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Effect of post-deposition annealing on crystal structure of RF magnetron sputtered germanium dioxide thin films

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ABSTRACT

In this work, we demonstrate the growth and phase stabilization of ultrawide bandgap polycrystalline rutile germanium dioxide (GeO₂) thin films. GeO₂ thin films were deposited using RF magnetron sputtering on *r*-plane sapphire (Al₂O₃) substrates. As-deposited films were x-ray amorphous. Postdeposition annealing was performed at temperatures between 650 and 950 °C in an oxygen or nitrogen ambient. Annealing at temperatures from 750 to 950 °C resulted in mixed-phase polycrystalline films containing tetragonal (rutile) GeO₂, hexagonal (α -quartz) GeO₂, and/or cubic (diamond) germanium (Ge). When nitrogen was used as the anneal ambient, mixed GeO₂ phases were observed. In contrast, annealing in oxygen promoted stabilization of the *r*-GeO₂ phase. Grazing angle x-ray diffraction showed a preferred orientation of (220) *r*-GeO₂ for all crystallized films. The combination of O₂ annealing and O₂ flux during growth resulted in *r*-GeO₂ films with highly preferential alignment. Using electron microscopy, we observed an interfacial layer of hexagonal-oriented GeO₂ with epitaxial alignment to the (1102) Al₂O₃ substrate, which may help stabilize the top polycrystalline *r*-GeO₂ film.

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I. INTRODUCTION

Ultrawide bandgap (UWBG) semiconductors are key to enabling high voltage and high power electronics as well as deep ultraviolet (UV) detectors and emitters.¹ For instance, the UWBG oxide semiconductor β -Ga₂O₃ is being intensively investigated due to its large breakdown field that results in a high Baliga figure of merit (BFOM), indicating its potential for high voltage power electronic devices.^{1–5} However, β -Ga₂O₃ has numerous drawbacks: it cannot be doped p-type, limiting it to unipolar device architectures, and it has a very low thermal conductivity, complicating heat extraction and thermal management.^{3,6} The UWBG semiconductor germanium dioxide (GeO₂) has recently gained attention as a possible alternative.^{7–9} At ambient temperatures and pressures, GeO₂ primarily has two UWBG phases: an α -quartz-like phase (P3₂21) that has a hexagonal structure and a rutile phase (P4₂/mm) that has a tetragonal structure.^{9–12} Recently, it has been reported that rutile germanium dioxide (*r*-GeO₂) has a high thermal conductivity¹⁰ and is predicted to have ambipolar doping capability.^{7,9,13–15}

These advantageous properties open the door for many potential applications in power electronic devices.

Synthesis of GeO₂ is challenging because the rutile and the α -quartz-like phases have a similar free energy of formation, making it difficult to obtain a single phase material.⁸ It has been found previously that the glassy phase of GeO₂ is the most likely phase to form at room temperature.¹⁶ Bulk synthesis of GeO₂ polymorphs has previously been reported, but many of these studies have been conducted under high pressure conditions.^{17,18}

Thin film growth of *r*-GeO₂ has been reported using molecular beam epitaxy (MBE),⁸ mist chemical vapor deposition (mist CVD),^{19,20} flux method,²¹ pulsed laser deposition (PLD),^{22–24} and metal-organic chemical vapor deposition (MOCVD).²⁵ Due to the challenge of stabilizing GeO₂, various approaches have been used to obtain single crystalline rutile GeO₂ films. For example, in the case of MBE, a buffer layer of SnO₂/Sn_xGe_{1–x}O₂ was used. For PLD and CVD, epitaxially matched substrates such as *m*-plane sapphire,²² *c*-plane sapphire,²³ *r*-plane sapphire,²⁴ and rutile TiO₂^{19,25} were used to reduce misfit strain. Physical vapor deposition (PVD)

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has an advantage over CVD because it does not require the use of specialized precursor materials. Previously, by using PVD magnetron sputtering of Ge targets with an oxygen flux during deposition, nanotextured hexagonal and tetragonal cristobalite (space group $P4_12_12$) phases of GeO_2 were achieved on silicon (100) and quartz substrates.¹⁶ In that work, Nalam *et al.* used a Ge target with oxygen flux during deposition, which provided limited control of oxidation during growth.

In this study, to harness PVD to achieve rutile-phase GeO_2 films, we used a GeO_2 target and oxygen flux during magnetron sputtering to improve control of oxygen incorporation into GeO_2 thin films. We used *r*-plane sapphire as the substrates because of its epitaxial relation with rutile structures, reported previously.^{8,24} We investigated the effects of oxygen-to-argon flux during growth and of the ambient during postdeposition annealing (PDA) on the structural properties of GeO_2 thin films and determined the conditions necessary to reduce crystallization of the hexagonal phase and promote formation of the rutile phase. We demonstrated that a combination of 1:5 O_2 :Ar ratio during growth followed by postdeposition anneal in O_2 results in rutile polycrystalline GeO_2 films with highly preferential alignment. We observed that an interfacial layer of epitaxial *h*- GeO_2 formed *in situ* on the sapphire substrate helps to stabilize the top polycrystalline *r*- GeO_2 film. Optical measurements were performed on the *r*- GeO_2 preferred oriented films, which confirmed the UWBG nature of the material.

II. EXPERIMENTAL DETAILS

To grow GeO_2 thin films, we used commercially available *r*-plane sapphire $10 \times 10 \text{ mm}^2$ substrates. The substrates were solvent cleaned with acetone and isopropyl alcohol in a 40 °C ultrasonic tank for 10 min each. Using RF magnetron sputtering (RFMS) in a Kurt J. Lesker PRO Line PVD 75, GeO_2 was deposited on top of the substrates. A 3-in. GeO_2 (99.999%) target (Princeton Scientific) was used with a target to-substrate distance of ~ 16 cm. All depositions used an RF power of 300 W, a process pressure of 5×10^{-3} Torr, a deposition time of 1200 s, and had no intentional heating or cooling of the substrate during deposition. These conditions were selected to achieve a reasonable growth rate and film thickness of approximately 100 nm through initial experiments depositing GeO_2 on silicon wafers. The O_2 flux during growth was varied between 0% and 30%, with the balance made up of Ar. Following thin film deposition, PDA was performed at temperatures ranging from 650 to 950 °C in either an oxygen or a nitrogen ambient. An Angstrom Engineering low pressure chemical vapor deposition furnace was used for the PDA, with a heating ramp rate of 100 °C/min. X-ray diffraction (XRD) experiments were performed using a Rigaku SmartLab diffractometer ($\lambda = 1.5406 \text{ \AA}$). The incident angle was set to $\omega = 0.5^\circ$ to maximize the peak intensity for all grazing incidence x-ray diffraction (GIXRD) measurements. To study the morphology of the films, atomic force microscopy (AFM) was performed using a Veeco Dimension Icon AFM tool.

To study the structural nature of the films, scanning transmission electron microscopy (STEM) and selected area electron diffraction (SAED) were performed on a TFS Talos F200X G2 transmission electron microscope system equipped with a SuperX

energy-dispersive x-ray spectrometer (200 keV operating condition). Focused ion beam (FIB)-assisted lift-out was conducted using a TFS Helios 650 Nanolab SEM. Prior to lift-out, carbon and platinum capping layers were deposited *in situ* to protect the film from FIB damage. Optical spectroscopy (UV-vis) was performed using a Cary 50 Bio UV-Visible Spectrophotometer.

III. RESULTS AND DISCUSSION

The first films were deposited with no oxygen flux during sputtering. The thickness of the as-deposited film was measured by electron microscopy to be approximately 100 nm. AFM was used to measure an RMS roughness of 0.3 nm. Figure S1 in the [supplementary material](#) shows a cross-sectional high-angle annular dark-field (HAADF) image and the AFM scan of an as-deposited film.

The structural properties of the GeO_2 thin film were studied using GIXRD. Using films deposited with no oxygen flux during growth, we performed PDA in a nitrogen ambient [Fig. 1(a)]. The PDA temperature ranged from 650 to 950 °C. The as-deposited film is x-ray amorphous. Crystallization starts at annealing temperatures of 650 °C and above. The films annealed at 650, 750, 850, and 950 °C are polycrystalline with mixed phases of rutile and hexagonal GeO_2 , as well as Ge diamond cubic crystals. The presence of *r*- GeO_2 crystallites is a promising first step.

Next, we sought to determine whether incorporating oxygen during growth and annealing would promote rutile germanium oxide formation. A second set of samples was prepared with 20% oxygen flux used during growth, and the PDA was performed in an oxygen ambient [Fig. 1(b)]. These samples are also x-ray amorphous as deposited. Crystallization begins at annealing temperatures of 750 °C and above. This is different from the films prepared without oxygen flux, for which crystallization started at 650 °C. For the samples prepared with oxygen flux during deposition and oxygen PDA at 750 and 850 °C, the films are polycrystalline with a mixed phase of rutile and hexagonal GeO_2 , as well as Ge diamond cubic. As the anneal temperature increases from 750 to 950 °C, we observe an increasing preference for *r*- GeO_2 with a predominant (220) orientation. We performed a similar experiment using 30% oxygen flux and found that the film grown with 20% O_2 flux has a relatively stronger (220) peak and more rutile peaks (Fig. S2 in the [supplementary material](#)), and therefore, we used 20% O_2 flux during growth for the remaining experiments. Thus, we conclude that by using 20% O_2 flux during deposition and an O_2 annealing ambient, we can obtain films that are predominantly *r*- GeO_2 with preferential (220) orientation, compared to films deposited with no oxygen flux or 30% oxygen flux during growth and annealed under N_2 ambient.

High-resolution 2-theta/omega XRD measurement was performed on the O_2 annealed 950 °C film [Fig. 2(a)]. Based on prior work, (101) *r*- GeO_2 is the expected orientation aligned to the *r*-plane substrate.^{8,24} However, this orientation was not observed in our 2-theta/omega measurements. Rather, a (100)-oriented *h*- GeO_2 component of the film was observed, oriented to the (1 $\bar{1}$ 02) Al_2O_3 substrate peak. Recently, Rahaman *et al.* reported the growth of polycrystalline GeO_2 by MOCVD, in which they observed a

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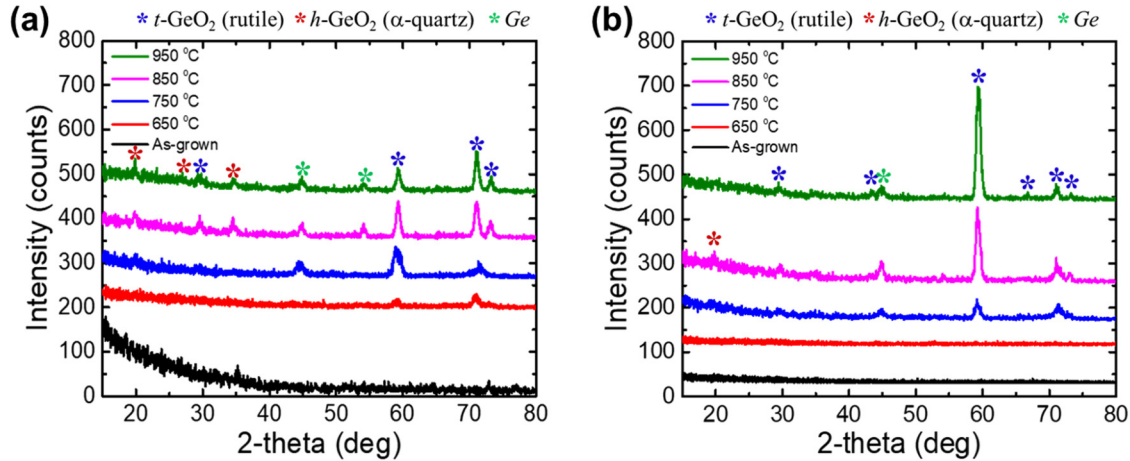


FIG. 1. Grazing incidence XRD of films deposited on *r*-plane sapphire with (a) no oxygen flux during growth and N_2 -ambient PDA; (b) oxygen flux during growth and O_2 -ambient PDA. The (220) *r*- GeO_2 peak is located near 60° .

polycrystalline *h*- GeO_2 phase oriented to the *r*-plane sapphire substrate.²⁶

By HAADF-STEM and SAED [Fig. 2(b)], we observe that the *h*- GeO_2 (100)-oriented crystals form a thin interfacial layer between the sapphire substrate and the top (220)-oriented *r*- GeO_2 polycrystalline film. The thin *h*- GeO_2 (100)-oriented layer, which is epitaxially aligned to the *r*-plane Al_2O_3 substrate, may help stabilize the (220)-oriented *r*- GeO_2 polycrystalline film.

While *r*- GeO_2 polycrystalline films have been achieved, so far it is not clear whether the morphology is due to the use of O_2 flux during deposition or the use of an O_2 ambient during

postdeposition annealing. To investigate this, we took two samples that were grown identically with 20% O_2 flux and subjected them to PDA at $950^\circ C$. One of the samples was annealed in O_2 , while the other was annealed in N_2 . After annealing, GIXRD scans were performed on both samples. The GIXRD traces for these films are shown in Fig. 3. The sample annealed in O_2 has significantly stronger *r*- GeO_2 peaks compared to the film annealed in N_2 . We conclude that both O_2 flux during growth and O_2 postdeposition annealing are needed to obtain the predominant (220)-oriented *r*- GeO_2 film. We hypothesize that the use of oxygen during both film synthesis and postdeposition annealing decreases the density

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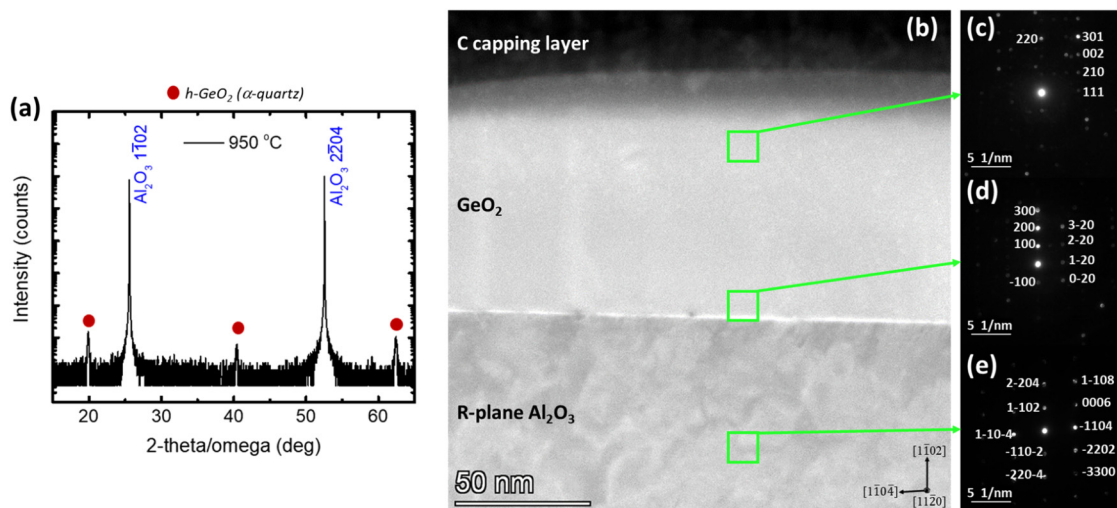


FIG. 2. Characterization of GeO_2 films deposited with 20% O_2 flux and annealed at $950^\circ C$ in O_2 . (a) High-resolution 2-theta/omega XRD showing that (100) *h*- GeO_2 is epitaxially aligned to (1102) Al_2O_3 . (b) HAADF STEM cross-sectional image of the GeO_2/Al_2O_3 interface and the GeO_2 film. (c)–(e) SAED patterns of (c) the polycrystalline GeO_2 film; (d) the GeO_2 film above the interface, showing (100) *h*- GeO_2 epitaxially aligned to (1102) Al_2O_3 ; and (e) the Al_2O_3 substrate.

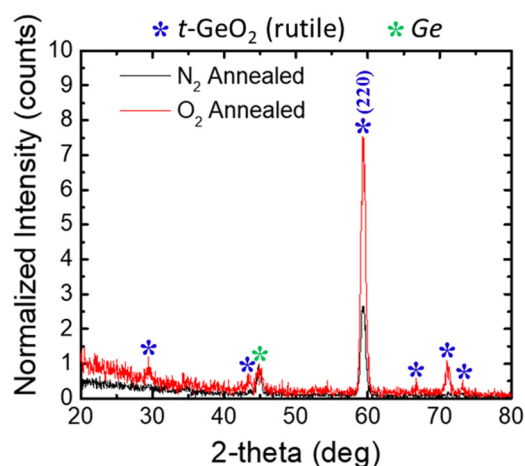


FIG. 3. Grazing incidence XRD results for films grown with 20% oxygen flux annealed at 950 °C using either nitrogen or oxygen as the anneal ambient. For comparison, the intensities of each trace are normalized that trace's peak value at the Ge diamond cubic peak near 45°, indicated with a green star.

of oxygen-related defects and promotes the oxidation of Ge to obtain *r*-GeO₂.

Optical characterization of the GeO₂ film deposited with 20% O₂ flux and annealed at 950 °C in O₂ was performed at room temperature to correlate its structural and optical properties. The Tauc plot is shown in Fig. 4. To determine the direct bandgap, we fit the data to the equation $(\alpha h\nu)^2 = B(h\nu - E_g)$, where α is the absorption coefficient, $h\nu$ is the photon energy, and B is a constant. The extracted bandgap is 5.1 eV, confirming the UWBG nature of the

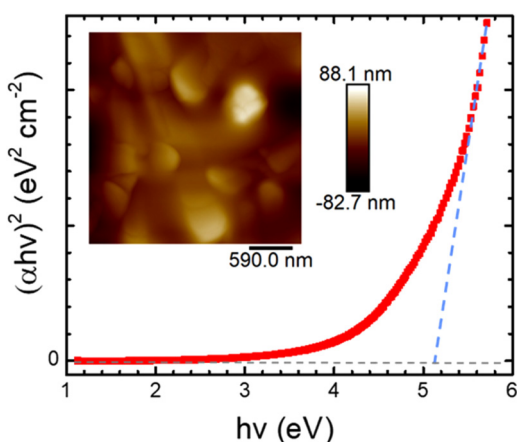


FIG. 4. Tauc plot based on absorption measurements of the GeO₂ film deposited with 20% O₂ flux and annealed at 950 °C in O₂. The linear extrapolation (dashed line) indicates that the bandgap of the film is 5.1 eV. The inset shows the surface morphology of the film measured by AFM, with an RMS roughness of ~20 nm.

film. The obtained bandgap of the GeO₂ film is wider than the reported values of 4.6 (Ref. 27) and 4.68 eV¹³ for bulk *r*-GeO₂. However, the 5.1 eV bandgap we measured is in agreement with recent experimental work and theoretical predictions of the first allowed optical transition on *r*-GeO₂ thin films.^{14,22–24} This result confirms the structural analysis, which showed that our film has a polycrystalline *r*-GeO₂ morphology.

Finally, the surface roughness of morphology of the GeO₂ film deposited with 20% O₂ flux and annealed at 950 °C in O₂ was studied using AFM. The scan is shown in the inset of Fig. 4. The RMS roughness of the film surface is approximately 20 nm.

IV. SUMMARY AND CONCLUSIONS

In this paper, we investigated the effects of oxygen flux during growth of GeO₂ thin films and of the ambient used during postdeposition anneal on the films' structural morphology. A new method to grow and phase-stabilize rutile polycrystalline GeO₂ films was established. For samples grown with 20% oxygen flux followed by a PDA in oxygen at temperatures ranging from 750 to 950 °C, *r*-GeO₂ with preferential (220) orientation was observed. In contrast, when nitrogen was used as the anneal ambient, a mixed GeO₂ phase results for all annealing temperatures studied (650–950 °C). This shows that oxygen annealing promotes the stabilization of the *r*-GeO₂ phase, and that a combination of O₂ annealing and O₂ flux of 20% during growth results in *r*-GeO₂ films with highly preferential alignment. From STEM of the GeO₂ film deposited with 20% O₂ flux and annealed at 950 °C in O₂, we observed that an epitaxial *h*-GeO₂ film forms *in situ* at the *r*-plane Al₂O₃ substrate interface, which may help stabilize the top polycrystalline *r*-GeO₂ film.

In conclusion, this study has demonstrated a new synthesis route to achieve *r*-GeO₂ on sapphire using PVD from GeO₂ targets, 20% O₂ flux during deposition, and postdeposition anneal in O₂ ambient. This growth is a key step in the fabrication process of future power electronics devices based on this promising UWBG semiconductor. Future work is needed to better understand how other deposition conditions such as the fraction of oxygen flux, the substrate temperature during deposition, and the choice of substrate may affect the formation of *r*- and/or *h*-GeO₂. In addition, further work is needed to understand the formation and role of the interfacial layer of *h*-GeO₂ on the *r*-GeO₂ film properties. To improve the GeO₂ films' crystal quality, in the future it would be interesting to investigate the effect of elevated substrate temperature during sputtering on the film phase purity and uniformity.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for a cross-sectional HAADF STEM image, an AFM image of a film deposited with no oxygen flux and no subsequent PDA, and GIXRD traces for films deposited with 20% and 30% O₂ flux during growth and annealed at 950 °C in O₂ ambient.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Ahmad Matar Abed: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Rebecca L. Peterson:** Conceptualization (equal); Data curation (equal); Funding acquisition (equal); Methodology (equal); Project administration (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

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

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