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LETTER TO THE EDITOR

Atomic Imaging of Clean Surface of Superconducting $YBa_2Cu_3O_{7-\delta}$

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Clean surfaces on the (001), (110), (11*l*), and (103) planes of superconducting $YBa_2Cu_3O_{7-\delta}$ have been obtained by electron irradiation, and investigated using high-resolution electron microscopy. Observed "Amorphous" coating layers on $YBa_2Cu_3O_{7-\delta}$ specimens crushed in air and argon were found to be different. Possible mechanisms of formation of these coating layers are discussed. © 1992 Academic Press, Inc.

Despite raising the transition temperature of several superconducting metal oxide systems to well over 90 K, applications of these materials are still restricted, mainly because of the low transport critical current density (J_c) and relatively high radio frequency (rf) surface resistance (R_s). Experience derived from many investigations is that surface impurities and insulating grain boundaries are the main source of the low intergranular J_c (*1–3*). As water and carbon oxides can easily be adsorbed, it would appear likely that $YBa_2Cu_3O_{7-\delta}$ (T_c = 90 K) could form an insulating surface layer containing carbonates and other metal oxides (*4*) when exposed to air. Even when crushed in vacuum to avoid contact with water and carbon oxides, the composition of the fracture surface of $YBa_2Cu_3O_{7-\delta}$ has also been observed to change (*5*). Therefore, a clean surface of this material has not been observed previously. We present here, for the first time, some clean surface atomic images of $YBa_2Cu_3O_{7-\delta}$, using electron beam recrystallization in the high-resolution electron microscope. The ability to create and observe clean surfaces of $YBa_2Cu_3O_{7-\delta}$ not only provides valuable information concerning the nature of intergranular contacts in this class of superconducting materials but may also eventually lead to a way of overcoming the low critical current density in these ceramic materials. This represents an important step in the research toward the practical applications of oxide superconductors.

Clean surfaces of several superconducting oxides related to $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, La_2CuO_4, and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n-4}$ can be observed in the high-resolution electron microscope (HREM) following cleaning of the surface contamination of amorphous carbon by electron beam irradiation (*6–8*). The sur-

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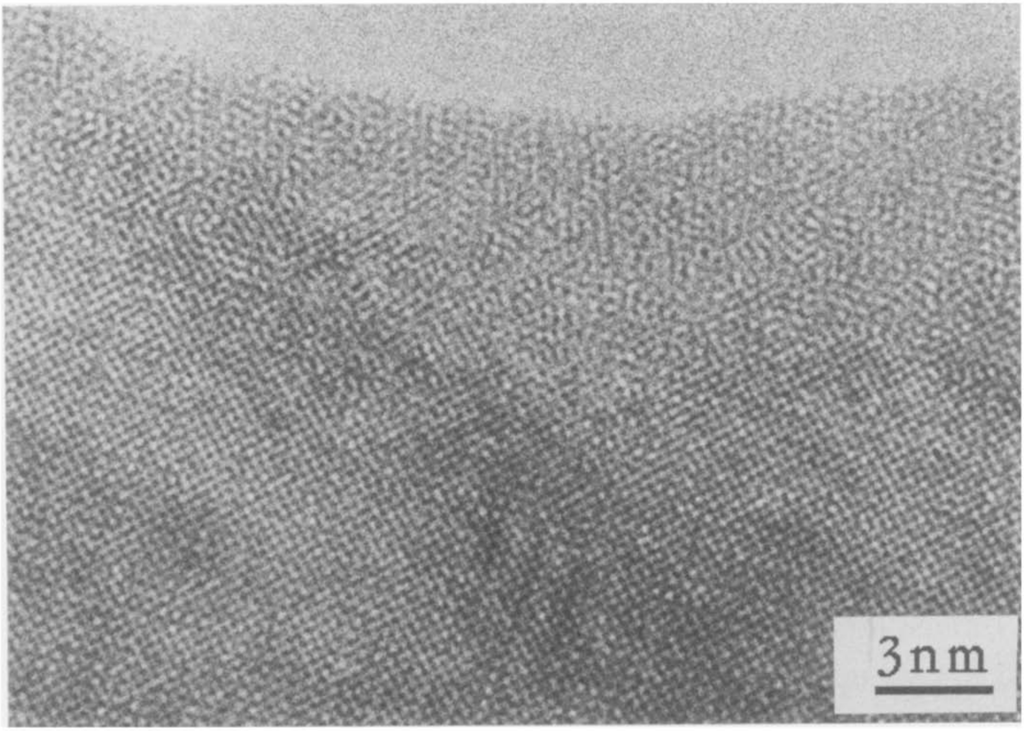

FIG. 1. HREM image of $YBa_2Cu_3O_{7-\delta}$ viewed down the [001] direction, showing considerable surface disorder. This crystal was ground in air.

face structures observed in these materials were assumed to be relatively stable, although some reconstructions have been found to take place in the topmost surface atomic layers. However, the "amorphous" coating found on $YBa_2Cu_3O_{7-\delta}$ crystals observed in the HREM proved impossible to clean by this method. An example of such an "amorphous" surface layer observed by HREM is shown in Fig. 1, viewing down the [001] direction of the crystal. This sample was ground in air before transfer into a Jeol JEM-200CX electron microscope operating at 200 keV. The typical thickness of the amorphous coating layer was about 50 Å. We found that the overall thickness of the coating layer was unchanged on exposure to the electron beam, but some microcrystals appeared to form within it. The coating seemed to intergrow with the crystal very well, leaving no clear boundary between it and the crystal proper. These facts suggest that the coating material on the crystal is certainly not amorphous carbon produced by contamination in the microscope, but consists of carbonates and/or metal oxides formed when the specimen was prepared.

A second sample of $YBa_2Cu_3O_{7-\delta}$ was prepared, this time by crushing in a glove box under an atmosphere of pure argon. A large number of new surfaces were thus created. The dry powder sample was then deposited on a copper grid with a holey carbon film and transfered to the electron microscope by means of a specially designed air-lock holder. The vacuum in the microscope was maintained at about 2×10^{-7} Torr. The first observation of the edge of the crystal (Fig.

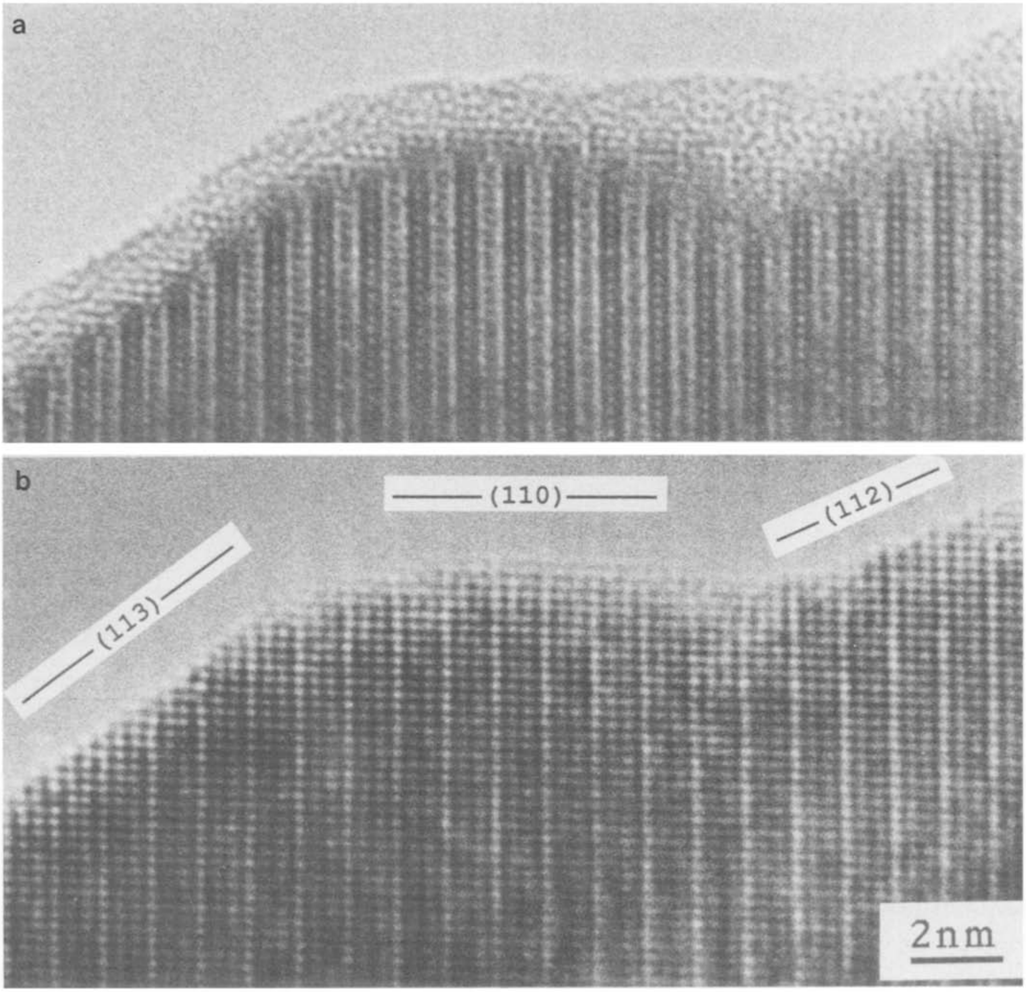

FIG. 2. HREM images of $YBa_2Cu_3O_{7-\delta}$ viewed down the [110] direction. (a) The initial image showing a thin layer of disordered coating, and (b) the image recorded from the same area after electron beam irradiation for 3 hr. The surface now appeared free from any disorder. Objective lens defocus in image (a) was chosen to highlight the "amorphous" layer by a white fringe at its outer edge; consequently the contrast in the bulk part of the material did not show the arrangement of metal atoms directly. In image (b), however, the defocus is correct for the bulk material.

2a) gave a very similar picture to that of Fig. 1, except that the amorphous coating on this sample was thinner (about 20 Å). Remarkably, after electron beam irradiation for about 3 hr, this coating layer recrystallized into the $YBa_2Cu_3O_{7-\delta}$ structure, in the same orientation as the bulk crystal, and a very clean surface was observed (Fig. 2b). The recrystallization started at the boundary between the surface coating and the crystal, then extended throughout the entire surface coating layer. As one can see in Fig. 2a, the degree of disorder in the coating decreases regularly from the top surface to the boundary. No isolated microcrystals can be observed in the disordered area, unlike those

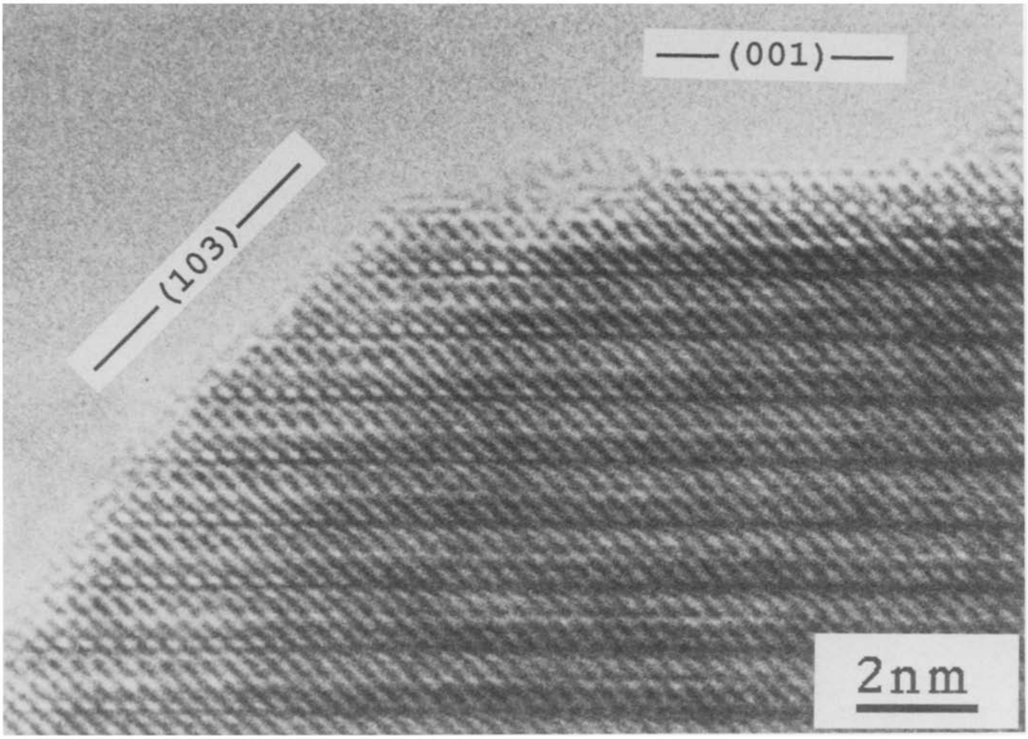

FIG. 3. HREM image from $YBa_2Cu_3O_{7-\delta}$ viewed down the [100] direction. Clean (103) and (001) surfaces were formed after 2 hr recrystallization under electron beam irradiation.

observed in samples prepared in normal fashion (Fig. 1).

Figure 2b shows no evidence of any surface reconstruction on the (113), (110), and (112) surfaces of $YBa_2Cu_3O_{7-\delta}$, with a tetragonal unit cell with $a = 3.85$ and $c = 11.7$ Å. This behavior is quite different from that of La_2CuO_4, where a single La atomic layer and C–La_2O_3 were found to cover the (113) and (001) surface, respectively, and of $Tl_2Ba_2Ca_2Cu_3O_{10}$, where excess Ba atoms deposited on the (110) surface (*7*, *8*). The surface homogeneity of $YBa_2Cu_3O_{7-\delta}$, both in composition and in chemical structure, seems to be much higher than other high T_c superconductors. The crystal shown above was then exposed to the electron beam for more than 10 hr. The surface remained perfect, with no evidence of reconstruction, although the holey carbon film nearby was heavily contaminated. We conclude that the clean surface of $YBa_2Cu_3O_{7-\delta}$ is very stable under the HREM operating conditions.

A series of HREM surface atomic images have been recorded for several crystals of $YBa_2Cu_3O_{7-\delta}$ using the above technique. Figure 3 shows a different crystal viewed down [100]. Clean (001) and (103) surfaces were formed from the amorphous layer after about 2 hr of electron irradiation. Again there was no significant difference in image contrast at the surface and within the bulk, except for the effects due to variations of specimen thickness and lens defocus. One interesting aspect visible in Fig. 3 is that the (001) surface of $YBa_2Cu_3O_{7-\delta}$ terminates with the Cu–O layer, which belongs originally to the Cu–O chain layer in $YBa_2Cu_3O_{7-\delta}$. On the other hand, in La_2CuO_4 and $Tl_2Ba_2Ca_2Cu_3O_{10}$, the topmost atomic layer on the (001) surface was invariably found to be La–O or Ba–O, respectively (*7*, *8*); surfaces terminating in copper have not been reported.

In conclusion, the fracture surface of $YBa_2Cu_3O_{7-\delta}$ is normally very active and decomposes both in air and in argon. The surface coating formed in air, almost certainly containing carbonates, is thicker and does not recrystallize into the $YBa_2Cu_3O_{7-\delta}$ structure. However, the coating formed in argon is thin and can recrystallize into the parent structure after electron beam irradiation, giving rise to a clean surface. We assume that the structure of the latter coating is not completely amorphous, but relates to that of $YBa_2Cu_3O_{7-\delta}$. One possible modification is that, when the surface is formed in argon, the oxygen network remains almost the same as the original one; only the arrangement of cations is disordered. Using this model, computer image simulation studies do indicate an amorphous-like crystal. On the other hand, the surface coating formed in air contained carbonates, and both the oxygen network and the metal arrangement were perturbed. Although the carbonate present could then be decomposed into metal oxides and CO or CO_2, the structure of $YBa_2Cu_3O_{7-\delta}$ could not be regenerated in the surface coating, as the oxygen arrangement was lost. Instead, separate microcrystals (presumably of the individual oxides) were then formed.

The present work suggests that it is possible to prepare $YBa_2Cu_3O_{7-\delta}$ ceramic and thin films with better intergranular contact by controlling the preparation conditions and using special treatment. Further detailed surface structures of $YBa_2Cu_3O_{7-\delta}$ are emerging and a better method of specimen preparation suitable for J_c measurements is being carried out in our laboratories.

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