

Chapter 5

Sample Surface Ageing

5.1 Introduction

Despite the reduction in surface sensitivity offered by 6 eV ARPES, sample surface ageing is still a concern. As the sample sits in the vacuum chamber at low temperature, gasses can freeze onto the surface, eventually altering the ARPES spectra. In this section I present a brief study on sample ageing using laser ARPES combined with extremely surface sensitive x-ray photoemission spectroscopy (XPS) (Hüfner, 2003).

5.2 Experimental

The samples for the ageing study were grown by Lou Lombardo and Aharon Kapitulnik at Stanford University using the directional solidification technique. Single domain samples were cut from the raw material, and annealed in air at 700° C, resulting in optimally doped Bi2212 with a transition temperature near 90 K. A detailed discussion of general sample preparation techniques is presented in section 6.2.

An Al cathode x-ray source (Physical Electronics 10-610) coupled with a toroidal quartz monochromator (Physical Electronics 10-420) was used to produce 1487 eV photons with a bandwidth of about 0.5 eV. The XPS data was acquired with the Scienta spectrometer in transmission mode, at either 200 eV or 50 eV pass

energy, using a curved analyzer entrance slit. These experiments were performed before the angle-mode calibrations of section 3.5 were completed. Nonetheless, we were able to observe bands in Bi2212 with 6 eV photons, and could diagnose some changes in the spectra as the samples aged. However, changes in the fine structure were not possible to track.

5.3 XPS and laser ARPES

Figure 5.1 shows an XPS spectrum from freshly cleaved Bi2212, indicating which core levels correspond to the various peaks. Keep in mind that we are now looking hundred of volts below the Fermi surface, far beyond the range of laser ARPES. To save time, data was only acquired in small regions surrounding the peaks. The Sr 3d, Bi 4f, Ca 2p, and Cu 2p peaks originate solely from within the sample, while the N 1s and C 1s peaks are expected from gas molecules deposited on the surface. The O 1s peak contains contributions both from oxygen within the sample, and from oxygen gas deposited on the cold surface. By far the most abundant gas in the chamber is hydrogen, which, unfortunately, is difficult to measure with XPS.¹

In order to better understand the sample ageing process, we measured Bi2212 at low temperature, alternating between laser ARPES and XPS, over the course of several days. After 2 days, the nodal electronic bands became broader and less intense, and after 8 days in the vacuum chamber at $T = 20$ K, we were no longer able to observe well defined electron bands at all with laser ARPES. This was accompanied by several changes in the the XPS spectra. Figure 5.2 shows a close up of the O 1s peaks taken over the course of these 8 days. The data in this figure is peak normalized and has a constant offset subtracted in order to com-

¹ If hydrogen is chemisorbed, then it has no electrons left to photoemit. Even if we do eject electrons from it, they are at an energy with many other strong features (like the valence band).

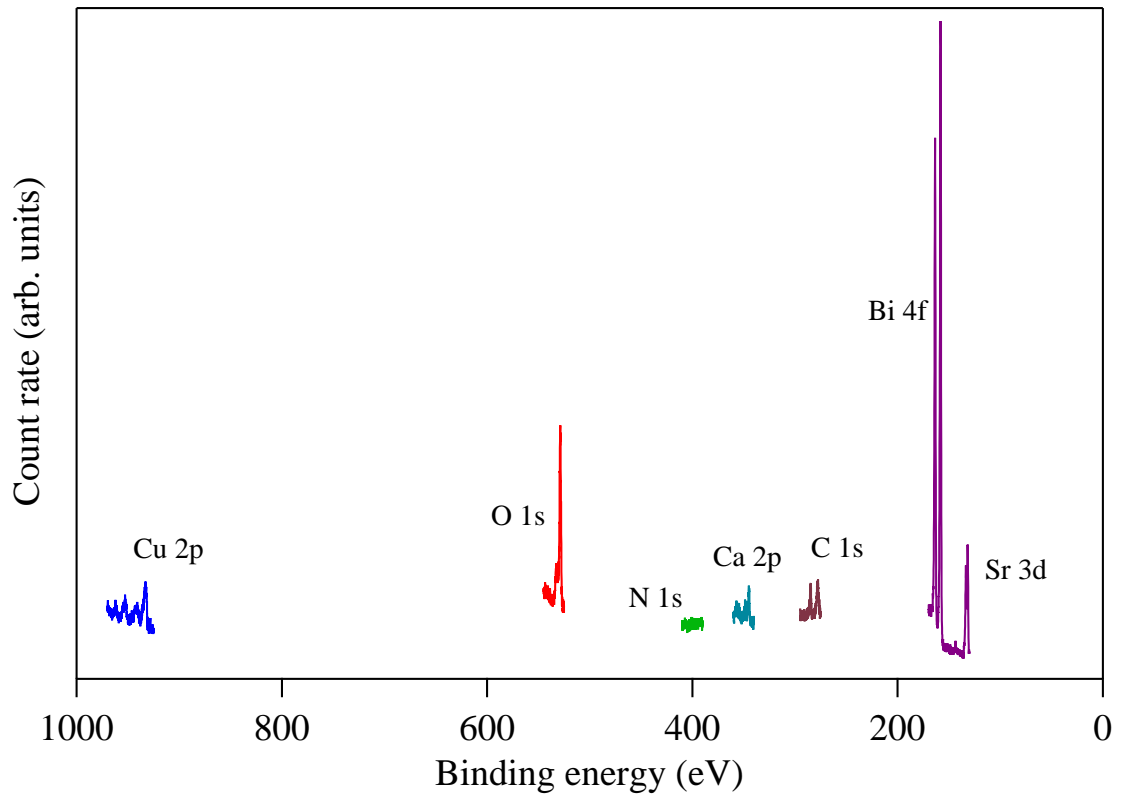


Figure 5.1: (color) High resolution XPS spectra from vacuum-cleaved Bi2212 at $T = 20$ K. The peaks are from core levels as indicated.

pare the oxygen peak lineshapes. While the lineshape of the peak labeled 'bulk oxygen' remains constant over time, the 'surface oxygen' peak grows as more gas is deposited onto the sample surface. When we warm the sample to 200 K, frozen gasses sublime from the sample surface (this is verified by the observation of a rise in oxygen pressure measured with a residual gas analyzer (RGA)), the surface oxygen peak disappears from the XPS spectrum, and we are again able to resolve dispersive bands with laser ARPES.

The fact that the laser ARPES features broaden as the sample ages may result from an increase in scattering of photoelectrons off the surface contaminants. Photons may also be absorbed by frozen gas on the sample surface, but this alone is not expected to cause any broadening of the ARPES spectra, only a reduction in intensity. There is some evidence for an increase in photoelectron scattering which is shown in figure 5.3, where the same oxygen peaks are plotted without the removal of constant offset. When plotted in this way, we can observe the change in the size of the background that these peaks sit on. As more gas molecules stick on the sample surface, more photoelectrons will lose energy by scattering off them, causing an increase in the overall strength of the XPS background. This is observed in the O 1s peaks where the magnitude of the background is correlated with the strength of the surface oxygen peak, which both increase with time. After the sample is warmed to 200 K, the inelastic background is reduced to near its original magnitude.

This study suggests that scattering of photoelectrons off surface contaminants is a main contributor to changes in the ARPES spectra over time. However, cleaning of the surface by warming does not necessarily restore the sample to its original state. Oxygen in particular may be problematic since it is the hole dopant used in Bi2212. Oxygen molecules chemisorbed on the sample surface will donate holes to the sample, therefore locally changing the doping level.

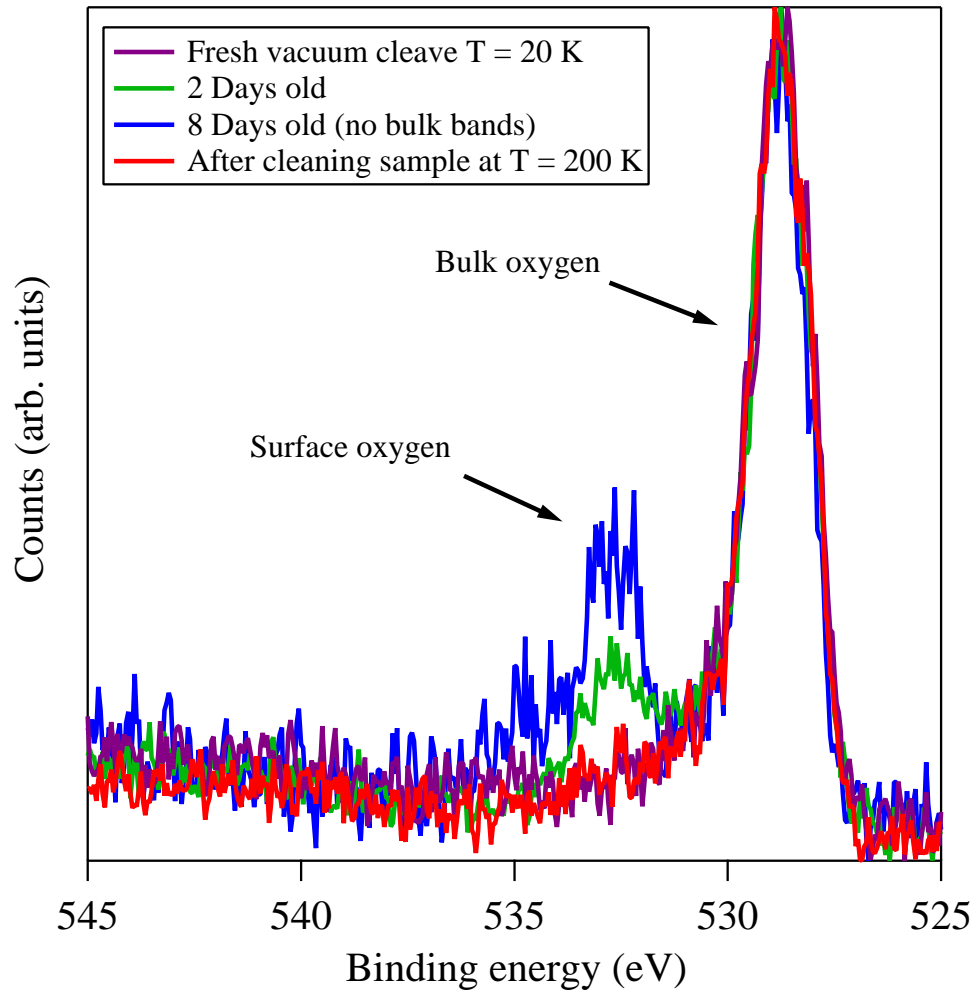


Figure 5.2: (color) The oxygen 1s peaks from Bi2212 at different times after the cleave. A constant background was subtracted from each spectrum to allow direct comparison. The peak derived from bulk oxygen is stable over time, while the surface oxygen peak grows as more oxygen sticks to the cold surface.

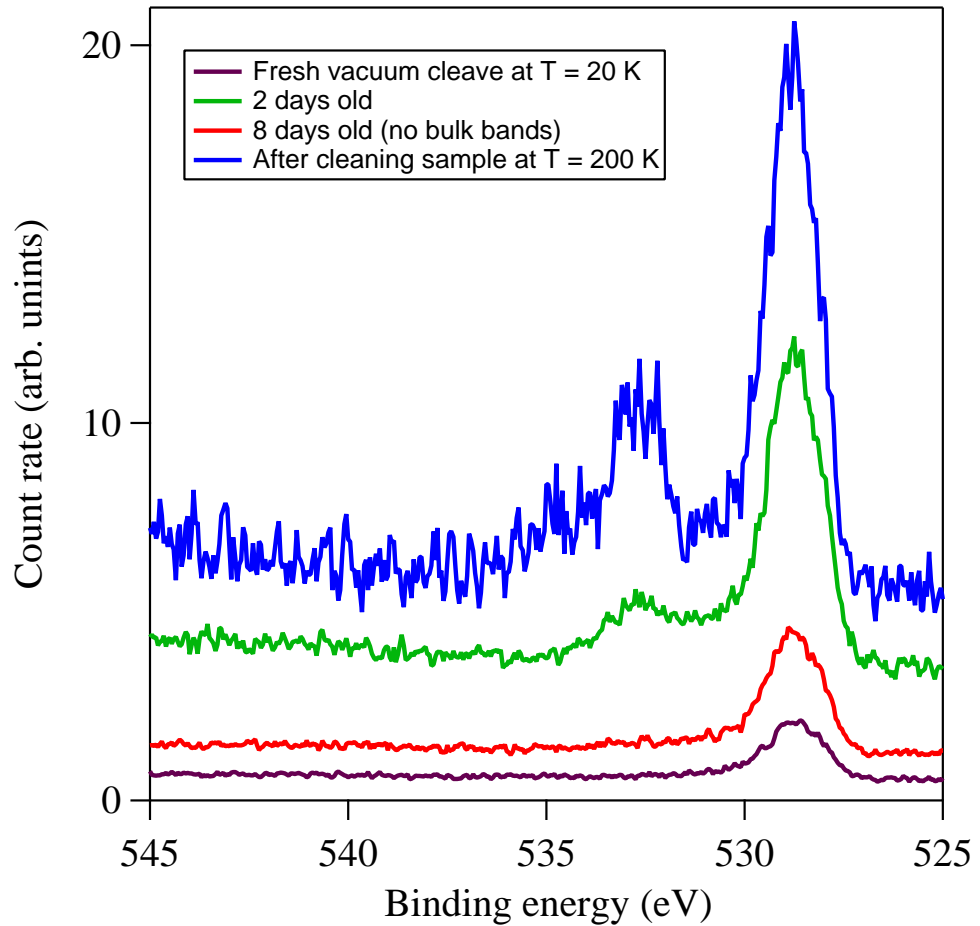


Figure 5.3: (color) The same O 1s data from figure 5.2 are shown, this time with no constant background subtraction. When plotted in this way, we can observe the change in the size of the background which these peaks sit on. As more gas molecules stick on the sample surface, more photoelectrons will lose energy by scattering off them, causing an increase in the overall strength of the XPS background.