Direct angle resolved photoelectron spectroscopy (DARPES) on high-Tc films: doping, strains, Fermi surface topology and superconductivity

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Abstract. Since 1997 we systematically perform Direct ARPES (=DARPES) on in-situ grown, non-cleaved, ultra-thin (<25nm) cuprate films. Specifically, we probe low energy electronic structure and properties of high-Tc films under different degree of epitaxial (compressive vs tensile) strain. In overdoped in-plane compressed La₂₋ₓSrₓCuO₄ (LSCO) thin films we double Tc from 20K to 40K, yet the Fermi surface (FS) remains essentially 2-dimensional (2D). In contrast, tensile strained films show 3-dimensional (3D) dispersion, while Tc is drastically reduced. It seems that the in-plane compressive strain tends to push the apical oxygen far away from the CuO₂ plane, enhances the 2D character of the dispersion and increases Tc, while the tensile strain seems to act exactly in the opposite direction and the resulting dispersion is 3D. We have the FS topology for both cases. As the actual lattice of cuprates is ‘Napoleon-cake’-like i.e. rigid CuO₂ planes alternate with softer ‘reservoir’ (that strains distort differently) our results tend to rule out 2D rigid lattice mean field models. Finally, we briefly discuss recent successful determination of the FS topology from the observed wavevector quantization by DARPES in cuprate films thinner than 18 units cells (<24nm). Such an approach is of broader interest as it can be extended to other similar confined (ultra-thin) functional oxide systems.

1. Introduction
Despite all the experimental and theoretical efforts, the mechanism of high-Tc superconductivity in cuprates remains highly controversial topic [1-3,15], partly due to the fact that most groups do not fabricate and/or fully control and thoroughly analyse their (non-trivial) cuprate samples [1-7]. Theorists prefer to use the reciprocal space data, the ARPES measurements on cleaved high quality samples across the phase diagram of representative compounds in the form of single crystals (mainly on cleaved Bi-cuprates) and thin films (very few reports; none on strained films, except our present work) continue to be very important [2]. It is precisely in that context that we focus our systematic research activities as we do fabricate the state-of-the-art thin films [8] (with and without growth induced strain) and in most cases the corresponding single crystal samples (H. Berger, EPFL). Moreover, we do most of our measurements within the EPFL collaborations (Forro et al., Grioni, Margaritondo et al.).
Back in 1990 when Ivan Bozovic (BNL; at that time at Varian & Stanford) proposed direct ARPES (= DARPES) concept, very few people shared his vision. In 1995-96 when one of us (DP) boldly begun this challenging project, most referees were very sceptical or downright negative. They claimed that it cannot work: one has to cleave the samples before performing ARPES measurements on high-\(T_c\) cuprate oxides. However, as we have demonstrated and is clearly visible in Figure 1, DARPES on cuprate films does work. Therefore, in this brief overview we summarize our main results obtained in more than 10 years of extremely demanding, systematic studies of electronic properties and DARPES on cuprate films, and specifically on LSCO-214. We also briefly discuss our recently observed the wave vector quantization in LaSrCuO films thinner than 12 unit cells, grown on SrTiO\(_3\) substrates. We have determined low energy dispersions in-situ for different photon energies by DARPES. From the observed wavevector quantization we have extracted 3D dispersions within a tight-binding model and obtained the Fermi surface topology, without resorting to the nearly-free-electron approximation. Such method can be extended to similar confined nano-structures and thin layers of functional materials and in general shows the remarkable potential of our DARPES approach in various thin film oxides.

2. DARPES on High-\(T_c\) Cuprate Films: Doping, Strain and Superconductivity

Following several ARPES studies on cleaved Bi-2212 single crystals [9,10], we have by now completed more than ten years of systematic DARPES work at the Wisconsin synchrotron. After numerous experimental problems, we have finally succeeded to perform a DARPES (= direct ARPES, without cleaving the film) on ultra-thin (<25nm) LSCO high-\(T_c\) cuprate films [12] with a special emphasis on the role of strain and its influence on electronic properties [9]. In-plane compressive strain is known to increase the critical temperature (T\(_c\)) of high temperature superconductors (HTSC) [5], and is obviously related to the mechanism of high-\(T_c\) superconductivity [1,5]. The phenomenon is quite dramatic in \(La_{2-x}Sr_xCuO_4\) (LSCO) thin epitaxial films: for \(x = 0.1\), T\(_c\) doubles with respect to relaxed LSCO (and increases by a factor of five with respect to films with in-plane tensile strain).

![Figure 1](image.png)

**Figure 1.** Convincing DARPES demonstration: Unprocessed, ‘raw’ MDCs in \(\Gamma-X\) (left) and \(\Gamma-M\) (Right) high symmetry directions, measured on \textit{in-situ} grown, compressively strained LSCO thin superconducting films (for further details see ref. [12]).
Published theoretical studies predicted the in-plane compressive strain to flatten the bands: this could provide a simple explanation for the dramatic $T_c$ increase, since band flattening implies an enhanced density of states (DOS) near the Fermi energy. Our DARPES study on compressively strained LSCO films contradicts [12] such picture by revealing a dispersing band that crosses Fermi level.

Moreover, our DARPES measurements on films with huge tensile strain (c-axis of ~13.10 Å, corresponding to the c-axis compression of 1%) show the evidence for a 3D dispersion, in clear contrast with strictly 2D dispersion observed in the aforementioned compressively strained films and relaxed, unstrained LSCO (for details see Cloetta et al. [13]). Although these results are striking and somewhat unexpected, they do make sense. Namely, already the conduction band of the relaxed $La_{2-x}Sr_xCuO_4$ is atypical among high-$T_c$ cuprates. It has considerable apical-oxygen $p_z$ and Cu 3$d_{2z^2}$ out-of-plane character, while, for the rest of the cuprates, those orbitals hybridize far less with the conduction band. Hence we can relate the observed z-axis dispersion with the significant displacement of the apical-oxygen towards the CuO$_2$ plane, induced by the epitaxial strain. Resistivity measurements show an insulating behavior of films under extreme tensile strain and no $T_c$. Films with weaker tensile strain still exhibit superconductivity, but diminished as compared to the relaxed films.

In summary, it seems that the in-plane compressive strain tends to push the apical Oxygen far away from the CuO$_2$ plane, enhances the 2D character of the dispersion and increases $T_c$, while the tensile strain seems to act exactly in the opposite direction [13] and the resulting dispersion is 3 dimensional [14]. At present we have no data on electron doped compound to verify the proposed scheme.

![Figure 2. Schematic presentation of the electronic phase diagram of $La_{2-x}Sr_xCuO_4$ (and its electron-doped counterpart $Nd_{2-x}Ce_xCuO_4$) as a function of doping, taking into consideration compressive and tensile strain for the superconducting phase (SC). For $Nd_{2-x}Ce_xCuO_4$ there are still no strain data.](image)

3. On DARPES Experiments in Different Cuprate Compounds

For completeness, here is also a summary of other relevant results obtained so far in our ongoing systematic studies on DARPES on various films of high-$T_c$ compounds [11,12]:

i) We have measured virtually identical ARPES dispersion on cleaved LSCO-214 single crystals and with DARPES on as-made relaxed (i.e. no strain) films. That clearly removes any ambiguity on whether results on crystals are different from those on films (apart from the changes deliberately induced by the growth induced strain as we do in our studies) [12]. That also
confirm that the extension of ARPES i.e. DARPES (with no cleavage of the films) is truly viable and very useful in heteroepitaxy of all layered functional materials as one can literally learn how to control the E(k) dispersion that evidently controls the properties and functionality.

ii) Cuprate films with ‘chains’: RBCO-123 (R=Y,Nd), YBCO-124 (double-chain compound) tend to lose oxygen from the so-called ‘chains’ above 100K, so their surfaces do not show clear, stable evidence of the Fermi edge when measured by using a cylindrical mirror analyser (CMA). Therefore, such films that lose oxygen from the topmost surface layer (in general those that have insulating surface) are not suitable for DARPES studies, so we now concentrate on other compounds, notably LSCO and the La-doped BSCCO-2201 films [12,13].

iii) Interesting new observations were made on ultra-thin films of Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ (Bi-2212) grown on STO substrates. All films (even those whose thickness corresponds to 1/4 of a unit cell) show metallic-like Fermi edge in the PES spectra. However, a structural phase transition occurs at a nominal thickness of one unit-cell (UC), converting the precursor Bi$_2$O$_{2.33}$ (Bi$_6$O$_7$) highly coherent ultra thin film into the Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ epitaxial structure. In other words, the BSCCO-2212 phase forms for deposits above 1UC, yet the very first UC represents metallic Bi$_6$O$_7$ that can be considered as a natural (self-organised) buffer for the growth of BSCCO-2212 films. In contrast, our results indicate that thin LSCO films form by gradually connecting deposited ‘islands’ ~60nm in diameter [11-13].

iv) Unlike other groups that perform ARPES on cleaved single crystals (that we do as well), we note that almost 90% of our work is dedicated to fully optimize the growth and properties of the film phase that is being studied. Such dedicated work is not glamorous, is extremely demanding and generally largely neglected by most physics groups, by most funding agencies and even top impact journals, as they all want spectacular ’new’ physics reports, that actually can be wrong or incomplete, precisely as the materials work hasn’t been properly performed. As an illustration let us just emphasize that in the past 10 years we have grown and studied several thousand films and only a small fraction was actually measured by DARPES. Most films were discarded on the ground of insufficient quality (the presence of unwanted phases, rough surface ...) for the demanding in-depth electronic properties studies. All leading groups in our field are aware of these difficulties, yet few experimental data on high-Tc cuprates can be trusted on these grounds.

In addition, various ex-situ measurements were performed in collaboration: EXAFS with S. Conradson (LANL) and paraconductivity (F. Vidal et al., Santiago), and the work has recently been completed on oxygen and ozone treated LBCO films grown by MBE (I. Bozovic et al, BNL). All these measurements allow us to study the normal and the superconducting state, and the property changes for each film sample. However, more studies are necessary to arrive at a more quantitative picture and discuss subtle consequences for the microscopic mechanism of high-Tc superconductivity. It is evident that our results on strained films cannot be simply explained within any simple 2D rigid lattice model. This is mainly due to the fact that the lattice is like a ‘Napoleon-cake’ i.e. CuO$_2$ planes are rigid while the out-of-plane ‘reservoir’ is softer so strain differently distorts different parts of the lattice and to determine the exact changes of all various coordinates (by strain) is an almost impossible task. Still, considering the strong influence of strain, both tensile and compressive, on T$_c$, the electronic phase diagram for LSCO (and cuprates in general) has to be extended by a third axis for strain. The resulting, illustrative phase diagram most likely resembles to the one shown in Figure 2, and shows that our experimental work is rather promising to eventually understand the high-Tc superconductivity. Since our demonstration of successful direct photoemission spectroscopy (DARPES) on thin cuprate films [11-13], similar approach is now being pursued by many groups worldwide. The technique will undoubtedly become very important as one can control the E(k) relation (and properties) of any sublayer of the heteroepitaxially grown functional oxide (cuprate, manganite, ruthocuprate … and related. The control of the surface and inteface and the metal-insulator transition can all be monitored when one combines the in-situ epitaxial growth with DARPES (see as an example our new EPFL integrated
system shown in Figure 3). Moreover, in BNL, Bozovic, Davis and Valla are developing even a better system with MBE-growth, DARPES and in-situ STM studies. Within one generation, we predict a development of some dozen advanced, fully integrated DARPES-STM-PLD (or MBE) heteroepitaxial materials systems in all leading synchrotron facilities worldwide.

![Figure 3. DARPES = Direct Angle Resolved Photoelectron Spectroscopy system at the EPFL. The (ultrathin) films grown *in-situ* by pulsed laser ablation are directly transferred to the Scienta chamber for systematic, advanced DARPES studies.](image)

**4. Fermi Surface Determination from the Wavevector Quantization in Ultrathin Films**

It is well known that the effect of wavevector quantization is due to the discrete nature of the energy spectra associated with the standing wave solutions of the Schroedinger equation in a finite medium. However, due to the roughness of the surfaces and interfaces it is often not observed in very thin films. Namely, the observation of such quantum behavior requires interfaces that are smoother than the electron wavelength, which is of the order of few atomic monolayers. In addition, it requires specific conditions in order to be directly observable by DARPES on thin cuprate films: a) the existence of the band dispersion along the confinement direction and b) the resolution in the electron wavevector better than the separation between the adjacent levels. As we have shown in our earlier publications [15,16], the condition a) is fulfilled in the particular case of our recent work on films, as we have observed a pronounced 3D character in the electronic band dispersion of ultrathin LSCO films with growth induced in-plane tensile strain. Condition b) is also fulfilled: our measurements were performed at the Synchrotron Radiation Center in Wisconsin on the 6m PGM beamline, by means of SCIENTA SES 2002 analyser with an energy resolution better than 10 meV and a momentum resolution of about 0.004/nm. Hence we were able to report a series of DARPES measurements on ultra-thin LSCO and BSCCO films performed at different photon energies exhibiting the wavevector quantization (see also a Figure 4). We have demonstrated how one can extract the 3D dispersions and the Fermi surface topology within a tight-binding scheme, without resorting to nearly-free-electron approximation [17]. Such an approach is of interest and can be extended to other similar confined
systems and most likely plays a role within the metal-insulator physics and emerging nanotechnology of ultra-thin multilayers and heteropitaxial functional oxides.

**Figure 4.** Discrete band dispersion obtained by DARPES with a photon energy of 67 eV, along the nodal direction in a 12-unit cell thin BSCCO film; for more details see ref. [17].

5. **Concluding Remarks and Ongoing Work**

In addition to our original DARPES results, another result that caught a lot of attention is in our confirmation of Naito’s discovery that $T_c$ can be enhanced by compressive strain in LSCO-214 films [5]. As summarised in Table 1, the superconducting critical temperature, $T_c$, is enhanced in all our compressively strained films [12]. It is diminished and ultimately disappears in tensile strained films[13]. What is truly striking is that by using essentially the same growth and oxidation procedure in underdoped ($x=0.1$) and overdoped ($x=0.2$) films we essentially double $T_c$ in both cases simply by changing the substrate of the film (thereby altering the compressive strain). Most theoretical models at this stage do not include the strain or pressure effects in high-$T_c$ cuprates.

| Doping, x | Unstrained film/$T_c$(K) | Compressive Strain / $T_c$(K) |
|-----------|------------------------|-----------------------------|
| 0.10      | 20                     | 40                          |
| 0.15      | 8                      | 44                          |
| 0.20      | 24                     | 40                          |

It is highly unlikely that the aforementioned changes in the in-plane electronic structure alone (see the discussion in section 2) can account for the measured $T_c$-enhancement effects. Especially striking
is the case of overdoped films (x=0.2); in that regime, where samples are expected to behave almost as in the Fermi liquid / BCS picture, an enhancement of density of states would be a natural explanation, yet that doesn’t seem to be the case according to our DARPES results [12, 13]. As the compressive strain clearly alters the lattice and increases the c-axis length, one has to take seriously models that take into account the role of the lattice and of the strain. It seems difficult to argue that some sort of ‘magnetic’ mechanism that completely neglects the lattice effects would give such a Tc-enhancement, especially in the overdoped samples, yet this possibility still cannot be ruled out without further work. However, better understanding of basic mechanisms that govern superconductivity and/or magnetism in these complex oxide heteroepitaxies is an immediate prerequisite and our ongoing key goal.

By now we have the DARPES data on Fermi surface (FS) topology in both, relaxed, compressively and tensile strained optimal and overdoped LSCO films [13]. We also have a series of spectra for the La-doped Bi-2201 films. We intend to grow and study the electron doped compounds Nd2-xCexCuO4 that were never been studied under strain (see also Fig. 2). And we shall use the resonant inelastic X-ray scattering technique (RIXS), that is currently being developed by M. Grioni et al. The RIXS should enable us to verify in-depth electronic features (as compared to ARPES and DARPES). Clearly, we will focus even more attention onto ultrathin films, their surfaces and interfaces and the search for an enhanced interface superconductivity. Last but not least, our DARPES approach can be and will be extended to other functional (oxides) heteroepitaxies.

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