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Epitaxial growth and magnetic properties of the first five members of the layered $Sr_{n+1}Ru_nO_{3n+1}$ oxide series

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Epitaxial thin films of the $n=1-5$ members of the layered $Sr_{n+1}Ru_nO_{3n+1}$ oxide series were produced by reactive molecular-beam epitaxy. X-ray diffraction and high-resolution transmission electron microscopy confirm that these films are epitaxially oriented and nearly phase pure ($>98\%$). The Sr_2RuO_4 ($n=1$) and $Sr_3Ru_2O_7$ ($n=2$) samples show no ferromagnetic transition in the range from 5 to 300 K, while the $Sr_4Ru_3O_{10}$ ($n=3$), $Sr_5Ru_4O_{13}$ ($n=4$), and $Sr_6Ru_5O_{16}$ ($n=5$) samples show ferromagnetic transitions at 85, 95, and 130 K, respectively. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2430941]

The discovery of superconductivity[1] and the establishment of spin-triplet pairing[2,3] in single-layer Sr_2RuO_4, quantum metamagnetism in double-layer $Sr_3Ru_2O_7$,[4,5] and the possible presence of momentum-space magnetic monopoles in ferromagnetic, pseudocubic $SrRuO_3$ (Ref. 6) have led to intensive research on the layered $Sr_{n+1}Ru_nO_{3n+1}$ perovskite oxide series (the positive integer n corresponds to the number of perovskite layers sandwiched between double-SrO rocksalt layers). It was suggested that being in close proximity of the ferromagnetic phase $SrRuO_3$ is key for the occurrence of spin-triplet superconductivity in Sr_2RuO_4.[7] The crossover from ferromagnetism in $SrRuO_3$ to paramagnetism and spin-triplet superconductivity in Sr_2RuO_4 appears to originate from a structural crossover from a three-dimensional perovskite network in $SrRuO_3$ to a two-dimensional perovskite sheet in Sr_2RuO_4. Therefore, a systematic study of the behavior of $Sr_{n+1}Ru_nO_{3n+1}$ as dimensionality decreases may provide insight into the interplay between magnetism and superconductivity.

Attempts to explore the magnetic properties of intermediate $Sr_{n+1}Ru_nO_{3n+1}$ members ($1<n<\infty$) have been thwarted by the substantial challenges associated with the synthesis of phase-pure samples. Conflicting results on the magnetic properties of $Sr_3Ru_2O_7$ and $Sr_4Ru_3O_{10}$ have been reported,[4,8–14] even though "single crystals" (as determined by x-ray diffraction) of these phases have been produced.[4,8,10–14] Growing evidence in support of $Sr_3Ru_2O_7$ being a paramagnetic metal in zero field[4,8,13] has led to the widely held belief that intergrowths of higher n members were responsible for the ferromagnetic transition ($T_C=104$ K) previously observed in some $Sr_3Ru_2O_7$ single crystals.[9] Indeed, single crystals deemed phase pure by x-ray diffraction (XRD) were found to contain intergrowths when examined by transmission electron microscopy (TEM).[15] The challenge to the conventional synthesis of phase-pure $Sr_{n+1}Ru_nO_{3n+1}$ compounds considerably restricts access to these materials and lies at the heart of the controversy in the interpretation of existing experimental results.

Here we show that using reactive molecular-beam epitaxy (MBE), i.e., monolayer-by-monolayer deposition with a correct absolute dose of cations, $>98\%$ phase-pure $Sr_{n+1}Ru_nO_{3n+1}$ compounds can be made. The synthesis of nearly phase-pure samples by MBE allows their properties to be characterized.

The first five ($n=1-5$) members of the $Sr_{n+1}Ru_nO_{3n+1}$ series were synthesized by reactive MBE on (001) $SrTiO_3$ and (001) $(LaAlO_3)_{0.29}(SrAl_{1/2}Ta_{1/2}O_3)_{0.71}$ (LSAT) substrates. Prior to growth, the (001) $SrTiO_3$ substrates were etched with a buffered HF solution to achieve a TiO_2-terminated surface.[16] During growth the substrates were held at 620 °C and immersed in a continuous flux of molecular oxygen, yielding a background pressure of 1×10^{-6} Torr. Monolayer doses of Sr and Ru were deposited alternately on the substrates to form the perovskite layers in these structures. For the double-SrO rocksalt layers in these structures, a Sr dose corresponding to twice the monolayer dose was delivered. Shuttered reflection high-energy electron diffraction intensity oscillations during growth were used to monitor film stoichiometry.[17] The duration of the Sr and Ru doses from molecular beams was adjusted to ensure that a complete monolayer of each cation was deposited during each shuttered cycle. The growth of each Ruddlesden-Popper film was begun with a $SrRuO_3$ buffer layer to precisely calibrate the shuttering times.[17] Once calibrated, the shuttering sequence was altered to grow the desired $Sr_{n+1}Ru_nO_{3n+1}$ film. In this letter we focus on five $Sr_{n+1}Ru_nO_{3n+1}$ films with thicknesses of 877, 523, 648, 614, and 670 Å for the $n=1-5$ films, respectively.

Four-circle x-ray diffraction (XRD) studies on these thin films revealed the formation of single-phase and high quality samples with the desired $n=1-5$ Ruddlesden-Popper structures. Figure 1 shows the XRD θ-2θ scans of a Sr_2RuO_4 film

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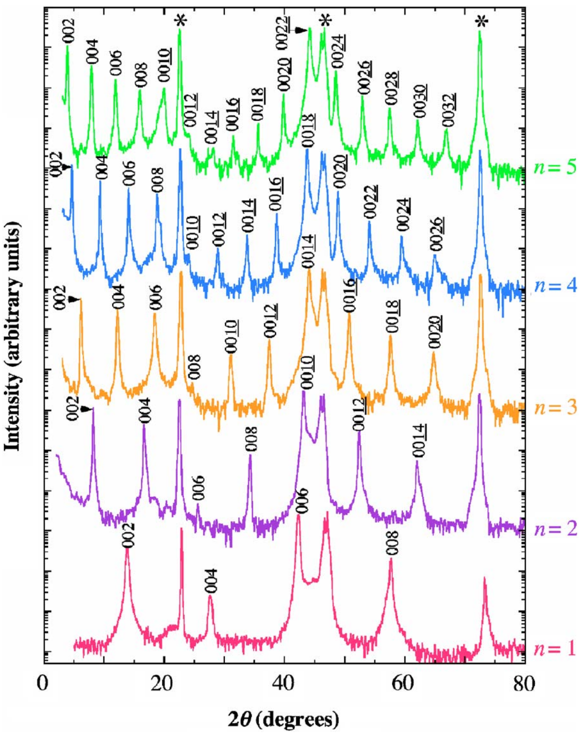

FIG. 1. (Color online) θ-2θ XRD scans of a Sr_2RuO_4 (n=1) film grown on a (001) LSAT substrate and n=2, 3, 4, and 5 $Sr_{n+1}Ru_nO_{3n+1}$ phases grown on (001) $SrTiO_3$ substrates. Substrate peaks are labeled with an (*), and the plots are offset for clarity.

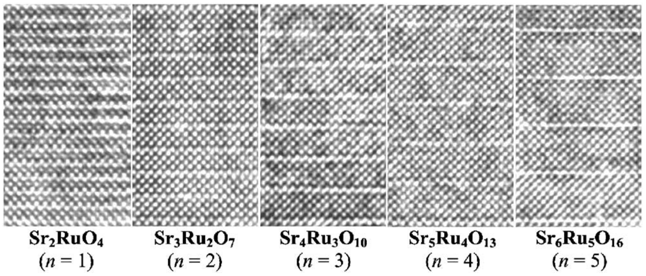

FIG. 2. Cross-sectional HRTEM images (from left to right) of the same n =1–5 $Sr_{n+1}Ru_nO_{3n+1}$ films shown in Fig. 1. The two adjacent white rows in the images correspond to the [100] projections of the rocksalt SrO layers. Between the double SrO layers lies the [100] projection of the $SrRuO_3$ perovskite sheet.

grown on a (001) LSAT substrate and $Sr_3Ru_2O_7$, $Sr_4Ru_3O_{10}$, $Sr_5Ru_4O_{13}$, and $Sr_6Ru_5O_{16}$ films grown on (001) $SrTiO_3$ substrates. All of the XRD peaks occur at 2θ positions consistent with the c axis of the films normal to the surface of the substrates. The c-axis lattice constants of these films as determined by a Nelson-Riley analysis[18] of the diffraction peak positions are 12.82±0.02, 20.85±0.05, 28.8±0.2, 37.2±0.4, and 44.7±1.0 Å for the n=1–5 phases, respectively. These values are slightly larger than the previously reported bulk values of $Sr_{n+1}Ru_nO_{3n+1}$ phases[11,19,20] with low n and lengthen by the amount expected (two $SrRuO_3$ sheets per unit cell) as n goes from n to $n+1$, consistent with an in-plane biaxial compressive strain being imparted on the films by the epitaxial growth on the (001) LSAT and $SrTiO_3$ substrates. The full width at half maxima of the rocking curves of the 006, 0010, 0014, 0018, and 0022 peaks of the n =1–5 samples are 0.091°, 0.049°, 0.056°, 0.042°, and 0.045°, respectively, indicating a high degree of structural perfection. XRD ϕ scans of off-axis (asymmetric) peaks were used to establish the in-plane orientations of the films. ϕ scans of the 103, 105, 107, 109, and 1011 peaks of the n=1–5 films, respectively, indicate an epitaxial in-plane orientation relationship of [100] $Sr_{n+1}Ru_nO_{3n+1} \parallel$[100] $SrTiO_3$ (LSAT).[23] Although the epitaxial films appear to be single phase by XRD, we used TEM to check for thin aperiodic intergrowths that are difficult to discern by XRD.[21,22]

High-resolution TEM (HRTEM) within a JEOL 4000EX operated at 400 kV was used to characterize the microstructure and atomic structure of the films. Figure 2 shows cross-sectional HRTEM images of the n=1–5 films with the incident electron beam along the [100] zone axis of the sample (film and substrate). The two adjacent white rows in the images correspond to the [100] projections of the rocksalt SrO layers. Between double-SrO layers lies the [100] projection of the $SrRuO_3$ perovskite sheet. The alternate stacking of the rocksalt SrO layers and the perovskite sheets observed in the image confirms the formation of the desired Ruddlesden-Popper structures. Selected area electron diffraction studies of these films corroborate the epitaxial orientations established by XRD. All of the imaged areas of the n=1 film display the identical contrast characteristic of the region shown in Fig. 2, with no intergrowths observed. Intergrowths of Ruddlesden-Popper layers with other n values (a half-unit-cell in thickness along the c direction) were, however, infrequently observed in the n=2–5 films. Such intergrowths exist in very localized regions and have insufficiently ordered volume to give rise to discernable diffraction spots in either XRD or electron diffraction. Although observable, the populations of the intergrowths are very small. Several representative regions imaged by HRTEM, which are typically 200–300 nm wide and span the entire film thickness, of each sample were analyzed to determine the volume fractions of the intergrowths. The statistics showed that the total volume fraction of the intergrowths is less than 2% of the imaged volume in all samples and none of the volume fractions of the individual intergrowths exceeds 0.6%.[23] In addition, the majority of the intergrowths are those with n values less than that of the film phase. In the n=5 film, all of the intergrowths have n values less than 5. We believe that the intergrowths in these samples are most likely the result of slight errors and variations in the monolayer doses supplied during the MBE growth. A comprehensive description of the microstructure of the films will be published elsewhere.[23]

The magnetization versus temperature of the *same* films studied by XRD and TEM was measured using a commercial superconducting quantum interference device magnetometer in a 0.005 T magnetic field aligned perpendicular to the sample plane after precooling in a 1 T field. The temperature-dependent magnetization of bare LSAT and $SrTiO_3$ substrates was measured to subtract the magnetic contribution of the magnetic impurities present in the substrates. The contribution of the thin $SrRuO_3$ (ferromagnetic with a $T_C \approx 160$ K in bulk[24]) buffer layer to the out-of-plane magnetization was also subtracted by assuming that the magnetic moment per Ru atom in the $SrRuO_3$ buffer layer and its temperature dependence are identical to those obtained from an 847 Å thick $SrRuO_3$ film grown by MBE using the same growth conditions as the $Sr_{n+1}Ru_nO_{3n+1}$ films. This assumption should be valid since all of the $SrRuO_3$ buffer layers have a thickness ($\geq$6 pseudocubic $SrRuO_3$ unit cells) that in other studies has been found to yield the out-of-plane mag-

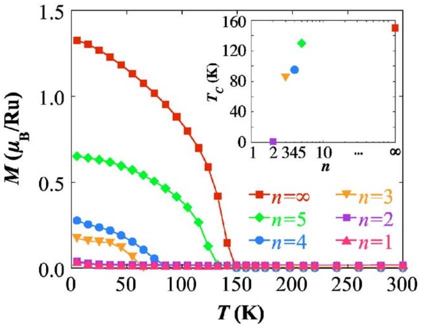

FIG. 3. (Color online) Magnetization as a function of temperature of the same $n=1-5$ $Sr_{n+1}Ru_nO_{3n+1}$ films shown in Figs. 1 and 2 and $n=\infty$ $Sr_{n+1}Ru_nO_{3n+1}$ film. Note that the $n=3$, 4, 5, and ∞ samples show ferromagnetism, while no sign of ferromagnetism is observed for the $n=1$ and $n=2$ samples. The inset shows a plot of the ferromagnetic transition temperatures of the $n=3$, 4, 5, and ∞ $Sr_{n+1}Ru_nO_{3n+1}$ samples vs n. For the sake of comparison, the metamagnetic phase transition temperature ($\sim$1.1 K) of the $n=2$ ($Sr_3Ru_2O_7$) single crystal in a magnetic field of 7.9 T (data from Ref. 5) is also shown.

netization of bulk $SrRuO_3$.[25,26] Figure 3 shows the magnetic moment per Ru atom as a function of temperature in the range from 5 to 300 K for the $n=1-5$ and ∞ samples, after the corresponding substrate and buffer layer subtraction. The curves reveal that the $n=3$, 4, and 5 samples are ferromagnetic, while no sign of ferromagnetism is observed in the $n=1$ and 2 samples. The transition temperatures (T_C) of the ferromagnetic phases were determined by the onset of the magnetization in the $M(T)$ curves. The obtained T_C values are 85, 95, 130, and 150 K for the $n=3$, 4, 5, and ∞ samples, respectively. The n-dependent magnetic behavior is evident (inset in Fig. 3). For the sake of comparison, the metamagnetic phase transition temperature ($\sim$1.1 K) of the $n=2$ ($Sr_3Ru_2O_7$) single crystals[5] in a magnetic field of 7.9 T is also shown in the inset.

The deviation of T_C for the $SrRuO_3$ thin film (150 K) from the bulk value [160±10 K (Ref. 24)] is consistent with previous reports that found such a T_C reduction to be due to the strain imparted by commensurate growth on a $SrTiO_3$ substrate.[27,28] Similarly, the deviation of T_C for the $Sr_4Ru_3O_{10}$ thin film from the reported value [$\sim$100 K (Ref. 29)] of single crystals is believed to be due to epitaxial strain. The saturation moment of the $SrRuO_3$ film ($\sim 1.3\mu_B$/Ru) is comparable to the values previously reported for epitaxial $SrRuO_3$ thin films grown on (001) $SrTiO_3$ substrates.[27,28] In contrast, the saturation moment ($\sim 0.2\mu_B$/Ru) of the $Sr_4Ru_3O_{10}$ thin film is significantly smaller than the values ($\sim 1.5\mu_B$/Ru) reported for single crystals.[29] The origin of the reduced moment for the thin film samples is unclear, although magnetism in the ruthenates is extraordinarily complicated and it is quite possible that the strain from the substrate is responsible for the difference. Further study, perhaps with neutron scattering, would be necessary to explore the details of the magnetic structure.

In closing, our data suggest that reduced dimensionality in the $Sr_{n+1}Ru_nO_{3n+1}$ series leads to a systematic reduction in ferromagnetism. The minimum value of ferromagnetism ($n=3$) corresponds to the case where at least one RuO_2 sheet in the structure is surrounded by RuO_2 sheets from above and below. For $n=1$ and 2 $Sr_{n+1}Ru_nO_{3n+1}$ phases, no RuO_2 sheets are surrounded by RuO_2 sheets, resulting in the loss of ferromagnetism.

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