_x:Zr_vN_z were grown in an AJA ATC Orion 8 RF sputtering system (vacuum pumped before growth to ${\approx}10^{-8}$ Torr) from ultrahigh-pure N_2 gas and a grade 702 Zr target purchased from the Kurt J. Lesker corporation. Two series of samples were grown: the first (a set of thick-film samples) were grown intentionally thick and on c-sapphire as well as Si(100) and Si(111) substrates (Si(111) was selected specifically for ease of measurement with RBS); the second (the set of thin-film samples) series of samples were grown thinner so that the thickness (a necessary parameter for the extraction of n and k from RT coefficients) could be accurately determined with XRR, a similar range of substrates were used. The set of thick-film samples was grown with consistent parameters of 300 °C, 200 W, 10 sccm Ar flow rate, 0.5 sccm N₂ flow rate, and 180 min except for the second sample Thick-B, which was grown for 45 min to test compatibility of thinner films in RBS. For the set of thick-film samples, pressure in the chamber was varied between 10, 5, 3, 2, and 1 mTorr for decreasing N fraction in the films Thick-A, Thick-B, Thick-C, Thick-D, and Thick-E, respectively. The set of thin-film samples consisted of five samples (Thin-A-Thin-E) grown as variations of the recipe for Thick-C. Ar and N₂ flow rates for the set of thin-film samples were consistent with the set of thick-film samples; varied parameters as well as thicknesses extracted from XRR measurements are shown in Table 3.

XRD and XRR Measurements: To characterize structural parameters, XRD and XRR were used in a Panalytical X'Pert X-ray diffractometer in the point-source configuration using Cu K radiation and a Ni Cu K filter generated at 45 kV and 40 mA. Samples were interrogated on a multipurpose stage. The Z-axis height of samples was set carefully using a mechanical depth stop to ensure repeated optimal positioning of the sample's top surface with respect to the X-ray beam. 1 and 4 mm perpendicular masks on the source were used to shape the X-ray beam. XRD: through a 1° incident beam slit, samples were scanned over $2\theta = 25^\circ - 90^\circ$ in the $2\theta - \omega$ geometry. Machine offsets were calculated by comparing substrate peak positions in the 2θ - ω and ω -scan geometries. Resultant diffractograms were analyzed with code developed in-house. ψ -tilts of the multipurpose stage were controlled in the X'Pert control software with sample Thin-A adhered via substrate corners to the stage with JVCC PPT-36G silicone splicing tape to minimize residues; $2\theta - \omega$ scans were measured as described before. XRR: in the same point-source configuration but through a 1/32° incident beam slit and in a diffracted beam slit, samples were scanned in the $2\theta - \omega$ geometry from $2\theta = 0^{\circ}$ to 4° . Resultant reflectograms were analyzed with GenX.^[40]

 $\ensuremath{\text{Table 3.}}\xspace$ Varied growth parameters for Thin-A–Thin-B with thickness calculated from XRR data.

Sample	Power [W]	Pressure [mTorr]	Time [min]	Temp [°C]	Thickness [Å]	Rate [Å s ⁻¹]
Thin-A	150	3 ± 0.24	10.0	17	541.4 ± 7.6	≈0.9
Thin-B	150	2 ± 0.24	35.0	300	$\textbf{362.6} \pm \textbf{3.0}$	≈0.2
Thin-C	150	1 ± 0.24	35.0	300	$\textbf{591.7} \pm \textbf{3.4}$	≈0.3
Thin-D	150	1 ± 0.24	11.3	300	$\textbf{288.1} \pm \textbf{1.4}$	≈0.4
Thin-E	150	1 ± 0.24	3.9	300	117.9 ± 1.2	\approx 0.5

RT Measurement: RT coefficients were measured through an inverted Zeiss microscope porting light into an Andor Shamrock spectrograph outfitted with an iDus CCD camera. A Thor PF10-03-P01-protected Ag mirror was used to calibrate the reflection coefficient by separate measurement with a Perkin-Elmer Lambda 1050 system. From the R, T, and A (absorption) parameters, n and k were extracted and used to calculate the real and imaginary parts of permittivity using the code developed in-house. This code used the transfer matrix method (TMM) to iteratively calculate R and T coefficients until the calculated R and T coefficients matched the experimental R and T coefficients. In practical use, the code showed good agreement between extracted permittivity values and actual permittivity values.^[34] Films were of high quality and showed low surface roughness—as measured with XRR—over the \approx 4 mm² X-ray beam spot size. All films studied here were thicker than the regime where thickness dependence (e.g., number of atomic layers in the film) played a significant role in the optical properties.^[43]

RBS Measurements: To characterize the atomic composition of films in the set of thick-film samples, RBS was selected, as it can measure concentrations of light elements like N with high sensitivity. For the set of thick-film samples, 2 MeV ⁴He⁺⁺ ions were incident on the samples at an 8° angle α with a spot size of $\approx 1 \text{ mm}^2$ in a General Ionex 4117HC 1.7MV tandetron accelerator operating in the Cornell geometry. The set of thick-film samples was measured in a 2024 MeV ⁴He⁺⁺ ion accelerator with a 22.50° incident angle α , 52.50° exit angle β , and 150° scattering angle θ with a spot size of $\approx 1 \text{ mm}^2$. SIMNRA was used to analyze the RBS measurement data.

Acknowledgements

S. B. thanks the support of the Department of Defense (DoD) through the National Defense Science & Engineering Graduate (NDSEG) Fellowship Program. This work was supported by NSF-ECCS-1907423. This work was conducted in part at the San Diego Nanotechnology Infrastructure (SDNI) of University of California, San Diego (UCSD), a member of the National Nanotechnology Coordinated Infrastructure (NNCI), which was supported by the National Science Foundation (grant ECCS-1542148). The authors also acknowledge the use of facilities within the Eyring Materials Center at Arizona State University supported in part by NNCI-ECCS-1542160 and acknowledge that some measurement was carried out in part in the Materials Research Laboratory Central Research Facilities, University of Illinois. Data supporting findings of this study are available from the corresponding author upon reasonable request.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords

extreme materials, hafnium nitride, nitrides, nonlinear optics, plasmonics, transition metal nitrides, zirconium nitride

Received: July 8, 2021 Revised: July 26, 2021 Published online: **ADVANCED** SCIENCE NEWS

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- [1] P. Patsalas, Thin Solid Films 2019, 688, 137438.
- [2] G. V. Naik, V. M. Shalaev, A. Boltasseva, Adv. Mater. 2013, 25, 3264.
- [3] O. Quevedo-Teruel, H. Chen, A. Díaz-rubio, G. Gok, A. Grbic, G. Minatti, E. Martini, S. Maci, G. V. Eleftheriades, M. Chen, N. I. Zheludev, N. Papasimakis, S. Choudhury, Z. A. Kudyshev, S. Saha, H. Reddy, A. Boltasseva, V. M. Shalaev, A. V. Kildishev, D. Sievenpiper, C. Caloz, A. Alù, Q. He, L. Zhou, G. Valerio, E. Rajo-Iglesias, Z. Sipus, F. Mesa, R. Rodríguez-Berral, F. Medina, V. Asadchy, S. Tretyakov, C. Craeye, J. Opt. 2019, 21, 073002.
- [4] N. Kinsey, M. Ferrera, V. M. Shalaev, A. Boltasseva, J. Opt. Soc. Am. B 2015, 32, 121.
- [5] K. Wang, H. Qian, Z. Liu, P. K. L. Yu, Prog. Electromagn. Res. 2020, 168, 25.
- [6] H. Qian, S. Li, C.-F. Chen, S.-W. Hsu, S. E. Bopp, Q. Ma, A. R. Tao, Z. Liu, Light Sci. Appl. 2019, 8, 13.
- [7] H. Qian, S. Li, Y. Li, C. Chen, W. Chen, S. E. Bopp, Y. Lee, W. Xiong, Z. Liu, Sci. Adv. 2020, 6, eaay3456.
- [8] U. Guler, A. Boltasseva, V. M. Shalaev, Science 2014, 344, 263.
- [9] M. Kumar, N. Umezawa, S. Ishii, T. Nagao, ACS Photonics 2016, 3, 43.
- [10] R. A. Maniyara, D. Rodrigo, R. Yu, J. Canet-Ferrer, D. S. Ghosh, R. Yongsunthon, D. E. Baker, A. Rezikyan, F. J. García de Abajo, V. Pruneri, *Nat. Photonics* **2019**, *13*, 328.
- [11] N. Formica, D. S. Ghosh, A. Carrilero, T. L. Chen, R. E. Simpson, Appl. Mater. Interfaces 2013, 5, 3048.
- [12] C. M. Zgrabik, E. L. Hu, Opt. Mater. Express 2015, 5, 478.
- [13] J. Meng, Z. Fu, M. Du, X. Liu, L. Hao, Mater. Lett. 2016, 164, 291.
- [14] Y. Ran, H. Lu, S. Zhao, Q. Guo, C. Gao, Z. Jiang, Z. Wang, Appl. Surf. Sci. 2021, 537, 147981.
- [15] W. Sun, C. J. Bartel, E. Arca, S. R. Bauers, B. Matthews, B. Orvañanos, B. Chen, M. F. Toney, L. T. Schelhas, W. Tumas, J. Tate, A. Zakutayev, S. Lany, A. M. Holder, G. Ceder, *Nat. Mater.* **2019**, *18*, 732.
- [16] P. Patsalas, N. Kalfagiannis, S. Kassavetis, G. Abadias, D. V Bellas, C. Lekka, E. Lidorikis, *Mater. Sci. Eng. R* 2018, 123, 1.
- [17] M. Kumar, S. Ishii, N. Umezawa, T. Nagao, Opt. Mater. Express, 2015, 6, 29.
- [18] S. Kassavetis, D. V. Bellas, G. Abadias, E. Lidorikis, P. Patsalas, Appl. Phys. Lett. 2016, 108, 263110.
- [19] Y. Ran, H. Lu, Z. Wang, S. Zhao, L. Jia, Q. Guo, C. Gao, Z. Jiang, Appl. Surf. Sci. 2019, 476, 560.
- [20] C. Metaxa, S. Kassavetis, J. F. Pierson, D. Gall, P. Patsalas, ACS Appl. Mater. Interfaces 2017, 9, 10825.
- [21] A. You, M. A. Y. Be, I. In, J. Vac. Sci. Technol., A 2018, 28, 541.
- [22] M. I. Stockman, K. Kneipp, S. I. Bozhevolnyi, S. Saha, A. Dutta, J. Ndukaife, N. Kinsey, H. Reddy, U. Guler, V. M. Shalaev, A. Boltasseva, B. Gholipour, H. N. S. Krishnamoorthy, K. F. MacDonald, C. Soci, N. I. Zheludev, V. Savinov, R. Singh,

P. Groß, C. Lienau, M. Vadai, M. L. Solomon, D. R. Barton III, M. Lawrence, J. A. Dionne, S. V. Boriskina, R. Esteban, J. Aizpurua, X. Zhang, S. Yang, D. Wang, W. Wang, T. W. Odom, N. Accanto, P. M. de Roque, I. M. Hancu, L. Piatkowski, N. F. van Hulst, M. F. Kling, *J. Opt.* **2018**, *20*, 043001.

- [23] K. Chaudhuri, A. M. Shaltout, U. Guler, V. M. Shalaev, A. Boltasseva, in 2016 Conf. Lasers Electro-Optics, CLEO 2016, OSA Technical Digest, Optical Society of America, 2016, FM3N.2; https://doi.org/10.1364/ CLEO_QELS.2016.FM3N.2.
- [24] M. Braic, M. Balaceanu, V. Braic, A. Vladescu, G. Pavelescu, M. Albulescu, Surf. Coat. Technol. 2005, 200, 1014.
- [25] Y. Xin, C. Liu, K. Huo, G. Tang, X. Tian, P. K. Chu, Surf. Coat. Technol. 2009, 203, 2554.
- [26] P. C. Johnson, H. Randhawa, Surf. Coat. Technol. 1987, 33, 53.
- [27] L. Y. Wang, M. S. Lee, J. Ind. Eng. Chem. 2016, 39, 1.
- [28] H. M. Benia, M. Guemmaz, G. Schmerber, A. Mosser, J. C. Parlebas, *Appl. Surf. Sci.* 2003, 211, 146.
- [29] H. M. Benia, M. Guemmaz, G. Schmerber, A. Mosser, J. Parlebas, *Appl. Surf. Sci.*, **2002**, 200, 231.
- [30] D. A. R. Fernandez, B. S. S. Brito, I. A. D. Santos, V. F. D. Soares, A. R. Terto, G. B. De Oliveira, R. Hubler, W. W. Batista, E. K. Tentardini, *Nucl. Inst. Methods Phys. Res. B* 2020, 462, 90.
- [31] M. Yuste, R. E. Galindo, O. Sánchez, D. Cano, R. Casasola, J. M. Albella, *Thin Solid Films* **2010**, *518*, 5720.
- [32] M. Mayer, presented at Workshop on Nuclear Data of Science and Technology: Materials Analysis 2003.
- [33] A. W. Czanderna, D. M. Hercules, *Ion Spectroscopies for Surface Analysis.*, Springer Science & Business Media, Cham, Switzerland 2012.
- [34] H. Qian, Y. Xiao, D. Lepage, L. Chen, Z. Liu, Nanophotonics 2015, 4, 413.
- [35] M. Mayer, AIP Conf. Proc. 1999, 475, 541.
- [36] P. Klumdoung, A. Buranawong, S. Chaiyakun, P. Limsuwan, Procedia Eng. 2012, 32, 916.
- [37] W. Chou, G. Yu, J. Huang, Thin Solid Films 2002, 405, 162.
- [38] N. J. Ashley, R. W. Grimes, K. J. McClellan, J. Mater. Sci. 2007, 42, 1884.
- [39] K. Balasubramanian, S. V. Khare, D. Gall, Acta Mater. 2018, 159, 77.
- [40] M. Bjo, G. Andersson, J. Appl. Crystallogr. 2007, 40, 1174.
- [41] G. V. Naik, J. Kim, A. Boltasseva, Opt. Mater. Express 2011, 1, 1090.
- [42] A. Wang, S. Shang, D. Zhao, J. Wang, L. Chen, Y. Du, Z. K. Liu, T. Xu, S. Wang, *Calphad Comput. Coupling Phase Diagrams Thermochem.* 2012, *37*, 126.
- [43] A. Boltasseva, A. Catellani, N. Kinsey, D. Shah, H. Reddy, V. Shalaev, A. Calzolari, ACS Photonics 2018, 5, 2816.