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Core and valence level photoemission study of the composition dependent metal to non-metal transition in thin film $Bi_{2.1}Sr_{1.7}Ca_{0.85-x}Y_xCu_2O_{8+\delta}$

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The composition dependent metal to non-metal transition in a series of single phase, two copper-layer, strongly c-axis oriented thin films of composition $Bi_{2.1}Sr_{1.7}Ca_{0.85-x}Y_xCu_2O_{8+\delta}$ has been studied using core and valence level photoemission. The decrease in itinerant hole concentration brought about by yttrium doping is accompanied by changes in both the valence and the core level photoemission spectra.

1. INTRODUCTION.

Despite many spectroscopic studies of high temperature superconductors[1], there are still a number of controversies surrounding their electronic structure. One such is the atomic nature of the electronic states near the Fermi level, E_F. In this respect the Bi-Sr-Ca-Cu-O (BSCCO) system has been extensively studied as it readily supports a measurable density of states (DOS) at the Fermi energy at room temperature in single crystal[2], thin film[3] and bulk polycrystalline samples[4].

In previous studies of the BSCCO system[3,4,5] we have correlated the size of the DOS at E_F with the superconducting transition temperature by comparing the 85K two copper-layer phase with the 110K three copper-layer $(Bi_{0.9}Pb_{0.1})_2Sr_2Ca_2Cu_3O_{10+\delta}$ phase. Not only was the DOS supported by the three

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Cu-layer material greater, but a distinct asymmetry was observed in the Pb:4f core peaks. This asymmetry is also present to a lesser degree in the Bi:4f peakshape of other members of the BSCCO system[6] and its interpretation remains controversial. In this paper, we investigate the correlation of both this asymmetry and changes in the Cu:2p core peaks with the itinerant hole concentration by successively replacing the Ca with Y in thin films of the two copper-layer $Bi_{2.1}Sr_{1.7}Ca_{0.85-x}Y_xCu_2O_{8+\delta}$ system.

2. EXPERIMENTAL.

Thin film samples of Y doped two Cu-layer BSCCO phase were prepared by spin pyrolysis[7] of 2-ethyl hexanoate precursors. Chloroform solutions of the precursors were mixed in the proportions Bi:Sr:Ca:Y:Cu of 2.1:1.7:0.85-x:x:2 as determined by ICPS, with x varying from 0 to 0.85, and deposited onto spinning MgO (100) substrates. The films were pyrolysed at 400°C for one minute in air and then annealed in air at temperatures ranging from 825-865°C for up to 10 hours. This produced single phase (from XRD and SEM including calibrated X-ray microanalysis), highly c-axis oriented films of thickness 0.4-0.5μm with no variation from the nominal composition. On adding Y, the c-axis parameter decreased from 30.66Å for x=0 to 30.24Å for the fully Y substituted sample.

Photoemission studies were carried out in a VG Escalab Mark II instrument, equipped with analysis and preparation chambers and a sample fast entry lock. Radiation for the photoemission experiments was supplied by a double-anode X-ray source (Mg:Kα and Al:Kα) and a noble gas discharge lamp. Analyser resolution was set at 0.4eV for the X-ray measurements and 0.1eV for He I photoemission. The position of the Fermi energy was determined (±0.025eV) from measurements on a cleaned Ni stub.

Samples were attached to platinum stubs and cleaned by annealing in one atmosphere of pure oxygen in the preparation chamber by coupling to the RF field provided by a water cooled copper work coil connected to a Radyne 1.5kW 400kHz power supply. Sample temperature was monitored using an emissivity-calibrated infrared pyrometer. Typically, samples were heated to 530°C for three hours and then cooled over half an hour and spectra recorded within one hour of the anneal.

3. RESULTS.

The substitution of Y for Ca in the BSCCO system is well established for bulk polycrystalline material[8] and leads to a formal reduction of the $Cu-O_2$ planes, T_c

falling to zero when approximately more than half the calcium has been replaced.One of the benefits of using Y substitution as a method to control the hole concentration in BSCCO is the lack of perturbation of the crystallographic environment of the other layers in the material, allowing detailed comparative studies across the metal to non-metal transition.

3.1. Core level photoemission.

XPS measurements on the cleaned surfaces showed no evidence of $SrCO_3$ or $CaCO_3$ contamination and in most cases no adventitious hydrocarbon - all common contaminants on uncleaned surfaces[3,4,5]. Integration of peak areas from XPS indicate that the surface Ca/Y ratio corresponds to the bulk nominal value, i.e. that no surface segregation effects have occurred. The superposition of the $Bi:4f_{7/2}$ line on the Y:3d peaks meant that the $Y:3p_{3/2}$ peak was used as a guide to the surface Y content. Figure 1 shows the evolution of this peak as a function of the Y doping level.
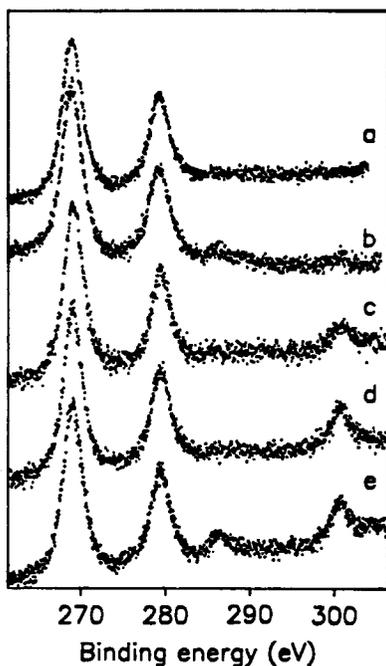

FIGURE 1
Al:Kα XPS of the Sr:3p region for Y doping levels x=0(a); 0.1(b); 0.25(c); 0.425(d) and 0.85(e). Note the appearance of the $Y:3p_{3/2}$ peak at 301 eV binding energy.

The Bi:$4f_{5/2}$ profile for the undoped sample together with that of the fully Y doped film are shown in Figure 2. Despite the slightly greater peak width (FWHM) of the non-metallic sample, it can be seen that the peak asymmetry is also less pronounced, although this effect is small. The presence of a Bi partial DOS at E_F leads to electron-hole excitations across the Fermi level at the atomic site, thus causing the asymmetry of the Bi:$4f_{5/2}$ peak[5]. The decrease in the asymmetry in the fully Y substituted sample correlates with the non-metallic nature of the Bi-O planes in this material, making such low energy loss mechanisms impossible.
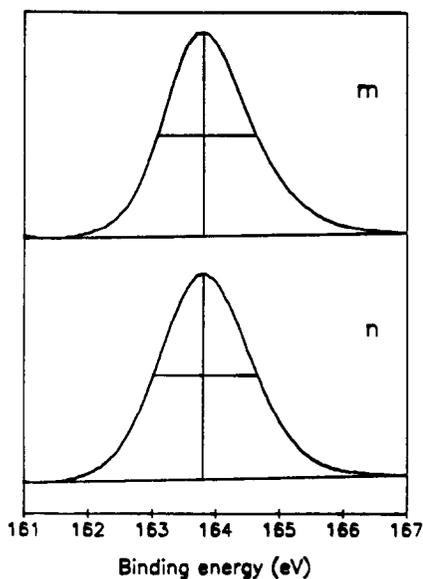

FIGURE 2
Al:Kα XPS profiles for Bi:4f5/2 region. Top spectrum (m) has Y doping level x=0. Spectrum (n) has Y level x=0.85. Lines are marked at the FWHM, peak centre and baseline as a guide to the eye. Spectra are area normalised.
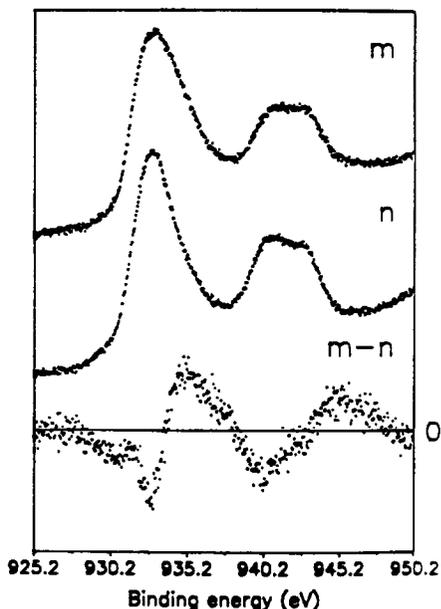
FIGURE 3
Al:Kα XPS spectra of Cu:2p3/2 region for doping levels x=0 (m) and x=0.85 (n). Spectra m and n are area normalised. Subtraction spectrum (m-n) is shown with a y-scale expanded by a factor of three.

Figure 3 shows the $Cu:2p_{3/2}$ spectra of the x=0 and x=0.85 films.The upper (x=0) spectrum displays the familiar double peak structure common to all the high T_c materials, produced by strong Cu/O covalency leading to valence electron transfer from the O:2p to the Cu:3d levels during photoionisation.

The main peak at 932.7 eV is due to well screened $|2p^53d^{10}\underline{L}^n>$ final states (where $\underline{L}^n$ denotes n ligand holes) and the broader feature centred at 941.8 eV arises from unscreened $Cu:3d^9$ final state processes.

The spectrum of the non-metallic sample shows similar overall structure but with greatly reduced FWHM of the main and satellite peaks. More information can be derived by consideration of the subtraction spectrum displayed underneath (labelled m-n): it shows significantly lower intensity on the high binding energy side of the well screened peak as well as greater spectral weight at the peak maximum.

The shifts in intensity from the metallic to the non-metallic sample are consistent with changes in the *formal* copper oxidation state. In the x=0 sample (with δ=0) the average copper valence is 2.3; in the fully Y substituted sample this value drops to 1.875, i.e. a mainly Cu^{2+} compound with a small amount of Cu^{1+}. The presence of Cu^{3+} in the metallic sample opens up the possibility of $|2p^53d^{10}\underline{L}^2>$ final states and it is these states that give rise to the intensity at higher binding energy than the main peak maximum. Likewise, increased intensity on the high binding energy side of the 941.8 eV satellite peak is associated with the availability of $|2p^53d^9\underline{L}^1>$ final states. The increase in intensity at 932.7 eV in the non-metallic sample is evidence of the greater Cu^{2+} content and is seen as a dip in the subtraction spectrum centred at that point. The contribution from Cu^{1+} in the same sample, where final states involving ligand-copper charge transfer are impossible, leads to an increase in intensity at lower binding energy than the peak maximum, causing a shoulder in the subtraction spectrum at 930.2 eV. These data are similar to those found in photoemission studies of $YBa_2Cu_3O_{7-x}$ (x=0.1 and x=1)[9], where the hole concentration can be readily controlled by variation in oxygen content.

3.2 Valence level photoemission.

In the last section it has been shown how changes in electronic structure across the metal to non-metal transition can lead to distinct changes in the core level photoemission spectra of Y doped BSCCO superconductors. Now we turn our attention to the valence level photoemission.

The He I (hv = 21.2 eV) spectra taken from films with four different Y doping levels are shown in Figure 4. The overall spectral profiles are similar to those that have been obtained from other Bi-based superconductors [3,4,5] including ceramic

samples in which Y has been substituted for Ca in the two copper-layer BSCCO phase[10,11]. A shift in valence band structure to higher binding energy is seen in comparing data from samples with x=0 and x=0.85. This is consistent with a model where hole doping introduces empty states into the previously filled bandstructure. Our data thus reinforce the conclusion of Fujimori et al[11] that photoemission of BSCCO superconductors is inconsistent with the idea that hole doping is itself responsible for the appearance of states above the main valence band edge.
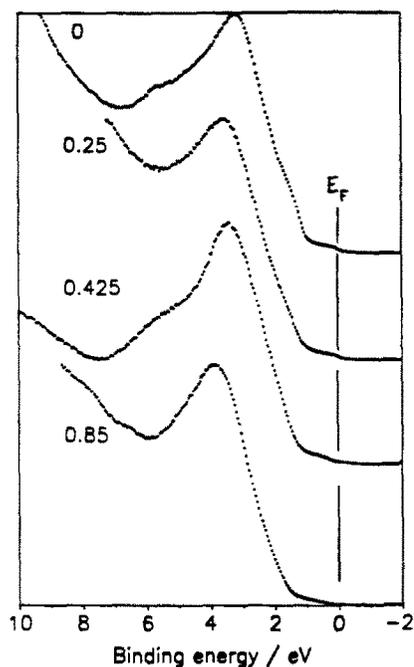

FIGURE 4

He I (hv = 21.2 eV) spectra of films with Y doping levels of 0, 0.25, 0.425 and 0.85. Spectra have been aligned at E_F using measurements from a cleaned Ni stub.
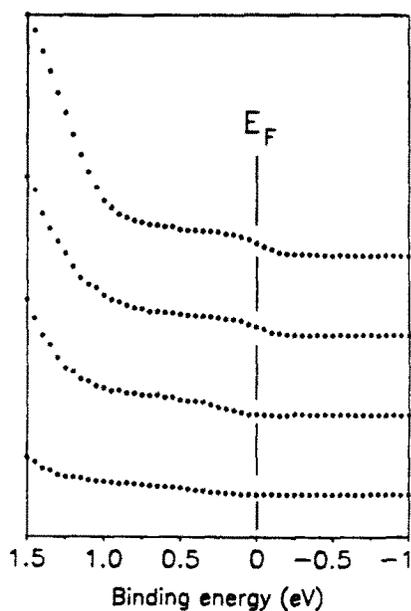
FIGURE 5

He I photoemission of the Fermi level region of samples with Y levels of 0, 0.25, 0.425 and 0.85. Spectra have been stripped of contributions from He Iβ and He Iγ satellite radiation. Note the decrease in DOS at E_F as the Y level increases.

The changes in the region around E_F can be seen in more detail in Figure 5. Here the spectra have been stripped of contributions from He Iβ and He Iγ radiation and are displayed on a y-scale equivalent to that in Figure 4 but expanded by a constant factor. The metallic samples (x=0 and x=0.25) exhibit a clearly resolved Fermi-Dirac cutoff in the density of states at E_F, the size of which is somewhat smaller for the x=0.25 sample. Figure 5 also emphasises the way in which the main valence band onset shifts progressively to higher binding energy with increasing Y content.

4. CONCLUSIONS.

It has been shown that substitution of Y for Ca in single phase thin films of the two copper-layer BSCCO phase results in a decrease in the itinerant hole concentration leading to a metal to non-metal transition. These changes in electronic structure are seen in features of both the core and valence level photoemission spectra.

In the core level photoemission, an absence of features associated with the presence of Cu^{3+} in the $Cu:2p_{3/2}$ spectra are correlated with the reduction of the nominal copper valency in the fully Y substituted sample. Note however that "Cu^{3+}" is manifest in terms of $|2p^5 3d^{10} \underline{L}^2\rangle$ and $|2p^5 3d^9 \underline{L}^1\rangle$ final states. The decrease in asymmetry of the $Bi:4f_{5/2}$ profile on total yttrium substitution is consistent with the lack of Bi partial DOS at E_F in the material at this doping level.

The valence level photoemission clearly shows the reduction of the density of states at the Fermi level and a shift of the main valence band photoemission onset to higher binding energy with increasing Y doping.

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