Local Control over Nucleation of Epitaxial Thin Films by Seed Layers of Inorganic Nanosheets

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Supporting Information

ABSTRACT: Nanosheets of TiO₂ and Ca₂Nb₃O₁₀ were synthesized and transferred onto Si substrates by Langmuir–Blodgett deposition. Using pulsed laser deposition, SrRuO₃ films were formed on top of these samples. The underlying nanosheets determined both the morphology and crystallographic orientation of the films. SrRuO₃ grew preferentially in the [110]pc direction on TiO₂ nanosheets, while growth proceeded in the [001]pc direction on Ca₂Nb₃O₁₀ nanosheets (pc refers to the pseudocubic unit cell of SrRuO₃). Besides macroscopic control over the out-of-plane crystal direction, single crystal orientations were measured by electron backscatter diffraction on the level of individual nanosheets, indicating that epitaxial growth was achieved on the nanosheets as imposed by their well-defined crystal lattices. The nanosheets also had a clear effect on the magnetic properties of the films, which showed anisotropic behavior only when a seed layer was used. A monolayer consisting of a mixture of both types of nanosheets was made to locally control the nucleation of SrRuO₃. In this context, SrRuO₃ was used as a model material, as it was used to illustrate that nanosheets can be a unique tool to control the orientation of films on a (sub-)micrometer length scale. This concept may pave the way to the deposition of various other functional materials and the fabrication of devices where the properties are controlled locally by the different crystallographic orientations.

KEYWORDS: inorganic nanosheets, pulsed laser deposition, anisotropy, mixed orientation, controlled nucleation, ferromagnetic perovskite, SrRuO₃

INTRODUCTION

In thin film laboratories, the structure-property relations of various materials are studied. One particular approach to control the properties of a thin film is by changing its crystallographic orientation. For example, Tebano et al. showed that for films with thicknesses in the range from 3 to 12 nm, La₀.₆₇Sr₀.₃₃MnO₃ was insulating on (001) oriented LaAlO₃ but behaved as a metal on (110) oriented LaAlO₃.5 Also, the magnetization characteristics of several manganites were reported to vary with the orientation of the substrate.6–8 In the field of ferroelectrics, the ferroelectric activity of a material can be tuned by changing its orientation.9–12 For instance, the ferroelectric response of epitaxial films of Nd-doped Bi₁₋ₓTiₓO₃ could be tuned down to the point where ferroelectricity was completely suppressed by using differently oriented SrTiO₃ substrates.6 A third example of a field where the structure and properties of films were found to vary markedly with the orientation of the substrate is that of nanocomposites made by pulsed laser deposition (PLD). These nanocomposite films are generally formed by self-assembly processes that take place during the simultaneous deposition of two immiscible phases.9–12

The previous examples show that the crystallographic orientation is an important parameter that determines the properties of a film. The reason can be found in geometric constraints defined by the unit cell5–8 but may also be different. For instance, strain imposed by the substrate,1–4 or anisotropies in the interfacial, surface, or elastic energies, may play a crucial role.9–12 In all of the examples, the orientations of the films were completely determined by the lattices of the single crystalline substrates. A versatile method to control the orientation of a film on a smaller scale than the typical dimensions of a substrate has so far not been proposed. If such control would be possible, functional films could be designed where certain position dependent properties are determined by the orientations of the crystallites. Thus, an extra degree of freedom would become available for the fabrication of materials with advanced local functionalities.

In this paper, we propose that different types of nanosheets can be used to locally control the nucleation of a film. The concept to use nanosheets for epitaxial growth was first introduced by Kikuta and co-workers in 2007.13 They showed that the texture of LaNiO₃ and Pb(Zr₀.₃Ti₀.₇)O₃ on glass plates could be controlled by the introduction of a seed layer of Ca₂Nb₃O₁₀ nanosheets. The films, which were made by chemical solution deposition, showed improved ferroelectric

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properties compared to films made without the nanosheet layer. Later, Shibata et al. used sol–gel processes to deposit textured films of SrTiO₃, TiO₂, and ZnO on glass substrates containing monolayers of Ca₃Nb₂O₉ or MnO₂ nanosheets. Also, PLD was used to form films with certain orientations, even on plastic substrates.  

In these previous studies, crystalline nanosheets were deposited on amorphous substrates in order to imitate costly single crystal substrates. The, in general, unsurpassed quality of films on single crystal substrates could not be mimicked, though, since the films were in-plane randomly oriented. In this work, we show that nanosheets can be a unique tool to control the nucleation of films on a level that can not be attained on single crystal substrates. In brief, the influence of Ca₃Nb₂O₉ and Ti₄O₇ nanosheets on the nucleation and properties of SrRuO₃ is discussed. SrRuO₃ is a conductive perovskite that is ferromagnetic typically below ∼160 K. The model material was selected mainly because strong magnetic anisotropy was expected. PLD was used to grow the films on Si substrates, most of which were pre-coated with a single layer of nanosheets. The morphology and crystallographic orientation of these films were controlled by the type of nanosheets that covered the substrates. Epitaxial growth was illustrated and explained by lattice matching with the underlying nanosheets together with continuation of the oxygen octahedral backbones, as illustrated by the graphical abstract. Anisotropic magnetic properties were found when a layer of nanosheets was present but not when SrRuO₃ was directly deposited on a Si substrate. The two types of (sub-)micrometer-sized nanosheets were also combined on a single substrate to locally control the orientation of SrRuO₃. This experiment illustrates that nanosheets can be used to create films with position dependent properties that are determined by the local crystallographic orientations.

### EXPERIMENTAL METHODS

#### Materials

Anhydrous K₂CO₃ (≥ 99%) was purchased from Fluka; CaCO₃ (ACS reagent, chelometric standard), Nb₂O₅ (99.99%, trace metals basis), and MoO₃ (> 99.5%, ACS reagent) were obtained from Sigma-Aldrich; TiO₂ (≥ 99%, technical) and Li₂CO₃ (≥ 99%, purum) were purchased from Riedel-de Haën; nitric acid (65% v/v in water) and tetrabutylammonium hydroxide (40% w/w in water) were provided by Acros Organics and Alfa Aesar, respectively. Ultrapure water with a resistivity of 18.2 MΩ·cm was used. Both solutions were shaken vigorously for 1 min after dilution. While the other solution was decanted 30 min after it had been prepared, the Ti₀.₈₇O₂ nanosheets were diluted 3.3 times after 21 days. Prior to making these stock solutions, the solution containing Ca₃Nb₂O₉ nanosheets was stirred until all of the precipitate had dispersed in the solution, while the other solution was decanted 30 min after it had been removed from the rocking shaker.

#### Langmuir–Blodgett Deposition.

The silicon wafers with native oxide layer were cut into pieces of about 1 × 1.5 cm². The substrates were first cleaned on a hot plate at 250 °C with a jet of supercritical CO₂ and then in an oxygen plasma cleaner (Harrick plasma) at 30 W for 15 min. A KSV minicrystal double-barrier Langmuir trough with a vertical lifting configuration was used to deposit the nanosheets on the substrates.

Three types of monolayers were deposited on the substrates, that is, Ti₄O₇, Ca₃Nb₂O₉, and a mixture of both types of nanosheets. For the samples with a dense packing and in the case of Ti₄O₇ nanosheets, depositions were performed at a surface pressure Π = 20 mN·m⁻¹. A 12.3 times dilution of the stock solution was used for these depositions. Without further diluting the stock solution of Ca₃Nb₂O₉ nanosheets and by using Π = 14 mN·m⁻¹, a high coverage of nanosheets was obtained. In the case when a mixture of both types of nanosheets was desired, 10 mL of each stock solutions was mixed with 30 ml water. The resulting solution was added to the Langmuir trough 15 min after its preparation and a deposition was performed at Π = 17.5 mN·m⁻¹. The isotherms showing the surface pressure versus compression and atomic force microscopy images of the resulting monolayers can be found in the Supporting Information.

#### Pulsed Laser Deposition of Strontium Ruthenate.

SrRuO₃ films were deposited by pulsed laser deposition using the conditions of Kuiper et al. ²⁶ All depositions were performed in a 1:1 O₂ and Ar environment of 0.30 mbar. The substrate temperature was controlled by a thermocouple inside the heater at 670 °C.

The laser beam was produced by a 248 nm KrF excimer laser (LPXPro from Coherent, Inc.) with a typical pulse duration of 20 to 30 ns. A 45° mirror was used to select the most homogeneous part of the laser beam. The laser was then focused on the stoichiometric SrRuO₃ target to a spot size of 1.8 mm². The voltage was adjusted to yield a laser fluence of 2.1 J·cm⁻² on the target. The laser repetition rate was set at 1 Hz and the target to substrate distance was kept at 5 cm.

The target was pre-ablated at 5 Hz for 6 min to remove possible surface contaminations. All depositions were carried out for 60 min,

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<tr>
<td>K₀.₆[T₁₀.₇₃L₁₀.₂₇]O₄</td>
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solution and was stirred with a stirring magnet at 300 rpm for 72 h. Similarly, about 10 g K₀.₆[T₁₀.₇₃L₄₀.₂₇]O₄ was stirred in nitric acid (500 mL, 2 mol·L⁻¹) for 96 h. The latter dispersion was allowed to sediment every 24 h after which the solution was removed by decantation and replaced by a fresh one. After protonation, both powders were filtered by vacuum filtration (Whatman 1450-SSS) and washed with a copious quantity of water (10 times).

To obtain Ca₃Nb₂O₉ nanosheets, 0.4 g of HC₆₅Na₉O₃·1.₅H₂O was suspended in 100 mL water and 480 μL of the 40% aqueous solution of tetrabutylammonium hydroxide (exfoliation agent) was added. The Ti₄O₇ nanosheets were formed by adding 0.3 g of H₁₉[T₁₀.₇₃]O₄·H₂O and 635 μL exfoliation agent to 200 mL water. Both solutions were shaken vigorously for 1 min after preparation and then kept on a rocking shaker. To increase stability, the solution containing Ca₃Nb₂O₉ nanosheets was diluted 9 times after 14 days of exfoliation and the solution containing Ti₄O₇ nanosheets was diluted 3.3 times after 21 days. Prior to making these stock solutions, the solution containing Ca₃Nb₂O₉ nanosheets was stirred until all of the precipitate had dispersed in the solution, while the other solution was decanted 30 min after it had been removed from the rocking shaker.

### Table 1. Annealing Sequences Used in a Chamber Furnace (Carbolite) for Solid State Synthesis of the Parent Compounds (A Holdback Temperature of 20 °C Was Used)

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<tr>
<td>K₀.₆[T₁₀.₇₃L₁₀.₂₇]O₄</td>
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yielding a layer thickness of $34 \pm 7$ nm. After deposition, the samples were allowed to cool to room temperature at a maximum rate of 20 °C/min$^{-1}$ in an environment of 100 mbar O$_2$.

**Analysis and Characterization.** The topography of the samples was analyzed with a Dimension Icon atomic force microscope (Bruker AXS) using the standard tapping mode option. For selected samples, the relative coverage of nanosheets on the substrates was determined. In these cases, atomic force microscopy scans were made on at least seven different locations on the sample. The data were subsequently processed using Gwyddion 2.29 and the resulting images were analyzed by Imager 1.45s to obtain a value for the relative coverage of nanosheets.

Crystallographic information was obtained with a D8 Discover diffractometer (Bruker AXS). Electron backscatter diffraction was performed on a Merlin field emission microscope (Zeiss) equipped with an angle selective backscatter detector. The electron backscatter diffraction data were analyzed by assuming a cubic SrRuO$_3$ crystal structure. In addition, an ultra-high vacuum Orion Plus helium ion microscope (Zeiss) equipped with an Everhardt–Thornley helium ion source was used.

The samples were cut to sizes of $17 \pm 2$ mm$^2$ after which magnetization measurements were conducted on a vibrating sample magnetometer (Physical Properties Measurement System by Quantum Design). The magnetic moments were determined as a function of the magnetic field and temperature, with the magnetic field applied parallel and perpendicular to the surfaces of the samples. The error bars and deviations used in this article all represent a confidence of 95% (two times the standard deviation).

### RESULTS AND DISCUSSION

**Influence of Nanosheets on the Morphology of Strontium Ruthenate.** As can be seen from the tapping mode atomic force microscopy (TM-AFM) images in Figure 1, the topography of SrRuO$_3$ was influenced by the underlying nanosheets. On the parts of the substrates that were not covered by nanosheets, larger and more separated grains were found than on the areas that did contain nanosheets. This observation is corroborated by the values for the root mean square (RMS) roughness. For SrRuO$_3$ on Ca$_2$Nb$_3$O$_{10}$ nanosheets, Ti$_{0.87}$O$_2$ nanosheets, and parts free from nanosheets, the RMS roughnesses were $R_q = 5.8$ nm, 4.4 nm, and 11 nm, respectively. These values are significantly larger than those measured for SrRuO$_3$ deposited on single crystalline substrates such as (001) SrTiO$_3$ (SrRuO$_3$ deposited on this substrate using the same conditions had an RMS roughness of $R_q = 0.24$ nm; see Supporting Information). Note that the AFM images of Figure 1 were made on samples with a relative sparse distribution of nanosheets. The reason to show these images is that the different morphologies of SrRuO$_3$ on and off the nanosheets are well visible. Similar film morphologies were obtained on densely packed monolayers of nanosheets (see Supporting Information), which were used for all further analysis and characterization.

Marked differences were observed between the morphologies of the films on Ca$_2$Nb$_3$O$_{10}$ and Ti$_{0.87}$O$_2$ nanosheets. The films on Ca$_2$Nb$_3$O$_{10}$ nanosheets (Figure 1a,b) were atomically smooth but contained deep trenches that formed a maze of nanostructures that meandered over the substrate. The trenches preferentially ran into two directions on a single nanosheet. This observation is also illustrated by the inset in Figure 1b, which shows the existence of fourfold symmetry in the two dimensional slope distribution analysis of the AFM image. The symmetry in the slope distribution analysis is a strong indication for epitaxy on the Ca$_2$Nb$_3$O$_{10}$ nanosheets, where facets follow preferred crystallographic planes of SrRuO$_3$. On Ti$_{0.87}$O$_2$ nanosheets the SrRuO$_3$ layer had a typical grain structure in which no such symmetry could be found (Figure 1c,d). Regardless of the type of nanosheets that was used, the morphologies of the films were not significantly influenced by changing the deposition pressure between 0.03 and 0.6 mbar, or the substrate temperature between 600 and 700 °C.

The observed strong variation in morphologies may be explained both by thermodynamic and kinetic considerations. Kinetically, roughness is determined by surface chemistries (e.g., surface charges, contaminations, or dislocations), which may affect sticking coefficients or diffusivities during deposition. Thermodynamically, roughness can be caused by stress or by large surface or interfacial energies.

X-ray diffraction and electron backscatter diffraction results discussed below indicated epitaxial growth of SrRuO$_3$ on the individual (single crystalline) nanosheets. Relatively large lattice mismatches between the nanosheets and SrRuO$_3$ and consecutive large elastic strain from registry of the two lattices led to rapid development of stress and may explain roughening of these films. The lattice mismatch for (001)$_{pc}$ oriented growth of SrRuO$_3$ ($d_{pc} = 3.928$ Å) on Ca$_2$Nb$_3$O$_{10}$ nanosheets ($d = 3.86$ Å) is +1.7 %. The mismatch for (110)$_{pc}$ oriented growth of SrRuO$_3$ on Ti$_{0.87}$O$_2$ nanosheets ($d = 3.76$ Å, $b = 2.97$ Å) is +4.3% parallel to the $a$-axis and −6.9% parallel to the $b$-axis of

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**Figure 1.** TM-AFM height images of SrRuO$_3$ deposited on Si substrates containing nanosheets. (a, b) Ca$_2$Nb$_3$O$_{10}$ nanosheets used as seed layer; (c, d) Ti$_{0.87}$O$_2$ nanosheets used. The inset in part b shows the slope distribution analysis from the corresponding AFM height image. The height profiles in part e were measured on the lines in parts b (upper red line) and d (lower blue line).
the nanosheets. (labels pc and c refer to a pseudo-cubic and cubic unit cell, respectively). For comparison, the lattice mismatch is +0.6% with SrTiO₃. The excessive growth of crystallites that was observed in between the nanosheets may be explained by suppression of nucleation due to absence of a periodic potential in the amorphous oxide layer on Si.

Large interfacial energies may also have caused roughening of the films. In particular, the (110)pc oriented film may have coarsened due to anisotropy in the surface energy. Generally in perovskite oxides, the (001)c planes have the lowest surface energy. The fact that the (001)pc oriented crystallites on Ca₂Nb₃O₁₀ nanosheets had atomically smooth surfaces and square-shaped facets, indicates that SrRuO₃ forms no exception to this generality. Therefore, the (110)pc oriented film may have preferentially formed (001)pc surface planes, thereby increasing its roughness. This theory is further enforced by the high roughness that was measured on the film deposited on (110) SrTiO₃ (Rₚ = 3.5 nm).

**Influence of Nanosheets on the Orientation of Strontium Ruthenate.** The X-ray diffraction (XRD) data in Figure 2a shows the result of θ−2θ scans on different films. The bottom curve was obtained from a sample where SrRuO₃ was deposited directly on a silicon substrate, the middle curve was obtained when a layer of Ti₀.₈₇O₂ nanosheets with a relative coverage of 96.3 ± 0.9 % was used and the top curve was obtained with a seed layer of Ca₂Nb₃O₁₀ nanosheets having a relative coverage of 95.7 ± 1.6%. When SrRuO₃ was directly deposited on silicon, no significant peaks other than those from the substrate were found. When Ti₀.₈₇O₂ nanosheets were used, the strongest peak was found at 2θ = 32.3°. A rocking curve was made at this angle by scanning ω in a window of 18° (Figure 2b). The full width at half maximum (FWHM) of this curve was 3.4°. A different orientation was measured on Ca₂Nb₃O₁₀ nanosheets, where peaks were observed at 2θ = 22.7° and 46.3°. In this case an additional peak was observed at 2θ = 44.4°, having an intensity of 4% compared to the peak at 2θ = 46.3°. The rocking curve that was made at 2θ = 46.3° had a FWHM of 1.3° (Figure 2c).

Control over crystallographic orientation by nanosheets is illustrated by the fact that film peaks were observed only when SrRuO₃ was deposited on nanosheets. The absence of film peaks in the case where SrRuO₃ was directly deposited on silicon can be explained by the lack of preferred orientation in this case, together with the absolute amount of material in our films. The peak observed for the film on Ti₀.₈₇O₂ nanosheets is matching well with the (110)pc orientation of SrRuO₃. Also, the (001)pc and (002)pc planes of SrRuO₃ diffract at angles where the two main peaks were found for the film on Ca₂Nb₃O₁₀ nanosheets. The ω rocking curves further confirmed preferred orientations of the crystallites when deposited on nanosheets. Thus, preferred out-of-plane orientations of the films were confirmed when interlayers of nanosheets were present.

The observed preferential out-of-plane orientation was in both cases expected from the lattice matching with the underlying nanosheets. After all, pseudo-cube on cube epitaxy of SrRuO₃ on Ca₂Nb₃O₁₀ nanosheets is most likely in the [001]pc direction, while the rectangular structure of the Ti₀.₈₇O₂ nanosheets will most likely promote growth in the [110]pc direction. Besides, epitaxy is likely in these directions because then the oxygen octahedra of the films and nanosheets are aligned, resulting in a continuous octahedral backbone through the nanosheets and films. The FWHM of the two rocking curves are significantly different, suggesting that the crystallites were more strongly oriented on Ca₂Nb₃O₁₀ than on Ti₀.₈₇O₂ nanosheets. This observation was also in accordance with our expectations, since the lattice mismatch between Ca₂Nb₃O₁₀ and SrRuO₃ is significantly smaller than the mismatch between Ti₀.₈₇O₂ and SrRuO₃.

The positions of the peaks for both SrRuO₃ on Ca₂Nb₃O₁₀ and Ti₀.₈₇O₂ nanosheets indicate that the films were free from strain (d₀₀₁ = 3.91 nm and d₁₁₀ = 2.77 nm). Most probably, elastic relaxation was accommodated by a large number of dislocations and grain boundaries in the films, which is in line with the observed morphologies, as discussed above. Another cause for release of strain may be found in the ‘flexible nature’ of the nanosheets, which may have resulted in a relaxed film on a strained seed layer. A rational condition for the latter explanation is that the nanosheets should not clamp to the substrate at the high deposition temperatures. Fractions of the film on Ca₂Nb₃O₁₀ nanosheets may have been compressively strained, as that would explain the presence of the small peak (d₂₀₁ = 2.04 nm). It is possible that a fraction of SrRuO₃ was strained by the unilamellar nanosheets or by thicker crystallites that had not been completely exfoliated into unilamellar sheets.

**Magnetic Anisotropy.** Temperature dependent magnetization measurements showed anisotropy when either a layer of Ti₀.₈₇O₂ or Ca₂Nb₃O₁₀ nanosheets was used, but not when
SrRuO$_3$ was directly deposited on Si (Figures 3 and 4). For both films on nanosheets, the easy axis was parallel to the surfaces. Fits of the saturation magnetization versus temperature to theoretical Brillouin functions with $J = 1, 4, \infty$ showed that all data were best followed by the Langevin functional dependency (i.e., $J = \infty$). Ferromagnetic behavior was measured up to $\sim 160$ K in all three cases (Figures 4 and 5). The only exception was found when the field was applied in the plane of the surface for the case of SrRuO$_3$ on Ca$_2$Nb$_3$O$_{10}$ nanosheets, where the Curie temperature was $\sim 6$ K lower.

The anisotropy in the magnetic response for films deposited on nanosheets clearly illustrates that the control over orientation had a significant effect on the properties of the films and was therefore of magnetocrystalline nature. In contrast to these results, the preferred direction of magnetization was measured to be out-of-plane when SrRuO$_3$ was deposited under the same conditions on (110) and (001) oriented SrTiO$_3$ substrates (see Supporting Information). The SrRuO$_3$ films on SrTiO$_3$ were compressively strained while those on nanosheets were free from strain. Due to the strong spin-orbit coupling in SrRuO$_3$, strain has a substantial effect on the magnetization. This was previously observed for SrRuO$_3$ on both (110) and (001) oriented SrTiO$_3$, where the strain was tuned between compressive and tensile by the introduction of a buffer layer.$^{34,35}$ In both of these cases, the easy axis rotated into the plane of the surface after changing the strain from compressive to tensile. Besides by strain, the direction of the easy axis may have been influenced by the roughness. Our films were found to be rougher on the nanosheets than on the SrTiO$_3$ substrates. The preference for out-of-plane magnetization due to the surface anisotropy may have been reduced because of the higher roughness of SrRuO$_3$ on the nanosheets. It is noted that on a macroscopic scale, our SrRuO$_3$ films were randomly oriented in the surface plane, because the nanosheet templates were also randomly oriented. On the other hand, the orientations of the films on the single crystalline substrates were

Figure 3. Magnetic hysteresis curves of SrRuO$_3$ films at 20 K, 120 K, and 160 K. The data were obtained from SrRuO$_3$ on (a) Ca$_2$Nb$_3$O$_{10}$ nanosheets, (b) Ti$_{0.87}$O$_2$ nanosheets, and (c) silicon without a layer of nanosheets. The data represented by the closed symbols were obtained by applying the magnetic field parallel to the plane of the surface, while the field was applied out of the plane for the data represented by the open symbols. The curves were obtained after extracting the diamagnetic background signals from the silicon substrates.

Figure 4. Temperature dependency of the saturation magnetization of SrRuO$_3$ on (a) Ca$_2$Nb$_3$O$_{10}$ nanosheets, (b) Ti$_{0.87}$O$_2$ nanosheets, and (c) silicon without nanosheets. The in-plane measurements (closed circles) and out-of-plane measurements (open circles) were fitted to Brillouin functions calculated from Weiss theory of ferromagnetism. With the assumption of zero external field and for different angular momenta ($J$), the theoretical curves were fitted (up to 155 K) to the data. Best fits were produced for different values of $J$ by an iterative process, where alternately the absolute saturation magnetization ($M_{S,abs}$) and the Curie point ($T_C$) were varied. $M_{S,abs}$ and $T_C$ where then chosen from the fit with the lowest least squares. Brillouin curves are shown for $J = 1, 4$ and $\infty$, where $J$ increases in the direction of the arrow.

Figure 5. Coercive field as a function of temperature for SrRuO$_3$ deposited on silicon containing Ca$_2$Nb$_3$O$_{10}$, Ti$_{0.87}$O$_2$, and no nanosheets. The data obtained with the field applied in the plane of the surface are represented by closed symbols, while the open symbols represent data obtained with the field applied out-of-plane. The solid lines are fits to a third order function and serve only to guide the eye.
fixed in all directions. The two classes of films were therefore especially different and only for this reason differences in the magnetization behavior are expected.

The measured Curie temperatures are close to the value measured for bulk SrRuO$_3$ ($T_c \approx 165$ K). When SrRuO$_3$ is strained, for example, by clamping on a substrate, the Curie temperature decreases. For example, Gan et al. found a Curie temperature of 150 K for SrRuO$_3$ on a (001) oriented SrTiO$_3$ substrate and showed that this temperature could be increased by 10 K after decoupling the film from the substrate. With respect to this study, the comparatively high Curie temperatures found in this work form yet another indication of relaxation of our films. The deviant value for the Curie temperature of SrRuO$_3$ on Ca$_2$Nb$_3$O$_{10}$ nanosheets may be explained by assuming that this film was partly strained, which is in line with the side peak observed in the XRD spectrum of Figure 2.

Signatures of high concentrations of defects were seen from the magnetization measurements, for instance by the high coercivity as plotted in Figure 5 and the large switching areas in the hysteresis curves of Figure 3. These observations can be explained by a large number of free poles, which add up to the magnetostatic energy of the system. Free poles are formed both at the grain boundaries and at imperfections (e.g. dislocations) inside the grains, the latter ones cause pinning of the domains during domain wall motion resulting in an increase of the coercive force (compared to films with less imperfections). We note that the magnetic characterization is in accordance with the AFM and XRD analyses, as all results indicate an abundance of grain boundaries and imperfections in the films. The coercive field was significantly lower when SrRuO$_3$ was deposited on Ca$_2$Nb$_3$O$_{10}$ than when it was deposited on Ti$_{0.87}$O$_2$ nanosheets. This observation is also in agreement with the XRD data, which indicated that crystal growth was controlled to a higher extent by Ca$_2$Nb$_3$O$_{10}$ than by Ti$_{0.87}$O$_2$ nanosheets.

The large concentration of defects and high roughness may explain the observed classical magnetic behavior by the Langevin functional dependency. Furthermore, the absence of a preferred in-plane orientation may have caused the total of all magnetic spins in our films to show classical rather than quantum mechanical behavior. Note that a vibrating sample magnetometer (VSM) is sensitive only for the complete magnetization of a sample. Therefore, no conclusions can be drawn on the magnetic behavior of SrRuO$_3$ on individual nanosheets.

**Control over the Crystallographic Orientation on a Single Substrate.** One of the great promises of nanosheets is that different kinds can be deposited on a single substrate to locally control the orientation of a film deposited thereon. To illustrate this concept, a mixture containing both Ca$_2$Nb$_3$O$_{10}$ and Ti$_{0.87}$O$_2$ nanosheets was made and transferred onto a single substrate. On top of this monolayer, SrRuO$_3$ was deposited.

After the deposition of nanosheets, a densely packed monolayer with a relative coverage of 95.7 ± 2.0 % was obtained (Figure 6). The two types of nanosheets could be distinguished in the AFM height images by their respective heights (Ti$_{0.87}$O$_2$ nanosheets have a thickness of 0.75 nm, while Ca$_2$Nb$_3$O$_{10}$ nanosheets are 1.44 nm thick). From the contrast in height, the relative coverage of Ti$_{0.87}$O$_2$ nanosheets was determined to be 69.6 ± 2.3 % and the relative coverage of Ca$_2$Nb$_3$O$_{10}$ to be 26.1 ± 2.8%. After PLD, both AFM (Figure 6b) and helium ion microscopy images (Figure 7) showed two clearly distinct surface morphologies on the SrRuO$_3$ film. Both a smooth layer containing trenches (typical for films on Ca$_2$Nb$_3$O$_{10}$ nanosheets) and more regular grains (typically observed on Ti$_{0.87}$O$_2$ nanosheets) were observed.

In the XRD spectrum (Figure 8), both peaks corresponding to the (00l)$_{pc}$ and (hh0)$_{pc}$ planes were found. The FWHM of the two peaks were a bit larger than those found when SrRuO$_3$ was deposited on a substrate with just one of the two

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**Figure 6.** TM-AFM height images of a monolayer of mixed Ca$_2$Nb$_3$O$_{10}$ and Ti$_{0.87}$O$_2$ nanosheets on silicon (a) before and (b) after deposition of SrRuO$_3$. The height profiles of the lines drawn in parts a and b are shown in part c.

**Figure 7.** Helium ion microscopy images of SrRuO$_3$ on mixed Ca$_2$Nb$_3$O$_{10}$ and Ti$_{0.87}$O$_2$ nanosheets on silicon. Two different regions are shown that are characteristic for SrRuO$_3$ on (a) Ca$_2$Nb$_3$O$_{10}$ and (b) Ti$_{0.87}$O$_2$ nanosheets (acceleration voltage was 35 kV, working distance was 5.5 mm and sample tilt was 20°).

**Figure 8.** (a) XRD patterns of SrRuO$_3$ on silicon containing both Ca$_2$Nb$_3$O$_{10}$ and Ti$_{0.87}$O$_2$ nanosheets. Rocking curves b and c were obtained with 2θ fixed at respectively 46.30° and 32.36°. Both rocking curves were fitted with two Gaussian functions.
The inverse pole figure maps and pole figures demonstrate that the orientation of the crystallites was controlled both parallel and perpendicular to the direction of growth. Particularly, the two pole figures clearly show that both (001)$_p$ and (110)$_p$ oriented SrRuO$_3$ had a single preferential orientation in all directions. This observation forms a strong indication for epitaxy, where the crystallographic orientations in the film were determined by the underlying nanosheets. The preference was clearer for the (001)$_p$ oriented part than for the (110)$_p$ oriented part. The difference is partly explained by the higher roughness of the film in the (110)$_p$ oriented areas, which led to a smaller band contrast in the diffraction patterns (Figure 9a). Besides, stronger deviations from the (110)$_p$ orientation were also indicated by the XRD patterns. Nevertheless, the single crystal orientations that were most clearly demonstrated by the two pole figures indicate that SrRuO$_3$ grew epitaxially on both Ca$_2$Nb$_3$O$_{10}$ and Ti$_{0.87}$O$_2$ nanosheets.

The magnetic characterization of the film on the mixed nanosheets is shown in Figure 10. We expect the magnetization properties of this sample to be the convolution of SrRuO$_3$ on Ca$_2$Nb$_3$O$_{10}$ and Ti$_{0.87}$O$_2$ nanosheets. Markedly, the preference was clearer for the (001)$_p$ oriented part than for the (110)$_p$ oriented part. The difference is partly explained by the higher roughness of the film in the (110)$_p$ oriented areas, which led to a smaller band contrast in the diffraction patterns (Figure 9a). Besides, stronger deviations from the (110)$_p$ orientation were also indicated by the XRD patterns. Nevertheless, the single crystal orientations that were most clearly demonstrated by the two pole figures indicate that SrRuO$_3$ grew epitaxially on both Ca$_2$Nb$_3$O$_{10}$ and Ti$_{0.87}$O$_2$ nanosheets.

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completely random in this case, and we are currently working on methods to control the positioning of nanosheets on a substrate. Such control may pave the way to advanced functional films where the properties are controlled locally by the crystallographic orientation.

**CONCLUSIONS**

Inorganic nanosheets of Ca$_2$Nb$_3$O$_{10}$ and Ti$_{0.87}$O$_2$ were placed on silicon substrates and used to control the nucleation of SrRuO$_3$ during growth by PLD. The nanosheets proved to influence both the crystallographic orientation and magnetic properties of the films. Magnetic anisotropy was measured when SrRuO$_3$ was deposited on one of the two nanosheets but not when it was deposited directly on a silicon substrate. The concept was explored by formation of SrRuO$_3$ films on a mixed monolayer comprising both types of nanosheets. Compared to films where the properties are controlled locally by functional films on a mixed monolayer comprising both types of nanosheets, nanosheets are still considered inferior because of poor control over their dimensions, shape, positioning, and orientations. However, nanosheets may offer unique advantages over costly single crystalline substrates. For example, previous work proves that nanosheets can be placed on all sorts of (amorphous) substrates to gain control over the crystallinity of films deposited thereon. With this article, we aim to show that another advantage is the local control over the nucleation of material, which allows tailoring the properties of a material on a (sub-)micrometer scale. Possibly, such control will be having important implications in various fields and will prove useful for applications in data storage and micro-electromechanical systems (MEMS).

**ASSOCIATED CONTENT**

**Supporting Information**

Surface pressure versus compression isotherms and AFM images of densely packed Ca$_2$Nb$_3$O$_{10}$ and Ti$_{0.87}$O$_2$ nanosheets before and after deposition of SrRuO$_3$. Analysis and magnetic characterization of SrRuO$_3$ on (001) and (110) oriented SrTiO$_3$. EBSD band contrast image showing the two areas from which pole figures were constructed. This material is available free of charge via the Internet at http://pubs.acs.org/.

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**Notes**

The authors declare no competing financial interest.

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