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## High temperature interface superconductivity

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#### 1. Introduction

Interfaces between different materials can have quantitatively modified properties compared to the bulk of the constituents, and even display qualitatively new phenomena. This can happen for several reasons and perhaps the foremost is expected to be structural. Symmetry at an interface is also different than in the translationally invariant bulk. As a result, artificial and metastable phases of matter, the so called "interface compounds", can become energetically favorable so as to ensure a smooth layering sequence in terms of stoichiometry and bonding, see Fig. 1 [1]. Another reasons are the proximity effects: the physical properties in near-interface region of one of the constituent materials may be modified due to the influence of the other constituent. This can be especially interesting for complex oxides which display a plethora of functional properties like magnetism, ferro-electricity or superconductivity. Combining them in a single interface compound can be useful for a variety of applications. Last but not least, the dimensionality of the surfaces and interfaces is lower, and hence one would expect that correlations, screening, disorder or fluctuations can play a more important role in the electronic dynamics. In conjunction with surface localized states and excitations, these can lead to novel phenomena.

In terms of superconductivity, the sign and the strength of pairing interactions at surface can be different than in the bulk. Half a century ago Ginzburg proposed that in an otherwise insulating ma-

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#### ABSTRACT

High- $T_c$  superconductivity at interfaces has a history of more than a couple of decades. In this review we focus our attention on copper-oxide based heterostructures and multi-layers. We first discuss the technique, atomic layer-by-layer molecular beam epitaxy (ALL-MBE) engineering, that enabled High- $T_c$  Interface Superconductivity (HT-IS), and the challenges associated with the realization of high quality interfaces. Then we turn our attention to the experiments which shed light on the structure and properties of interfacial layers, allowing comparison to those of single-phase films and bulk crystals. Both 'passive' hetero-structures as well as surface-induced effects by external gating are discussed. We conclude by comparing HT-IS in cuprates and in other classes of materials, especially Fe-based superconductors, and by examining the grand challenges currently laying ahead for the field.

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terial a near-surface layer can acquire metallic character and even superconduct if surface states are partially filled [2]. Such ideas have found experimental validation in the last few decades.

So far two main routes have been investigated in order to produce high-quality interfaces. One is hetero-epitaxy which implies the growth of two or more compounds on commercially available substrates. Multi-layers made out of copper-oxide based high temperature superconductors (HTS) or those made of band or Mott-type insulating oxides with perovskite-like structures, e.g. LaAlO<sub>3</sub>/SrTiO<sub>3</sub> (LAO/STO) are among the most prominent realizations in the field [3-6]. A second method is to intervene postgrowth and change the properties of a surface or interface layer by applying an external agent, for example by exposure to a chemically reactive environment or by applying a voltage bias to the hetero-structure.

#### 2. ALL-MBE: the technology behind HT-IS

However, as natural occurrences of perfect and useful interfaces in bulk crystalline solids are scarce, they have to be artificially engineered. This process requires state-of-the-art synthesis and control capabilities.

Atomic layer-by-layer molecular beam epitaxy (ALL-MBE) has been used for nearly three decades for fabrication of HTS films, multi-layers and devices [7,8]. The technique allows for precise control of the growth conditions and of atomic fluxes aimed at the substrates, down to about 1% of monolayer coverage. The main part of the oxide ALL-MBE system at Brookhaven, see Fig. 2, is an ultra-high vacuum (UHV) chamber ( $p \le 10^{-9}$  Torr) which hosts 16 elemental sources along with characterization tools. Atomic species



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**Fig. 1.** HR-TEM picture of the interface between a  $La_{2-x}Sr_xCuO_4$  film grown on a LaSrAlO<sub>4</sub> substrate. At the interface the layering sequence corresponds to 1 UC of  $La_3AlCuO_7$ ; this is an example of spontaneous formation of an interface compound (from [1]).

are evaporated from thermal effusion cells at a shallow angle  $(\theta = 20^{\circ})$  with respect to the substrate. On one hand this allows for insertion of additional real-time characterization devices, e.g. ion scattering or low energy electron spectroscopy instrumentation but, more importantly, it enables achieving a finite gradient in the spread of atomic concentration at the substrate level. This is crucial for growth of combinatorial samples with unprecedented fine separations in composition, a topic which will be discussed in more detail later in this review.

A brief description of the instrumentation for growth monitoring in the main chamber is as follows (see also Fig. 3). Accurate stoichiometry is ensured by parallel automatic control of the 16 pneumatic source shutters in conjunction with flux monitoring tools. The deposition rates are calibrated before growth by a quartz crystal monitor simultaneously with the 16-channel (one for each source) parallel atomic absorption spectroscopy setup. The latter is then used for real time flux monitoring during growth. Each source has its own turbo pumping station and is separated by a gate valve from the main chamber. This configuration reduces the down-time of the system considerably because it is possible to replace/replenish each source independently without breaking UHV in the main growth chamber. Samples are grown in a mixture of  $O_2:O_3$  that is distilled by condensation, delivering pure ozone to the film surface. The sample manipulator can host a 3 in. wafer onto which one can mount up to a  $4 \times 4$  array of  $1 \text{ cm}^2$  substrates. Heating is realized by four individually adjustable quartz lamps and the temperature of the wafer is controlled by four thermocouples and measured by a black-body infrared pyrometer. The crystal quality of the growing film is monitored in real time by reflection high-energy electron diffraction (RHEED).

The main MBE chamber is connected by a UHV transfer tube to a processing chamber so that samples can be transferred between them without being exposed to air. The processing chamber is placed into a class 1000 clean room and has a few in-situ device fabrication capabilities: electron-beam evaporation of various materials used for insulation or metallization, Ar-ion milling and ozone plasma treatments. The clean room hosts an additional battery of device fabrication and characterization utilities: profilometry, micro-controlled probe station for room temperature transport, mask aligner for UV-lithography, and a wire bonder. The clean room capabilities of the laboratory are accompanied by additional characterization setups like hard X-ray diffraction (XRD), dedicated vacuum and ozone annealing chamber and atomic force microscopy (AFM). These characterization and fabrication capabilities are further extended by a few advanced research tools: 0.3–300 K range DC transport for combinatorial and Hall measurements in liquid He4 and He3, as well as in extremely temperature-stabilized closed-cycle cryocooler setups [9]. We also use state-of-the-art custom-made AC mutual inductance and sheet conductance setups for susceptibility measurements in the superconducting state.

#### 3. HT-IS: history and development

In this section we review early results as well as data up to about a few years ago on HT-IS. Additional information can be found in several previously published reviews [4,10]. The first results on HT-IS in cuprates were obtained by J. Eckstein and I. Bozovic at Varian Research in California [7] only a few years after the discovery of HTS materials [11]. The structure shown in Fig. 4 was made by virtue of the ALL-MBE technique and it also represents the first realization of an artificial superconductor. The metastable Bi-22(n)(n + 1) compound is realized by insertion of  $n \times (CaCuO_2)$  layers in the basic structure of Bi-2201 (Bi<sub>2</sub>Sr<sub>2</sub>CuO<sub>6</sub>). Fig. 4 shows an example of a structure containing a single layer of Bi-2278 (n = 7), see Fig. 5. These results confirmed that HTS is essentially a 2D phenomenon and also provided the first hints of unusual proximity effects in these materials.

The year 2002 marked the first report of an interfacial-induced  $T_c$  enhancement in hetero-structures based on La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4+ $\delta$ </sub> (LSCO) family of compounds [12]. A bilayer system consisting of a 5 UC oxygen doped superconducting LCO materials grown on

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