Perspective: Rapid Synthesis of Complex Oxides by Combinatorial Molecular Beam Epitaxy

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The molecular beam epitaxy technique is well known for producing atomically smooth thin films as well as impeccable interfaces in multilayers of many different materials. In particular, molecular beam epitaxy is well suited to the growth of complex oxides, materials that hold promise for many applications. Rapid synthesis and high throughput characterization techniques are needed to tap into that potential most efficiently. We discuss our approach to doing that, leaving behind the traditional one-growth-one-compound scheme and instead implementing combinatorial oxide molecular beam epitaxy in a custom built system.

Complex oxides that contain transition metals have garnered a great deal of interest in recent years due to the potential they hold for next generation technologies. A wide variety of electronic and magnetic phases can be found in these materials, such as multiferroicity, high-temperature superconductivity (HTS), colossal magnetoresistance, and high mobility electron gases.[1] The diversity of behaviors realized in these systems typically originate from strongly correlated electrons bound up in the *d*-orbitals of these compounds. When two different complex oxides are brought together charge transfer, chemical interactions, and competition between ground states in the constituent materials can all give rise to an even wider range of interesting phenomena at the interface than can be observed in the base materials alone.[2]

The synthesis of high quality samples of complex oxides frequently poses substantial challenges. Because these compounds contain at least two, and frequently more, elements in addition to oxygen, several thermodynamically stable phases can form from the same constituents. Hence, producing single-phase samples with good control over stoichiometry is not always straightforward and may require sophisticated techniques. Moreover, these materials frequently exhibit complicated electronic phase diagrams as a function of doping, and hence a thorough examination of the doping-dependent properties of a given material family necessitates the production of numerous samples. In addition, for many applications we are in fact interested in interfacial effects between different complex oxides, or in the properties and operation of engineered multilayer devices. In this case, the method used to produce the samples should allow for layer-by-layer growth so that interfaces are clearly defined.

To address these issues we employ a custom-built oxide molecular beam epitaxy system that allows for atomic-layer-by-layer (ALL) synthesis with a high degree of control over film growth[3]. Molecular beam epitaxy (MBE) is an ultra-high vacuum technique for the deposition of thin films that is well known for the high quality of samples that can be produced[4,5]. This is particularly true for complex oxides when compared to other thin film growth techniques.[6] Atomic or molecular beams, typically produced from resistively heated thermal evaporation sources (electron-beam and other specialty sources are used for some particular materials) slowly deposit material onto heated substrates. The substrate temperature is held within a temperature window that is high enough that the arriving atoms have a large surface mobility, which ensures that they can fill the empty places in the growing atomic layer and we obtain single crystal films that are atomically smooth. However, the growth temperature is low enough that bulk mobility and diffusion are almost negligible, allowing us to grow superlattices with clean interfaces as well as other metastable structures. Our system[3] is equipped with sixteen metal sources, which are shuttered, and a sixteen-channel real-time rate monitoring system based on atomic absorption spectroscopy. A scanning quartz crystal monitor is used to determine the absolute flux rate to within one percent error before each growth. The sources are held at a constant temperature (± 0.1 ºC) so that the flux from each source remains very stable (<< 1% change). With the real-time feedback and computer control of the shutter times and sequencing the entire deposition

process is controlled very accurately, at a level of better than one percent of an atomic monolayer, thus providing atomic-layer-by-layer growth. The control software allows one to modify the stoichiometry within each monolayer that is grown, providing great flexibility in depositing different HTS compounds and other oxides. In particular, the ALL-MBE technique is well suited to depositing alternating layers with a precision better than a single atomic-layer, and hence for synthesis of artificial superlattices. The MBE system is also provided with a reflection high-energy electron diffraction (RHEED) system for real-time information about the film surface morphology and a time-of-flight ion scattering and recoil spectroscopy (TOF-ISARS) system for *in situ* chemical analysis of the film surface.[3]

While the quality of thin films produced by the ALL-MBE technique can be very high the tradeoff is that the growth rate of these films is quite low. This is clearly undesirable when trying to perform experiments that call for a wide range of doping levels within a specific class of materials or when carrying out new materials discovery in general. In these situations techniques that provide one composition per growth are too slow and inefficient. A better alternative is combinatorial synthesis in which several compounds are grown simultaneously on the same substrate. Combinatorial synthesis of oxides has been performed by several groups through creative use of arrangements of physical masks that are stationary, movable, or a combination of each.[7-14] A very wide range of compounds can be produced this way. Depending on the deposition method, the resulting library of compounds is then thermally treated to promote mixing of the constituent materials that were deposited through the masks.[7-11] One drawback to this is that after the solid-state reactions what may form at each of the different "pixels" (individual members of the library) are different mixtures of various thermodynamically stable phases. Annealing after film growth is not always necessary, however, as in the case of combinatorial pulsed laser deposition. The moving masks in these systems are used to grow layer-by-layer films on heated substrates with layers that are wedge shaped and do not need a post growth thermal treatment to mix.[12,13]

Another approach to oxide combinatorial synthesis relies on producing deliberately a gradient in the deposition rates at the substrate surface, for each of multiple deposition sources. The variable rates at different locations on the substrate from each source results in a continuous coverage of stoichiometrically different compounds being deposited at each location. This has proven successful with off-axis sputtering[15] and pulsed laser deposition[16-18] and is the approach that we take here.[19] The sources in our MBE system are not aimed perpendicularly to the substrate but rather at a shallow angle (20º from parallel). The effect at the substrate is that the molecular beam flux on the side closest to the source is higher than on the side furthest from the source, which produces a compositional gradient along the substrate surface (Fig. 1a). Note that this gradient can be removed by using two sources that are on opposite sides of the vacuum chamber from one another, and that deposit the same material at the same rate. Use of these conjugate pairs of sources is important to maintain the proper balance of atoms arriving at the substrate (Fig. 1b). If it is not controlled carefully then secondary phases will unintentionally form that will ruin the quality of the combinatorially grown film. Note that films are grown on crystallographically matching single-crystal substrates, at a high substrate temperature (typically 650-750 ºC) and exposed to pure ozone. Thus, we synthesize epitaxial films that are locally single-phase and highly crystalline, and thus very suitable for study of intrinsic physical properties of materials with different doping levels.

To fully realize the benefits in terms of speed of materials exploration that the combinatorial growth technique offers it is necessary to study these types of samples using high throughput characterization methods. An excellent example of rapid characterization of combinatorial material libraries is found in the discovery of phosphors for display applications.[9-12] The entire combinatorial library of materials is illuminated at once by UV light and a simple visual check is all that is needed to determine which materials are suitable for further investigation and which are not. Optical properties remain an important trait for quickly studying certain classes of materials. For some others, such as dielectrics and materials that display electric and/or magnetic ordering, scanning probe techniques can be used to quickly characterize combinatorial libraries.

The important properties in the cuprate superconductors that we are interested in are their longitudinal and Hall resistivities as functions of temperature and magnetic field. Our one-dimensional combinatorial libraries are patterned into a Hall bar (Fig. 1c) that runs nearly the entire length of our (10 mm × 10 mm) substrates. Pairs of voltage contacts are located at 31 equally spaced positions along the Hall bar so that 30 longitudinal resistivity or 31 Hall resistivity measurements can be taken in each library. The sample is mounted in a gas-flow cryostat that contains an array of 64 pogo pins that make connections to electrical contact pads on the sample surface. The Hall bar is biased with a low frequency AC current while custom built electronics with 32 lock-in amplifiers measure the relevant voltages along the bar.[20] A multiplexer switches between longitudinal and transverse measuring modes.

With this system we can examine the entire combinatorial library in just one day, which neatly matches our rate of sample production so there are no bottlenecks in the process.

The material synthesis and measurement techniques described above have been applied in several of our studies of cuprate superconductors. For instance, superconductivity was discovered in bilayers of undoped $LaCuO_4$ grown on top of heavily overdoped $La_{1.55}Sr_{0.45}CuO_4$, even though neither compound itself is superconducting ($LaCuO_4$ is an insulator while $La_{1.55}Sr_{0.45}CuO_4$ is a metal).[21] Owing to the ALL-MBE technique the interface between these two materials is sharp with very little strontium interdiffusion, limited to a length scale of less than one unit cell, as determined by resonant inelastic x-ray scattering. Rather, mobile charge carriers move from the overdoped side to the underdoped side of the bilayer and it is this "doping without disorder" scenario that accounts for the interface superconductivity in this material system.[22] The width and the exact location of the highest temperature superconductivity were pinpointed by a study using zinc δ-doping tomography, i.e., zinc substitution in a selected single copper oxide plane, which was varied from one film to another.[23] After all of this, however, the question remained about what the role of the doping level in the base layer was, as it was shown several years earlier that in trilayers with insulating $LaCuO_4$ and optimally doped $La_{1.84}Sr_{0.16}CuO_4$ the respective anti-ferromagnetic and HTS phases do not mix, even at the level of one unit cell.[24]

Combinatorial molecular beam epitaxy was employed to help answer this question. Several samples were grown with a combinatorial spread in the doping of the base layer such that we covered the range from very overdoped ($x = 0.45$) all the way to optimal doping ($x = 0.16$). Because of the large number of compounds that can be fabricated at one time by combinatorial growth techniques we were able to examine more than 800 unique base layer doping levels while performing only 5% that number of film growths, saving considerable time and resources. Surprisingly, we found that the base layer doping has little effect on the observed critical temperature, T_c, in these bilayers.[25] This can be understood qualitatively by taking into account the charge profile on each copper oxide plane in the vicinity of the interface and what that tells us about where the highest critical temperature superconductivity is located. The zinc doping study showed that for heavily overdoped base layers ($x = 0.45$), HTS occurs in the second copper oxide plane from the geometrical interface. The first copper oxide plane from the interface is overdoped with a lower T_c. As the base layer doping is reduced there are less mobile charge carriers available to spill over into the $LaCuO_4$ and eventually that second copper oxide layer from the interface becomes underdoped while at the same time the first copper oxide layer from the interface becomes doped close to the optimal level. So while the position of the highest T_c layer changes, one of the layers is always close to optimally doped and has the corresponding high critical temperature. While this explanation captures our observations qualitatively, the expected variation in T_c from such a simple model is actually much larger than what is observed. Our data are much better fit quantitatively by further assuming an atypical chemical potential which varies linearly on the overdoped side of the phase diagram but becomes doping independent below optimal doping. While certainly unusual, this picture is corroborated by independent studies of cuprate films by angle resolved photoemission spectroscopy.[26]

The manner in which we obtain a range of compositions from shallow-angle sources is ideally suited for studying compounds that exhibit quantum critical points driven by chemical doping. The combinatorial spread in beam flux is linear over a distance of at least 4 cm in our system as measured by a scanning quartz crystal monitor and is about 4% from one side of our 10 mm × 10 mm substrate to the other. Therefore when we grow $La_{2-x}Sr_xCuO_4$ the resulting spread in strontium doping is 4% of the average doping across the substrate. A larger spread could be achieved with larger substrates but in our case crystalligraphically appropriate substrates are not available (or are prohibitively expensive) in larger sizes. At the critical point on the underdoped side of the superconducting dome, $x = 0.06$, a total spread of $\Delta x = 0.0024$ is obtained. If the one dimensional combinatorial library is then patterned as shown in Fig. 1c then the difference in nominal doping from pixel to pixel is extremely small, $\Delta x = 0.000072$. Several $La_{2-x}Sr_xCuO_4$ thin film samples with this layout were studied with a focus on observing what happens to the Hall effect at the superconductor-to-insulator quantum critical point. The magnetoresistance of those pixels with doping levels that put them in the insulating phase become hysteretic at low-temperature ($T < 1.5$ K), with erratic switching that increases upon further cooling. Pixels with doping levels slightly higher than the critical doping are superconducting, however hysteretic behavior can be restored by application of an external magnetic field. These observations point to the existence of a charge glass, with quantum charge fluctuations that disappear when superconductivity emerges but that can be restored by an applied magnetic field.

Complex oxides display many interesting phenomena and are potentially useful in future applications making them an important part of current materials research. Combinatorial atomic layer-by-layer molecular beam

epitaxy is the choice synthesis technique for producing the highest quality thin film and multilayer samples of these materials rapidly and over a range of alloying that can span an entire family of compounds.

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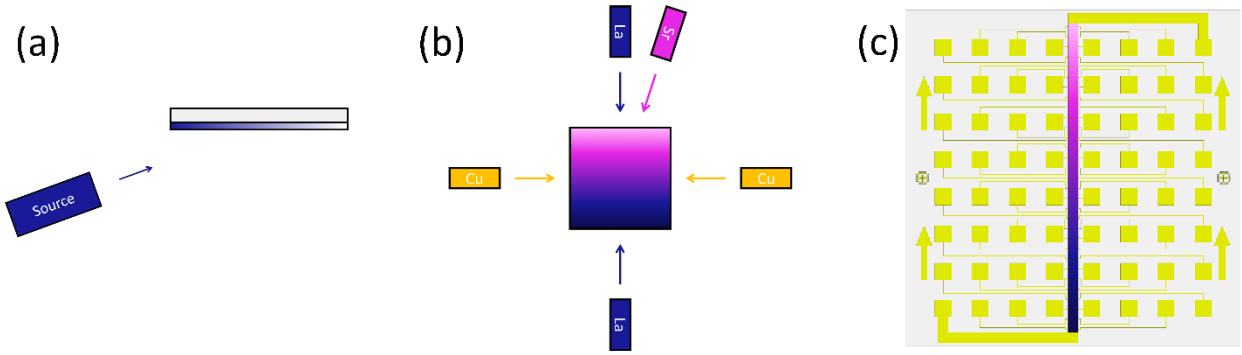

FIG. 1. (a) Side view illustration of a shallow angle source that makes combinatorial MBE synthesis possible. The beam flux varies linearly across the substrate surface with the side of the substrate that is closest to the source receiving the highest flux. (b) During the growth of a combinatorial sample of a complex oxide several sources are used in unison, as shown in this diagram depicting the growth of a one dimensional combinatorial library of $La_{2-x}Sr_xCuO_4$ (the view here is from below looking up at the sample surface). The beam flux gradients from the opposing copper sources cancel each other, leading to a constant copper deposition rate. The strontium deposition rate is adjusted to fix the desired doping level at the center of the library. The deposition rate from the lanthanum source next to the strontium source is adjusted so that their combined rate matches that of the opposite lanthanum source (which is the same as the combined rate from the two copper sources). Two dimensional libraries can be produced by using even more sources. For instance, in the example above a zinc source could be used with one of the copper sources to examine the effect of zinc substitution in the copper oxide planes in addition to doping of a cuprate. (c) One dimensional combinatorial libraries are patterned into a long Hall bar with 31 pairs of voltage contacts equally spaced along the bar's length. The contacts along the bar trace out to an 8×8 array of contact pads that match a corresponding 8×8 array of pogo pins in our high throughput electrical characterization system that allows us to quickly measure longitudinal and Hall resistance down to low temperature and in magnetic field.