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Citation: [Journal of Applied Physics](#) **117**, 185706 (2015); doi: 10.1063/1.4921060

View online: <http://dx.doi.org/10.1063/1.4921060>

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Lattice dynamics of a mist-chemical vapor deposition-grown corundum-like Ga_2O_3 single crystal

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(Received 20 March 2015; accepted 1 May 2015; published online 12 May 2015)

The lattice dynamical properties of the corundum-like α -phase of Ga_2O_3 are investigated by means of Raman scattering experiments and *ab-initio* calculations. A high-quality, single-crystal thick epilayer was grown on sapphire by the mist-chemical vapor deposition method. The phonon frequencies at the Brillouin zone center of all the Raman-active modes are determined by polarized Raman scattering measurements on an α - Ga_2O_3 single crystal. By performing backscattering measurements from (0001) and (10 $\bar{1}$ 0) faces, all Raman active modes are unambiguously identified. Density functional perturbation theory calculations were carried out to determine the symmetry and the frequency of the α - Ga_2O_3 lattice modes. We find a good agreement between the theoretical predictions and the Raman spectra. The relative intensity of the different modes and their polarizability are discussed. The Raman spectrum is dominated by a narrow A_{1g} peak which indicates the high crystalline quality of the layers grown by the mist chemical vapor deposition method. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4921060>]

I. INTRODUCTION

Gallium oxide is a wide-band-gap semiconductor with important applications in transparent conductive oxides,¹ deep ultraviolet solar-blind detectors,^{2,3} spintronics,⁴ high temperature gas sensors,⁵ and novel functional oxides.⁶ The monoclinic β -phase is thermodynamically the most stable phase at ambient conditions.⁷ Owing to its unique physical properties, such as chemical and thermal stability at high temperatures, large bandgap ($E_g = 4.9$ eV), large breakdown field (estimated at 8 MV cm^{-1}), and high dielectric constant (~ 10)^{8,9} as well as to its widely tunable conductivity,¹⁰ a great effort has been devoted in the past decade to the development of β - Ga_2O_3 -based device technology. Ga_2O_3 is a promising material to realize low-cost power devices outperforming those based on GaN or SiC. Recently, a metal semiconductor field effect transistor with good I - V characteristics and a breakdown voltage over 250 V has been demonstrated.¹¹ Ga_2O_3 may also provide low-cost substrates for epitaxial growth of GaN. In spite of the dissimilarity between their crystalline structures and lattice parameters, by adjusting the nitridation conditions that transform the β - Ga_2O_3 surface to GaN, homoepitaxial growth of high quality hexagonal GaN on β - Ga_2O_3 was achieved by molecular beam epitaxy.¹²

While most of the progress in Ga_2O_3 -based devices has been developed on the β -phase, the less-studied metastable, corundum-like α -phase has also a great potentiality in the integration of transparent conductive oxide technology with other corundum structure functional oxides, such as Cr, Fe, and V oxides. The potential of alloying with α - Fe_2O_3 and α - Cr_2O_3 opens up the possibility of harnessing multiferroic and magnetoelectric effects.^{4,13} On the other hand, the α - Ga_2O_3 has a moderate *in-plane* a -lattice parameter misfit

($\sim 4.8\%$)¹⁴ with α - Al_2O_3 and a substantially lower bandgap (~ 5 eV for α - Ga_2O_3)^{15,16} compared to sapphire. This makes the α - $\text{Ga}_2\text{O}_3/\alpha$ - Al_2O_3 system an interesting possibility for the development of intersubband devices operating at telecommunication wavelengths. Very recently, it has been shown that three monolayers of pseudomorphic α - Ga_2O_3 stabilized by strain are present at the interface between c -plane sapphire and β - Ga_2O_3 .¹⁷

The growth of highly crystalline α - Ga_2O_3 by mist chemical vapor deposition (CVD) on c -sapphire was demonstrated by Shinohara and Fujita.¹⁶ More recently, highly conductive n -type layers of tin-doped α - Ga_2O_3 grown by mist CVD have been reported.¹⁸ A semi-coherent growth with the α - Al_2O_3 substrate has been proposed to account for misfit relaxation at the interface and the low density of screw dislocations¹⁴ which contribute to obtain samples with excellent crystalline quality. The growth of high quality α - Ga_2O_3 epilayers on sapphire is also favored by the fact that both epilayer and substrate have the same crystalline structure. The mist-CVD technique is an environmentally friendly growth method that can provide a cost-effective way of producing large-area, high-quality α - Ga_2O_3 buffer layers. These could have a great potential as novel buffer layers for the growth of hexagonal GaN layers as they have the same rhombohedral crystalline structure as sapphire and an excellent lattice match of GaN with the nitridated α - Ga_2O_3 surface is expected.

Raman scattering is a powerful, nondestructive tool to characterize the crystal quality and strain state of thin film layered materials. While the polarized Raman spectra of β - Ga_2O_3 was reported on (010) Mg-doped, (100) Si-doped, and (001) unintentionally doped layers obtained by the floating-zone and edge-defined film-fed growth,¹⁹ no similar

study exists on α -Ga₂O₃. The only Raman-scattering data on phonons of α -Ga₂O₃ were reported by Machon *et al.*⁷ in a study of β - to α -phase transition under hydrostatic pressure. The high-pressure form of Ga₂O₃ contains a substantial degree of structural disorder, and to help identify the features in the Raman spectrum it was compared with an unpolarized spectrum recorded on a sample obtained from a precipitated gel in aqueous solution.⁷ In the present work, we present polarized Raman scattering spectra obtained in backscattering configuration from (0001) and (10 $\bar{1}$ 0) faces of a corundum-like α -Ga₂O₃ monocrystalline layer grown by mist CVD. The thickness of the high-quality α -Ga₂O₃ layer was high enough to allow micro-Raman measurements to be carried out on a lateral fracture face. This enabled us to verify Raman selection rules and to identify all Raman active modes in the α -Ga₂O₃ crystal.

II. EXPERIMENT

A corundum-like α -Ga₂O₃ layer of thickness around 0.8 μ m was grown by the ultrasonic mist chemical vapor deposition on a *c*-face sapphire substrate. A liquid solution of Ga(C₅H₇O₂)₃ in H₂O (0.05 mol/l) was used as Ga source. Mist particles were formed by a 2.4 MHz ultrasonic transducer and carried by a flow of N₂ gas to the heated reaction chamber where the (0001) sapphire substrate was placed on a sample holder kept at 200 °C. The sample was characterized by x-ray diffraction (XRD). As can be seen in Fig. 1, the $2\theta/\theta$ scan spectra show a distinct (0006) α -Ga₂O₃ reflection peak, and the XRD rocking curve (inset of Fig. 1) displays a full width at half maximum of 69 arcsec, indicating the high crystalline quality of the sample.

Raman measurements were excited with the 532 nm line of a diode-pumped solid-state laser. The light was collected in backscattering geometry through a 100 $\times$ objective with a numerical aperture of 0.95 and analyzed using a Jobin-Yvon T64000 spectrometer. Confocal micro-Raman measurements were performed with a 100 μ m pinhole aperture at the back focal plane. To aid the identification of the Raman active phonons, a theoretical investigation of the lattice dynamics of α -Ga₂O₃ was carried out. The numerical calculations were

FIG. 1. X-ray diffraction $2\theta/\theta$ scan profile. Inset: (0006) XRD diffraction rocking curve. The full width at half maximum is 69 arcsec.

performed in the framework of the density functional theory (DFT) in the local density approximation (LDA) as implemented in the ABINIT code.²⁰ In the calculations, we used Perdew-Wang parametrization of the exchange interaction, Troullier-Martins pseudopotentials with the 3*d* electrons included as valence states, a $4 \times 4 \times 4$ Monkhorst-pack *k*-point sampling and a plane-wave basis set with an energy cutoff of 95 Ha.²⁰ After a full structural relaxation of the α -Ga₂O₃ unit cell, hexagonal lattice parameters $a = 5.004$ Å and $c = 13.410$ Å were obtained, in excellent agreement with the reported high-resolution x-ray diffraction value ($a = 4.983$ Å and $c = 13.433$ Å).²¹ Phonon modes were obtained by diagonalization of the dynamical matrix derived from the perturbation theory linear response approach. The frequencies of the zone-center Raman active phonons are listed in Table I.

III. RESULTS AND DISCUSSION

The α -Ga₂O₃ crystal has a rhombohedral structure that belongs to the $R\bar{3}c$ (D_{3d}^6) space group with two molecular Ga₂O₃ groups per unit cell. Since the α -Ga₂O₃ crystal is centrosymmetric, all the Raman active phonons are infrared inactive and vice versa. The irreducible representations for the zone-center optical modes are $\Gamma = 2A_{1g} + 2A_{1u} + 3A_{2g} + 2A_{2u} + 5E_g + 4E_u$. The A_{1g} and E_g vibrations are Raman active, the A_{2u} and E_u are infrared active, and the A_{1u} and A_{2g} have no optical activity (silent modes). The Raman tensors for the Raman active modes are

$$\mathcal{R}(A_{1g}) = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \quad (1)$$

$$\mathcal{R}(E_g) = \begin{pmatrix} c & 0 & 0 \\ 0 & -c & d \\ 0 & d & 0 \end{pmatrix}, \begin{pmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{pmatrix}.$$

Thus, in backscattering from the *c* face the fully symmetric A_{1g} vibrations are allowed in parallel polarization and forbidden in cross polarization, whereas the doubly degenerate E_g vibrations are always allowed. Figure 2 shows the Raman spectra obtained in backscattering from the *c* face. For clarity, the Raman spectrum of the sapphire substrate has been subtracted. The assignment of the symmetry of modes has been made by comparison with the DFT calculations. The $z(\chi\chi)z$ spectrum is dominated by a strong and narrow

TABLE I. Frequencies of the Raman active modes of α -Ga₂O₃.

Symmetry	Phonon frequency (cm ⁻¹)	
	measured (Raman)	calculated (DFT)
A_{1g}	218.2	211
E_g	240.7	233
E_g	285.3	281
E_g	328.8	314
E_g	430.7	426
A_{1g}	569.7	551
E_g	686.7	667

FIG. 2. Polarized Raman spectra of α -Ga₂O₃ obtained in backscattering configuration from the c face.

A_{1g} mode at 218.2 cm^{-1} . This low-frequency A_{1g} mode corresponds mainly to Ga atoms vibrating against each other along the c axis. By contrast, the high-frequency A_{1g} mode at 569.7 cm^{-1} involves mainly the lighter O atoms vibrating perpendicularly to the c axis. The low-frequency A_{1g} peak exhibits the lowest linewidth (full width at half maximum of 3.3 cm^{-1} , compared to 18.4 cm^{-1} for the high-frequency A_{1g} mode). The narrow linewidth of the low-frequency A_{1g} mode reflects a substantially higher phonon lifetime which can be explained in terms of the availability of anharmonic decay channels. Similar to the case of the low-frequency E_2 mode in ZnO²² and InN,²³ the low density of phonon states with lower frequencies strongly reduces the probability of anharmonic decay into lower-energy phonons.

In addition to the A_{1g} peaks, three other Raman peaks are observed in the upper spectrum of Fig. 2, which are assigned to E_g modes, in accordance with the DFT calculations. These E_g modes are also present in the $z(xy)\bar{z}$ spectrum, where the symmetry forbidden A_{1g} modes are extinguished. However, no clear observation of the remaining E_g modes (predicted at 233 and 314 cm^{-1} by the DFT calculations) can be made in these spectra.

To experimentally detect the remaining Raman active modes, micro Raman measurements were performed on a lateral fracture surface of the sample. While the brittle corundum structure does not have natural cleavage planes, crystals tend to part more easily in certain directions. The lowest surface energies are found for the $\{10\bar{1}0\}$ and $\{1012\}$ planes.²⁴ The orientation of the lateral surface in our sample was determined to be $(10\bar{1}0)$ by means of XRD measurements.

Figure 3 shows the polarized Raman spectra obtained from the $(10\bar{1}0)$ lateral face. By suitably rotating the Raman tensors [Eq. (1)] to describe the experimental scattering configuration, the Raman selection rules listed in Table II are obtained. On the $(10\bar{1}0)$ face, the A_{1g} modes are allowed in parallel polarization and forbidden in cross polarization. The A_{1g} low-frequency mode is again dominant in the $x'(y'y')\bar{x}'$

FIG. 3. Polarized Raman spectra of α -Ga₂O₃ obtained in backscattering configuration from the $(10\bar{1}0)$ face.

spectrum. In fact, the relative intensities between Raman peaks in $x'(y'y')\bar{x}'$ and $z(xx)\bar{z}$ spectra are very similar, as for each mode the same polarizability component is probed in both configurations (see Table II). In contrast, the intensity of the low-frequency A_{1g} mode is substantially reduced in the $x'(zz)\bar{x}'$ configuration, which indicates that the polarizability of this mode along the c -axis is significantly lower ($b \ll a$). Even though this mode mainly involves vibrations of the Ga atoms against each other along the c direction, the resulting radial stretching of the Ga–O bonds yields a substantial *in-plane* polarizability.

Although E_g modes are forbidden in $x'(zz)\bar{x}'$ configuration, a weak E_g peak at 285.3 cm^{-1} is detected in the Raman spectrum. This may probably be attributed to a slight sample misalignment that introduces some leakage from the $x'(y'y')\bar{x}'$ geometry. Note that the E_g peak at 285.3 cm^{-1} is by far the most intense feature in the $x'(y'y')\bar{x}'$ spectrum. Besides the Raman modes detected in backscattering from the c -face, two additional peaks are clearly seen in the $x'(y'y')\bar{x}'$ spectrum at 240.7 and 328.8 cm^{-1} which are assigned to E_g modes. These modes are barely visible in the $x'(y'y')\bar{x}'$ spectrum, which implies that $c \ll d$. Conversely, the E_g modes at 430.7 and 686.7 cm^{-1} display a substantially higher intensity in the $x'(y'y')\bar{x}'$ spectrum than in the $x'(y'z)\bar{x}'$ spectrum, and

TABLE II. Raman selection rules ($|e_i \mathcal{R} e_s|^2$) for the different incident (e_i) and scattered (e_s) polarizations used in the Raman experiments. Here, $x' = \frac{\sqrt{3}}{2}x - \frac{1}{2}y$ and $y' = \frac{1}{2}x + \frac{\sqrt{3}}{2}y$.

	Backscattering from (0001) face		Backscattering from $(10\bar{1}0)$ face		
	$z(xx)\bar{z}$	$z(xy)\bar{z}$	$x'(zz)\bar{x}'$	$x'(y'y')\bar{x}'$	$x'(y'z)\bar{x}'$
A_{1g}	a^2	0	b^2	a^2	0
E_g	c^2	c^2	0	c^2	d^2

therefore for these modes we have $c \gg d$. In contrast, the E_g mode at 285.3 cm^{-1} displays a similar intensity in both geometries, and consequently $c \simeq d$ for this mode.

The Raman measurements on the lateral face of the $\alpha\text{-Ga}_2\text{O}_3$ epilayer have revealed all Raman active modes ($2 A_{1g} + 5 E_g$). Their frequencies are listed in Table I, compared with the frequencies obtained from DFT calculations. A good overall agreement is found between experimental and calculated values, although the measured Raman frequencies are systematically higher than the theoretical values by $\sim 3\%$ on average. The presence of a compressive residual strain in the $\alpha\text{-Ga}_2\text{O}_3$ cannot be ruled out, given the *in-plane* lattice mismatch with the sapphire substrate ($\sim 4.8\%$). Transmission electron microscopy studies suggests semi-coherent growth of $\alpha\text{-Ga}_2\text{O}_3$ on sapphire, with some degree of misfit relaxation at the interface giving rise to periodic structures along the $[1\bar{1}00]$ direction.¹⁴ The misfit dislocations do not thread through the layer, which explain the high crystalline quality observed in these crystals by x-ray and Raman measurements. We have not observed significant frequency shifts between samples of different thicknesses, which is consistent with the localization of the misfit defects primarily on the interface.

IV. SUMMARY AND CONCLUSIONS

A high-quality, single crystalline layer of the corundum-like α -phase of Ga_2O_3 has been grown by the mist-CVD method on a (0001)-sapphire substrate. The vibrational modes of $\alpha\text{-Ga}_2\text{O}_3$ have been studied by means of Raman scattering. The thickness of the $\alpha\text{-Ga}_2\text{O}_3$ layer permits micro-Raman measurements to be carried out on a $(10\bar{1}0)$ lateral face, which gives access to additional scattering configurations. This allowed us to observe all Raman active modes of $\alpha\text{-Ga}_2\text{O}_3$. Whereas both A_{1g} and E_g modes are allowed in the customarily used backscattering geometry on the c face, two of the E_g modes are only unambiguously revealed in backscattering from a lateral face in cross polarization. The frequencies of the modes are in good agreement with DFT calculations. The polarized spectra are consistent with the Raman selection rules, indicating the high crystalline quality of the sample, and yield information about the polarizability of the different modes. The Raman spectrum is dominated by the low frequency A_{1g} mode, which corresponds mainly to Ga atoms vibrating against each other along the c axis and displays a remarkably narrow linewidth. Raman spectroscopy can be a versatile tool for the characterization of $\alpha\text{-Ga}_2\text{O}_3$ layers in a new emerging device technology based on functional oxides.

ACKNOWLEDGMENTS

This work has been supported by the Spanish Ministry of Economy and Competitiveness under Contract Nos. MAT2010-16116 and MAT2014-59199. N.D. acknowledges financial support from the FPU program of the Spanish Ministry of Education. T.H. and T.Y. acknowledge financial support from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) under the Strategic Research Foundation Grant-aided Project for Private Universities 2011-2015 (S1101005) and the Grants-in-Aid for Scientific Research Nos. 25420341 and 25706020, as well as from the Advanced Low Carbon Technology Research and Development Program, JST, Japan.

- ¹N. Ueda, H. Hosono, R. Waseda, and H. Kawazoe, *Appl. Phys. Lett.* **70**, 3561 (1997).
- ²T. Oshima, T. Okuno, N. Arai, N. Suzuki, S. Ohira, and S. Fujita, *Appl. Phys. Express* **1**, 011202 (2008).
- ³L. Li, E. Auer, M. Liao, X. Fang, T. Zhai, U. K. Gautam, A. Lugstein, Y. Koide, Y. Bando, and D. Golberg, *Nanoscale* **3**, 1120 (2011).
- ⁴K. Kaneko, T. Nomura, I. Takeya, and S. Fujita, *Appl. Phys. Express* **2**, 075501 (2009).
- ⁵U. Hofer, J. Frank, and M. Fleischer, *Sens. Actuators, B* **78**, 6 (2001).
- ⁶Z. Dai, Z. Pan, and Z. Wang, *Adv. Funct. Mater.* **13**, 9 (2003).
- ⁷D. Machon, P. McMillan, B. Xu, and J. Dong, *Phys. Rev. B* **73**, 094125 (2006).
- ⁸M. Passlack, E. F. Schubert, W. S. Hobson, M. Hong, N. Moriya, S. N. G. Chu, K. Konstantinidis, J. P. Mannaerts, M. L. Schnoes, and G. J. Zydzik, *J. Appl. Phys.* **77**, 686 (1995).
- ⁹M. Higashiwaki, K. Sasaki, A. Kuramata, T. Masui, and S. Yamakoshi, *Phys. Status Solidi A* **211**, 21 (2014).
- ¹⁰M. Orita, H. Ohta, M. Hirano, and H. Hosono, *Appl. Phys. Lett.* **77**, 4166 (2000).
- ¹¹M. Higashiwaki, K. Sasaki, A. Kuramata, T. Masui, and S. Yamakoshi, *Appl. Phys. Lett.* **100**, 013504 (2012).
- ¹²S. Ohira, N. Suzuki, H. Minami, K. Takahashi, T. Araki, and Y. Nanishi, *Phys. Status Solidi C* **4**, 2306 (2007).
- ¹³N. Kida, Y. Kaneko, J. He, M. Matsubara, H. Sato, T. Arima, H. Akoh, and Y. Tokura, *Phys. Rev. Lett.* **96**, 167202 (2006).
- ¹⁴K. Kaneko, H. Kawanowa, H. Ito, and S. Fujita, *Jpn. J. Appl. Phys., Part 1* **51**, 020201 (2012).
- ¹⁵G. Sinha, K. Adhikary, and S. Chaudhuri, *J. Cryst. Growth* **276**, 204 (2005).
- ¹⁶D. Shinohara and S. Fujita, *Jpn. J. Appl. Phys., Part 1* **47**, 7311 (2008).
- ¹⁷R. Schewski, G. Wagner, M. Baldini, D. Gogova, Z. Galazka, T. Schulz, T. Remmele, T. Markurt, H. von Wenckstern, M. Grundmann *et al.*, *Appl. Phys. Express* **8**, 011101 (2015).
- ¹⁸K. Akaiwa and S. Fujita, *Jpn. J. Appl. Phys., Part 1* **51**, 070203 (2012).
- ¹⁹T. Onuma, S. Fujioka, T. Yamaguchi, Y. Itoh, M. Higashiwaki, K. Sasaki, T. Masui, and T. Honda, *J. Cryst. Growth* **401**, 330 (2014).
- ²⁰X. Gonze, J. M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G. M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet *et al.*, *Comput. Mater. Sci.* **25**, 478 (2002).
- ²¹M. Marezio and J. P. Remeika, *J. Chem. Phys.* **46**, 1862 (1967).
- ²²M. Millot, R. Tena-Zaera, V. Muñoz-Sanjós, J. M. Broto, and J. González, *Appl. Phys. Lett.* **96**, 152103 (2010).
- ²³N. Domènech-Amador, R. Cuscó, L. Artús, T. Yamaguchi, and Y. Nanishi, *Phys. Rev. B* **83**, 245203 (2011).
- ²⁴A. Azhdari and S. Nemat-Nasser, *Mech. Mater.* **28**, 247 (1998).