

Oxide nanosheets as seed layers for growth of complex oxides on Si and glass



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Oxide thin films

Functional oxides: ferroelectricity, ferromagnetism, multiferroism, electric conductivity, ionic conductivity, electro-optics, catalysis ...



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Epitaxial growth on single crystalline oxide substrates: SrTiO₃, LaAlO₃, MgO, ...



M. F. Sarott, E. Gradauskaite, J. Nordlander, N. Strkalj, M. Trassin. J. Phys.: Condens. Matter. **33** (2021) 293001



Workshop OSEPI. May 2024

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Complex oxides substrates:

- Expensive
- Difficult to process
- Limited size
- Limited use in industry



Difficulty to integrate oxides on silicon and glass:

- High reactivity of Si with O₂: propensity to form amorphous SiO₂ at the interface
- Structural and chemical dissimilarities
- Differences in thermal expansion coefficients
- Reaction of oxides with Si

Very low crystalline qualityDegradation of the properties



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- Reaction of oxides with Si

Very low crystalline quality
Degradation of the properties

Breakthrough 1998: McKee *et al*. PRL 81 : first demonstration that SrTiO₃ can be grown directly on Si with an atomically sharp interface using MBE

Heteroepitaxy of a thin template layer

of SrTiO₃ on Si

(001)Si

SrTiO₃ Y₂O₃:ZrO₂ (YSZ) template layer by Pulsed Layer Deposition (PLD) Fork et al. APL 57 (1990) 1137 CeO₂/YSZ Perna et al. J. Phys. Cond. Matter. 21 (2009) 30 Diaz-Fernandez et al. Appl. Surf. Sci. 455 (2018) 227

ZrO₂ template layer by Atomic Layer Deposition (ALD)

Dogan et al. J. Phys. Chem. C 123 (2019) 15053

Limitations: Complex technics

Advantages: High crystalline quality of the template layer



Pioneer work of Sasaki's group (NIMS, Japan), 2007

Layered metal oxide





Pioneer work of Sasaki's group (NIMS, Japan), 2007

Exfoliation in solution





Pioneer work of Sasaki's group (NIMS, Japan), 2007

Exfoliation in solution





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Exfoliation in solution







[Ca₂Nb₃O₁₀]⁻: nanosheets for the growth of (001) perovskite

Layered perovskite Dion-Jacobson phase: AA'_{k-1}B_kO_{3k+1}

A: alkaline metal, A': alkaline-earth metal, B: transition metal



P2₁/m a = 7.741 Å, b = 7.707 Å, c = 14.859 Å, β = 97.51° (larger tetragonal cell description: a = 7.727 Å, b = 29.466 Å)



M. Dion, M. Ganne, M. Tournoux. *Mater. Res. Bull*. <u>16</u> (1981) 1429 T. Tokumitsu, K. Toda, T. Aoyagi, D. Sakuraba, K. Uematsu, M. Sato. *J. Ceram. Soc. Jpn*. <u>114</u> (2006) 795

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Nanosheets for preferential orientation of oxides on any substrate

Nanosheets (NS)	2D lattice	Grown films on NS	Substrates	
		(001)SrTiO ₃ (001)(Ba,Sr)TiO ₃	Glass	
[Ca ₂ Nb ₃ O ₁₀] ⁻	Square $a_{\rm NS}$ = 3.85 Å x 3.85 Å	(001)LaMnO₃/STO SLs	Si	
		(001)LAO/STO SLs	Si	
		(001)LaNiO ₃	Si	
		(001)BaTiO ₃	Si	
		(001)(K,Na)NbO ₃	Pt/Ti/SiO ₂ /Si	
		(001)BiFeO ₃	Pt/Si, Pt/TiO ₂ /Si, 316LSS	
		(001)Pb(Zr,Ti)O ₃	Si, Pt/TiO ₂ /Si, glass, 316LSS	
	. 1 .	(001)SrRuO ₃	Si, Glass	
		(001)(Ca,Sr)Bi ₄ Ti ₄ O ₁₅	Pt/TiO₂/Si	
		(110)(Sr,Eu) ₂ (Sn,Ti)O ₄	Glass	
		(001)TiO ₂	Glass	

PLD, Sputtering, Sol-gel



Synthesis of KCa₂Nb₃O₁₀



Solid state reaction:

 $1/2 \text{ K}_2\text{CO}_3 \text{ (+ excess) + 2 CaCO}_3 + 3/2 \text{ Nb}_2\text{O}_5 \rightarrow \text{KCa}_2\text{Nb}_3\text{O}_{10} + 5/2 \text{ CO}_2$



Protonation: ion exchange $K^+ \rightarrow H^+$



P4/mbm, a = 5.452 Å, c = 14.414 Å



A.J. Jacobson, J.T. Lewandowski, J.W. Johnson. J. Common Met. 116 (1986) 137 Y. Chen, X. Zhao, H. Ma, S. Ma, G. Huang, Y. Makita, X. Bai, X. Yang. J. Solid State Chem. 181 (2008) 1684 L.V. Yafarova, O.I. Silyukov, T.D. Myshkovskaya, I.A. Minich, I.A. Zvereva. J. Therm. Analysis. Calorim. (2020)

X-ray diffraction



Exfoliation



Tetra(n-butyl)ammonium hydroxide (TBAOH)



R.E. Schaak, T. Mallouk. *Chem. Mater.* <u>12</u> (2000) 2513 H. Yuan, D. Dubbink, R. Besselink, J.E. Elshof. *Angew. Chemie. Int. Ed.* <u>54</u> (2015) 9239 J.E. Elshof. H. Yuan, P Gonzalez Rodriguez. *Mater. Views.* <u>6</u> (2016) 1600355

Exfoliation



Tetra(n-butyl)ammonium hydroxide (TBAOH)

- Acid-base reaction between OH⁻ from TBAOH and H⁺ from HCN



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Tetra(n-butyl)ammonium hydroxide (TBAOH)

Nanosheets in solution: $[H_{1-y}TBA_y]^+[Ca_2Nb_3O_{10}]^- + H_2O$

- Acid-base reaction between OH⁻ from TBAOH and H⁺ from HCN

- TBA keep nanosheets in a well-dispersed state in water

R.E. Schaak, T. Mallouk. *Chem. Mater.* <u>12</u> (2000) 2513 H. Yuan, D. Dubbink, R. Besselink, J.E. Elshof. *Angew. Chemie. Int. Ed.* <u>54</u> (2015) 9239 J.E. Elshof. H. Yuan, P Gonzalez Rodriguez. *Mater. Views.* <u>6</u> (2016) 1600355





[Ca₂Nb₃O₁₀]⁻ nanosheets



Nanosheet colloidal suspension: Tyndall effect







Weak superlattice { $\frac{1}{2}$, $\frac{1}{2}$, 0} reflections: $\sqrt{2}a$ lattice constant ~ 5.46 Å

A. Maia, F. Cheviré, V. Demange, V. Bouquet, M. Pasturel, S. Députier, R. Lebullenger, M. Guilloux-Viry, F. Tessier. *Solid State Sci*. <u>54</u> (2016) 17-21 F. Baudouin, V. Demange, S. Ollivier, L. Rault, A. S. Brito, A. S. Maia, F. Gouttefangeas, V. Bouquet, S. Députier, B. Bérini, A. Fouchet, M. Guilloux-Viry. *Thin Solid Films* <u>693</u> (2020) 137682



Nanosheets seed layer deposition by drop-casting method

Y. Shi, M. Osada, Y. Ebina, T. Sasaki. ACS Nano <u>14</u> (2020) 15216



Easy Fast (dozens samples/day) No waste of material Large substrates (several cm²)

Limitations:

« Coffee-ring » marks **Operator dependent**





After deposition: atomic force microscopy/SEM



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After deposition: in-plane X-ray diffraction



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Random in-plane distribution of nanosheets on the substrate

Texturation of the film grown on nanosheets covered substrate







In-plane RSM





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Growth of complex oxides: KNbO₃ on [Ca₂Nb₃O₁₀]⁻/glass



Amm2 a = 3.9741(0) Å; b = 5.6965(0) Å; c = 5.726(1) Å Pseudo-cubic cell: $a_{pc} = 3.971$ Å, $b_{pc} = 4.027$ Å, $c_{pc} = 4.045$ Å

L. Katz and H.D. Megaw. *Acta Cryst*. <u>22</u> (1967) 639 S. Kawamura *et al. Jpn J. Appl. Phys*. <u>52</u> (2013) 09KF04



Workshop OSEPI. May 2024

Growth of complex oxides: KNbO₃ on [Ca₂Nb₃O₁₀]⁻/glass



Sciences Chimiaúes

*Amm*2 *a* = 3.9741(0) Å; *b* = 5.6965(0) Å; *c* = 5.726(1) Å Pseudo-cubic cell:

300 nm

 a_{pc} = 3.971 Å, b_{pc} = 4.027 Å, c_{pc} = 4.045 Å

L. Katz and H.D. Megaw. *Acta Cryst*. <u>22</u> (1967) 639 S. Kawamura *et al. Jpn J. Appl. Phys*. <u>52</u> (2013) 09KF04

Pulsed Laser Deposition: on SrTiO₃, on glass, on [Ca₂Nb₃O₁₀]⁻/glass





F. Baudouin, V. Demange, S. Ollivier, L. Rault, A.S. Brito, A.S. Maia, F. Gouttefangeas, V. Bouquet, S. Députier, B. Bérini, A. Fouchet, M. Guilloux-Viry. *Thin Solid Films* <u>693</u> (2020) 137682

Growth of complex oxides: KNbO₃ on [Ca₂Nb₃O₁₀]⁻/Si

KNbO₃/Si



 $K_6 Nb_6 Si_4 O_{26}$ *P*-62*m a* = 9.032 Å *c* = 8.041 Å

J. Choisnet *et al. Mater. Res. Bull*. <u>11</u> (1976) 887 KNbO₃/[Ca₂Nb₃O₁₀]⁻/Si





Workshop OSEPI. May 2024

Growth of complex oxides: KNbO₃ on [Ca₂Nb₃O₁₀]⁻/Si

KNbO₃/3 layers [Ca₂Nb₃O₁₀]⁻/Si

de Rennes

KNbO₃/4 layers [Ca₂Nb₃O₁₀]⁻/Si





Magnetic La_{0.67}Sr_{0.33}MnO₃ films on glass (PLD)



A. Boileau, M. Dallocchio, F. Baudouin, A. David, U. Lüders, B. Mercey, A. Pautrat, V. Demange, M. Guilloux-Viry, W. Prellier, A. Fouchet. ACS Appl. Mater. Int. 11 (2019) 37302

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Transparent conducting SrVO₃ and CaVO₃ films on glass (PLD) Resistivity Transmittance



A. Boileau, S. Hurand, F. Baudouin, U. Lüders, M. Dallocchio, B. Bérini, A. Cheikh, A. David, F. Paumier, T. Girardeau, P. Marié, C. Labbé, J. Cardin, D. Aureau, M. Frégnaux, M. Guilloux-Viry, W. Prellier, Y. Dumont, V. Demange, A. Fouchet. Adv. Func. Mater. <u>32</u> (2022) 2108047

TiO₂ thin films grown by atomic layer deposition (ALD)

5 nm TiO₂ on Si: amorphous



ALD GEMaC Geeder

A. Grishin B. Bérini

HR(S)TEM

S tructures P roperties M odeling of S olids

M. Vallet





A. Grishin, B. Bérini, M. Vallet, S. Hurand, F. Maudet, C. Sartel, M. Frégnaux, S. Nowak, G. Amiri, S. Hassani, D. Aureau, V. Sallet, V. Demange, Y. Dumont. Appl. Surf. Science. 641 (2023) 158446

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CNRS de Rennes

Crystal size of the parent phase: KCa₂Nb₃O₁₀

Molten salts:

Excess of K₂CO₃

Growth temperature

Cooling rate

Salts: KCl, K₂SO₄, K₂MoO₄

Ratio salt/precursors

Pure phase

Crystals size

Solid state reaction

Molten salt: K₂SO₄



Molten salt: $K_2MoO_4(1)$



Molten salt 2: K_2MoO_4 (2)







Effect of growth methods of the parent phase on nanosheets size Solid state reaction Molten salt: K₂SO₄



~ 0.1 – 0.2 μm

Molten salt: K₂MoO₄(1)



<u>1μm</u>

~ 2 – 5 µm

Molten salt 2: K₂MoO₄(2)



> 50 µm



45

26.0

um

18

11.0

10.0

Other nanosheets for oxide growth



Nanosheets for preferential orientation of oxides on any substrate

Nanosheets (NS)	2D lattice	Grown films on NS	Substrates
[Ti _{0.87} O ₂] ^{0.52-}	Rectangle	(110)SrTiO ₃	Glass
	c _{NS} ~ 2.97 Å	(110)SrRuO₃	Si
		(110)Pb(Zr,Ti)O ₃	Si, Si ₃ N ₄
		(011)VO ₂	Si, Pt/TiO ₂ /Si
[Cs ₄ W ₁₁ O ₃₆] ²⁻	Hexagonal <i>a_{Ns}</i> = 7.261 Å	(001)ZnO	Glass, polymer
[MnO ₂] ^{0.45-}	Hexagonal a _{NS} = 2.94 Å	(001)ZnO	Glass
[MoO ₂]δ-	Hexagonal a _{NS} = 2.90 Å	(111)SrTiO ₃	Glass
[NbWO ₆] ⁻	Square a _{NS} = 4.68 Å x 4.68 Å	(-402)VO ₂	Si, Si ₃ N ₄



Refs: Sasaki's articles, Ten Elshof articles, ...

[Ti_{0.865}O₂]^{0.54-} nanosheets for (110) perovskite growth





[Ti_{0.865}O₂]^{0.54-} nanosheets for (110) perovskite growth

 $K_{0.8}Ti_{1.73}Li_{0.27}O_4$









In-plane XRD

de Rennes





[Ti_{0.865}O₂]^{0.54-} nanosheets for (110) perovskite growth

 $K_{0.8}Ti_{1.73}Li_{0.27}O_4$









In-plane XRD





[(Ti,Co,Fe)_{0.865}O₂]^{0.54-}



[MnO₂]^{0.45-} nanosheets for (111) perovskite growth





[MnO₂]^{0.45-} nanosheets for (111) perovskite growth





a_{NS} = 2.94 Å

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Yano *et al*. (3 months) See Sahar Gaddour's poster



Yano et al. Cryst. Growth Des. (2022) 22



Master 2

First attempt of exfoliation



Conclusions

- Integration of various oxides (including oxides that react with Si) on Si and glass thanks to nanosheets

- Excellent properties of thin films grown on Si or glass
- Easy process, large surface
- Synthesized nanosheets: [Ca₂Nb₃O₁₀]⁻, [Sr₂Nb₃O₁₀]⁻, [Ti_{0.865}O₂]^{0.54-}, [MnO₂]^{0.45-}

and also : $[K_{4-x}Nb_6O_{17}]^{x-}$, $[Cs_4W_{11}O_{36}]^{2-}$, $[(Ti,Co,Fe)_{0.865}O_2]^{0.54-}$



Acknowledgements

Florent Baudouin	Amélia Baucher	<section-header></section-header>	Sahar Gaddouu	UAR Sca Ludivine Francis Gou Loïc Jo	anMAT e Rault ittefangeas oanny
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