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Surface restructuring in sputter-damaged $Bi_2Sr_2CaCu_2O_{8+\delta}$

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The high-T_c cuprate Bi-2212 is sputtered with 500 eV Ar^+ ions, and changes to the surface composition are investigated with low energy (2 keV) Na^+ ion scattering. It is shown that ion bombardment leads to the development of a Bi-O overlayer, differing in structure from the underlying material and making the surface highly resistant to further sputtering-induced changes. In contrast, sputtering and ion-scattering simulations would suggest that atoms from lower layers should be present at the surface as a consequence of the kinematics of the sputtering process. It is thus concluded that the Bi-O layer forms because the surfactant effects of Bi reduce the surface energy.

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I. INTRODUCTION

Ion-beam mixing of surfaces under particle bombardment is a phenomenon of considerable importance, especially with respect to the resolution of secondary-ion mass spectrometry (SIMS) depth profiling[1] and to the formation of surface structures in thin films via sputtering.[2] The projectile species, energy, and the composition of the target crystal all greatly affect these processes, the result of which could be the formation of 2D or 3D structures.[3] Collision cascades created during sputtering either result in thermal spikes that activate what are essentially chemical interactions, or they proceed in a largely ballistic way with binary collisions accounting for the final arrangement of atoms. The miscibility of target atoms, sputtering yield, and mass of the projectile all contribute to the final structure, with purely kinematic effects being in competition with chemical or energetic processes.

Despite its importance, there are still significant open questions about the details of the rearrangement that atoms undergo in ion-beam mixing. This is especially true when it comes to the outermost layer of atoms, as the analytical techniques used typically probe many atomic layers, thus missing detail on the monolayer length scale. While the density of species can be depth profiled by Rutherford backscattering spectrometry (RBS) after sputtering,[4] it is often impossible to say where the atoms in the resulting layers originated. Forming structures with marker layers (ones with more than one atomic species formed into layers) partially solves this problem, but systems fabricated for this purpose have been large scale (>50 nm) in size and hence miss the fundamental atomic scale details of the ion-beam mixing process.

The problem of creating a heterostructure with many distinct marker layers is obviated by using a substance that naturally organizes into pristine planes of differing atomic species. One such material is $Bi_2Sr_2CaCu_2O_{8+\delta}$ (abbreviated Bi-2212), a high-T_c superconductor. It can be reliably cleaved in ultra-high vacuum (UHV), producing atomically flat and clean terraces. Each of the first four layers of the structure contains metallic atoms that differ in mass from 40 to 209 amu, all within about 6 Å along the c-axis. It is thus unlike two-component materials, such as TiO_2 or GaAs, where the origin of the post-irradiation surface atoms cannot be identified. The application of a surface sensitive and mass-resolved measurement technique to Bi-2212 would enable a determination of not only what comprises the surface, but would also specify where the atoms originated from with atomic-layer resolution.

Bi-2212 is also an interesting material because the outer layer is composed of Bi, a well-known surfactant. The effect of surfactants on materials is to reduce their overall surface energy. This has the result of allowing layers to exist even with a large lattice mismatch and strain.[5] As such, there is the opportunity to see if it is either kinematics, due to the atomic collisions, or energetic mechanisms, such as surface segregation of surfactants, that ultimately win out in the sputtering process.

We employed low-energy ion scattering (LEIS) with sodium (Na^+) projectiles to determine the specific composition of the outermost atomic layer after sputtering. Note that the same information could not have been obtained with scanning tunneling microscopy (STM), as it is difficult to specifically identify the species responsible for image contrast.[6] Initial ion-scattering studies of the Bi-2212 surface were recently conducted by our group both with and without adsorbates.[7] This work clearly showed that the as-cleaved surface is terminated solely by Bi-O, as was previously posited, independent of cleave temperature. SIMS studies of Bi-2212 material were mostly ambiguous in detailing any sputter-induced changes,[8] as they only investigated relatively large etch rates and were unable to say anything about the structure of the surface following sputtering.

LEIS owes its extreme surface sensitivity to the fact that single binary collisions that result in backscattering occur only with atoms that are directly visible to the ion beam. The ions that undergo single elastic collisions with these exposed surface atoms scatter with energy commensurate with the target mass so that the atomic species at the surface can be positively identified using simple classical mechanics. By employing time-of-flight (TOF) detection, the surface sensitivity is independent of the ion neutralization as the detector responds identically to ions and neutrals. This provides a more realistic picture of the atomic composition at a surface than does traditional ion scattering spectroscopy (ISS) using He projectiles[9] or SIMS studies, which detect only secondary ions. Single scattering from Bi, Sr, Ca, and

Cu atoms would be well separated in LEIS spectra, so it becomes possible to specifically infer which layers of the structure contribute atoms to the resulting surface layer when the sample is sputtered. (Note that oxygen is too light to identify with Na^+ projectile backscattering.) Although sputter beam studies have been performed looking at the restructuring of three-component solids such as $SrTiO_3$,[10] none to our knowledge have been conducted with more than two easily identifiable species.

In this study Na^+ TOF-LEIS was collected as the Bi-2212 surface was sputtered by Ar^+ with fluences ranging from very light sputtering to that of one incident Ar^+ ion per surface atom. Ballistic simulations (detailed subsequently) indicate that this energy results in collision cascades that affect several layers in the crystal, and the depth affected at these sputtering energies is estimated to be greater than 20 Å.[11] The results show, however, that an unexpectedly large amount of Bi remains on the surface as Sr becomes uncovered. Thus, the expectations of a purely kinematic process differ from the experimental findings. We conclude that a layer of Bi-O is formed at the surface by the sputtering process, and this layer blunts the effect of further sputtering due to the immiscibility of Bi and its surfactant effect on flat semiconductor growth. The make-up of this layer has essentially no contribution from Ca or Cu, implying that ion-beam mixing does not occur due to this protective layer.

II. EXPERIMENTAL PROCEDURE

The experiment was conducted in a UHV chamber with a base pressure of 3×10^{-10} torr. Single crystal Bi-2212 samples were grown by a floating zone method,[12] and the superconductivity of the single crystals was measured by SQUID. The superconducting transition temperature of the as-grown Bi-2212 crystals was 91 K. Samples were cleaved *in situ* using the following method provided by A.N. Pasupathy[13]: The $\sim 7 \times 7$ mm^2 samples were affixed to a copper sample holder with a very thin layer of H20E epoxy (Epotek), which was cured for 30 minutes at 100 °C. Then a small piece of aluminum was affixed to the top of the sample by way of a small amount of Torr-Seal, which was cured for 15 minutes at 70 °C. After transferring the sample into the UHV chamber, the aluminum-Torr-Seal amalgam was mechanically knocked off, cleaving the sample and revealing a pristine Bi-O layer with a mirrorlike surface.[7]

To investigate the effects of beam damage, samples cleaved at room temperature were bombarded with an Ar^+ beam at 500 eV with a current density of approximately 5 μA·cm^{-2}. Sputtering was carried out with a back-filled PHI sputtering gun at a chamber pressure of 1×10^{-5} torr of Ar. TOF LEIS spectra and secondary electron cutoff measurements aimed at measuring work function shifts were collected following each round of sputtering after the Ar was pumped out, and the cycle was repeated for several rounds. Fluence was increased past where the ratio of surface Bi/Sr reached a plateau up to a fluence corresponding to one incident Ar^+ ion per surface Bi atom. We note that in prior work[7] no significant structural differences were observed between ISS of samples cleaved at room temperature and those cleaved at low temperature.

The details of the TOF ion-scattering apparatus have been described elsewhere.[14] For these experiments a 2-keV beam of Na^+ ions is produced from a Kimball Physics IGS-4 alkali ion gun, which is pulsed at 80 kHz and focused onto the sample at an incoming angle of 30° with respect to the surface normal. The flight time of the scattered projectiles emitted along the surface normal is recorded by measuring the time difference between the ion pulses and counts recorded on a microchannel-plate detector located in the end of a flight tube at approximately 0.5 m from the sample. Although the pulse width can be as small as $\sim$20 ns, in this study we found that increasing the pulse width to $\sim$200 ns gave satisfactory time resolution and much better signal strength. Exposure to the alkali ion beam was limited to ensure less than 1% dosage to any spot on the specimen. The shift of the surface work function was determined by bombarding the sample with 100 eV electrons and measuring the low-energy cutoff of the secondary electron spectra with a Comstock AC-901 electrostatic analyzer, giving work function shifts to within an accuracy of 0.04 eV.[15]

Computer simulations using two different software packages were carried out to help understand the LEIS and sputtering results. Both use the screened Ziegler-Biersack-Littmark (“universal”) potential in the binary collision model to approximate the final trajectories of ions and surface atoms in the scattering and sputtering processes.

The first simulation package utilized was KALYPSO,[16] which is ideally suited for ion scattering. Although limited to two target elements, it can quickly simulate the energy spectrum of backscattered ions for a predetermined crystal structure and set of initial trajectories. Because of the two-element limitation, scattering from Bi and Sr in the crystalline structure had to be modeled separately, as subsequently described. The sum of these results would be identical to the result of performing the simulations together, as there were essentially no backscattered trajectories that interacted with both of these elements.

The second simulation software package, MARLOWE,[17] was used to estimate the efficiency with which each atomic species in the crystal was sputtered, assuming that the process is essentially ballistic. The software can accommodate the entire crystal structure of Bi-2212 and keeps track of the dynamics of collisions in a cascade created by an incident ion. Atoms displaced in a collision can remain in the displaced position during subsequent cascades, allowing simulation of the effect that crystal damage has on the sputtering rate. The software keeps track of all ejected atoms, and so it is ideal for simulating the sputtering yield for this system. Because the program has a limit of five atomic species, it was not possible to also specify Ar as the incident ion. Instead, Ca was used for the projectile, as its mass is nearly the same. Although the accuracy of the screened potential will be slightly incorrect due to the different number of electrons in Ar and Ca, this small deviation is assumed to be negligible.

In MARLOWE the unit cell of Bi-2212 was specified, and a $3 \times 3 \times 3$ crystal constructed from it. Incident Ca ions were given a kinetic energy of 500 eV, and the initial trajectories were chosen randomly on the target surface. Using identical binding energies of 0.5 eV for all species, atoms escaping from the crystal by way of collision cascades were recorded and tabulated as a function of accumulated damage. In this way

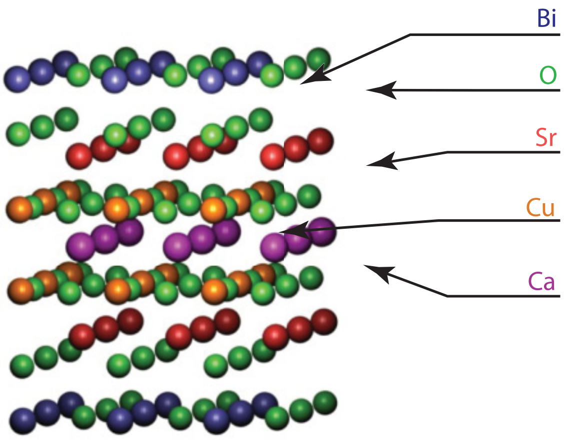

FIG. 1. (Color online) A side view of the crystal structure of $Bi_2Sr_2CaCu_2O_8$. The dimensions depicted are 7.33 Å × 7.33 Å × 12 Å.

the sputtering rate of each species can be modeled relative to all the others as the crystal is subjected to lattice vacancies and displacements. After a collision cascade has terminated, the crystal can either be reset or the current damaged configuration can be retained for further calculations. In our simulations the program accumulated damage until the crystal reached a steady state (chosen to be after 100 cascades), whereupon it was reset. The number of outgoing atoms was then tabulated to give the distribution of sputtered atoms by species. We note that the system is quite insensitive to the value of binding energy, as is normally reported for these energy ranges.[18] As such, the model does not update binding energies for displaced atoms.

III. RESULTS AND DISCUSSION

Figure 1 shows the atomic structure of Bi-2212. The material is a layered crystal with repeated inverted layers. The oxygen atoms are in-plane with the metal atoms for all layers except the Sr-O layer, in which the oxygen atoms are located slightly closer to the Bi-O layer. Weak van der Waals binding between the adjacent Bi-O layers ensures that samples always cleave at this interface.[19]

A TOF spectrum from as-cleaved Bi-2212 is shown as the bottom curve of Fig. 2. The sharp peak representing quasisingle-scattering binary collisions of Na^+ with Bi is clearly seen at about 4-μs flight time. The broad background at longer flight times corresponds to projectiles that have escaped the surface after suffering multiple collisions, or species recoiled into the detector (presumably oxygen). No scattering from Sr or any other metallic element is visible from the virgin surface, as was previously observed.[7]

TOF-LEIS spectra collected as the sputtering fluence is increased are shown in Fig. 2. Note that it is estimated that there are 1.5×10^{15} surface atoms·cm^{-2} in Bi-2212, so these spectra represent the range of fluences from 0 to 1 Ar^+ ion per surface Bi atom (although it should be noted that each collision cascade is expected to eject on average about 1.6 atoms[20]). The single-scattering peak (SSP) that emerges at ∼6 μs after 1 minute of sputtering is attributed to scattering from Sr, as the flight time indicates that the energy of that peak corresponds to an elastic binary collision of Na^+ with Sr, consistent with the simulations (cf. Fig. 3). The Bi peak is somewhat attenuated as the Ar^+ fluence increases, while the intensity of the Sr SSP increases. After a fluence of 2×10^{14} cm^{-2}, these intensities saturate. In addition the underlying Cu and Ca species are never visible with LEIS. Although not shown in the figure, even quadrupling the fluence produces no further noticeable effects.

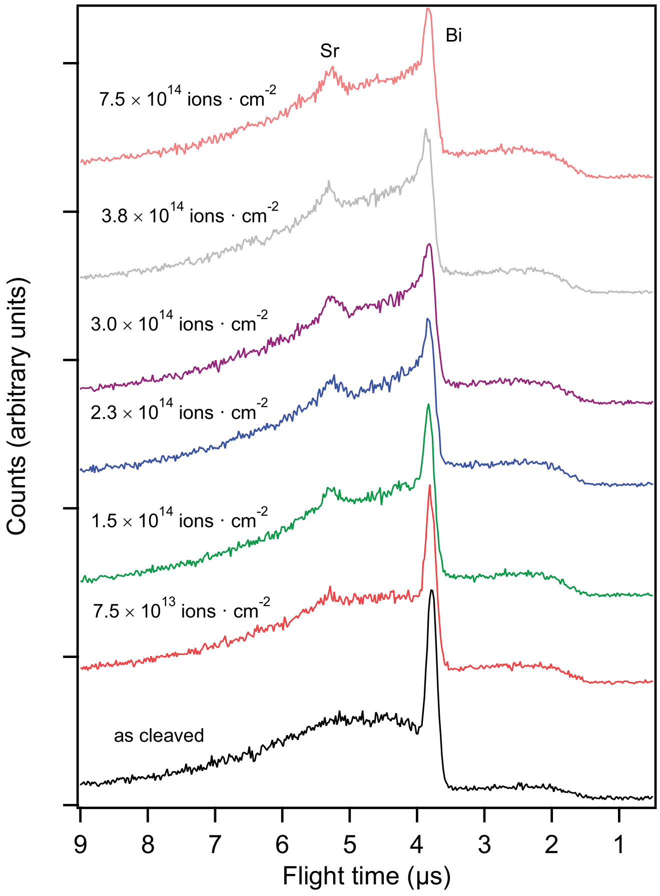

FIG. 2. (Color online) TOF spectra for 2 keV Na^+ scattered from Bi-2212 with increasing amounts of Ar^+ sputtering damage given as fluence (total ion flux per area).

The cross section for scattering is dependent on the mass of the target atom and is thus not the same for all species in this material. It is possible, however, to estimate the cross sections for scattering of Na^+ from these species using Thomas-Fermi theory.[21] The purpose is to give a rough estimate of the minimum amount of Cu that would need to be at the surface due to ion-beam mixing so that the signal would be visible. The calculated ratios of the differential cross sections for Na scattering from Sr, Ca, Cu compared to Bi are $\sigma_{\mathrm{Bi}}/\sigma_{\mathrm{Sr}} = 1.65$, $\sigma_{\mathrm{Bi}}/\sigma_{\mathrm{Ca}} = 1.90$, and $\sigma_{\mathrm{Bi}}/\sigma_{\mathrm{Cu}} = 2.29$. Thus, since Cu has only a slightly smaller cross section than Sr, it should also be seen if it were present in a similar concentration. By employing a fitting procedure (described subsequently), it is shown that the fraction of surface atoms made up of Cu is less than 1%. We can conclude from this that the LEIS spectra probe only the outermost layer of the sample; moreover, although Sr becomes visible quickly, Cu, though located only one atomic layer below, is never present at the surface. Thus, Cu atoms are not promoted in any significant number by the ion bombardment

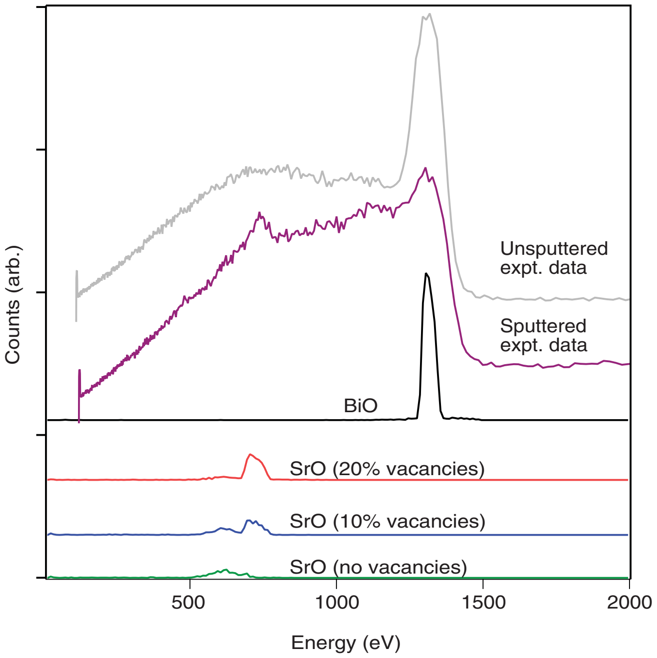

FIG. 3. (Color online) Ion-scattering spectra predicted by KALYPSO simulation of the Bi-2212 upper layers (Bi-O and Sr-O). Sr-O is shown for differing levels of oxygen vacancies in the Bi-O layer. Also shown for comparison are measured TOF spectra of the as-cleaved and sputtered surfaces.

from the third layer to the higher layers where they could be detected.

To investigate whether the absence of single scattering from Sr is reasonable from the as-cleaved surface and to clarify the role of oxygen vacancies in the eventual emergence of a Sr peak, simulations were performed using KALYPSO. The two-element limitation of the software required that Na^+ scattering from two model crystals be simulated separately. The first model crystal is the flat uppermost atomic layer of Bi-O as depicted in Fig. 1. The second includes the Sr atoms, the oxygen atoms associated with the Sr layer, and the oxygen atoms that lie directly above the Sr atoms in the Bi-O layer. We used an incoming altitudinal angle of 30°, along the low-index direction, and an incoming energy of 2 keV, consistent with the experiment.

The normal emission intensity for scattering from the Sr system is plotted vs outgoing energy in Fig. 3 for differing levels of first-layer oxygen vacancies (bottom three curves). Oxygen vacancies were created explicitly in the target crystal by removing a specific fraction of equivalent surface oxygen atoms from the second model structure. The vacancies were chosen so that there would not be any effect of correlations, e.g., there could be additional effects if two adjacent surface oxygen atoms were removed. Although some scattering from Sr is observed in the simulations in the absence of vacancies, at normal emission the trajectories are blocked along the outgoing trajectory by the first-layer oxygen atoms positioned directly above the Sr atoms. Some events do scatter from Sr and then glance off of a surface O atom on the way out, however, which results in a small, wide peak at about 600 eV. The peak is at a lower energy than the single-scattering energy of Na^+ from Sr because of extra losses incurred in the grazing collisions with oxygen. This small signal for single scattering from Sr would be very difficult to resolve against the large background in the experimental spectra and for small detection angles may not appear at all. As oxygen is removed from the surface, however, a clear SSP from Sr emerges at about 700 eV, while the 600 eV peak corresponding to scattering from both Sr and O diminishes. Also shown in Fig. 3 are the simulated data for scattering from the Bi-O layer and the experimental data, plotted with respect to energy, for the cleaved and sputtered surfaces. The agreement of the SSP positions for Bi and the revealed Sr is quite good.

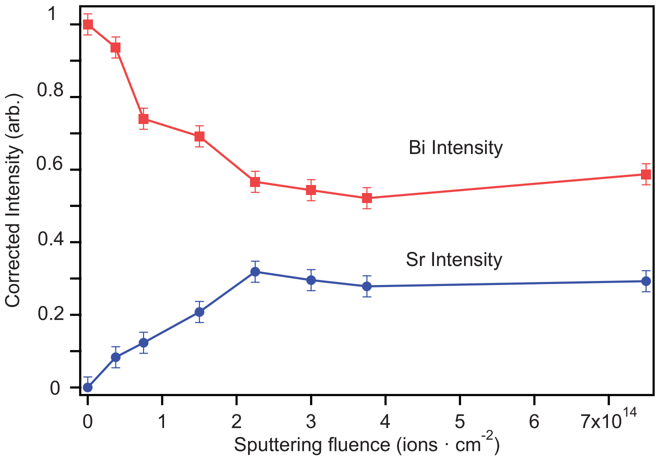

FIG. 4. (Color online) Measured single-scattering intensities determined from the TOF spectra. The values are calculated by taking the area of the peaks in Fig. 3 and correcting for the scattering cross section.

A quantitative analysis of the scattering yield from Bi and Sr is displayed in Fig. 4, where the Bi intensity is seen declining simultaneously with the Sr intensity rising. This scattering intensity is calculated using a fit procedure to fit the peaks in the TOF spectra as follows: The background in the neighborhood of the peak is considered to be linear with a Gaussian superimposed on it. After this curve is fit, the area under the Gaussian is calculated and used as the measured intensity, whereas the area under the line is considered to be background. Note that the Bi and Sr signal strengths have been normalized to each other using the cross-section ratios provided previously. The graphs simultaneously level off at a fluence of 2.2×10^{14} cm^{-2}.

The observed ratio of Bi/Sr atoms at the surface, corrected for scattering cross section, is shown in Fig. 5 as a function of sputtering fluence along with the surface work function. The highest fluence corresponds to one incident Ar^+ ion per surface Bi. Ion scattering indicates that the ratio (right axis) saturates at a value of 2 Bi to 1 Sr atom at the surface. After abruptly shifting down (presumably due to the quick desorption of oxygen), the work function (left axis) increases to its quasistatic value of 0.4 eV above the clean Bi-2212 work function (4.85 eV). The intensity ratio and the work function reach their final values at nearly the same fluence. This steady state is surprisingly long lived, as quadrupling the fluence does not noticeably change it.

What is notable about this result is the lack of apparent ion-beam mixing past the point of Sr saturation.

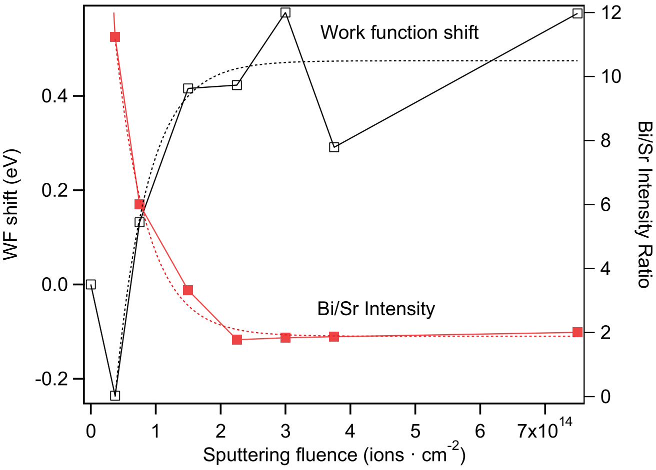

FIG. 5. (Color online) Ratio of the intensities of the Bi and Sr backscattering peaks and the surface work function shift plotted as a function of sputtering fluence.

Low-energy bombardment in heterostructures has been shown (e.g., Ref. 22) to broaden the apparent interface on the order of 1 nm at fluences similar to ours, which would include all of the first seven layers of the Bi-2212 structure. This being the case, it would seem that all layers of the Bi-2212 structure would be evenly mixed at the surface and not merely the first and second layers. Correspondingly, if the oxygen were removed it would make these other metallic species very easy to see in the TOF spectra, as the broad background would diminish. Moreover, supposing that the process were relatively slow, the work function should reflect a more gradual change as buried species diffuse to the surface; whereas, our findings show that the work function promptly decreases and then stays there.

Figure 6 shows the number and type of atoms ejected in a sputtering collision cascade as simulated by MARLOWE, where the horizontal axis can be thought of as time or sputtering fluence. The histogrammed number of ejected particles is tabulated by how many runs had been performed without resetting the crystal, so that time evolution of the sputtering yield could be ascertained as a function of crystal damage. There were approximately 4×10^4 target atoms, with 14% each of Bi, Sr, and Cu, 7% of Ca, and 51% oxygen to begin. As can be seen, oxygen is readily removed with Bi at a third of that rate and Sr at a mere quarter of that. The simulation predicts that after a small number of runs most of the Bi has been sputtered away, while the Sr is considerably more resistant to sputtering. This is not, however, consistent with the experimental observations.

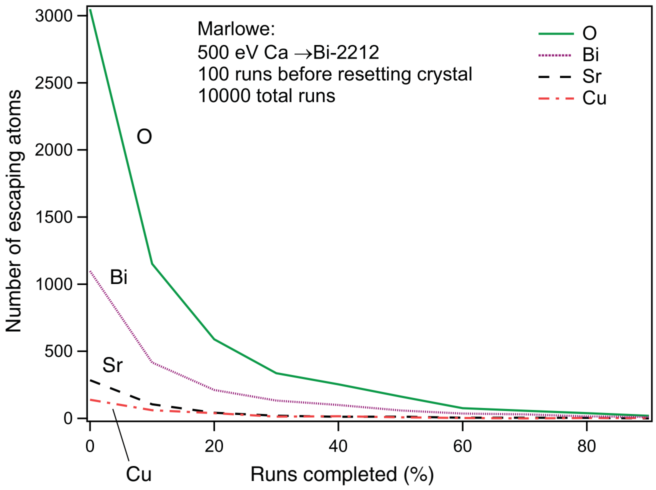

FIG. 6. (Color online) Number of sputtered atoms of O, Bi, Sr, Cu, as predicted by MARLOWE simulation, as a function of sputtering damage. One hundred trials of 100 incident ions of Ca were separately performed, and the results added afterwards. The data is histogrammed by time (number of ions incident on the surface out of 100).

Any oxygen vacancies in the top layer should result in a continual increase of the Sr signal, as MARLOWE predicts that many Bi and O atoms, but not many Sr atoms, should be sputtered. Instead, however, the Sr stays partially obscured. Considering that the initial ratio of Bi to Sr in the substrate was 1:1 and that Bi is much more readily sputtered, one would expect a mixed surface to have much more Sr signal in the data. By the end of the simulated crystal damage, there is a ratio of 1.45 Sr to 1 Bi. In other words the simulation predicts that there will be more Sr than Bi, which is the reverse of what is observed in the experiment.

The sputtering simulation assumes that the atoms are displaced only due to actual collision cascades. Bi, however, has a low miscibility and at the surface is likely to be highly mobile. Oxygen, too, is apt to migrate from lower layers to the surface, which has been suggested to explain the results of SIMS studies of Bi-2212.[8]

With this in mind there is a very real possibility that a flat layer of Bi-O, or the somewhat less likely Bi_2O_3, forms at the surface, even though its structure is incommensurate with the underlying crystal. Growth of semiconductors such as Bi-O is observed in surfactant-like behavior in 2D CVD experiments.[23] Bi, a natural donor, lowers the energy of the surface layer, forming a smooth surface even when there is a large lattice mismatch between the overlayer and the substrate. Indeed, thin films of Bi-O are found to have a particularly low internal stress in the presence of excess oxygen.[24] Because of its low miscibility and its low surface energy, we expect that the capping layer is around one atomic layer in thickness. Studies of the roughness of this system by *in situ* AFM would be interesting, though they are not possible in our apparatus.

Because the scattering signal from Sr remains lower than expected and that of Bi higher than expected implies a layer of Bi-O at the surface. This layer would then obscure the Sr, even as oxygen was sputtered away, and would also negate any ion-beam mixing from occurring. The result is that Bi and Sr signals saturate at the values measured. Since the structure of this Bi-O overlayer may not be the same as that of the as-cleaved surface, the measured Bi/Sr ratio does not necessarily imply that the approximately 20% oxygen vacancies that was predicted using KALYPSO is quantitatively correct.

Note that we cannot strictly discount the possibility that the top layer is composed of amorphous Bi rather than Bi-O. There are, however, several reasons why it is reasonable to assume that the top layer has oxygen. Because of the relatively low surface energy, it has been observed that lighter species segregate to the surface in systems such as Pt/TiO_2.[25] Furthermore there is evidence to suggest that oxygen in

Bi-2212 is highly mobile in vacuum, diffusing from the bulk to the surface.[8,26] In addition, the work function would be expected to decrease if oxygen were being removed from the outermost layer, while in fact the work function increases as steady state is attained. A high surface work function is normally associated with the dipoles created at an oxide surface. Note that x-ray photoelectron spectroscopy (XPS) data of the Bi-core level shifts between the as-cleaved and the sputtered surface could clarify this since the oxygen-induced Bi 4f binding energy shifts are on the order of a few eV. We are unable, however, to perform an XPS study on these samples with our equipment.

IV. CONCLUSIONS

Behavior of the Bi-2212 surface under sputtering was investigated by 2 keV Na^+ LEIS. The surface oxygen and Bi are readily removed at the start, which is in good agreement with simulation. Further sputtering unexpectedly results in a quasisteady state, which leads to a stable Bi/Sr ratio. The results imply that a protective layer of Bi-O forms due to the high mobility of oxygen and the low miscibility of Bi. This process can form an amorphous layer because of the lowering of surface energy characteristic of the Bi surfactant effect, which forms a layer independent of the crystal structure of Bi-2212 itself. This layer then blunts the effects of local ion-beam mixing so that Bi and O atoms block incoming ions from reaching the majority of Sr and other species in the crystal.

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