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Structural and mechanical properties of nanocrystalline Ga$_2$O$_3$ films made by pulsed laser deposition onto transparent quartz substrates

Vishal Zade$^{1,2,3}$, Nanthakishore Makeswaran$^{1,3}$, Brad L. Boyce$^2$, Francisco Paraguay-Delgado$^4$ and C. V. Ramana$^{1,3}$

$^1$ Center for Advanced Materials Research (CMR), University of Texas at El Paso, 500 W University Ave, El Paso, Texas 79968, United States of America
$^2$ Center for Integrated Nano Technologies (CINT), Sandia National Laboratory, Albuquerque, New Mexico, United States of America
$^3$ Department of Mechanical Engineering University of Texas at El Paso, 500 W University Ave, El Paso, Texas 79968, United States of America
$^4$ Centro de Investigación en Materiales Avanzados SC, Miguel de Cervantes 120, CP 31109, Chihuahua, Chih., México

E-mail: rvchintalapalle@utep.edu

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Abstract

This work reports on the correlation between structure, surface/interface morphology and mechanical properties of pulsed laser deposited (PLD) β-Ga$_2$O$_3$ films on transparent quartz substrates. By varying the deposition temperature in the range of 25 °C–700 °C, ~200 nm thick Ga$_2$O$_3$ films with variable microstructure and amorphous-to-nanocrystalline nature were produced onto quartz substrates by PLD. The Ga$_2$O$_3$ films deposited at room temperature were amorphous; nanocrystalline Ga$_2$O$_3$ films were realized at 700 °C. The interface microstructure is characterized with a typical nano-columnar morphology while the surface exhibits the uniform granular morphology. Corroborating with structure and surface/interface morphology, and with increasing deposition temperature, tunable mechanical properties were seen in PLD Ga$_2$O$_3$ films. At 700 °C, for nanocrystalline Ga$_2$O$_3$ films, the dense grain packing reduces the elastic modulus $E_r$ while improving the hardness. The improved crystallinity at elevated temperatures coupled with nanocrystallinity, the β-phase stabilization is accounted for the observed enhancement in the mechanical properties of PLD Ga$_2$O$_3$ films. The structure-morphology-mechanical property correlation in nanocrystalline PLD β-Ga$_2$O$_3$ films deposited on quartz substrates is discussed in detail.

1. Introduction

Gallium oxide (Ga$_2$O$_3$) offers exciting possibilities in the design and development of advanced technologies based on wide bandgap semiconductor devices. Ga$_2$O$_3$ is the ideal candidate in the field, especially, in the context of integrating wide bandgap semiconductors into practical devices and applications [1–7]. The device applications list of Ga$_2$O$_3$ is growing fast and, with the further expansion in the knowledge database from theoretical studies and nanoscale architectures, the advent of a new era of devices is imminent. To name a few applications or the potential technological domains, significant progress has been made for utilization of properties of Ga$_2$O$_3$ in the field of transparent conducting oxides (TCO) [8, 9], deep-UV photodetectors [10–12], photocatalysis [13, 14], flat panel devices [15], photoluminescence [16]. The physical and chemical properties, that are of particular interest in using β-Ga$_2$O$_3$, are primarily due to its high thermal and chemical stability compared to its other polymorphs, which often exhibit unstable behavior and convert to the more stable β-Ga$_2$O$_3$ at elevated temperatures [17]. Even with the advancements in the research and current developments with regards to GaN and SiC power devices, search for a viable alternative to these materials act as a catalyst to the Ga$_2$O$_3$ research. The better and faster power devices that operate at ultrahigh voltages will advance a range of technological fields and help us explore new and unexplored areas [17, 18].

The present work mainly focuses on two critical aspects of Ga$_2$O$_3$ thin films deposited onto the transparent quartz substrates. Before diving deep into the current work, it is pertinent to understand the importance of this
work in terms of using transparent quartz as a substrate while understating the properties of thin films at an elevated temperature. Deposition of oxide films on transparent amorphous substrates such as quartz have been investigated due to their potential applications on transparent conductive contacts, solar cell, and liquid crystal displays, amid others. Due to the nature of the amorphous substrate, deposition at room temperature creates a high stress at the interface of the film [19, 20]. Increasing the substrate temperature or post-deposition annealing treatment reduces the stress of the material, improves the crystallinity of the film, and generally increases the band gap [19, 21–23]. Nevertheless, transmittance is slightly compromised at higher temperatures, yet researchers have claim that values are still high and comparable to those of conventional transparent electrodes [22]. Indeed, quartz substrate is effective on the deposition of conductive oxide films.

Going back to the two critical aspects of this work, first is the mechanical properties due to varying fabrication conditions and, second, the evolution of surface/interface morphology as a function of deposition temperature. The relationship between hardness and elastic modulus can significantly affect the overall toughness of the coatings making them to be wear-resistant in practical applications [24]. Even the current direction of the scientific developments focus on coatings that can withstand wear under normal operating conditions as well as at extreme environments [25, 26]. Industrial applications, which are susceptible to impact loadings or variation in temperatures during the lifecycle of the service components, demand a high level of performance [27–29]. Hence, it becomes imperative to study the grains size evolution and property evolution for such applications. Also, when films are grown either using a physical vapor deposition method or a chemical vapor deposition method, the overall properties of the Ga2O3 thin films are highly dependent on the processing parameters. The most important parameters influencing the properties are base operating pressure [30], reactive pressure, deposition rate and growth temperature [31–33]. Hence, a deeper understanding of the effect of processing parameters and resulting materials at the nanoscale dimensions can help to establish strategies and derive tunable properties and enhanced performance of Ga2O3 films. For instance, the chemical valence state of Ga and its corresponding surface chemistry dictates the electronic properties which can be beneficial for certain applications [34]. Similarly, for optoelectronic applications, tunable optical constants are quite important; however, the optical properties are highly influenced by the microstructure. In fact, the optical and mechanical properties of oxide films are highly sensitive to the lattice parameters, strain, packing density, interfacial structure, and defect structure [34–38]. Therefore, the present work was performed to understand the effect of deposition temperature on the crystal structure, surface/interface morphology and mechanical properties of Ga2O3 thin films deposited onto quartz by pulsed laser deposition (PLD). The results presented and discussed in this work can help to establish a structure-morphology-mechanical property correlations, which may be useful to optimize conditions to produce excellent quality nanocrystalline PLD Ga2O3 films.

2. Experimental details

2.1. Fabrication

The thin films were deposited by the pulsed laser deposition (PLD) technique using a COPMEx Pro setup equipped with an excimer laser supplied by COHERENT. The depositions were carried out on quartz substrates by varying the deposition temperature from room temperature (RT = 25 °C) to 700 °C. For the target ablation, the KrF excimer laser with a wavelength of 249 nm was applied. The films were deposited at a deposition pressure of 5 mTorr with the laser pulses set at a repetition rate of 5 Hz for 2000 pulses with a pulse energy of 220 mJ. The target-substrate distance was set at 45 mm for an efficient plume-substrate interaction. The home-made Ga2O3 target was used in this work. The thickness of deposited films was fixed at ~500 nm. However, the crystallization-induced thickness variation is taken into account under post-deposition conditions.

2.2. Characterization

2.2.1. X-ray diffraction (XRD)

The XRD analysis of the Ga2O3 thin films was performed using a PANalytical X’Pert Multipurpose Diffractometer with a vertical θ–θ goniometer (220 mm radius) in the Bragg- Brentano geometry. The x-ray source was set at operating parameters of 45 kV and 40 mA for the long fine-focus x-ray tube with a Cu anode. The diffraction data analysis or phase matching was carried out using JADE 9.5.1 (Materials Data, Inc.) and the PDF4+ – 2018 database from The International Centre for Diffraction Data (ICDD).

2.2.2. Transmission electron microscopy (TEM)

The structure and element composition were studied using an JEOL transmission electron microscope JEM-2200FS with spherical aberration corrector in probe mode. The instrument was operated at 200 kV and the electron diffraction patterns were acquired in TEM mode using selected area electron diffraction (SAED) mode. The X-ray energy dispersion spectrometer (EDS) was used in a STEM mode to get elemental mapping images.
The thin film cross section sample for TEM study was made using an JEOL JEM-9320FIB device. The sample for this purpose was covered with a thin layer of gold using sputter technique and the specific zone was covered by carbon to protect the sample.

2.2.3. Scanning electron microscopy (SEM)

The Ga2O3 thin films were subject to surface morphological studies using a FEI Magellan 400 scanning electron microscope which provides sub-nanometer spatial resolution. The imaging was done with secondary electrons (SE) at 5 kV beam energy and a working distance (WD) of 3.4 mm. The samples were gold coated before imaging to optimize the surface properties under SEM.

2.2.4. Nanoindentation

The mechanical properties of the PLD deposited Ga2O3 thin films were tested with a Hysitron TI950 Triboindenter. A triangular pyramid Berkovich diamond indenter was used for the indentation which has a normal angle of 65.3° between the tip axis and the pyramid faces. The effective size of the tip apex is estimated to be 100 nm. The loading and unloading curves were determined using the set standard procedures [39, 40], while the hardness and the reduced modulus were calculated using the methods developed elsewhere [41, 42].

3. Results and discussion

3.1. Crystal structure

The XRD patterns of the PLD Ga2O3 thin films are shown in figure 1. The XRD data clearly indicate the structural evolution as a function of deposition temperature. It can be noticed that, except the films deposited at 700 °C, there are no diffraction peaks observed in the XRD patterns. All the XRD patterns exhibit diffuse nature at lower temperatures (<700 °C). This indicates that the films are amorphous. However, the growth of nanocrystalline PLD Ga2O3 thin films is found at 700 °C. As evidenced from the XRD patterns, the 700 °C PLD Ga2O3 films are crystalline, and the diffraction peaks identified as: (400), (402), (603) and (801) corresponding to monoclinic β-phase Ga2O3. The respective peaks and their positions are indicated in figure 1. The crystal structure is identified in space group C2/m. The crystal structure is identified with space group C2/m. The most dominant peak i.e., (400), is located at 2θ = 30.05°. The peaks are indexed and match according to the JCPDS (00-043-1012) [43]. The absence of diffraction reflexes for PLD Ga2O3 films deposited at <700 °C signifies the strong effect of deposition temperature on the growth of crystalline films. At lower temperatures, the kinetic energy of the flux may be not sufficient, or time may be short in reference to conditions required for the crystallization Ga2O3. In a pulsed laser deposition technique, Ga2O3 target ablation in this case, the plume consist of gaseous species of Ga, O and Ga2O and possibly other Ga-O forms in an excited state or fundamental otherwise [44, 45]. The films were deposited at a relatively low oxygen partial pressure (50 mTorr) with an intent of lowering down the oxygen content in plume expansion of the target. Also, the substrate temperature significantly influences the surface kinetics alongside the properties of the gaseous phase precursor coming.
towards the substrate in the form of a plume [44]. The formation of nanocrystalline Ga$_2$O$_3$ at lower temperature is insufficient to get a crystalline thin film which results in the formation of amorphous thin films at lower deposition temperatures. The crystalline growth of Ga$_2$O$_3$ is supported at higher substrate temperature due to the favored kinetics and thermal effects of the system on the substrate-plume interaction resulting in improved crystallinity. This further asserts the crystallinity improvement as a function of substrate temperature.

### 3.2. Surface morphology

The scanning electron microscopy (SEM) images for PLD Ga$_2$O$_3$ films are shown in figure 2. As it can be seen from the images, the films deposited at room temperature shows no sign of grain formation indicating an amorphous state. As the temperature increases, there is an evident grain evolution occurring in the films. This can be attributed to the increment in temperature and the subsequent thermal kinetics at the substrate surface during the plume-substrate interaction. To further understand the surface morphology evolution, AFM micrographs were recorded in contact mode, as shown in figure 3. At elevated temperatures, an evolved grain structures can be seen in the 3D representative micrographs.

The microstructural information of the films, thickness in particular, is also measured for the PLD Ga$_2$O$_3$ films. The physical thickness as a function of the temperature revealed the trend that it remains constant at all temperatures but shows a sudden drop at 700 °C, where the film material crystallization is evident. This correlates well with all the structural data from XRD, SEM and AFM analyses in addition to nanoindentation testing, as discussed later. The significant increase in crystallinity at 700 °C, as indicated in the XRD and SEM images, would not only account for the similarly abrupt increased hardness and decrease in modulus of elasticity at that temperature, but it would also explain the reduced thickness of the sample via a more compact microstructure. Finally, to understand the effect of temperature, the most important thermodynamic parameter, on the growth behavior in PLD Ga$_2$O$_3$ films and the fundamental mechanism involved we considered the structural characterization data from XRD and surface characteristics obtained from AFM. Particularly, to the data obtained from XRD and AFM were analyzed in terms of simple models available in the literature. Substrate temperature generally plays a role on the crystallization and, hence, the resulting microstructure and properties of oxide thin films deposited by physical vapor deposition methods [46, 47]. The two most important features, as evident from XRD and AFM data analyses, are the amorphous-to-crystalline transformation and surface roughness increase with increasing temperature. The crystallization and grain or crystallite size increase related to the increase in diffusion coefficient on the substrate and typically depend on temperature by means of Arrhenius relation. However, due lack of appreciable size estimation in amorphous films, we consider the AFM surface roughness data as a function of deposition temperature.

![Figure 2. SEM images of Ga$_2$O$_3$ PLD thin films fabricated at (a) 24 °C, (b) 500 °C, (c) 600 °C and (d) 700 °C.](image-url)
The variation of RMS surface roughness with deposition temperature is shown in figure 4. It is evident that the surface roughness of PLD Ga$_2$O$_3$ films follows a trend at higher deposition temperature although it not much affected in the growth temperature range of 25 °C–400 °C. It appears that kinetic roughening occurs in PLD films, especially for those deposited at elevated temperature. The kinetic roughening in the growth of metal, alloy, and compound thin films by physical vapor deposition has been considered as an important topic of scientific and technological significance [48–50]. While many theories exists and/or developed in recent years explain the growth processes and roughening mechanisms [48–50], we believe that the temperature induced roughening mechanism is operative in these PLD Ga-oxide films. Specifically, thermally activated surface diffusion can account for the general trend in morphology evolution, while surface roughness increase at higher temperatures can be due to the combined effect high deposition temperatures and stresses in nanocrystalline PLD Ga$_2$O$_3$ films. Furthermore, the roughness increase with increasing temperature can be due to crystallization induced local stresses within the film. Perhaps, that could be the reason for the observed more or linear increase in surface roughness in the PLD Ga$_2$O$_3$ films deposited in the temperature range of 400 °C–700 °C.

3.3. Phase stability and composition

The variation of RMS surface roughness with deposition temperature is shown in figure 4. It can be noted that the variation is not affected until 400 °C, at which point the trend noted is the linear increase with increasing temperature.

Figure 3. AFM 3D profiles representing the Ga$_2$O$_3$ PLD thin films fabricated at different temperatures.

Figure 4. Variation in RMS surface roughness of PLD Ga$_2$O$_3$ films with temperature deposition temperature. It can be noted that the variation is not affected until 400 °C, at which point the trend noted is the linear increase with increasing temperature.
since the sample is not completely crystalline. The fuzzy circles seen in the SAED pattern could belong to the film material. The pattern from the zone Z3 is a superposition of signals from the oxide sample and gold layer. In this pattern, the first wide circle belongs to the oxide material and the second and third clear thinner circles belong to gold. These results are in good relationship with the XRD patterns recorded for the sample obtained at 700 °C, where it was classified as nanocrystalline material.

The elemental composition of thin film cross-section was determined by EDS technique. The mapping images are show in figure 6, where each one shows the images for Oxygen, Gallium and Silicon distributions. It can be noticed that Ga and O show higher intensity for the layer zone and the Si can be seen in the substrate zone. These images show qualitatively that we have clear presence of the constituent elements and confirm the clear layer zone of Ga₂O₃.

3.4. Mechanical properties

3.4.1. Indentation load (L) and penetration depth (d)

The deposited thin films were inspected with nanoindentor as it is a versatile technique to obtain reliable information regarding the mechanical properties of thin films. The simplicity of this technique helps attain quick and valuable insights of the deposited thin films [29]. The effect of indentation load on the indentation depth is shown in figure 7. It is widely known that the substrate dictates the indentation response in any thin film characterization technique [29, 41, 51]. As the depth of indentation increases, the hardness increases correspondingly due to the formation of a plastic zone under the indenter tip [29]. As the plastic zone increases in size and reaches the film-substrate interface, the hardness is predominantly comes from the substrate [29]. A continuum analysis implemented by Bhattacharya and Nix addresses the issue with an assertion that the indentation depth over 20% of film thickness would lead to gradually increasing hardness but will be lower than the actual substrate hardness due to the fact that the indenter is resting in the deposited film [52]. To better address the mechanical properties of thin films rather than a mixture of film-substrate effects, the penetration depth was kept at a value of roughly 10% of film thickness in line with the literature [53–55]. In view of the above context, the Ga₂O₃ thin films exhibit a similar behavior with the indentation depth, as can be seen in figure 6(a). The load was varied from 100 μN to 2000 μN with increments of 100 μN while recording the indentation depth values at each load. The initial load of 100 μN yielded a small value for indentation depth (< 22 nm) which is within 5% of the film thickness. As we subsequently move towards higher loads, at 300 μN, the indentation
depth is in the preferred depth to thickness ration of ~10%. The penetration depth follows a linear trend with the increasing indentation load up to 2000 μN and, as it can be seen in figure 7(a), the values are in close proximity for all the thin films i.e. the indentation load has a less than overwhelming effect on the penetration depth of the films with the temperature change. This also indicates that the deposition technique (PLD) gives a high-quality thin film with dense packaging of the grains as can be corroborated from the SEM images (figure 2). The grain size evolution with temperature giving a slightly denser packing of grains with finer grain size can be seen to influence the indentation depth.

The loading and unloading curves for Ga₂O₃ films are shown in figure 7(b). The curves are plotted for a fixed load of 2000 μN. A typical load versus displacement curve is used to measure parameters viz elastic stiffness, maximum load, and corresponding maximum displacement. The values obtained are essential to determine the hardness (H) and the reduced elastic modulus (E_r) for the material in context. As it can be noted from figure 7(b), the slope varies with the change in the deposition temperature. It can be clearly seen that the film deposited at 700 °C shows a different characteristic slope as compared to the other films indicating a direct correlation between crystallinity and hardness of the Ga₂O₃ films. An improved hardness at elevated temperature arises due to the rearrangement of atoms and hence the changed kinetics. It is further discussed in the following subsection.

### 3.4.2. Effect of indentation load (L) on hardness (H) and reduced elastic modulus (E_r)

The variation of hardness and reduced elastic modulus as a function of incremental load up to the peak load of this experiment is shown in figure 8. As it can be seen in figure 8(a), the variation of hardness with the load increase for thin films deposited at different substrate temperatures indicates that there is a slight correlation between hardness and deposition temperature. It may be noted that, for the films deposited at room temperature, 500 and 600 °C, the hardness value has a plateau after the critical load of ~300 μN, whereas the 700 °C sample exhibits a different behavior with an elevated hardness that peaks at around 750 μN of applied indentation load. After this the hardness gradually plateaus similar to the other deposited samples. This phenomenon typically arises due to the interfering substrate effect and changes occurring directly under the indenter tip. It can be construed that, at lower temperatures due to the larger grain sizes, the material will be softer and, above a certain temperature, as the grain size further decreases, it gives rise to the thin film hardening [56–58]. To further refer to the findings of Siegel [59], at sufficiently smaller grain sizes, the dislocations generated by the Frank-Read sources are too difficult to activate and impart deformation, hence the elevated hardness. If we shift the gaze to the change in reduced elastic modulus E_r evolution due to the substrate temperature, it can be seen from figure 4(b) that the elastic modulus follows a similar trend with reference to the plateauing of the values but there is a contrast in values for different films. The Er level shows a decrease for the thin film deposited at 700 °C, indicating that there is an improvement in the grain packing, as evidenced by the SEM images. This also points out to a fact that, at lower temperatures, the films are either amorphous or exhibit larger grain size. Now as the grain size reduces, the improved volume of the grain boundary regions which has a
higher modulus in comparison with the in-grain crystals [60]. The atomic models predicted such a behavior that, with the reducing grain size, there is a drop in elastic modulus value [61, 62].

3.4.3. $H$ and $E_r$ at critical load
A thin film is adjudged with its physical properties for any practical application that requires it to operate at elevated or room temperatures. The physical attributes are an indicator of the life cycle of the thin film over time while maintaining its high level of performance. The hardness ($H$) and elastic modulus ($E_r$) were estimated for the PLD grown Ga$_2$O$_3$ thin films barring the substrate effect out of the equation. As noted earlier and seen in figure 8, the $H$ and $E_r$ values change over the range of applied indentation loads. At $\sim 300 \, \mu$N (critical load), the depths of indentation are qualified a measured effect only for a thin film. The elimination of substrate effect allows us to comprehend the properties of the thin films from a mechanical standpoint. It may be noted from figure 9 that the hardness of the thin films increases with the temperature increase and it is particularly high for the thin film deposited at 700 °C. This is due to the fact that the grain size decreases at higher temperature giving a compact arrangement which leads to elevated hardness. On the other hand, the elastic modulus declines for the film deposited at 700 °C and it represents the change in the capacity of the films to bear plastic deformation. The films deposited at relatively low temperatures would have higher resistance to applied force, as compared to those fabricated elevated temperatures. Although we see contrasting changes in the hardness and elasticity of the films, it may be noted that the variations of the values are within 10% and 15%, respectively, which some might argue is an insignificant amount of change in the properties. But these change can be vastly significant in the case of devices which are sensitive to temperature variation and mechanical properties in extreme conditions.

Figure 7. (a) Nanoindentation on thin films for initial critical load identification and (b) loading-unloading curves.
Figure 8. (a) Hardness and (b) elastic modulus of thin film as a function of increasing load.

Figure 9. Overall variation of hardness and elastic modulus as a function of deposition temperature.
4. Conclusions

Ga$_2$O$_3$ films were deposited by PLD technique onto quartz substrates by varying the deposition temperature in a wide range of 25 °C–700 °C. The XRD analyses reveal that the Ga$_2$O$_3$ films deposited at 700 °C were nanocrystalline while those deposited at lower temperatures are amorphous. The structure, elemental composition, and surface/interface morphology of Ga$_2$O$_3$ films were also analyzed under TEM; the results indicate the formation of nanocrystalline Ga$_2$O$_3$ films at 700 °C. The surface morphology studies conducted using SEM and AFM show a grain size evolution at elevated temperatures further attesting the enhanced kinetics giving rise to substrate-plume interaction. The higher temperature induced grain evolution affects the mechanical properties, which were studied using nanoindentation. The elevated temperature gives a compact arrangement propelling the hardness of the thin films giving a resultant effect in the decline of the elastic modulus. This work shows the importance of deposition conditions and its effects on the thin films evolution of gallium oxide to be used in device fabrication which require a certain level of mechanical properties for devices under extreme conditions.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Vishal Zade  https://orcid.org/0000-0001-6455-9629
C V Ramana  https://orcid.org/0000-0002-5286-3065

References

[1] Higashiwaki M, Kuramata A, Murakami H and Kumagai Y 2017 State-of-the-art technologies of gallium oxide power devices J. Phys. D: Appl. Phys. 50 333002
[2] Dong L, Jia R, Xin B, Peng B and Zhang Y 2017 Effects of oxygen vacancies on the structural and optical properties of beta-Ga$_2$O$_3$ Sci. Rep. 7 40160
[3] Guo D et al 2017 Zero–power–consumption solar-blind photodetector based on beta-Ga$_2$O$_3$/NSTO heterojunction ACS Appl. Mater. Interfaces 9 1619–28
[4] Higashiwaki M and Jessen G H 2018 Guest Editorial: The Dawn of Gallium Oxide Microelectronics Appl. Phys. Lett. 112 060401
[5] Higashiwaki M, Sasaki K, Kuramata A, Masui T and Yamakoshi S 2012 Gallium oxide (Ga$_2$O$_3$) metal-semiconductor field-effect transistors on single-crystal beta-Ga$_2$O$_3$ (010) substrates Appl. Phys. Lett. 100 013504
[6] Onuma T et al 2015 Valence band ordering in beta-Ga$_2$O$_3$ studied by polarized transmittance and reflectance spectroscopy Jpn. J. Appl. Phys. 54 112601
[7] Sasaki K, Higashiwaki M, Kuramata A, Masui T and Yamakoshi S 2013 MBE grown Ga$_2$O$_3$ and its power device applications J. Cryst. Growth 378 591–3
[8] Orita M, Ohita H, Hirano M and Hosono H 2000 Deep–ultraviolet transparent conductive beta-Ga$_2$O$_3$ thin films Appl. Phys. Lett. 77 3166–8
[9] Sinha G, Adhikary K and Chaudhuri S 2007 Effect of annealing temperature on structural transformation of gallium based nanocrystalline oxide thin films and their optical properties Opt. Mater. 29 718–22
[10] Chen D et al 2018 Structural, vibrational and thermal expansion properties of Sc$_2$W$_4$O$_{15}$ PCCP. 20 20160–6
[11] Li Y et al 2010 Efficient assembly of bridged beta-Ga$_2$O$_3$ nanowires for solar-blind photodetection Adv. Mater. 20 3972–8
[12] Lee S H et al 2017 High–responsivity deep–ultraviolet–selective photodetectors using ultrathin gallium oxide films ACS Photonics. 4 2937–43
[13] Zhang W et al 2015 Liquid metal/metal oxide frameworks with incorporated Ga$_2$O$_3$ for photocatalysis ACS Appl. Mater. Interfaces 7 1943–8
[14] Zhang X et al 2018 Phase transition of two-dimensional $3\text{-Ga}_2\text{O}_3$ nanosheets from ultrathin $\gamma\text{-Ga}_2\text{O}_3$ nanosheets and their photocatalytic hydrogen evolution activities ACS Omega 3 14469–76
[15] Fu L, Liu Y, Pa H, Xiao K, Yu L and Zhu D 2003 $\text{Ga}_2\text{O}_3$ nanoribbons: synthesis, characterization, and electronic properties Chem. Mater. 15 4287–91
[16] Farvid S S, Wang T and Radovanic P V 2011 Colloidal gallium indium oxide nanocrystals: a multifunctional light-emitting phosphor broadly tunable by alloy composition J. Am. Chem. Soc. 133 6711–9
[17] Pearson S J et al 2018 A review of $\text{Ga}_2\text{O}_3$ materials, processing, and devices. Appl. Phys. Rev. 5 011301
[18] Stepanov S, Nikolaev V, Bougrov V and Romanov A 2016 Gallium oxide: properties and applications—a review Rev Adv Mater Sci. 44 63–86
[19] Beena D et al 2009 Effect of substrate temperature on structural, optical and electrical properties of pulsed laser ablated nanostructured indium oxide films Appl. Surf. Sci. 255 8334–42
[20] Shi W, Ageyman O and Xu C 2002 Enhancement of the light emissions from zinc oxide films by controlling the post-treatment ambient J. Appl. Phys. 91 5640–4
[21] Khoshman J, Khan A and Kordesch M 2008 Amorphous hafnium oxide thin films for antireflection optical coatings Surf. Coat. Technol. 202 2500–2
[22] Park S M, Ikekaggi T and Ebihara K 2005 Investigation of transparent conductive oxide Al-doped ZnO films produced by pulsed laser deposition Jpn. J. Appl. Phys. 44 8027
[23] Chen M, Pei Z, Sun C, Wen L and Wang X 2000 Surface characterization of transparent conductive oxide Al-doped ZnO films J. Cryst. Growth 220 254–62
[24] Leyland A and Matthews A 2000 On the significance of the $H/E$ ratio in wear control: a nanocomposite coating approach to optimised tribological behaviour Wear 246 1–11
[25] Huang L-Y I-J and Troyon M 2006 Nanomechanical properties of nanostructured titanium prepared by SMAT Surf. Coat. Technol. 201 208–13
[26] Tjong S and Chen H 2004 Nanocrystalline materials and coatings Materials Science and Engineering: R: Reports 45 1–88
[27] Krell A 1998 A new look at the influences of load, grain size and grain boundaries on the room temperature hardness of ceramics Int. J. Refract. Met. Hard Mater. 16 3–5
[28] Lim Y Y and Chaudhuri M M 1999 The effect of the indenter load on the nanohardness of ducitle metals: an experimental study on polycrystalline work-hardened and annealed oxygen-free copper Philos. Mag. A 79 2979–3000
[29] Nix W D 1989 Mechanical properties of thin films Metall. Trans. A 20 2217
[30] Ogita M, Higo K, Nakamichi Y and Hatanaka Y 2001 $\text{Ga}_2\text{O}_3$ thin film for oxygen sensor at high temperature. Appl. Surf. Sci. 175 721–5
[31] Priyamvada W, Radhakrishnan G, Droopad R and Passlack M 2011 In-situ XPS and RHEED study of gallium oxide on GaAs deposition by molecular beam epitaxy J. Cryst. Growth 323 103–6
[32] Ou S L et al 2012 Growth and etching characteristics of gallium oxide thin films by pulsed laser deposition Mater. Chem. Phys. 133 70–76
[33] Kim H W and Kim N H 2004 Growth of gallium oxide thin films on silicon by the metal organic chemical vapor deposition method Materials Science and Engineering: B 110 34–7
[34] Ramana C et al 2014 Chemical bonding, optical constants, and electrical resistivity of sputter-deposited gallium oxide thin films J. Appl. Phys. 115 045308
[35] Ramana C et al 2008 Spectroscopic ellipsometry characterization of the optical properties and thermal stability of ZrO$_2$ films made by ion-beam assisted deposition Appl. Phys. Lett. 92 031917
[36] Kruchinin V N et al 2017 Optical properties of TiO$_2$ films deposited by reactive electron beam sputtering J. Electron. Mater. 46 6089–95
[37] Ramana C, Mudavaikka V, Bharathi K K, Atuchin V, Pokrovsky L and Kruchinin V 2011 Enhanced optical constants of nanocrystalline yttrium oxide thin films Appl. Phys. Lett. 98 013105
[38] Atuchin V, Lebedev M, Koroliov I, Kruchinin V, Maksimovski E and Trubin S 2019 Composition-sensitive growth kinetics and dispersive optical properties of thin Hf$_x$Ti$_{1-x}$O$_2$ ($0 \leq x \leq 1$) films prepared by the ALD method. J. Mater. Sci., Mater. Electron. 30 812–23
[39] Wirasat S and Boerio F 2005 Effect of adhesion, film thickness, and substrate hardness on the scratch behavior of poly (carbonate) films J. Adhes. 81 509–28
[40] Xi-Fang C, Mi Y, De-Ren Y and Yukio H 2003 A method for predicting critical load evaluating adhesion of coatings in scratch testing journal of Zhejiang University-SCIENCE A 4 709–13
[41] Oliver W C and Pharr G M 2004 Measurement of hardness and elastic modulus by instrumented indentation: advances in understanding and methodology J. Mater. Res. 19 3–20
[42] Kan Q, Yan W, Kang G and Sun Q 2013 Oliver–Pharr indentation method in determining elastic moduli of shape memory alloys—a phase transformable material J. Mech. Phys. Solids 61 2015–33
[43] Kumar S S et al 2013 Structure, morphology, and optical properties of amorphous and nanocrystalline gallium oxide thin films J. Phys. Chem. C 117 4194–205
[44] Guo D et al 2017 Evidence for the bias-driven migration of oxygen vacancies in amorphous non-stoichiometric gallium oxide AIP Adv. 7 065312
[45] Hebert C et al 2012 Phase separation in oxygen deficient gallium oxide films grown by pulsed-laser deposition Mater. Chem. Phys. 133 135–9
[46] Ramana C, Bharathi K K, Garcia A and Campbell A 2012 Growth behavior, lattice expansion, strain, and surface morphology of nanocrystalline, monolithic HfO$_2$ thin films The Journal of Physical Chemistry C 116 9955–60
[47] Makeneswaran N, Battu A K, Deemer E and Ramana C V 2020 Crystal Growth and Structure—Property Optimization of Thermally Annealed Nanocrystalline Ga$_2$O$_3$ Films Crystal Growth & Design, 20 2893–903
[48] Hachenberg J et al 2004 Kinetic roughening of laser deposited polymer films: crossover from single particle character to continuous growth Phys. Rev. Lett. 92 246102
[49] Liu Z-L, Jiang N, Shen Y and Mai Y-W 2002 Atomic force microscopy study of surface roughening of sputter-deposited TiN thin films J. Appl. Phys. 92 3559–63
[50] Dannenberg R, Stach E, Groza J and Dresser B J 2000 TEM annealing study of normal grain growth in silver thin films Thin Solid Films 379 133–8
[51] Gong J et al 2010 Micro- and nanomaterials: metal organic compounds and polymeric substances by indication lithography Nano Lett. 10 2590–8
[52] Bhattacharyya A and Nix W 1988 Analysis of elastic and plastic deformation associated with indentation testing of thin films on substrates Int. J. Solids Struct. 24 1287–98
[53] Battu A K, Manandhar S and Ramana C V 2018 Nanomechanical characterization of titanium incorporated gallium oxide nanocrystalline thin films *Materials Today Nano.* **2** 27–14

[54] Battu A K, Manandhar S, Shutthanandan V and Ramana C 2017 Controlled optical properties via chemical composition tuning in molybdenum-incorporated $\beta$-Ga$_2$O$_3$ nanocrystalline films *Chem. Phys. Lett.* **684** 363–7

[55] Battu A K and Ramana C V 2018 Mechanical properties of nanocrystalline and amorphous gallium oxide thin films *Adv. Eng. Mater.* **20** 1701033

[56] Suryanarayana C, Mukhopadhyay D, Patankar S and Froes F 1992 Grain size effects in nanocrystalline materials *J. Mater. Res.* **7** 2114–8

[57] Kobelev N, Soifer Y M, Andrievski R and Gunther B 1993 Microhardness and elastic properties of nanocrystalline silver *Nanostruct. Mater.* **2** 537–44

[58] Lian J, Baudelet B and Nazarov A 1993 Model for the prediction of the mechanical behaviour of nanocrystalline materials *Mater. Sci. Eng. A* **172** 23–9

[59] Siegel R W 1990 Nanophase Materials Assembled from Atomic Clusters. *MRS Bulletin* **15** 60–67

[60] Valat-Villain P, Durinck J and Renault P 2017 Grain size dependence of elastic moduli in nanocrystalline Tungsten *J. Nanomater.* **2017**

[61] Wang J, Wolf D, Phillpot S and Gleiter H 1996 Computer simulation of the structure and thermo-elastic properties of a model nanocrystalline material *Philos. Mag. A* **73** 517–55

[62] Chen D 1995 Computer model simulation study of nanocrystalline iron *Mater. Sci. Eng. A* **190** 193–8