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TOPICAL REVIEW — Physics research in materials genome

Combinatorial synthesis and high-throughput characterization of copper-oxide superconductors

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Fast synthesis and screening of materials are vital to the advance of materials science and are an essential component of the Materials Genome Initiative. Here we use copper-oxide superconductors as an example to demonstrate the power of integrating combinatorial molecular beam epitaxy synthesis with high-throughput electric transport measurements. Leveraging this method, we have generated a phase diagram with more than 800 compositions in order to unravel the doping dependence of interface superconductivity. In another application of the same method, we have studied the superconductor-to-insulator quantum phase transition with unprecedented accuracy in tuning the chemical doping level.

Keywords: Materials Genome Initiative, combinatorial growth, high-throughput characterization, copper-oxide superconductors

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1. Introduction

Many key advances in condensed matter physics and materials science have been driven by the discoveries of new materials and new phenomena therein. These, in turn, have engendered new applications and technologies. The era of electronics and information has sprung out of the discovery and study of semiconductors. The magnetic storage industry has been boosted by the study and development of magnetic heterostructures. The utilization of clean energy demands new classes of materials for absorbing solar energy or storing electric energy more efficiently.

The Materials Genome Initiative[1] was launched to meet the challenge of accelerating the synthesis and characterization of new materials. It requires close interplay between multiple disciplines[2,3] including physics, chemistry, materials science, computer science, etc. By integrating the endeavors of theoretical modeling, numerical simulation, and experimenting, one hopes to increase the pace of designing and manufacturing novel functional materials with desired properties.

Within the framework of the Materials Genome Initiative, one key area is the development of high-throughput experimental techniques for materials synthesis and characterization. In contrast to the exponentially increasing computation power expressed by Moore's law, the efficiency of materials synthesis and characterization has remained difficult to improve. For instance, the time and cost to grow a thin film — the standard platform for almost all electronics applications — are usually constrained by the employed procedures, leaving little room for significant improvements. One promising route to overcome this hurdle is to synthesize combinatorial material libraries — composite samples containing many 'pixels' of different and position-addressable chemical compositions, all at the same time.[4–11] Thus, one can greatly accelerate the search through the chemical-composition phase space, provided one can also test all of these pixels fast. This calls for high-throughput methods for sample characterization. Ideally, all these compositions should be measured simultaneously. By implementing both high-throughput synthesis and characterization, one may improve the overall efficiency by orders of magnitude. In what follows, we report on our progresses in this direction, illustrated by several examples that involve copper-oxide high-temperature superconductors.

2. COMBE

In molecular beam epitaxy (MBE), we deposit atoms of source materials onto an appropriate substrate under high- or ultra-high vacuum conditions. We control the substrate temperature and the background pressure of reactive gas (ozone) to fix the thermodynamic conditions. We also control the growth kinetics by monitoring and adjusting the source rates, the source shuttering times, and the shuttering sequence. The aggregate set of these parameters is referred to colloquially as the 'growth recipe'. Once this is established (usually after some sometimes tedious experimentation and study), the deposited atoms arrange themselves in crystal lattices with the correct stoichiometry. MBE is thus one of the best existing techniques to produce the highest quality, atomically flat, single-crystal thin films.

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Combinatorial molecular beam epitaxy (COMBE) is a variation of the MBE technique in which the deposition rate of one or more elements is varied intentionally and in a controlled manner.[4] In this way, the chemical composition of the deposited film varies with the position on the substrate.[4–11] In our setup, this is realized by aiming the thermal effusion cells at a shallow angle (20°) with respect to the substrate, see Fig. 1. The atom flux generated by an effusion cell decreases as the distance from the cell increases. As a result, the deposition rate at a given position on the substrate plane depends on its location.

The position-dependent deposition rates are measured by a scanning quartz-crystal oscillator monitor. We have verified that, for each source, the measured rate is an almost perfectly linear function of the displacement from the center axis of the flux. The area of the substrates we used here is 10 mm×10 mm. Given the 20° incidence angle and the known source-to-substrate distance, the maximum difference in the deposition rate between the two edges of the substrate is about 4%. This gradient can be partially or completely compensated by using a pair of identical sources placed at opposite azimuth positions.

Using the latter technical solution, we have been able to synthesize thin films of the copper-oxide superconductor $La_{2-x}Sr_xCuO_4$ (LSCO) in which the concentration of Sr dopant atoms is varied by 4% across the substrate, while keeping the atomic ratio (La+Sr):Cu at exactly 2:1. The latter constraint is quite indispensable; even small departures from this ideal 2:1 stoichiometry lead to nucleation of secondary-phase precipitates and are thus detrimental to the film quality.

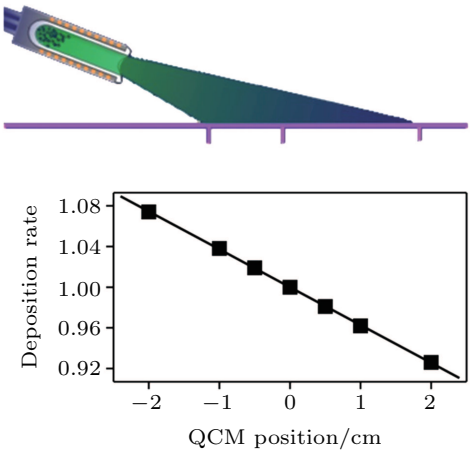


Fig. 1. (color online) (a) Sketch of the geometrical relation between the effusion cell and the substrate plane. The atom flux is colored in proportion to its density. The deposition rate is designed to vary with the position on the substrate, enabling COMBE experiments. (b) The spatially-resolved distribution of the deposition rate at the substrate plane, measured by a scanning quartz-crystal oscillator monitor.

3. Device fabrication by photolithography

To enable accurate and high-throughput measurements of transport properties, we use photolithography to pattern the films into linear arrays of geometrically identical devices — one-dimensional combinatorial libraries. Thus, each LSCO film grown by the COMBE method is patterned into a 10 mm long Hall bar contacted by 64 gold lines and contact pads (see Fig. 2). The Hall bar is aligned along the Sr doping gradient direction. In this way, we ensure that every segment (pixel) between two neighboring contact lines has a slightly different chemical composition. Then we run the electric current along the Hall bar and simultaneously measure the longitudinal resistance of each of 30 pixels by choosing contact pairs like 1 and 3. Similarly, we measure the Hall resistance of each of 31 pixels by utilizing contact pairs like 1 and 2.

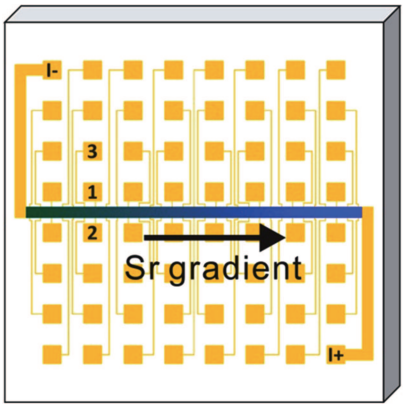


Fig. 2. (color online) The lithography pattern transferred to the film to fabricate the central Hall bar, 10 mm long, contacted by 64 gold lines and contact pads. The doping gradient is generated by the COMBE synthesis technique with a single Sr source at a shallow angle. The Hall bar is aligned along the direction determined by the doping gradient. The current runs from contact $I+$ to $I-$ and the voltages are measured between contact pairs like 1 and 3 or 1 and 2, to determine longitudinal or Hall resistances, respectively. All pixels (30 for longitudinal and 31 for Hall resistance) can be measured simultaneously.

4. High-throughput transport measurements

A patterned film is mounted onto a sample stage customized to be compatible with the particular system for cryogenic transport measurements. In our laboratory, we have a helium-4 flow-through cryostat that is equipped with a 1.1 T electromagnet, and two helium-3 top-loading cryogenic setups equipped with 9 T superconducting magnets. This enables us to conduct experiments at sample temperatures ranging from 300 mK to 300 K, with temperature stability better than ±1 mK.

The electrical connection from the gold contact pads on the patterned film to the sample stage can be made by either a mechanical contact (using spring-loaded pogo-pins) or by wire-bonding. The sample probes for different cryogenic systems are customized to accommodate a bundle of 64 wires to carry the electronic signals from the contact pads to the feed-through ports on the probes. These wires are grouped in twisted pairs to reduce the electronic noise, and carefully thermally-anchored to minimize the heat load onto the sample.

Aiming for a good signal-to-noise ratio, we apply the excitation current in the low frequency range, e.g., 100 Hz. The electronics include several home-built 32-channel lock-in amplifiers, enabling simultaneous and accurate measurements of the differential voltages between each contact pair. We have been using both analog and digital electronics to perform the lock-in amplification, and these two techniques have a similar noise floor in our setups.

5. Application: determining the detailed phase diagram

Combining COMBE synthesis technique with high-throughput transport measurements, we extract 30 times more experimental data from one cycle of sample growth and characterization process. This greatly reduces the average time, effort, and cost to study one chemical composition. Taking full advantage of this, we can determine the accurate doping dependence of the key transport properties with an unprecedented precision and for very large data sets.

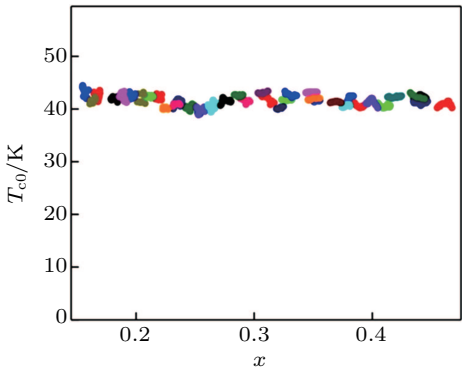


Fig. 3. (color online) The (onset) superconducting transition temperature T_{c0} plotted as a function of the chemical doping x in $La_2CuO_4/La_{2-x}Sr_xCuO_4$ bilayer films grown by the COMBE technique. The data[8] include more than 800 different doping levels, from 38 combinatorial libraries, with each library containing 24 distinct samples.

In the investigations of the interface superconductivity[12,13] in $La_2CuO_4/La_{2-x}Sr_xCuO_4$ bilayer films (Fig. 3), one key question has been the dependence of superconductivity on the chemical doping level x in the metallic $La_{2-x}Sr_xCuO_4$ layer.[8] The COMBE methodology enables us to synthesize and measure one combinatorial library per one substrate, each library consisting of 30 samples with slightly different values of x. (In this study, to reduce scatter, the 3 samples closest to each substrate edge were not included in the data analysis.) We have studied a total of 38 COMBE libraries, and hence the data set includes more than 800 different doping levels, covering densely the doping ranges from optimal to heavily overdoped.[8] The onset superconducting transition temperature T_{c0} was determined from the measured temperature dependence of the longitudinal resistivity. We have found it to be nearly independent of the doping level x in the metallic LSCO layer. This peculiar experimental finding has been explained by an equally peculiar doping dependence of the chemical potential in cuprates, which stays almost constant from undoped LCO to optimally doped LSCO, then drops in a linear manner with at least one order-of-magnitude larger slope.[8]

In $La_2CuO_4/La_{2-x}Sr_xCuO_4$ bilayers, mobile holes transfer through the interface from the overdoped $La_{2-x}Sr_xCuO_4$ layer to the undoped La_2CuO_4 layer, driven by the difference in the chemical potentials in these two compounds. Due to the charge redistribution, one CuO_2 plane located near the interface may achieve a density of holes close to what is optimal for superconductivity. In the framework of Fermi liquid theory, the chemical potential should be dependent on the carrier density; for a single cylindrical Fermi surface, as is the case in overdoped $La_{2-x}Sr_xCuO_4$, the dependence should be nearly linear. Consequently, varying the doping level x in the $La_{2-x}Sr_xCuO_4$ layer is expected to tune the hole density continuously in the interfacial CuO_2 planes in La_2CuO_4, prompting T_c to change dramatically with x. But this is in sharp contrast to our experimental results. We have demonstrated[12,13] that in $La_2CuO_4/La_{2-x}Sr_xCuO_4$ bilayers, superconductivity resides in a single layer near the interface. And, as seen from Fig. 3, clearly its T_c is almost independent of x. To resolve this apparent paradox, we have inferred that the chemical potential in the 'hot' CuO_2 layer (that is, the one with the highest T_c) must be staying pinned very close to the optimal value, regardless of the variations in x. This is possible only if the chemical potential in $La_{2-x}Sr_xCuO_4$ stays constant from the undoped ($x = 0$) to the optimally doped ($x = 0.16$) composition. This hypothesis has found support in other, independent, experiments, including transport in tunnel junctions and angle-resolved photoelectron spectroscopy, and it reflects the non-Fermi liquid behavior of cuprates.[8] A more detailed theoretical discussion of this topic is beyond the scope of this paper and has been presented elsewhere.[8,14]

6. Application: studying quantum phase transitions

In the studies of phase transitions, it is essential to have the capability of tuning the control parameter(s) in very fine steps. For instance, in studies of the critical behavior in thermal phase transitions, the system temperature is varied in steps which are as small as is achievable, typically at milli-Kelvin level or better. A comparable levels of fine-tuning the control parameter are achievable in studies of phase transitions driven by tuning the external electric or magnetic field. However, the accuracy with which the chemical doping x can be tuned has lagged behind; e.g., the uncertainty in the absolute value of x remains at about a few percent even with the state-of-art MBE

technique (Note that while the chemical composition of bulk single crystals grown from the melt is sometimes quoted with 2 or 3 significant digits, this is almost always just the nominal composition of the melt, rather than the measured stoichiometry of the actual crystal).

The COMBE methodology has the potential to revolutionize this type of study. The difference in the doping level Δx of two neighboring pixels in a COMBE library can be smaller than the above uncertainty by orders of magnitude. For example, if the doping level at the center of an LSCO film is $x = 0.06$, the pixel-to-pixel doping step is $\Delta x = 0.06 \times 0.04 \times 300\ \mu\text{m}/10\ \text{mm} = 0.00007$. This resolution in doping is unprecedented in the condensed matter physics literature. Moreover, all the samples (i.e., pixels in the COMBE library) are grown on the same substrate under the same thermodynamic and kinetic conditions, and have undergone the same thermal and processing history. This greatly reduces random sample-to-sample variation that results from inevitable variations in the control parameters of the synthesis and device fabrication processes.

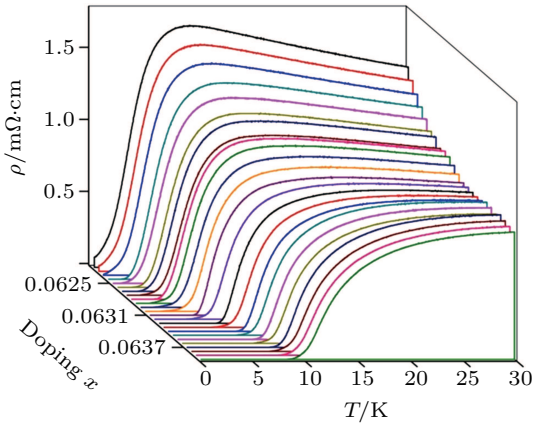


Fig. 4. (color online) The insulator-to-superconductor quantum phase transition in underdoped LSCO, studied using the COMBE synthesis and high-throughput (parallel) transport measurements.[11] The step in doping level reaches 0.00007, an extremely fine resolution, more than two orders of magnitude better than what is achievable using the conventional synthesis methods.

As an example, we have studied the insulator-to-superconductor quantum phase transition[15,16] in underdoped LSCO (Fig. 4). As x increases, the longitudinal resistivity $\rho(T)$ decreases monotonically and the superconducting transition temperature increases accordingly.[11] More importantly, the extremely fine pixel-to-pixel doping step ($\Delta x = 0.00007$) makes it possible to study in detail the quantum critical behavior in the vicinity of the critical point.

7. Conclusions and outlook

In this brief review, we have described our technique of COMBE synthesis coupled with high-throughput characterization. We have also shown some applications of this methodology to the study of physical phenomena of great current interest. While here we have used copper-oxide high-temperature superconductors[17,18] as an example, the principles discussed here can be easily generalized to other classes of materials. The resulting improvement in the efficiency of synthesis and screening can represent a significant step forward in the quest for the discovery and optimization of new functional materials. Combined with data mining and machine learning algorithms, which are being rapidly developed within the Materials Genome Intitiative, this may herald a new era in materials science.

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