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Face-Centered Cubic $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$

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Abstract

We report the discovery of a face-centered cubic $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ solid solution [$0.60 < x < 0.70$] in films grown onto Si substrates using reactive dual magnetron sputtering from Al and Cr targets at 400 °C. The proposed structure is NaCl-like with 33% vacancies on the metal sites. The unit cell parameter is 4.04 Å as determined by x-ray diffraction. The films have $\langle 100 \rangle$ preferred orientation and exhibit hardness values up to 26 GPa and elastic modulus of 220-235 GPa.

Keywords: Alumina, Chromia, Sputtering, Physical vapor deposition (PVD), Solid solution

We report the synthesis of a face-centered cubic (fcc) $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ solid solution [$0.60 < x < 0.70$] thin films grown by reactive magnetron sputter deposition, for which we propose a vacancy-stabilized NaCl-like structure with 33% vacancies on the metal sites. The unit cell parameter is 4.04 Å as determined by x-ray diffraction. Previously, only one type of solid solution is known; the thermodynamically metastable corundum-structure $(\text{Al,Cr})_2\text{O}_3$ [1-6] of the stable binary oxides, $\alpha\text{-Al}_2\text{O}_3$ (corundum) and $\alpha\text{-Cr}_2\text{O}_3$ (eskolaite), which are well-studied in terms of synthesis and characterization [see, e.g, 7-10]. The only known cubic phase in the archetypical oxide system of alumina is the defect spinel-structure $\gamma\text{-Al}_2\text{O}_3$ [11, 12]. In the chromia system, there are reports on the formation of local fcc-like stacking in just a few monolayers in thin films [13-15]. There is also a patent on industrial synthesis by cathodic arc deposition of $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ films which are claimed to be cubic, but without suggestion for the actual crystal structure [16].

Al-Cr-O films were deposited at a substrate temperature of 400 °C using reactive radio frequency magnetron sputtering in a flow controlled Ar (99.999 % pure) / O₂ (99.99 % pure) gas mixture. The base pressure was $\sim 3 \times 10^{-5}$ Pa. During the depositions, the lowest and highest amount of oxygen was 5 and 10 % of the total gas flow, respectively. The targets were circular (50 mm in diameter) metallic aluminum (99.99% purity) and chromium (99.95% purity). The deposition chamber is described in detail elsewhere [17]. The substrates were 17 mm \times 17 mm polished single crystal Si(001) wafers with native oxide. They were ultrasonically cleaned in trichloroethylene, acetone, and isopropanol for 5 min each and finally blown dry in N₂ gas. The targets were sputter-cleaned prior to each deposition for 5 min with shutters in front of the targets and the sample holder. The films were deposited to a thickness in the range 1 to 1.6 μm . X-ray diffraction (XRD) $\theta/2\theta$ measurements were performed using a Philips Bragg-Brentano diffractometer operated at 40 kV and 40 mA using Cu K $_{\alpha}$ radiation. Texture analysis was performed in a Philips X'Pert Materials Research Diffractometer (MRD) with a low-resolution configuration. Time of flight elastic recoil detection analysis (ToF-ERDA) was used to determine the elemental composition of the films using a beam of 40 MeV $^{127}\text{I}^{9+}$ ions. Surface and cross-sectional observations of the films were performed using a Leo 1550 Gemini field emission gun scanning electron microscope (FEG-SEM) with accelerating voltage 10 kV. Transmission electron microscopy (TEM) and scanning TEM (STEM) were carried out

in a FEI Tecnai G² TF20 UT microscope equipped with a field emission gun and operated at 200 kV. Nanoindentation experiments were performed in a UMIS 2000 instrument with a Berkovich indenter tip and an applied load in the range of 15 to 27 mN depending on the film thickness. The determination of hardness and elastic modulus was done according to the Oliver-Pharr method [18] and averaging between 20 indents for each sample.

Fig. 1 shows the $\theta/2\theta$ x-ray diffractograms for three $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ films labeled *i*, *ii*, and *iii* with compositions $(\text{Al}_{0.40}\text{Cr}_{0.60})_{0.41}\text{O}_{0.59}$, $(\text{Al}_{0.31}\text{Cr}_{0.69})_{0.42}\text{O}_{0.58}$, and $(\text{Al}_{0.30}\text{Cr}_{0.70})_{0.42}\text{O}_{0.58}$, respectively. The compositions, as determined by ERDA, are accurate to within ~ 2 at. %. The ERDA results also showed that the level of impurities (C and H) was lower than 0.1 at. %, the detection limit of the measurement. The diffractograms show that all three measured films have only one strong out-of-plane peak at $2\theta = 44.80^\circ$, indicating a single preferred orientation. Additional $\theta/2\theta$ measurements (not shown) were performed to higher 2θ angles and showed a peak at $2\theta = 99.00^\circ$ with a relative intensity of one tenth, which apparently is a higher multiple of the peak at $2\theta = 44.80^\circ$. The inset in figure 1 is a pole figure from the $(\text{Cr}_{0.69}\text{Al}_{0.31})_{0.42}\text{O}_{0.58}$ film measured at $2\theta = 44.80^\circ$; the pole figures were essentially identical for all films. The only feature in the pole figure in Fig. 1 is the strong diffraction at the center ($\psi = 0^\circ$) corresponding to an orientation of the normal of the scattering lattice planes being parallel to the sample surface normal (from now on referred to as out-of-plane orientation) in the film. It is important to note that, for lattice planes fulfilling Bragg's law at $2\theta = 44.8^\circ$, there are none in the sample giving rise to any intensity at any other tilt angles than $\psi = 0^\circ$. This fact rules out the possibility of a corundum-like structure, because *if* this was a corundum-structured $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ solid solution, the peak at 44.80° and $\psi = 0^\circ$ would correspond to the (202)-planes. However, we do not observe the equivalent (022) planes, which, in such a case, would have produced a ring of intensity at $\psi = 56.9^\circ$ (the interplanar angle between (202) and (022) in the pole figure).

Instead, we consider the peak at 44.80° as the 200 peak from an fcc lattice with a lattice constant of 4.04 \AA . Such a lattice should exhibit diffraction at 2θ angles of 38.55° , 65.25° , 78.41° , and 82.63° , corresponding to (111), (220), (311), and (222) planes,

respectively. Fig. 2 (a-d) show the pole figures of the $(\text{Al}_{0.31}\text{Cr}_{0.69})_{0.42}\text{O}_{0.58}$ film at these 2θ angles. In these pole figures, the rings appear precisely at Ψ (tilt) angles corresponding to the interplanar angles between the (200) plane and the above mentioned planes in a cubic structure. Additional pole figure measurements (not shown) at 2θ angles of 21.97° and 31.27° corresponding to the (100) and (110) planes, which are forbidden in an fcc lattice, did not show any diffraction. These results show that the crystal structure of the as-deposited films is based on an fcc lattice.

Fig. 3(a) shows a cross-sectional SEM micrograph of the $(\text{Al}_{0.31}\text{Cr}_{0.69})_{0.42}\text{O}_{0.58}$ film. The film is dense with a columnar microstructure of 50-100 nm wide columns, and it has a relatively smooth surface. Fig. 3(b) is a low-magnification-cross-sectional TEM image, which shows that the film has a columnar sub-structure approximately five times finer than the one discerned in SEM. Fig. 3(c) shows a high-resolution image of the film. The interplanar spacing, d , is measured to be 2 \AA , consistent with the result from XRD. Fig. 3(d) shows a selected area electron SAED diffraction pattern. It confirms that the film has an fcc-like structure with an out-of-plane orientation of [002]. The discontinuities in the diffraction circles indicate that the film is textured and polycrystalline.

To investigate the possibility of phase separation during film growth STEM EDX line profiles were obtained from the $(\text{Al}_{0.30}\text{Cr}_{0.70})_{0.42}\text{O}_{0.58}$ film (*iii* in figure 1) in out-of-plane (Fig. 4.a) and in-plane (Fig. 4.b) orientations. These results show that the Cr-to-Al signal-intensity ratio is constant throughout the film and across grain boundaries, meaning that there is no phase separation of Al_2O_3 and Cr_2O_3 , to the ~ 1 nm resolution limit of the measurement.

As shown above, the synthesized films are $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ solid solutions whose crystal structure is based on an fcc lattice. To determine the exact crystal structure, several possibilities first need to be excluded. The possibility of our identified structure being a γ -alumina-like (defect spinel) structure was excluded by texture analysis. γ -alumina has a cubic structure with a unit cell of 7.90 \AA , which gives the 2θ angle of 19.45° for the (111) plane [ICDD JCPDF No.10-0425]. Considering the d spacing of 4.04 \AA in our case, the 2θ angle corresponding to $\{111\}$ planes in a hypothetical γ -alumina-like structure would

be 19.00° ($d = 8.08 \text{ \AA}$). A pole figure at this 2θ angle (not shown) showed no diffraction for the whole range of tilt ($0 < \psi < 90^\circ$) and azimuth angles. We can therefore exclude the possibility that this is a γ -alumina-like structure since a diffraction ring would have been observed at $\psi = 54.7^\circ$, the interplanar angle between (111) and (200). Furthermore, an interpretation of the present diffraction results as a fluorite crystal structure is refuted based on the observed lattice parameter of 4.04 \AA , which would render the metal-oxygen (i.e., cation-anion) bonding distance unrealistically short. In a fluorite structure, the cation-anion distance is $0.433a$ in which a is the lattice parameter of the fcc unit cell [19]. For a lattice parameter of 4.04 \AA , this would translate into a cation-anion distance of only 1.75 \AA . In contrast, the same distance in a NaCl structure is $0.5a$ or 2.02 \AA . Therefore, the possibility of our films having an oxygen-vacancy-stabilized fluorite structure like in the cubic ceria and zirconia systems (see, e.g., [20]) is ruled out. A zincblende-like structure can be excluded by similar arguments.

Based on these results and arguments, we conclude that our $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ films have a NaCl-like structure with $\sim 33\%$ vacancies on the metal sites. This phase is likely metastable with respect to the binary oxides. Further support for this interpretation is the work of Du et al. [13], who presented a chromium oxide thin film having a local ordering corresponding to a defected NaCl structure in Cr_2O_3 films on MgO(110) substrates. In this structure, every third Cr position was vacant along the MgO $\langle 110 \rangle$ direction in an ordered way. Furthermore, our results likely explain the observation in a patent on industrial synthesis by cathodic arc deposition of $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ films which were claimed to be cubic, but without identification of the crystal structure [16].

The mechanical properties (hardness, H , and reduced elastic modulus, E_r) of the fcc- $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ films were measured to 24-26 GPa and 220-235 GPa, respectively. This is similar to typical values for α - $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ thin films [2,6], but not as hard as α - Cr_2O_3 ($H = 29 - 30 \text{ GPa}$ [21,22]), which is the hardest of the common oxides.

In conclusion, we have discovered an fcc- $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ solid solution phase in films synthesized using reactive rf magnetron sputtering at a substrate temperature of $400 \text{ }^\circ\text{C}$. The proposed crystal structure is NaCl-like with a unit cell parameter of 4.04 \AA and one

third vacancies on the metal sites. It is noteworthy that our films do not form the corundum-structure $\alpha\text{-(Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ solid solution, as would be expected from the literature on this well-studied system [2-6]. It is further remarkable since pure chromia readily grows in the corundum structure also in the present experimental setup, as expected (results not shown). We propose a stabilization mechanism of the defect NaCl-like structure in which the introduction of vacancies on metal sites sets the metal-oxygen ratio to the chemically preferred 2:3. This, together with the more simple stacking order of an fcc lattice, may explain the formation of the NaCl-like structure in these films.

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References

- [1] L. A. Vieira, M. Döbeli, A. Domman, E. Kalchbrenner, A. Neels, J. Ramm, H. Rudigier, J. Thomas, B. Widrig, *Surf. Coat. Technol.* 204 (2010) 1722.
- [2] J. Ramm, M. Ante, T. Bachmann, B. Widrig, H. Brändle, M. Döbeli, *Surf. Coat. Technol.* 202 (2007) 876.
- [3] D. Diechle, M. Stueber, H. Leiste, S. Ulrich, V. Schier, *Surf. Coat. Technol.* 204 (2010) 3258.
- [4] J. Ramm, M. Ante, H. Brändle, A. Neels, A. Dommann, M. Döbeli, *Adv. Eng. Mater.* 9 (2007) 604.
- [5] M. Witthaut, R. Cremer, K. Reichert, D. Neuschütz, *Mikrochim. Acta* 133 (2000) 191.
- [6] K. Pedersen, J. Bottiger, M. Sridharan, M. Sillassen, P. Eklund, *Thin Solid Films* 518 (2010) 4294.
- [7] R. Cremer, K. Reichert, D. Neuschütz, G. Erkens, T. Leyendecker, *Surf. Coat. Technol.* 163-164 (2003) 157.
- [8] F. Luo, X. Pang, K. Gao, H. Yang, Y. Wang, *Surf. Coat. Technol.* 202 (2007) 58.
- [9] F. Fietzke, K. Goedicke, W. Hempel, *Surf. Coat. Technol.* 86-87 (1996) 657.
- [10] M. Ristić, S. Popović, S. Musić, *Mater. Lett.* 16 (1993) 309.
- [11] J. M. McHale, A. Auroux, A. J. Perrotta, A. Navrotsky, *Science* 277 (1997) 788.
- [12] I. Levin, D. Brandon, *J. Am. Ceram. Soc.* 81 (1998) 1995.
- [13] J.C. Rao, X.X. Zhang, B. Qin, K.K. Fung, *Ultramicroscopy* 98 (2004) 231.
- [14] J.S. Arlow, D.F. Mitcheli, M.J. Graham, *J. Vac. Sci. Technol.* A5 (1987) 572.
- [15] X.S. Du, S. Hak, T. Hibma, O.C. Rogojanu, B. Struth, *J. Cryst. Growth* 293 (2006) 228.
- [16] D. Kurapov, International Patent No. WO 2010/040494 A1, (15 april 2010)
- [17] D.H. Trinh, M. Ottosson, M. Collin, I. Reineck, L. Hultman, H. Högberg, *Thin Solid Films* 516 (2007) 4977.
- [18] W. C. Oliver and G. M. Pharr, *J. Mater. Res.* 7 (1992) 1564.
- [19] A. R. West, *Basic Solid State Chemistry*, second ed., John Wiley & Sons, 1999, p. 40.
- [20] N. V. Skorodumova, S. I. Simak, B. I. Lundqvist, I. A. Abrikosov, and B. Johansson, *Phys. Rev. Lett.* 89 (2002) 16660.
- [21] P. Eklund, M. Sridharan, M. Sillassen, J. Böttiger, *Thin Solid Films* 516 (2008) 7447.
- [22] P. Hones, M. Diserens, F. Lévy, *Surf. Coat. Technol.* 120–121 (1999) 277.

Figures

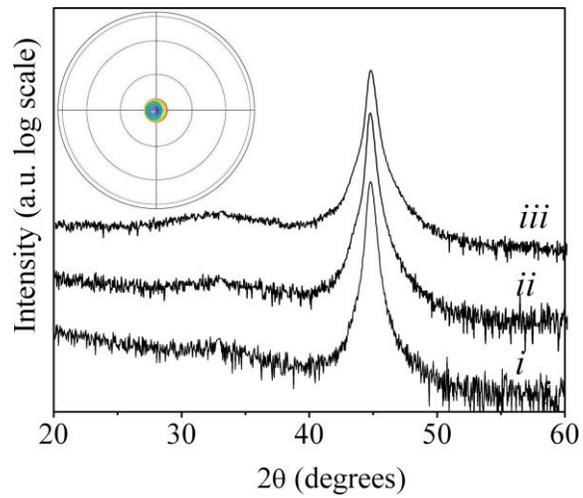


Figure 1. $\theta/2\theta$ X-ray diffractograms from three stoichiometric Al-Cr-O films *i*) $(\text{Al}_{0.40}\text{Cr}_{0.60})_{0.41}\text{O}_{0.59}$, *ii*) $(\text{Al}_{0.31}\text{Cr}_{0.69})_{0.42}\text{O}_{0.58}$, and *iii*) $(\text{Al}_{0.30}\text{Cr}_{0.70})_{0.42}\text{O}_{0.58}$, respectively. The pole figure inset corresponds to film *ii* and was measured at $2\theta = 44.8^\circ$.

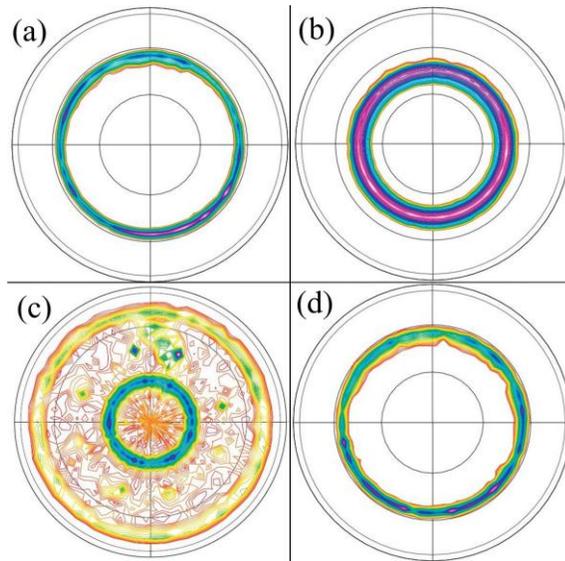


Figure 2. Pole figures obtained for the $(\text{Al}_{0.31}\text{Cr}_{0.69})_{0.42}\text{O}_{0.58}$ film at 2θ equal to (a) 38.55° , (b) 65.25° , (c) 78.41° , and (d) 82.63° . Polar and radial angles represent the azimuth, φ , and tilt, ψ , angles.

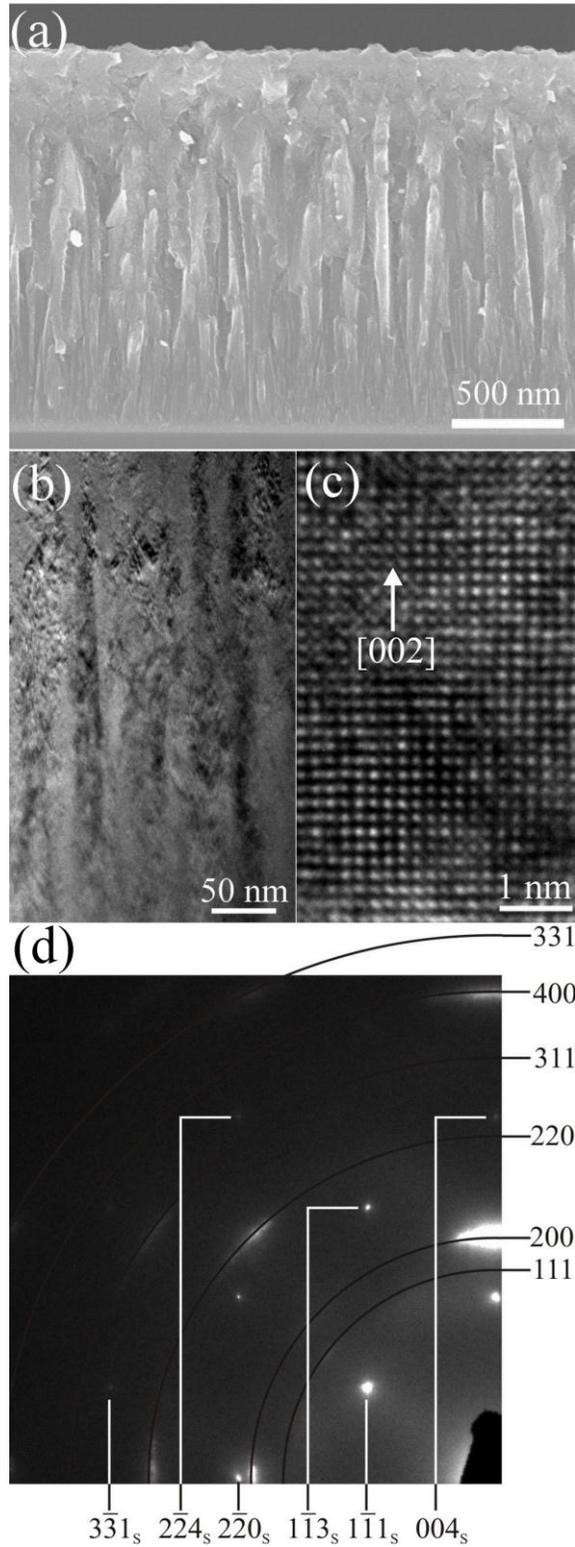


Figure 3. Cross-sectional (a) SEM and (b) TEM micrographs from the $(\text{Al}_{0.31}\text{Cr}_{0.69})_{0.42}\text{O}_{0.58}$ film, and (c) HRTEM image of the film with the [002] preferred growth direction indicated, and (d) diffraction pattern from substrate (subscript S) and film.

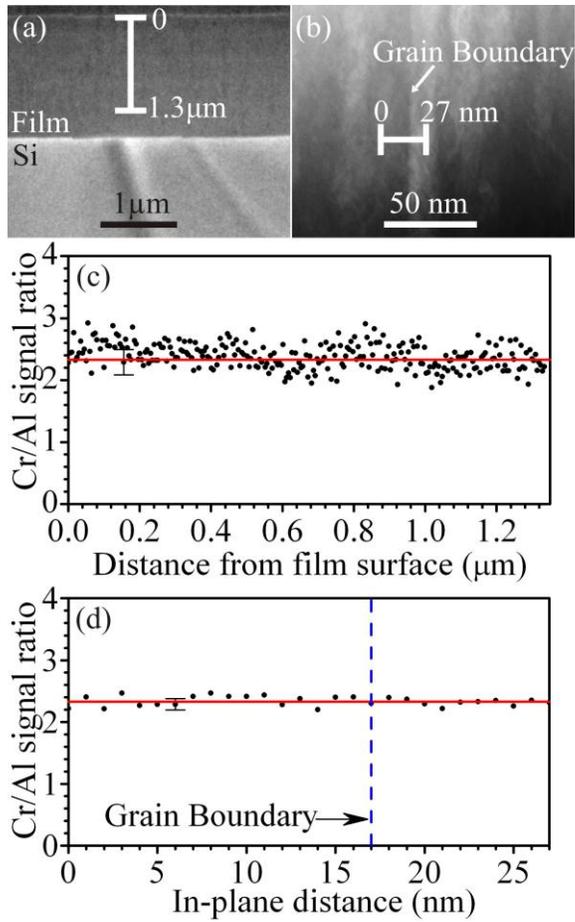


Figure 4. TEM EDX measurement (showing the Cr/Al signal-intensity ratio normalized to the compositional ratio) on $(\text{Al}_{0.30}\text{Cr}_{0.70})_{0.42}\text{O}_{0.58}$ film along (a) and (c) Out-of-plane orientation with step size of 5 nm, and (b) and (d) in-plane orientation with step size of 1 nm. The error limit of the measurement is indicated.