Epitaxially stabilized growth of orthorhombic $LuScO_3$ thin films

T. Heeg, M. Roeckerath, J. Schubert, W. Zander, Ch. Buchal, H. Y. Chen, C. L. Jia, Y. Jia, C. Adamo, and D. G. Schlom

Citation: Appl. Phys. Lett. **90**, 192901 (2007); doi: 10.1063/1.2737136
View online: https://doi.org/10.1063/1.2737136
View Table of Contents: http://aip.scitation.org/toc/apl/90/19
Published by the American Institute of Physics

Epitaxially stabilized growth of orthorhombic $LuScO_3$ thin films

T. Heeg,[a] M. Roeckerath, J. Schubert, W. Zander, and Ch. Buchal
Institute of Bio- and Nanosystems (IBN1-IT), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany and Centre of Nanoelectronic Systems for Information Technology (CNI), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

H. Y. Chen and C. L. Jia
Institute of Solid State Research (IFF), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany and Ernst-Ruska-Centre for Microscopy and Spectroscopy with Electrons (ER-C), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

Y. Jia, C. Adamo, and D. G. Schlom
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802-5005

(Received 20 March 2007; accepted 14 April 2007; published online 7 May 2007)

Metastable lutetium scandate ($LuScO_3$) thin films with an orthorhombic perovskite structure have been prepared by molecular-beam epitaxy and pulsed-laser deposition on $NdGaO_3(110)$ and $DyScO_3(110)$ substrates. Stoichiometry and crystallinity were investigated using Rutherford backscattering spectrometry/channeling, x-ray diffraction, and transmission electron microscopy. The results indicate that $LuScO_3$, which normally only exists as a solid solution of Sc_2O_3 and Lu_2O_3 with the cubic bixbyite structure, can be grown in the orthorhombically distorted perovskite structure. Rocking curves as narrow as 0.05° were achieved. A critical film thickness of approximately 200 nm for the epitaxially stabilized perovskite polymorph of $LuScO_3$ on $NdGaO_3(110)$ substrates was determined. © *2007 American Institute of Physics*.
[DOI: 10.1063/1.2737136]

The rare-earth scandates ($REScO_3$, RE being Y, La, or a lanthanide) have gained considerable attention as a high dielectric constant (high-κ) gate dielectric for silicon-based metal-oxide-semiconductor field-effect transistor devices.[1–4] Most of these scandates crystallize in an orthorhombically distorted perovskite structure; the space group is *Pbnm*(62).[5] $GdScO_3$, for example, has lattice parameters of $a=5.486$ Å, $b=5.750$ Å, and $c=7.935$ Å.[6] Thus, it has a lattice mismatch with Si(100) of 3.3%. This mismatch decreases as the size of the RE ion in $REScO_3$ gets smaller. The stability of $REScO_3$ in direct contact with silicon,[7] coupled with the improving lattice match, motivates the investigation of $REScO_3$ perovskites containing the smallest RE ions for high-κ gate dielectric applications. Indeed, silicon has been grown epitaxially on $GdScO_3(110)$ and $DyScO_3(110)$,[8] just as it has on $LaAlO_3(100)$.[9] Lutetium is the smallest of all RE ions, and previous attempts to form thin films of the orthorhombic phase of $TmScO_3$, $YbScO_3$, and $LuScO_3$ have failed.[10] Attempts to synthesize $LuScO_3$ in bulk form at pressures up to 60 GPa also failed and only produced cubic Lu_2O_3–Sc_2O_3.[6,11] This failure can be explained by the Goldschmidt tolerance factor $\alpha=(r_A+r_O)/(\sqrt{2}(r_B+r_O))$, which is a good indicator for the stability of ABO_3 perovskites.[12] Here, r_A and r_B are the ionic radii of the *A*- and *B*-site cations, and r_O is the ionic radius of oxygen. Roughly, the perovskite structure is stable for values of α between 0.8 and 1; α approaching 1 corresponds to a perfect (cubic) perovskite structure. As shown by Christen *et al.*, the crystallization temperature of thin scandate films is directly correlated to α (increasing α leads to decreasing T_{cryst}).[10] For $TmScO_3$, $YbScO_3$, and $LuScO_3$, the tolerance factors are 0.789, 0.786, and 0.784, respectively, using the ionic radii from Ref. 13 for $^{viii}A^{3+}$, $^{vi}Sc^{3+}$, and $^{vi}O^{2-}$. These values are close to the stability limit. This observation is in agreement with the assumed phase diagram for Sc_2O_3–Lu_2O_3,[14,15] which predicts a continuous solid solution of cubic Sc_2O_3 and Lu_2O_3, but no perovskite phase. It is well known, however, that otherwise unstable compounds or structures can often be stabilized by the formation of low-energy interfaces.[16] This and the small difference between the Goldschmidt factors of $LuScO_3$ and $TmScO_3$, which contains the smallest RE ion among the $REScO_3$ compounds that have been synthesized with the perovskite structure in bulk,[11] motivate the possibility of epitaxially stabilizing the otherwise nonexisting orthorhombic perovskite phase of $LuScO_3$. Key to such a quest is the choice of substrate.

Thin films of $LuScO_3$ were deposited onto different substrates using reactive molecular-beam epitaxy (MBE) and pulsed-laser deposition (PLD). MBE growth was done in an EPI 930 system designed for the growth of oxide materials.[17] Molecular beams of lutetium and scandium were generated using conventional effusion cells. Oxidation was achieved using molecular oxygen in a pressure range between 5×10^{-6} and 1×10^{-4} Pa. The deposition rate was measured by a quartz crystal microbalance, and film growth itself was monitored using reflection high-energy electron diffraction (RHEED). Substrate heating was provided by a radiative heater.

PLD growth took place in an on-axis geometry using KrF excimer laser radiation (wavelength of 248 nm, pulse width of 20 ns, and a fluence of 2.5 J/cm^2).[18] The target was made by mixing 99.99% pure Lu_2O_3 and Sc_2O_3 powder, ball milling in isopropanol for 24 h, calcining at 1300 °C for 24 h, pressing into 25 mm targets, and subsequent sintering first at 1500 °C for 12 h and finally at 1600 °C also for 12 h. The substrates were placed directly on a SiC resistive heater.

[a]Electronic mail: t.heeg@fz-juelich.de

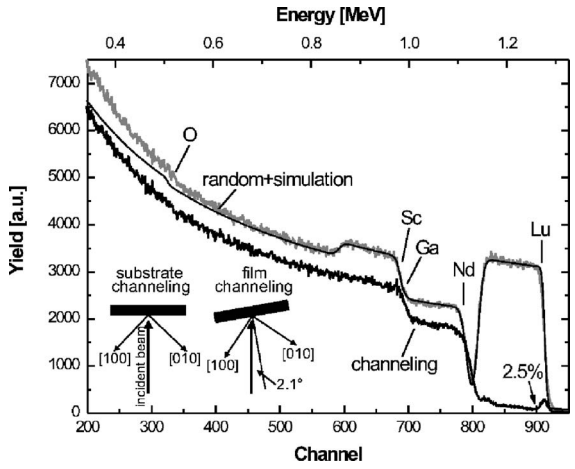

FIG. 1. RBS random and channeling spectra of a $LuScO_3$ film grown epitaxially with PLD on $NdGaO_3$ at 650 °C. The simulated curve gives a thickness of 130 nm and a Lu:Sc ratio of 1:0.97. Film and substrate channeling directions differ by about 2.1°, as shown in the inset. The incident energy of the He^+ ions was 1.4 MeV and the scattering angle 170°.

Growth on different substrates was investigated. In MBE, best results were achieved on $NdGaO_3(110)$ substrates, whereas films grown on $SrTiO_3(001)$ showed a lower quality of the $LuScO_3$ perovskite phase. On $LaAlO_3(012)$ [this corresponds to $(001)_p$ in pseudocubic notation, the meaning of the p subscript] and $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}(001)_p$ (LSAT), $LuScO_3$ did not form the perovskite phase. Using PLD, good results on $NdGaO_3$ were reproduced and extended to $DyScO_3(110)$ substrates.

During MBE growth the film crystallinity was monitored using RHEED with an electron energy of 10 keV. This allowed crystalline growth in the perovskite phase (RHEED pattern similar to that of the substrate) to be readily distinguished from formation of the bixbyite structure of the $Lu_2O_3-Sc_2O_3$ solid solution. For growth on $NdGaO_3(110)$ substrates, no substantial change in the pattern could be detected up to the maximum investigated film thickness of 50 nm. By contrast, on $SrTiO_3(001)$ substrates a structural change was visible. The film thickness at which it took place varied from a few nanometers to 30 nm, with no clear relationship to deposition conditions. On $LaAlO_3(012)$ and $LSAT(001)_p$ substrates, the RHEED image fully disappeared after the deposition of a few monolayers; the resulting film was amorphous.

Rutherford backscattering spectrometry/channeling (RBS/C) utilizing He^+ ions with an energy of 1.4 MeV was applied to investigate the composition and crystalline quality of the films. The computer software RUMP was employed to analyze the RBS data.[19] Figure 1 shows the RBS/C spectra of a 130 nm thick $LuScO_3$ film deposited on $NdGaO_3(110)$ by PLD at 650 °C and 2×10^{-1} Pa of O_2. The simulation reveals a Lu:Sc ratio of 1:0.97, indicating that the films are stoichiometric within experimental error. The low channeling minimum yield $\chi_{min}=2.5\%$ shows the good crystallinity of the film. It is notable that the best channeling direction in the film deviates slightly ($\approx2.1°$) from that of the substrate. To calculate the film thickness from the RBS spectrum, the known density of $DyScO_3$ was used. The error is estimated to be less than 5%, taking into account the pseudocubic unit cell of the perovskite polymorph of $LuScO_3$ calculated below.

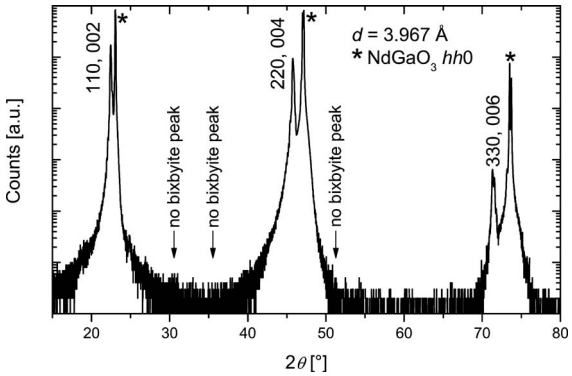

FIG. 2. XRD θ-2θ scan of $LuScO_3$ on $NdGaO_3(110)$ grown at 770 °C with MBE. Substrate peaks are marked with an asterisk (⋆). The out-of-plane lattice parameter is determined to be 3.967 Å and the rocking curve FWHM of the 220/004 reflection is 0.05°.

The structure of the films was characterized by x-ray diffraction (XRD) θ-2θ scans, rocking curves, and reciprocal space mapping (RSM).[20] Figure 2 shows a θ-2θ scan of a 75 nm thick $LuScO_3$ film grown with PLD on $NdGaO_3(110)$ at 650 °C. The $hh0$ or $00l$ peak series belonging to the perovskite phase is clearly visible. The out-of-plane lattice parameter is determined to be 3.967 Å using a Nelson-Riley plot.[21] There is no indication for the cubic solid solution phase of Lu_2O_3 and Sc_2O_3, from which prominent peaks would be expected around $2\theta\approx30.6°$ (222), $2\theta\approx35.5°$ (400), or $2\theta\approx51°$ (440). Even a (211)-oriented film would create peaks at least 1° away from the detected positions. The rocking curve full width at half maximum (FWHM) of $\Delta\omega=0.05°$ for the 220/004 reflection indicates good crystallinity of the film. Samples with similar properties could also be grown on $NdGaO_3(110)$ using MBE at 770 °C and 5×10^{-6} Pa of O_2, e.g., a 60 nm film showing an out-of-plane lattice parameter of 3.961 Å and a rocking curve FWHM of $\Delta\omega=0.08°$ measured at the 220/004 reflection. Comparable results were gained on PLD-deposited films on $DyScO_3(110)$ substrates, which showed an out-of-plane lattice parameter of 3.878 Å and also a FWHM of $\Delta\omega=0.05°$ for the 220/004 reflection. Figure 3 displays a RSM plot of a 130 nm thick, PLD-grown film around the 332 reflection of the $NdGaO_3(110)$ substrate, which corresponds to a 103 reflection in pseudocubic notation. The plot indicates an out-of-plane lattice parameter of 3.94 Å in agreement with the value determined using a Nelson-Riley plot technique, and an in-plane lattice parameter of 3.86 Å, showing that the film

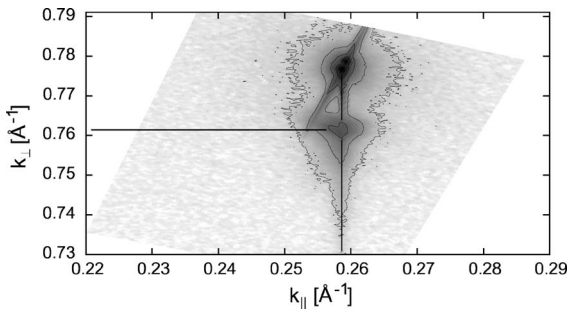

FIG. 3. XRD reciprocal space map around the 332 reflection of the $NdGaO_3(110)$ substrate (corresponding to the 103 reflection in pseudocubic notation). Angular offsets of the measurement axes were corrected using the substrate reflection. The substrate peak and the film peak have the same in-plane lattice spacing $k_{||}$, indicating that the $LuScO_3$ film is commensurate with the $NdGaO_3$ substrate on which it was grown.

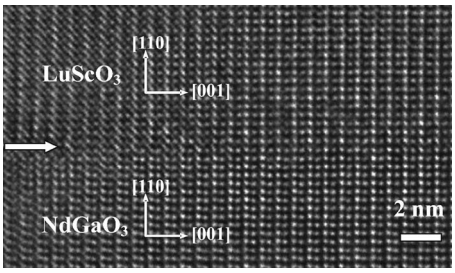

FIG. 4. High-resolution TEM lattice image of the interface between the $NdGaO_3(110)$ substrate and the $LuScO_3$ film prepared by PLD. The arrow denotes the film/substrate interface.

is fully strained to the $NdGaO_3(110)$ substrate. The resulting volume of the orthorhombic unit cell is 234.8 Å, which corresponds to a pseudocubic lattice spacing of $\sqrt[3]{234.8/4}$ Å^3 =3.89 Å assuming unit cell volume conservation (until now, no elasticity data for the scandates have been published).

The results presented so far are also corroborated by transmission electron microscopy (TEM). The investigation shows a similar microstructure of the films prepared by PLD and MBE. As seen in Fig. 4, at the interface the film adopts the crystallographic orientation of the substrate. From the lattice images and diffraction patterns, the $LuScO_3$ films have the same structure as the $NdGaO_3$ substrate.

Assuming that the perovskite phase of $LuScO_3$ is not stable without the influence of the underlying substrate, it can be expected that a critical thickness exists, above which growth continues in the bixbyite structure of the solid solution of Lu_2O_3 and Sc_2O_3, because the additional volume energy of the stabilized phase exceeds the gain in interface energy.[16] To determine this critical thickness of $LuScO_3$ on $NdGaO_3(110)$, $LuScO_3$ films with thicknesses varying from 65 to 780 nm were deposited by PLD at 650 °C and 2×10^{-1} Pa of O_2. Figure 5 shows a series of XRD θ-2θ scans of these samples. All films show a sequence of peaks close to the substrate peaks, which corresponds to the *hh*0 or 00*l* series of the orthorhombic perovskite structure of $LuScO_3$. The films thicker than about 200 nm exhibit a peak at 2θ =35.2°, which corresponds to the 400 reflection of the bixbyite structure of the Lu_2O_3–Sc_2O_3 solid solution. Between 260 and 390 nm, the intensity of this peak grows much faster than the film thickness increases. This indicates that the film has started to grow predominantly in the bixbyite structure. Additionally, the 222 and 440 reflections appear, together with a peak at 45.2°, which could not be identified. The crystalline quality of the films decreases with increasing thickness. The rocking curve FWHM of the 220/004 reflection starts at $\Delta\omega$=0.05° for the 65 nm thick film, is over $\Delta\omega$=0.3° for the 180 nm thick film, and broadens to $\Delta\omega$ =0.5° at a thickness of 780 nm. At the same time, the out-of-plane lattice parameter of the orthorhombic structure decreases from 3.956 Å for the 65 nm thick film over 3.945 Å for the 180 nm thick film to 3.935 Å for the 780 nm thick film. Both observations are an indication of increased relaxation at higher film thicknesses.

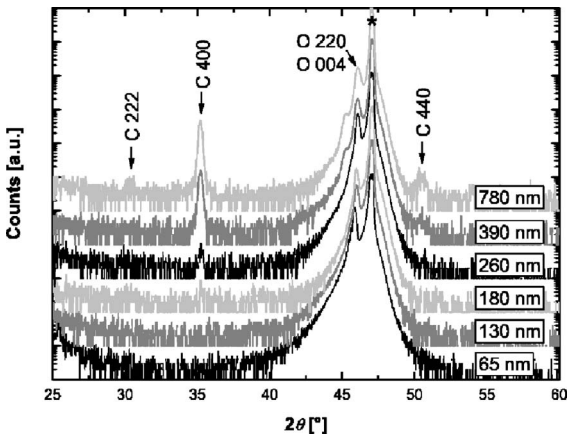

FIG. 5. Series of XRD θ-2θ scans of PLD-grown $LuScO_3$ on $NdGaO_3(110)$ with varying film thicknesses. The thickness values are taken from RBS measurements. Substrate peaks are marked with an asterisk (⋆); the peaks belonging to the orthorhombic perovskite polymorph are marked with "O," whereas those of the cubic bixbyite polymorph are marked with "C."

We have demonstrated the existence of the metastable perovskite polymorph of $LuScO_3$ in crystalline thin films. These films exhibit an orthorhombically distorted perovskite structure, which is epitaxially stabilized with a critical layer thickness of around 200 nm for growth on $NdGaO_3(110)$. The epitaxial stabilization, where the film adopts the orientation of the substrate, allowed the deposition of high-quality epitaxial $LuScO_3$ thin films on $NdGaO_3(110)$ and $DyScO_3(110)$ substrates using MBE and PLD. It remains an open question why on $SrTiO_3(100)$ substrates, the perovskite polymorph of $LuScO_3$ is less stable, even though its pseudocubic lattice parameter of 3.89 Å is much closer to the lattice parameter of $SrTiO_3$ than to those of $NdGaO_3$ and $DyScO_3$.

This work was supported by the Deutsche Forschungsgemeinschaft (Graduiertenkolleg 549 University of Cologne, "Non-centrosymmetric crystals").

[1] C. Zhao, T. Witters, B. Brijs, H. Bender, O. Richard, M. Caymax, T. Heeg, J. Schubert, V. V. Afanas'ev, A. Stesmans, and D. G. Schlom, Appl. Phys. Lett. **86**, 132903 (2005).
[2] V. V. Afanas'ev, A. Stesmans, C. Zhao, M. Caymax, T. Heeg, J. Schubert, Y. Jia, D. G. Schlom, and G. Lucovsky, Appl. Phys. Lett. **85**, 5917 (2004).
[3] M. Wagner, T. Heeg, J. Schubert, St. Lenk, S. Mantl, C. Zhao, and M. Caymax, Appl. Phys. Lett. **88**, 172901 (2006).
[4] T. Heeg, J. Schubert, C. Buchal, E. Cicerella, J. L. Freeouf, W. Tian, Y. Jia, and D. G. Schlom, Appl. Phys. A: Mater. Sci. Process. **83**, 103 (2006).
[5] *Crystal Structure of Data of Inorganic Compounds*, Landolt-Börnstein, New Series, Group III, edited by K. H. Hellwege and A. M. Hellwege (Springer, Berlin, 1976), Vol. 7e, pp. 11–13.
[6] R. P. Liferovich and R. H. Mitchell, J. Solid State Chem. **177**, 2188 (2004).
[7] D. G. Schlom and J. H. Haeni, MRS Bull. **27**, 198 (2002).
[8] J. Lettieri, H. Li, D. O. Klenov, S. Stemmer, and D. G. Schlom (unpublished).
[9] D. O. Klenov, D. G. Schlom, H. Li, and S. Stemmer, Jpn. J. Appl. Phys., Part 2 **44**, L617 (2005).
[10] H. M. Christen, G. E. Jellison, Jr., I. Ohkubo, S. Huang, M. E. Reeves, E. Cicerella, J. L. Freeouf, Y. Jia, and D. G. Schlom, Appl. Phys. Lett. **88**, 262906 (2006).
[11] J. B. Clark, P. W. Richter, and L. du Toit, J. Solid State Chem. **23**, 129 (1978).
[12] V. M. Goldschmidt, Naturwiss. **21**, 477 (1926).
[13] R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 751 (1976).
[14] J. M. Badie, Rev. Int. Hautes Temp. Refract. **15**, 183 (1978).
[15] J. M. Badie and M. Foex, J. Solid State Chem. **26**, 311 (1978).
[16] O. Yu. Gorbenko, S. V. Samoilenkov, I. E. Graboy, and A. R. Kaul, Chem. Mater. **14**, 4026 (2002).
[17] D. G. Schlom, J. H. Haeni, J. Lettieri, C. D. Theis, W. Tian, J. C. Jiang, and X. Q. Pan, Mater. Sci. Eng., B **B87**, 282 (2001).
[18] L. Beckers, J. Schubert, W. Zander, J. Ziesmann, A. Eckau, P. Leinenbach, and C. Buchal, J. Appl. Phys. **83**, 3305 (1998).
[19] http://www.genplot.com/RUMP/index.htm.
[20] P. van der Sluis, J. Phys. D **26**, A188 (1993).
[21] J. B. Nelson and D. P. Riley, Proc. Phys. Soc. London **57**, 160 (1945).