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Epitaxial growth of metastable Ba_2RuO_4 films with the K_2NiF_4 structure

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Epitaxial Ba_2RuO_4 films with the K_2NiF_4 structure have been grown by pulsed laser deposition on (100) $SrTiO_3$ substrates. X-ray diffraction and cross-sectional transmission electron microscopy results indicate that the films are *c*-axis oriented, single-domain, and contain relatively few stacking faults and intergrowths. Electrical measurements indicate metallic conductivity to low temperatures, but no evidence of superconductivity. © *1999 American Institute of Physics.* [S0003-6951(99)04923-2]

Sr_2RuO_4 is unique in several ways, including its being the only known layered perovskite superconductor that does not contain copper ($T_c = 1.5$ K in single crystals).[1,2] Sr_2RuO_4 has the K_2NiF_4-type tetragonal structure, making it isostructural with $La_{2-x}Ba_xCuO_4$ the first high-T_c superconductor discovered.[3] There is increasing evidence that Sr_2RuO_4 is an unconventional odd-parity (*p*-wave) superconductor.[4–8] Ruthenates with structures related to Sr_2RuO_4 are of great interest in terms of discovering other ruthenate superconductors, and establishing the characteristics of Sr_2RuO_4 responsible for its unusual superconducting behavior.

Owing to the observation that hydrostatic pressure reduces the superconducting transition temperature (T_c) of Sr_2RuO_4,[9] the substitution of the larger Ba^{2+} ion for Sr^{2+} is interesting from the standpoint of potentially increasing T_c. Substituting Ba^{2+} for Sr^{2+} is an obvious way to apply negative chemical pressure, provided the structure remains of the K_2NiF_4 type. Utilizing such ''chemical pressure'' (negative in this case) is common in superconducting research.[10]

However, Ba_2RuO_4 is not isostructural with Sr_2RuO_4 when synthesized at atmospheric pressure.[11–13] Nonetheless, using pressures of 64 000 atm., Kafalas and Longo[11] were able to synthesize (polycrystalline) Ba_2RuO_4 with the K_2NiF_4 structure, i.e., the same structure as Sr_2RuO_4. Although this high-pressure route is a reasonable way to make *polycrystalline* Ba_2RuO_4, such samples may not exhibit the intrinsic transport properties (including possible superconductivity) of Ba_2RuO_4. Superconductivity was not observed in polycrystalline Sr_2RuO_4.[1] Yet growing extremely pure (impurity levels of 430 ppm are sufficient to destroy superconductivity in Sr_2RuO_4)[5] single crystals at 64 000 atm. is unlikely to be easy. An alternative is to make epitaxial films of Ba_2RuO_4 at low pressures, by utilizing an epitaxial template that stabilizes the growth of the metastable K_2NiF_4-type polymorph of Ba_2RuO_4.

Here we report the use of epitaxial stabilization—the use of interfacial strain to favor the desired metastable phase over the equilibrium phase[14–16]—to grow tetragonal Ba_2RuO_4 with the desired K_2NiF_4 structure ($a = 3.99$ Å and $c = 13.43$ Å).[11] Commercially available (100)-oriented single crystal substrates were selected having lattice constants close to those of the desired metastable Ba_2RuO_4 structure. These substrates included MgO (cubic rocksalt, $a = 4.21$ Å),[17] $MgAl_2O_4$ (cubic spinel, $a = 8.08$ Å),[17] $LaSrGaO_4$ (tetragonal K_2NiF_4, $a = 3.84$ Å, $c = 12.68$ Å),[18] $LaAlO_3$ (cubic perovskite,[19] $a = 3.81$ Å at 500 °C),[17] $LaAlO_3$–Sr_2AlTaO_6 (LSAT, cubic perovskite, $a = 7.737$ Å),[20] and $SrTiO_3$ (cubic perovskite, $a = 3.905$ Å).[17] Of these substrates, only $SrTiO_3$ yielded epitaxial films of the desired metastable polymorph of Ba_2RuO_4. The good structural match of $SrTiO_3$ with the *a* axis of the desired form of Ba_2RuO_4 encourages it to grow with its *c* axis perpendicular to the (100) substrate (*c*-axis oriented Ba_2RuO_4 films). Although the perovskite $KTaO_3$ is available commercially and has a lattice constant of 3.99 Å (an excellent lattice match to the desired polymorph of Ba_2RuO_4), it suffers from significant potassium loss at substrate temperatures (T_{sub}) of about 800 °C or greater.[21] As described below, the growth of Ba_2RuO_4 by pulsed laser deposition (PLD) requires $T_{sub} \gtrsim 1000$ °C, making the use of $KTaO_3$ as a substrate material impractical. Note that although other nonisostructural substrates had better lattice match (e.g., $MgAl_2O_4$ with a 2:1 lattice match of 1.3%), it was only the isostructural perovskite substrate with the closest lattice match (−2.1%) that worked. Our results are in agreement with the theory of epitaxial stabilization emphasizing the importance of isostructural and lattice matched substrates.[14]

Films were grown *in situ* by on-axis PLD using a KrF excimer laser (248 nm, Lambda Physik EMG103MSC) on single crystal (100) $SrTiO_3$ wafers located 7.5 cm from a stoichiometric Ba_2RuO_4 target (99.9% purity, Target Materials, Inc.) and heated radiatively[22] to a substrate temperature of 1000 °C. Oxygen background pressures of 0.7×10^{-5} to 2.9×10^{-5} Torr, a laser pulse energy of 160 mJ, a laser energy density of 2.7 J/cm^2, and a laser repetition rate of 2 Hz were used for deposition. The resulting films were about 1500 Å thick. After growth the films were cooled in the same oxygen partial pressure in which they were grown. These

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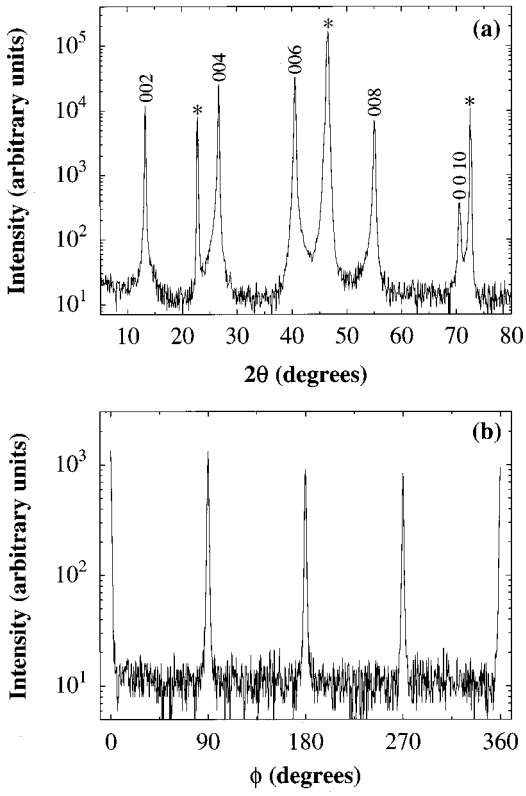

FIG. 1. Four-circle x-ray diffraction scans of a ~1500-Å-thick *c*-axis oriented Ba_2RuO_4 film grown on a (100) $SrTiO_3$ substrate at $P_{O_2}=2.5\times10^{-5}$ Torr. (a) θ–2θ scan and (b) ϕ scan of the Ba_2RuO_4 103 reflection. The substrate peaks are marked (*). $\phi=0$ is along the [001] $SrTiO_3$ direction.

growth conditions are similar to the conditions that we found to work for Sr_2RuO_4 epitaxial films.[23,24] We note that the low oxygen pressures and high temperatures found necessary for the synthesis of epitaxial Sr_2RuO_4 films are in reasonable agreement with the thermodynamic measurements of Mallika and Sreedharan.[25,26] For Ba_2RuO_4, oxygen pressures

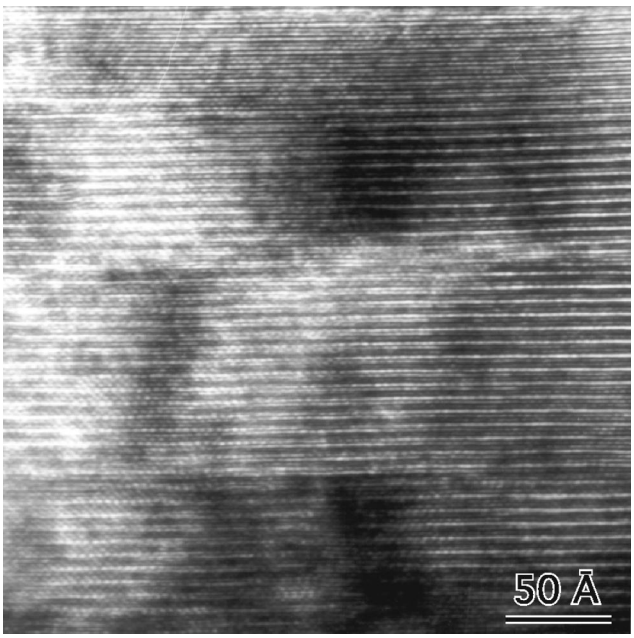

FIG. 2. Cross-sectional TEM image of a ~1500 Å thick *c*-axis oriented Ba_2RuO_4 film grown on a (100) $SrTiO_3$ substrate at $P_{O_2}=1.3\times10^{-5}$ Torr.

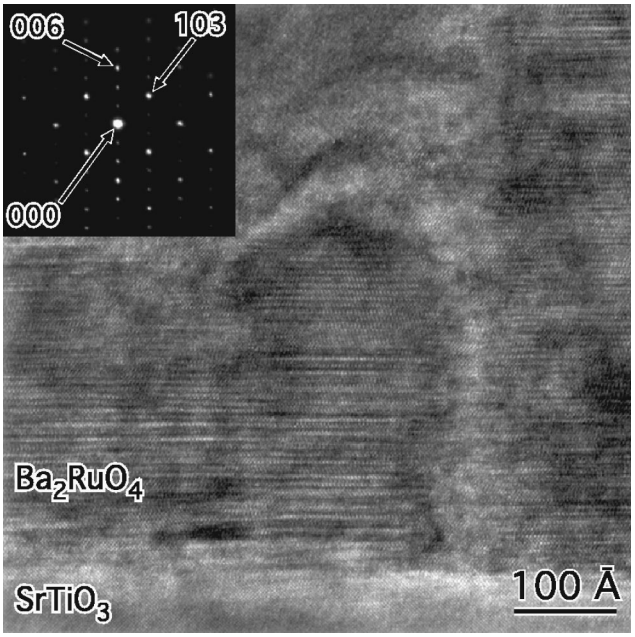

FIG. 3. Cross-sectional TEM image of the substrate/film interface of the same Ba_2RuO_4 film whose x-ray diffraction patterns are shown in Fig. 1. The inset electron microdiffraction pattern is from a single subgrain along the $[0\bar{1}0]$ zone axis. The Ba_2RuO_4 films are very sensitive to beam damage; several seconds after taking this image the amorphous region seen in this image grew to occupy the entire field of view.

about an order of magnitude higher than those used to grow Sr_2RuO_4 by PLD were found to be optimal.

The films were characterized using a four-circle x-ray diffractometer with Cu $K\alpha$ radiation. A θ–2θ scan of a Ba_2RuO_4 film [see Fig. 1(a)] shows it to be *c*-axis oriented with $c=13.35\pm0.01$ Å. The full-width at half-maximum (FWHM) of the 006 peak is 0.25°, and the rocking curve FWHM of the 006 peak is 0.70°.[27] Figure 1(b) shows a ϕ scan of the 103 Ba_2RuO_4 reflection of this same film. The sharp peaks at $\phi=0°$, 90°, 180°, and 270°, indicate that the film is single domain with the ⟨100⟩ directions of the film aligned with the ⟨001⟩ in-plane directions of the substrate. The FWHM of the 103 peak in ϕ is 1.3°. From this scan, the *a*-axis lattice parameter was calculated to be $a=4.00\pm0.05$ Å. The lattice constants of the film agree with those reported for the desired tetragonal polymorph of Ba_2RuO_4 with the K_2NiF_4 structure.[11]

Cross sections for high-resolution transmission electron microscopy (HRTEM) were prepared by slicing the substrate along (010), sandwiching the film-bearing face with a piece of silicon using M-Bond (Measurements Group, Inc.), and slicing the sandwich along the substrate [001] direction. TEM samples were prepared from the slices by polishing, mounting to a molybdenum ring, dimpling, and cold-stage ion milling (Gatan cold-stage duomill, Ar, 11°, 4 keV). TEM samples were examined in a Hitachi HF2000 field-emission TEM.

Several films were imaged by HRTEM. The results indicated relatively few stacking faults, as seen in Fig. 2. Slight circumferential smearing of the reflections was noted in some [010] microdiffraction patterns, indicating variation in the *c*-axis direction of subgrains of the tetragonal Ba_2RuO_4 thin film. The local order within subgrains was observed to be high, as shown by the image and microdiffraction pattern

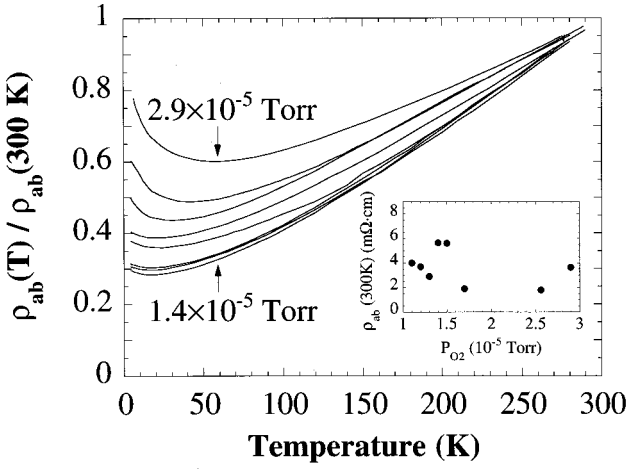

FIG. 4. In-plane resistivity normalized by its value at $T=300$ K [ρ_{ab} (300 K)] for epitaxial Ba_2RuO_4 films grown in various oxygen background pressures (P_{O_2}). From top to bottom, the P_{O_2} values in units of μTorr are: 29, 17, 15, 12, 25, 11, 13, and 14. The inset shows the resistivities of the films at room temperature.

in Fig. 3. The films are metastable, and may also be sensitive to water. Many films observed to be epitaxial by θ–2θ and ϕ x-ray diffraction scans were amorphized during TEM sample preparation. It is not known whether humidity, wet polishing, ion beam damage, or a combination of these caused the amorphization of the films. But, once sample preparation was modified to eliminate all exposure to water, to limit exposure to humidity and elevated temperatures, and to use only cold-stage ion milling techniques, good TEM samples were obtained. The films also amorphized rapidly during observation in the TEM, limiting the time allowed to image regions of the film.

The normalized in-plane electrical resistivity (measured using a four-point method) of several epitaxial films grown at various oxygen pressures yielding single-phase Ba_2RuO_4 are shown in Fig. 4. As the film thickness was not precisely measured for these films, the resistivity is nominal. The room temperature resistivities of these films are shown in the inset of Fig. 4. It is seen that these Ba_2RuO_4 films show metallic conductivity at high temperatures and are insulating at lower temperatures. Prior to the present work, the only electrical (or magnetic) property reported for the K_2NiF_4 polymorph of Ba_2RuO_4 is that in polycrystalline form it has a room temperature resistivity of 22 mΩ cm.[13] Although metallic properties were obtained, no superconductivity was found in these films down to 0.3 K. Given that only high purity single crystals of Sr_2RuO_4 exhibit superconductivity,[5] higher purity Ba_2RuO_4 targets and a better lattice-matched perovskite substrate for the growth of Ba_2RuO_4 might be required to address the question of superconductivity in this metastable ruthenate.

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[27] The narrowest FWHMs observed were 0.24° in 2θ and 0.38° in ω for the 006 peak of a Ba_2RuO_4 film grown at $P_{O_2}=1.4\times10^{-5}$ Torr.