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ALCHEMY OF XXI CENTURY: DIGITAL SYNTHESIS OF QUANTUM MATERIALS

Abstract: Atomic-layer-by-layer molecular beam epitaxy (ALL-MBE) is a new technique developed in the last few decades to synthesize functional quantum materials, including high-temperature superconductors, other complex oxides, and two-dimensional materials such as graphene and borophene. It even enables one to synthesize novel metastable materials that cannot be produced by standard methods. Several examples are presented of ALL-MBE alchemy — the creation of artificial materials with novel and unique electronic properties. The ability to engineer the materials atasingle-atomicmonolayerlevelenabled important discoveries, further illustrating the power of ALL-MBE.

Key words: *Atomic layer-by-layer Molecular beam epitaxy, Digital synthesis, Artificial metastable materials*

1. INTRODUCTION

Ancient alchemists attempted to purify and perfect certain materials, and I will use the word „alchemy“ in this sense. (The attempts to transmute elements, discover the panacea, and the philosopher's stone will be ignored.) The materials of our focal interest will be high-temperature superconductors (HTS) cuprates, but I will also mention other complex oxides and two-dimensional (2D) quantum materials such as graphene and borophene. As for the synthesis, purification, and perfection technique, the focus will be on Atomic-layer-by-layer molecular beam epitaxy (ALL-MBE), which I had the privilege of developing, in parallel with several other colleagues and collaborators, over the last three decades. In some cases, ALL-MBE has even

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enabled the creation of metastable novel artificial materials that the standard thermodynamic synthesis methods cannot obtain.

The paper is organized as follows; In Section 2, I describe our hardware — three ALL-MBE systems, each unique and custom-designed for a different purpose. Section 3 briefly describes the know-how — the technique of using ALL-MBE for materials synthesis, heterostructure engineering, and device fabrication. Section 4 is central to our topic, presenting concrete examples of ALL-MBE alchemy — the creation of several new, artificial metastable materials with novel and unique electronic properties. Section 5 briefly mentions several important discoveries enabled by ALL-MBE alchemy and notably by its ability to custom-engineer the materials and samples for the needs of a particular physics experiment. Conclusions are given in Section 6.

2. THE HARDWARE: ATOMIC LAYER-BY-LAYER MOLECULAR BEAM EPITAXY (ALL-MBE)

MBE-1 system at BNL. Atomic layer-by-layer (or „digital“) synthesis of novel quantum materials requires specialized and sophisticated hardware. An ALL-MBE system at Brookhaven National Laboratory, illustrated in Figures 1 and 2, is a prime example. [1] It is a cluster of several interconnected ultra-high vacuum (UHV) chambers distributed between two neighboring laboratories. The main growth chamber (Figure 1) is equipped with the following tools: (i) a 6-degree-of-freedom sample manipulator, (ii) a diode-laser heater, (iii) 16 metal atom sources, mostly thermal effusion (Knudsen) cells, but also including several rod-fed electron-beam evaporators used for depositing refractory (high-melting point) metals, (iv) a source of pure ozone gas, (v) a scanning quartz-crystal monitor for measuring deposition rates as a function of position, before and after the film growth, (vi) a 16-channel atomic absorption spectroscopy system for measuring the deposition rates in real-time, (vii) a 20-channel scanning reflection high-energy electron diffraction (RHEED) system, and (viii) a time-of-flight ion scattering and recoil spectroscopy (TOF-ISARS) system for measuring the surface chemical composition.

A pure ozone beam provides sufficient oxidation under high vacuum conditions, which permits in-situ monitoring of the surface structure by RHEED and TOF-ISARS.

The main growth chamber is highly modular. It is equipped with 16 spools (‘arms’), each of which houses a metal atom source. Each arm has a gate valve and autonomous pumping using a dedicated small (80 1/s) turbo-molecular pump and a roughing line. It is thus possible to valve off each

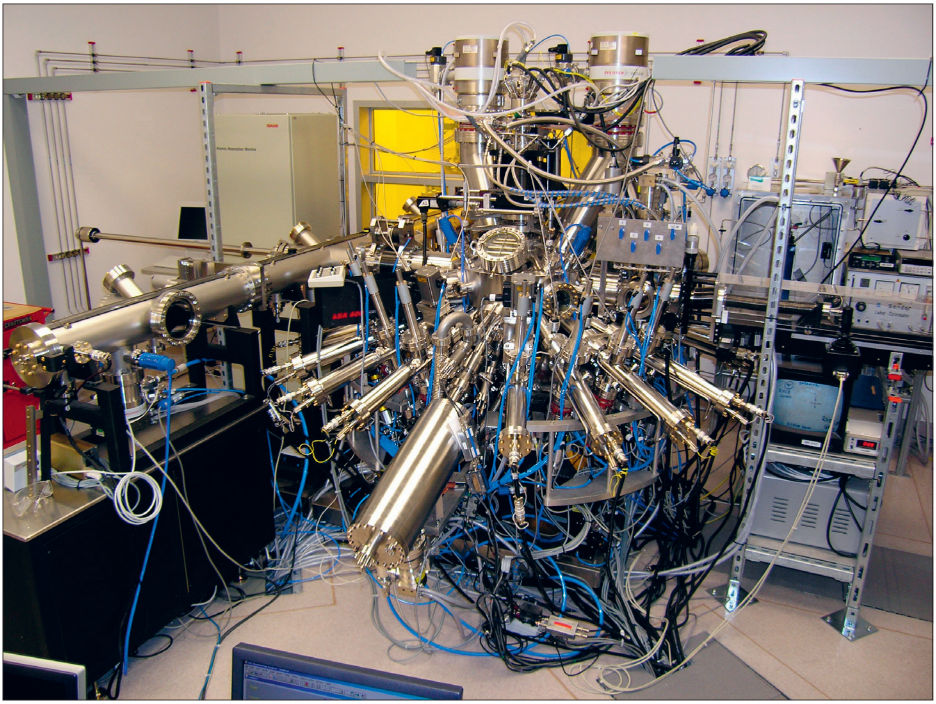

Figure 1. BNL oxide-MBE system: the synthesis chamber

arm and to recharge, service, interchange, replace, or outgas each source, within minutes, without breaking the vacuum in the main chamber, even while a film is being grown.

Various metal sources are used: low-temperature, high-temperature, and double-filament thermal effusion cells, as well as rod-fed electron-beam sources, for refractory metals. All the sources are easily interchangeable. Altogether, we can access most elemental metals in the periodic system with this range of sources.

The controlling software allows us to track the temperature of all the sources, the ozone pressure, the substrate position and orientation, the deposition rates from each source, etc., and to control or modify the stoichiometry within each monolayer.

The processing chamber (Fig. 2) is installed in the clean room. This way, the substrates can be prepared in a class-100 clean environment and loaded into the system without surface contamination. This chamber contains several tools for critical lithographic operations: a 5-pocket electron-beam evaporator used to deposit metallization and insulation layers, an oxygen plasma source for burning photoresist residue and cleaning the surface, a large-diameter (2”) ion-beam source for ion-milling, and a secondary-ion

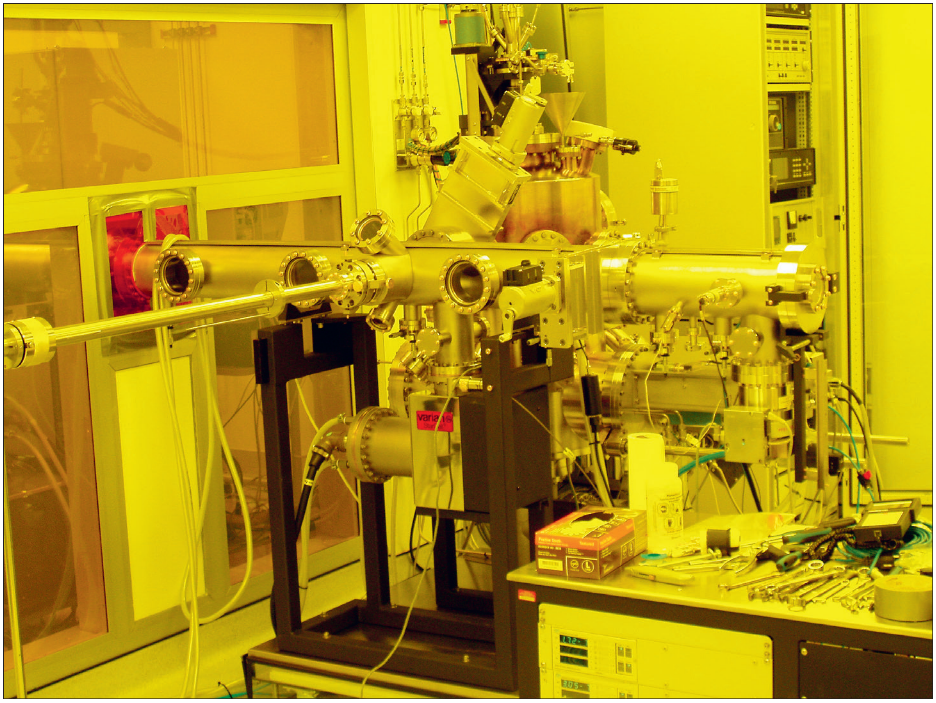

Figure 2. BNL oxide-MBE system: the chamber for lithographic processing

mass spectrometer (SIMS) enabling atomically precise control of the depth of ion-milling. The processing chamber allows the key micro-fabrication steps (metallization, insulation, surface cleaning and oxidation, and ion-milling) to be performed without breaking the vacuum.

The growth and processing chambers are connected via a 20' long UHV transfer chamber. Thus, the samples can be shuttled between the two chambers for multiple process steps without breaking the vacuum. This capability is critical, e. g., for the fabrication of sandwich junctions with superconducting contacts deposited to the top.

MBE2: OASIS system at BNL. Our second ALL-MBE system is a part of the OASIS facility at BNL. [2, 3] This new multi-module system consists of an Oxide molecular beam epitaxy module, Angle-resolved photoemission spectroscopy (ARPES) module, and a Spectroscopic Imaging Scanning tunneling microscopy (SI-STM) module. All these modules are interconnected under UHV; we can thus grow a film and transfer it to the ARPES or the STM module without breaking the vacuum and contaminating the surface.

This OASIS MBE module is conceptually akin to the ALL-MBE system described above, but there are some variations. The OASIS system is smaller and more compact, with just eight elemental sources (plus a source

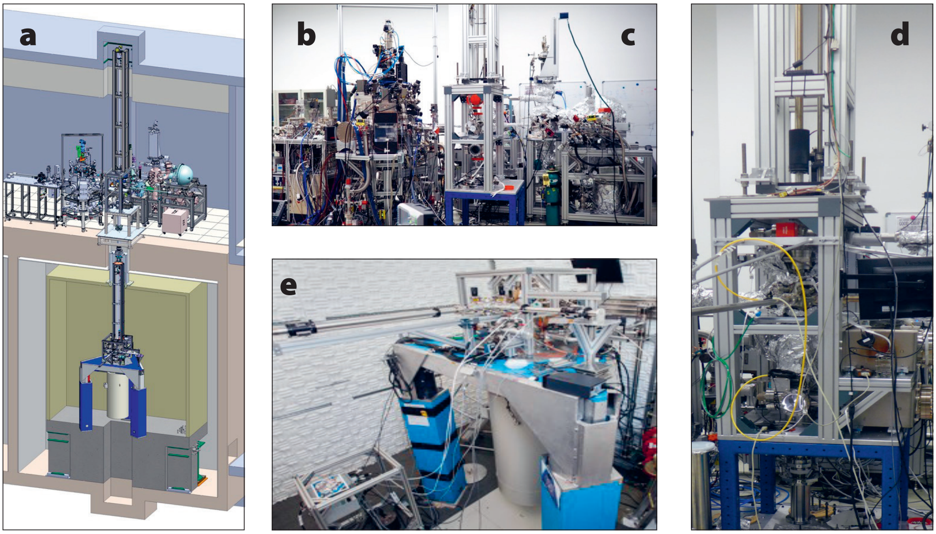

Figure 3. a, Schematics of the OASIS system at Brookhaven National Laboratory. b, the Oxide MBE module. c, the ARPES module. d, the horizontal and vertical transfer station. e, the SI-STM module.

of pure ozone gas). The sample holder and the transfer systems are very different, custom-designed to accommodate the conflicting demands of oxide MBE (high temperature, low thermal contact to the chamber, high oxidation power, horizontal transfer), STM (rigid contact to reduce vibrations, vertical transfer, cryogenic temperature), ARPES (precise sample rotation, cryogenic temperature, sample electrically grounded). To maintain UHV, the sample heater is an infrared source placed outside the MBE chamber, and a 100 cm long quartz crystal rod is used as a waveguide.

Traditionally, APRES and STM studies of HTS cuprates and other complex oxides were limited to materials that can be readily cleaved under UHV. The OASIS system is a solution for this problem, greatly expanding the list of materials amenable to ARPES and STM studies to include any material that can be synthesized by oxide MBE. Moreover, one can control and choose the surface termination layer and use heterostructures to study the effects of the epitaxial strain, various proximity effects, etc.

MBE3: The LEEM/MBE/multiprobe system at Yale. To synthesize and characterize novel quantum materials, including borophene, we have put together at Yale a unique system with a small MBE chamber attached to two additional modules for sample characterization. One is a low-energy electron microscope (LEEM), providing real-space microscopic images of the surface, with a resolution better than 10 nm, in real-time and at a

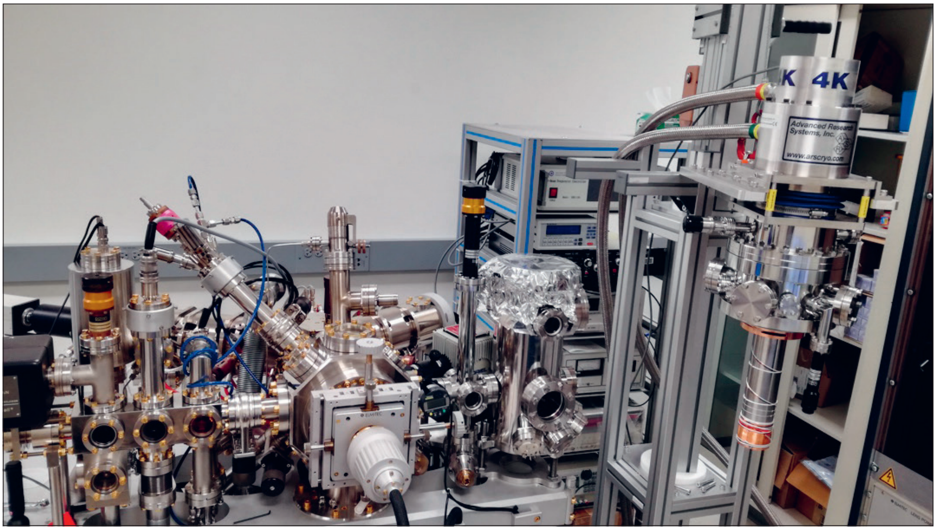

Figure 4. A system at Yale University that integrates MBE, LEEM/LEED/PEEM, and a multiprobe chamber for electrical transport and magnetic susceptibility measurements.

video rate. LEEM enables one to observe, study, and quantify the film nucleation and growth and identify the growth mechanism(s), such as island nucleation or step-flow growth. The same instrument can also be operated in the electron diffraction (LEED) mode, providing inverse-space information about the crystalline structure and order. In the photo-emission electron microscopy (PEEM) mode, the incoming electron beam is switched off and replaced by an ultraviolet light source, which is also implemented in our system. [4, 5]

The third module is a UHV chamber for in-situ cryogenic measurements of resistivity and magnetic susceptibility. All three modules are interconnected under UHV, so we can synthesize reactive and air-sensitive materials and study their fundamental electronic properties of interest without breaking the vacuum.

3. THE TECHNOLOGY: SYNTHESIS, HETEROSTRUCTURE ENGINEERING, AND DEVICE FABRICATION

Our advances in the MBE apparatus and technique enabled us to develop a technology for reproducible fabrication of atomically smooth films of cuprate superconductors and other related complex oxides. Over two decades, we synthesized well over 3000 thin films. These included single-crystal films of $La_{2-x}Sr_xCuO_4$ (with $0 \leq x \leq 0.45$), $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+2}$ (with n

= 1, 2, 3, 4,...), $DyBa_2Cu_3O_{7-x}$, $BaBiO_3$, $La_{2-x}Sr_xNiO_4$, $LaAlO_3$, $LaSrAlO_4$, $La_{2-x}Sr_xZnO_4$, etc., as well as a large number of heterostructures, multilayers, and superlattices. [6–17] Some contain layers that are just one unit cell (1 UC) thick and have virtually atomically perfect interfaces with little or no cation interdiffusion. [18–20]

Each film was characterized in real-time by RHEED and ex-situ by atomic force microscopy (AFM) and magnetic susceptibility measurements. RHEED oscillations provide a digital count of atomic layers and real-time film quality control. Selected films were also characterized *in situ* by time-of-flight ion scattering and recoil spectroscopy and ex-situ by X-ray diffraction (XRD), transport measurements, and Rutherford backscattering. Additional characterization was done by our collaborators using atomic-resolution scanning transmission electron microscopy and electron energy loss spectroscopy, resonant elastic and inelastic synchrotron X-ray scattering, synchrotron-based X-ray phase-retrieval techniques such as coherent Bragg rod analysis, muon spin rotation, ultrafast electron diffraction, ultrafast optical and THz pump-probe techniques, second-harmonic generation spectroscopy, shot-noise measurements, scanning SQUID magnetometry, etc.

Thin films of LSCO synthesized by ALL-MBE are single crystals without any secondary phase precipitates and feature atomically smooth surfaces and interfaces; we have seen the RMS surface roughness as low as 1 Å. The films can be made ultrathin, down to a single unit cell thick, without any pinholes; this is advantageous for transmission measurements. Much thicker films can also be grown for reflectance measurements.

To alleviate the problem of oxygen non-uniformity, we have performed over a thousand experiments that involved annealing in ozone, oxygen, or vacuum, spanning 13 orders of magnitude in pressure, from $10-^8$ Torr to 200 atm. Before and after each annealing step, the films were characterized by AFM, transport, and XRD. We have developed recipes that involve multiple annealing steps at different temperatures and pressures, yielding the most homogeneous films with the sharpest superconducting transitions based on these extensive studies.

Altogether, we have developed a reliable and robust technology for synthesizing thin films of high-T_c superconductors and other complex oxides, including various heterostructures and superlattices. We have also developed a large spectrum of device designs, lithographic masks, and well-tested recipes for the fabrication of electronic devices, including SNS and SIS tunnel junctions, SQUIDS, nanowires, nano-rings, sunbeam patterns of Hall bars for angle-resolved transport measurements, and many others. [16, 21–23]

4. THE ALL-MBE ALCHEMY

Tunnel junctions, modulation doping. ALL-MBE synthesis provides excellent flexibility in switching from one compound to another and tailoring surfaces and interfaces. This opens new avenues in the fabrication of tunnel junctions. [16, 21, 22] Traditionally, the barrier layer is inserted between the two naturally terminated layers of the host material (the bottom and the top electrode). ALL-MBE makes it possible to insert a layer of a foreign compound in-between two „inner“ planes of a host compound, which are not natural termination planes. The first HTS superconductor-insulator-superconductor (SIS) junctions were fabricated in this way. [21] Next, one can deposit just a fraction of a monolayer of a given atomic species and then complete the monolayer with another element. In this way, if there is no bulk diffusion, one can select the monolayers to be doped at will. The dopant may be picked to have a different valence, which enables one to control the local charge carrier density. Modulation doping in HTS materials has been accomplished in this manner. [19, 21]

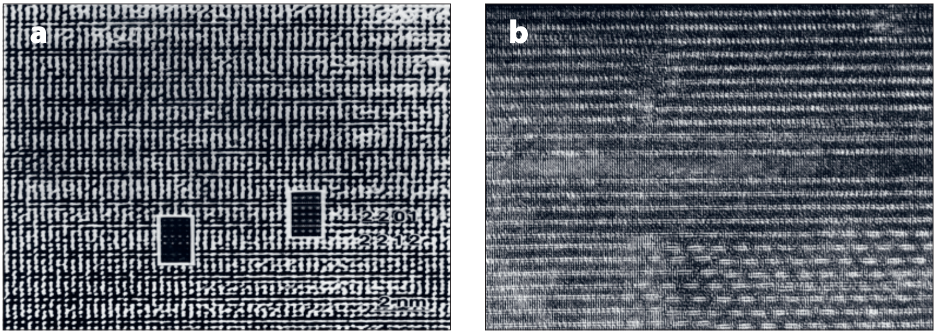

Figure5.a,Bi$_2$Sr$_2$CuO$_6$: Bi$_2$Sr$_2$CaCu$_2$O$_8$ superlattice. b, Bi$_2$Sr$_2$Ca$_7$Cu$_8$O$_{20}$: a novel artificial HTS meta-material. (Top and bottom electrodes: Bi$_2$Sr$_2$CaCu$_2$O$_8$)

Superlattices. ALL-MBE enabled synthesis of precise [(Bi-2201)$_n$ + Bi-2212]$_m$ superlattices, with n = 1, 2, ..., 10. [24] The cross-section TEM image in Fig. 5a shows essentially perfect Bi-2201 / Bi-2212 interfaces. In-plane transport measurements showed that in such superlattices, T_c was equal to that in thick single-phase Bi-2212 films, independent of the number of the spacer Bi-2201 layers inserted between one-half unit cell (15.4 Å) thick Bi-2212 monolayers. This indicated that Bi-2212 monolayers were well connected and continuous (in-plane) on a macroscopic length scale. The same observation demonstrated that the HTS phenomenon is essentially quasi-2D in nature. We have also seen undiminished T_c in superlattices with one-half unit cell (6.6 Å) thick LSCO layers spaced away by thicker, undoped, insulating LCO layers. [25]

Metastable phases. In layered oxides, one frequently finds several energetically nearly degenerate phases. A well-known example is provided by 2201, 2212, 2223, 2234, etc., phases in the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ family. In general, by cooling the Bi-Sr-Ca-Cu-O melt, one obtains a mixture of all these phases for entropy reasons. Layer-by-layer growth enables one to discriminate among such phases, i. e., to selectively grow the desired one only, including the phases that do not exist as bulk equilibrium compounds. Unless the temperature is raised too much, the topological barrier protects the phase grown because phase separation would require extensive bulk diffusion. In this way, it has been possible to assemble metastable compounds such as Bi-2234, Bi-2245, and Bi-2278 phases (see Fig. 5b). These films were superconducting, with the highest T_c = 60 K in single-phase Bi-2278 films and T_c = 75 K in Bi-1278. These were the first 'engineered' high-T_c materials. [26]

Artificial compounds. By our digital synthesis technique, we can stack various atomic layers trying to create new, synthetic, metastable compounds. One example is $Ba_3LaBi_2O_9$, a layered bismuthate related to the perovskite $BaBiO_3$ (BBO). The latter is a charge-density wave (CDW) insulator, but upon doping with potassium, it becomes metallic and superconducts with T_c = 30 K. This is very high for a cubic material; T_c higher than that only occurs in 2D materials. The question is what T_c one could get by forcing BKBO to be 2D. Our attempts at d-doping with K failed because it is volatile; at the lowest substrate temperature sufficient to make the film crystalline, K migrates away and out of the film.

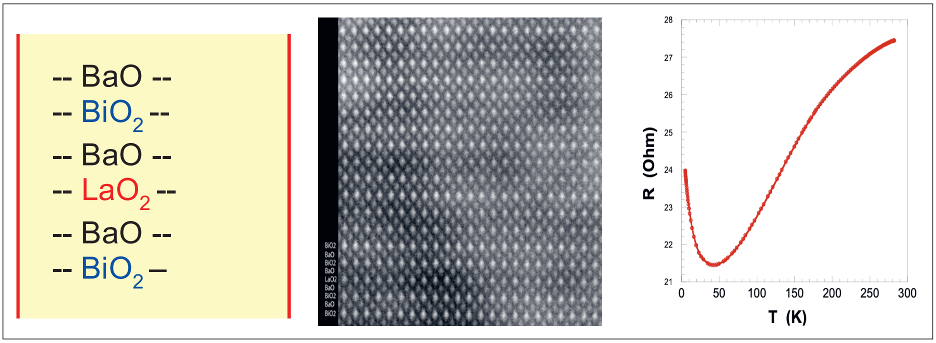

Figure 6. a., Schematic of $Ba_3LaBi_2O_9$ (BLBO). b, A cross-section image of BLBO film obtained by transmission electron microscopy. c, The high-temperature dependence of BLBO is metallic, but it develops a CDW at low temperatures.

For this reason, we tried d-doping with La3 +, the only cation with adequate size and charge. Replacing every third BiO_2 plane with a LaO_2 plane should provide one hole per two BiO_2 planes, making them metallic. The experiment was spectacularly successful insofar that we could synthesize this new, metastable compound that standard thermodynamic techniques cannot make. The films were atomically perfect and smooth. They were metallic but regrettably not superconducting so far because of the competing CDW instability. [27] In the future, we will try to suppress this CDW, and hopefully, superconductivity will emerge.

Borophene. Another spectacular example of new quantum alchemy is the discovery, after two centuries, of several new allotropes of boron, employing MBE synthesis. Generally, discoveries of new allotropes of elements are rare and hailed as milestone events in Chemistry. Take carbon as an example. Amorphous carbon has been known since prehistory. Diamond was known since 2000 BCE in China, although it was identified as carbon only in 1772 by Lavoisier. Seven years later, graphite was also identified as carbon by Schelle. Two centuries later, in 1985, fullerenes (buckyballs and carbon nanotubes) were discovered to be recognized with the Nobel Prize in 1996. Graphene was discovered next in 2004, earning another Nobel Prize in 2010.

Boron is the neighbor of carbon in the periodic system. While the borax glaze was used for pottery in China since at least the 3rd century, boron was identified as an element in 1808 by Humphrey Davy. Boron also forms several allotropes; one amorphous and four crystalline forms have been known for a long time. Two groups recently reported the first synthesis of a new allotrope, borophene — an atomically-thin, covalent-bonded boron sheet analogous to graphene. [28, 29] As the substrate, they used silver crystal that was polished to expose the (111) surface with hexagonal symmetry, like graphene. The drawback was that only nanometer-sized crystalline flakes of borophene were produced this way, precluding device fabrication and the measurements of interesting physical properties.

Using MBE synthesis empowered by real-time LEEM and LEED monitoring, we were able to grow, on copper substrates, monocrystal borophene islands of an area exceeding 100 square micrometers. [4, 5] More importantly, we discovered two new borophene structures, depending on whether we used the hexagonal Cu(111) or tetragonal Cu(100) facets. These new allotropes of boron captured much interest since they host electronic spectra and states with unusual topological properties and feature exotic electronic quasiparticles. Borophene bilayers were also fabricated recently. [30]

5. NEW PHYSICS ENABLED BY ALL-MBE

One distinguishing feature of our signature MBE design is complete system modularity. [1] Every system component — the main chamber, each atom source, RHEED, QCM, TOF-ISARS — is placed in a separate UHV compartment equipped with a gate valve and a turbo-molecular pump. The MBE-1 synthesis module thus hosts 24 turbo pumps. The great advantage of this design is that one component can be serviced without breaking the vacuum in the others; for example, an atomic source can be cooled down, vented, recharged, pumped down, and outgassed even while a film is being grown. This ensures a very high system up-time, essentially 100%, and excellent productivity. We have been routinely able to complete over 200 synthesis experiments per year.

This, in turn, enabled a focused and comprehensive study that spanned almost two decades and over three thousand HTS cuprate samples, probably without precedence in Condensed Matter Physics. We have measured the fundamental physical parameters of the normal and superconducting states and established their precise dependence on doping, temperature, strain, and external fields. This enormous database — several tens of thousands of data files — contains a wealth of information that has enabled critical new insights into the physics of cuprates. Our ability to engineer the material at the single-atomic monolayer level for the specific needs of a particular experiment has also played a crucial role. A brief list of some key discoveries is as follows.

An extraordinary insulating state. Undoped cuprates (the „parent“ compounds) are antiferromagnetic insulators. Upon doping, they become metallic and superconducting. For example, in $La_{2-x}Sr_xCuO_4$ this quantum phase transition occurs at $x = 0.06$. For $x < 0.06$, the material is insulating in the sense that its resistivity increases as the temperature is lowered. However, it does not behave as a standard semiconductor or insulator. The transport becomes erratic, hysteretic at very low temperatures, and shows memory effects. [31,32] These are signatures of an unusual quantum charge-cluster glass state. Moreover, the charge is quantized in the units of 2e (two electron charges) — electrons in this insulator are paired. [33]

An extraordinary metallic state. For $x > 0.06$, LSCO is metallic; its resistivity decreases as the temperature is lowered. But this is a „strange metal“; the dependences of the resistivity on the temperature and magnetic field are incompatible with the standard textbook description of metals as a gas of weakly-interacting quasiparticles. [15] Even more strange, the rotational symmetry of the electron fluid in the normal metallic state above T_c is always spontaneously broken — the so-called „electronic nematicity“. [14]

Moreover, magnetic excitations (paramagnons) indicate the vestiges of short-ranged, short-lived antiferromagnetic correlations at all doping levels. [34]

An extraordinary superconducting state. In standard superconductors, electrons pair and condense at some sharply-defined critical temperature T_c. In HTS cuprates, including both BSCCO and LSCO, we detected electron pairing and vestiges of superconductivity (superconducting fluctuations) way above T_c and at energies way above the superconducting gap. [16, 17, 36] Next, when the doping level is increased above $x = 0.16$, the superfluid density decreases and drops to zero at $x = 0.26$ instead of increasing; this strange behavior is unexpected and, so far, unexplained. [13]

Extraordinary proximity effects. Heterostructures also brought in some big surprises. For example, in $La_{2-x}Sr_xCuO_4/La_2CuO_4$ multilayers, for $x < 0.16$, there is no charge transfer; unexpectedly, the HTS state and the antiferromagnetic state separate sharply on the Ångstrom scale. In stark contrast, in $La_{1.84}Sr_{0.16}CuO_4/La_{2-x}Sr_xCuO_4$ multilayers, for $x > 0.06$, supercurrent runs through non-superconducting barrier layers that are 100 thicker than what is conceivable based on the standard theory — the „Giant proximity effect“, also unexplained so far. [37] Finally, in $La_{2-x}Sr_xCuO_4/La_2CuO_4$ multilayers, for $x > 0.16$, interface superconductivity is seen, with $T_c \approx$ 40 K independent on the doping level x and confined to a one-atom-thick CuO_2 layer — the thinnest superconductor known. [18–20]

6. CONCLUSIONS

ALL-MBE of HTS cuprates and other complex oxides has gone a long way from its humble origins, over three decades ago, at the margins of industrial R&D. By now, it has taken center stage in the fundamental Condensed Matter Physics and Materials Science, enabling a series of important experiments and discoveries, a few of which were listed above. By the strength of this fact, coupling ARPES or STM with an MBE in one complex UHV system has become the norm in the community today, while just a decade ago, this was generally considered excessive if not technically impossible.

Apart from the fabrication of state-of-the-art single-crystal HTS films and heterostructures, ALL-MBE has enabled engineering materials at a single-atomic monolayer level. By stacking atomic layers at will, new, artificial, metastable quantum materials have been created. They can be fine-tuned by various tricks — epitaxial strain, epitaxial stabilization, heterostructure engineering, interface effects, proximity effects — to tailor the desired electronic properties, including some unprecedented and very exotic ones. New alchemy has been developed, and we have just touched the tip of the iceberg. We can say one thing about the future: it will surpass our imagination.

ACKNOWLEDGEMENT

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ALHEMIJA XXI VEKA: DIGITALNA SINTEZA KVANTNIH MATERIJALA

Sažetak

Epitaksija molekularnim zracima, atomski sloj po sloj (ALL-MBE), nova je tehnologija, razvijena u poslednjih nekoliko decenija, za sintezu funkcionalnih kvantnih materijala, uključujući visokotemperaturne superprovodnike, druge kompleksne okside, i dvodimenzionalne materijale kao grafen i borofen. Ova tehnika omogućava sintezu novih metastabilnih materijala, koji se ne mogu proizvesti standardnim metodama. ALL-MBE alhemija — kreiranje sintetskih materijala sa novim i jedinstvenim elektronskim svojstvima je ilustrovana sa nekoliko primera. Mogućnost da se materijal oblikuje na nivou pojedinačnih atomskih monoslojeva je omogućila važna otkrića, koja ukazuju na prednosti ALL-MBE tehnologije.