Clean "As Grown" Surfaces of Ln_2CuO_4 and $(LnM)_2CuO_4(001)$ Single Crystals: Atomic and Electronic Structure

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The geometric and electronic structure of clean and oxygen-treated "as grown" (001) single crystal surfaces of Ln_2CuO_4 (where Ln = La, Nd, Pr) and $(LnM)_2CuO_4$ (M = Sr, Ce) was studied by LEED and spectroscopic techniques in the temperature range of 20–400 K. Clean surfaces were prepared by oxygen annealing, UHV annealing, and ion bombardment and annealing. A wide variety of superstructures were observed on the (001) "as grown" surfaces of Ln_2CuO_4 and $(LnM)_2CuO_4$: $(\sqrt{2} \times \sqrt{2})R45°$, $3\sqrt{2} \times 1$, 1×3, 3×3, etc. Intensity and symmetry of some LEED patterns were sensitive to electron beam exposure (LEED gun). Comparison of spectroscopic and LEED data, possible models of reconstruction and influence of electron stimulated oxygen diffusion were discussed.

1. Introduction

Investigations using different surface study techniques: low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), ultra-violet and X-ray photoelectron spectroscopy (UPS, XPS) and electron energy loss spectroscopy can greatly contribute to better understanding of physical properties of rare earth $(LnM)_2CuO_4$ cuprates. Such investigations can provide us with important information on the valence and charge states of atoms, density of electron states in the vicinity of the Fermi level (E_F) and below it, stoichiometry, surface atomic structures, etc.

It is obvious that crystal cleavage, scrapping or annealing can produce clean surfaces. However, those surfaces might be essentially different from each other. Actually, mechanical actions in the course of cleavage or scrapping can produce a lot of surface defects, steps and can probably even affect the surface stoichiometry and cause surface reconstruction.

In the case of single crystals or thin films, only annealing in ultra-high vacuum (or *in situ* growth) one can achieve the surface purity without introducing surface defects. However, the stoichiometry can be modified, including loss of the oxygen atoms. So, obtaining the clean surfaces of rare earth cuprate compounds with minimum artifacts and the investigation of the influence of the methods of preparation of clean surfaces on the atomic and electronic structure of cuprates still remains one of the main problem of surface studies of HTSC.

In this paper we present the experimental results of investigation of clean "as grown" (100) surfaces of single crystals of La, Nd, and Pr cuprates. The term "as grown" surfaces means the topmost layers of crystals in the equilibrium state obtained by crystal growth procedure (in our case from melt solution in oxidized atmosphere) without any kind of mechanical or chemical treatment (cutting, polishing, cleavage, scrapping).

2. Experiment

Experiments were performed in electron spectrometers ESCALAB-5 (with a low-temperature cryomanipulator), ADES-400 and X-ray spectrometer "M-Probe". Two series of $La_{1.85}Sr_{0.15}CuO_4$ single crystals were studied: non-super-conducting and superconducting ones with $T_c = 15$ K ($\Delta T = 5$ K) grown from the melt in a rotatable crucible. The crystals of plate habit were $8 \times 4 \times 1$ mm^3 in size and had the $La_{1.85}Sr_{0.15}CuO_4$ composition, a pseudotetragonal structure with the lattice parameters $a = 5.353$ Å, $c = 13.176$ Å and the resistivity $r = 0.1$ Ohm·cm at 300 K. $Nd_{1.8}Ce_{0.2}CuO_4$, Nd_2CuO_4 and Pr_2CuO_4 crystals were grown from the melt solution by low rate cooling in air using platinum crucible in oxidized atmosphere. The crystals were typically about $10 \times 5 \times 0.05$ mm^3 in size and had a composition corresponding to Nd_2CuO_4, Pr_2CuO_4 and $Nd_{1.8}Ce_{0.2}CuO_4$ (non-superconducting, metallic) with pseudotetragonal structure characterized by $a = 3.935$ Å, $c = 12.143$ Å and the resistivity $r = 10^4$ Ohm·cm for Nd_2CuO_4 and Pr_2CuO_4 and $r = 0.5$ Ohm·cm for $Nd_{1.8}Ce_{0.2}CuO_4$. The orientation of the "as grown" surfaces of these crystals was checked by the X-ray diffraction and was found to be close to (001).

We used the following procedures to prepare the clean "as grown" surfaces of $(LnM)_2CuO_4$ for surface studies: (i) developed in our laboratory procedure of annealing of crystals in oxygen (or air) at 600–700 K (2–3 hours) in the furnace near electron spectrometer followed by rapid (1 min) placing (using special oxygen mini-camera) of a hot sample holder with the crystal into the UHV analytical chamber of the spectrometer, (ii) annealing *in situ* in the UHV chamber of the electron spectrometers at 700–1200 K, and, for comparison, (iii) ion bombard-

ment of the surface (ion energy 500 eV and 5 keV, argon and oxygen) followed by annealing in UHV at 700–1200 K. Also for comparison we sometimes used chemical polishing *ex situ* and annealing *in situ* in the spectrometer analytical chamber.

Let us note that all the above mentioned cleaning procedures allow to obtain clean (from impurities, mainly carbon) (001) surfaces (according to our Auger and XPS data [1]) although only the first approach (i) allows one to prepare clean surfaces with minimized changes (if any) of stoichiometry, composition, structure, etc. Using all other procedures we obtain clean surfaces with some artifacts which can mask and spread phenomena on the surface. For example, ion bombardment and annealing generate irreversible superstructural reconstructions on the (001) surfaces of cuprates.

3. Results and discussion

First of all, let us pay attention to results of investigations of the composition, atomic structure and symmetry of the topmost layers of cuprate crystals. We have found that the cleaned "as grown" surfaces of $(LaM)_2CuO_4$, $Nd_{1.8}Ce_{0.2}CuO_4$, Nd_2CuO_4, and Pr_2CuO_4 display unreconstructed surfaces as well as a number of superstructures which do not qualitatively depend on temperature scanning in the temperature range of 20–600 K. The surfaces are well crystallographically ordered and demonstrate sharp LEED patterns. It should be noted that the clean (001) surfaces of $(LnM)_2CuO_4$ proved to be very stable in UHV and possess extremely low sticking coefficients for all residual gases (except for perhaps oxygen) in the UHV chamber. Actually, we were able to observe quite sharp diffraction patterns for 8–12 days under a pressure of 10^{-10} torr. We have also found that in spite of the fact that the surfaces are stable in UHV, they are rather sensitive to the electron beam irradiation. It was found that exposure under electron beam of the LEED gun produces remarkable changes not only in the quality but even in the symmetry of LEED patterns.

In order to clarify the composition of the topmost clean "as grown" (001) surfaces of these cuprates (prepared by procedure (i)) we have investigated the angular dependences of the XPS and AES signal intensities (see Fig.1). Variations of the AES (XPS) electron escape angle have shown that on increasing the angle from 0 to 45° the AES signal intensity ratio I_{Cu}/I_{La} grew by a factor of 1.5 (for $(LaM)_2CuO_4$ [1]). Similar results were obtained for Nd and Pr cuprates.

So we propose that after the final stages of the crystal growth process in the equilibrium state, such "as grown" (001) surfaces of rare earth cuprates are terminated by Cu-O layers. This is an important statement which should
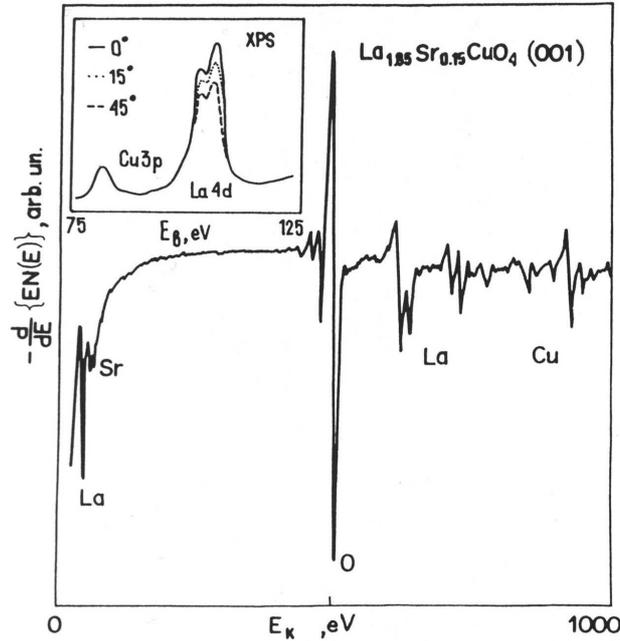
Figure 1. Auger electron spectrum of $La_{1.85}Sr_{0.15}CuO_4(001)$. Inset shows the angular dependence of the photoelectron peak intensities (normalized to the Cu $3p$ peak) (from Ref. [1]).

be taken into account when considering effects related to the surface electronic states, surface relaxation, adsorption of atoms, interface formation, etc.

Let us consider structural aspects of "as grown" surfaces of La, Nd, and Pr cuprates.

La_2CuO_4 and $(LaM)_2CuO_4$ (001)

We have found that the clean "as grown" (001) surfaces of La_2CuO_4 demonstrate the unreconstructed (1×1) and reconstructed $(\sqrt{2} \times \sqrt{2})R45°$ LEED patterns which are stable in UHV for several days and do not depend on temperature in the range of 20–300 K and during annealing up to 1000 K. We also observed that the stable surface of La cuprates (in UHV) are nevertheless sensitive to electron beam irradiation. Under the electron beam of a LEED gun ($E_p = 40 - 150$ eV, $I_p = 10^{-6}$ A) some qualitative changes in the pattern can occur with time: LEED pattern (spots) becomes sharper and the signal to background ratio increases after a few hours of exposure. Typical Auger spectrum for clean $La_{1.85}Sr_{0.15}CuO_4$ is shown in Fig.1. We have found that in UHV the Auger spectrum is not essentially changing for the 1–2 hours although after sev-
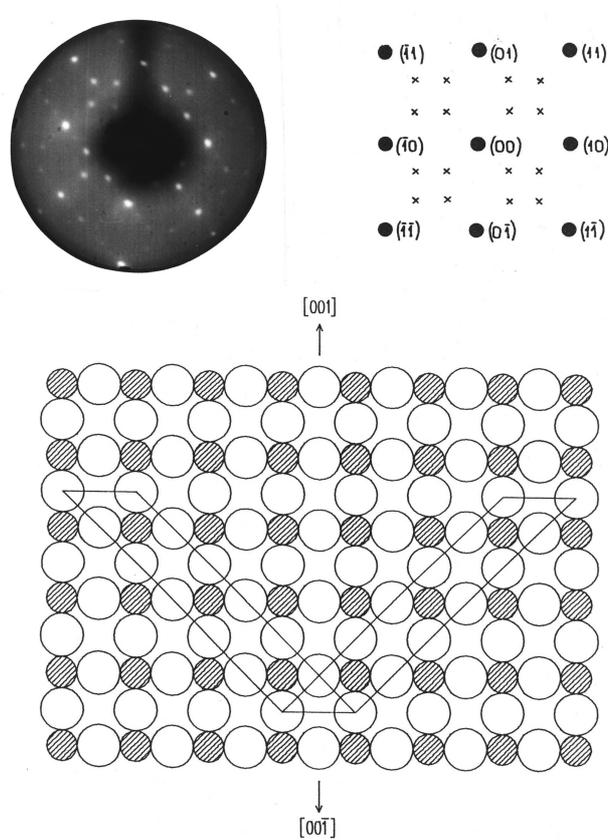
Figure 2. LEED pattern and the ball model of the (NdCe)$_2$CuO$_4$ and Pr$_2$CuO$_4$(001) oxygen-derived surface showing the two rotational domains corresponding to the $(3\sqrt{2} \times 1)$R45° LEED pattern.

eral hours of exposure (5–8 hours) to the electron beam (LEED gun) the ratio I_O/I_{La} gets slightly increased by 10–15 % (where I_O and I_{La} are the O and La Auger signal intensities, respectively). A shift of the electron beam (by about 1 mm) results in the recovery of the previous value of I_O/I_{La} proving the diffusion of oxygen into the irradiating area.

These facts apparently mean that the electron beam stimulated additional re-ordering of surface accompanied by the oxygen atoms and vacancies diffusion processes "improving" the atomic perfection of the surface. A similar phenomenon of oxygen diffusion under electron beam has been reported in Ref. [2] where the electronic structure of La$_{1.85}$Sr$_{0.15}$CuO$_4$ ceramics was studied by the inverse photoemission.

It should be noted that without the electron irradiation, in the 10^{-10} torr vacuum only the signal of carbon contamination slightly increased during 8–10 hours. One can therefore assume that the oxygen adsorption and/or its diffusion (from the bulk to the surface) can probably be stimulated by the electron beam thus increasing the I_O/I_{La} ratio and improving the LEED picture (see above).

It should be noted that in contrast to our results other types of superstructures reported in literature are due to the changes in cation composition on the surface. Thus the (1×8) (or 1×7 ?) superstructure reported by Brookes [3] is undoubtedly the result of repeated ion bombardment and annealing cycles (the copper content on the surface was found to increase [3]). The 1×5 LEED picture observed by Weirich [4] might be due to the peculiarity of crystal growth processes (La content is higher as compared with Cu).

Nd_2CuO_4, $(NdCe)_2CuO_4$, Pr_2CuO_4

Surfaces of $Nd_{1.8}Ce_{0.2}CuO_4$, Nd_2CuO_4, and Pr_2CuO_4 also demonstrate a number of superstructural reconstructions of the topmost layer.

We have found that after rapid placing of $Nd_{1.8}Ce_{0.2}CuO_4$, Nd_2CuO_4, and Pr_2CuO_4 samples into the UHV analytical chamber (after annealing in air or oxygen at 700–800 K) the surfaces demonstrate LEED pattern with superstructural spots consistent with the periodicity tripling along the [110] direction (Fig. 2). The LEED picture can be interpreted as the result of the existence of the two domains:

$$\begin{pmatrix} 0 & 1 \\ 3\sqrt{2} & 3\sqrt{2} \end{pmatrix}$$

The superstructure proves to be rather stable in UHV at 10^{-10} torr (during several days) and did not qualitatively depend on temperature in the range of 20–500 K [5]. We have also found that in spite of the fact that this superstructure is stable in UHV, the existence and the intensity of the superstructural spots is sensitive to the electron beam exposure (LEED gun, $E_p = 40 - 200$ eV, $I_p = 0.5 - 1.0$ μA). During irradiation, intensity of the superstructural spots decreases and after 30–40 min of exposure these spots become invisible: the superstructural disordering takes place and the LEED pattern transforms to (1×1). Annealing at $T = 800 - 1000$ K in UHV (for 1–2 min) or in air/oxygen (600–700 K, 3 hours) recovers the superstructure and the original intensity of superspots. Note that cycles of soft ($E_p = 500$ eV) ion bombardment followed by annealing irreversibly change the LEED pattern from $(3\sqrt{2} \times 1)$ to (1×3) and then to (3×3) superstructures. Chemical polishing and annealing of the crystal surfaces restores the (1×1) LEED pattern but not the $3\sqrt{2} \times 1$ superstructure: in this case only the 1×1 pattern exists.
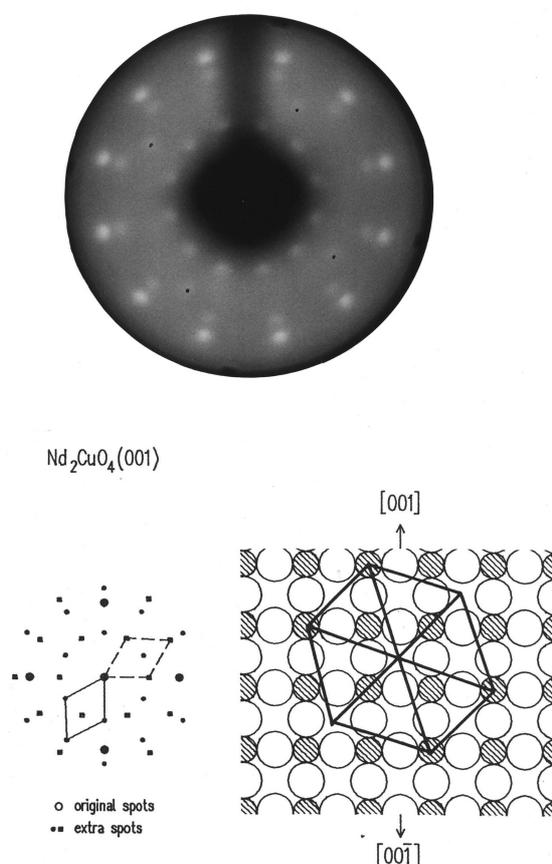
Figure 3. LEED pattern, schematic representation and a possible ball model of the reconstruction (hexagonal, in addition to the (1×1) structure) of the copper-derived Nd_2CuO_4 surface lattice.

The $(3\sqrt{2} \times 1)R45°$ superstructure was reported by Schulz and Cox[6] on the (001) Cu_2O polar Cu-terminated surface. Simple geometric considerations reveal that the surface mesh of Cu_2O rotated by 45° coincides with the (001) surface of Nd_2CuO_4 and Pr_2CuO_4 so that the doubled lattice parameter of Cu_2O in the [110] direction is close to the tripled parameter of Nd214 and Pr214. It seems that the oxygen ordering on the surfaces of $Nd_{1.8}Ce_{0.2}CuO_4$, Nd_2CuO_4, and Pr_2CuO_4 produces the oxygen-derived $(3\sqrt{2} \times 1)$ superstructure. Electron beam destroys oxygen-derived structure demonstrating 1×1 LEED pattern, and *visa versa* annealing in UHV or oxygen reproduces the previous $(3\sqrt{2} \times 1)$ superstructure.

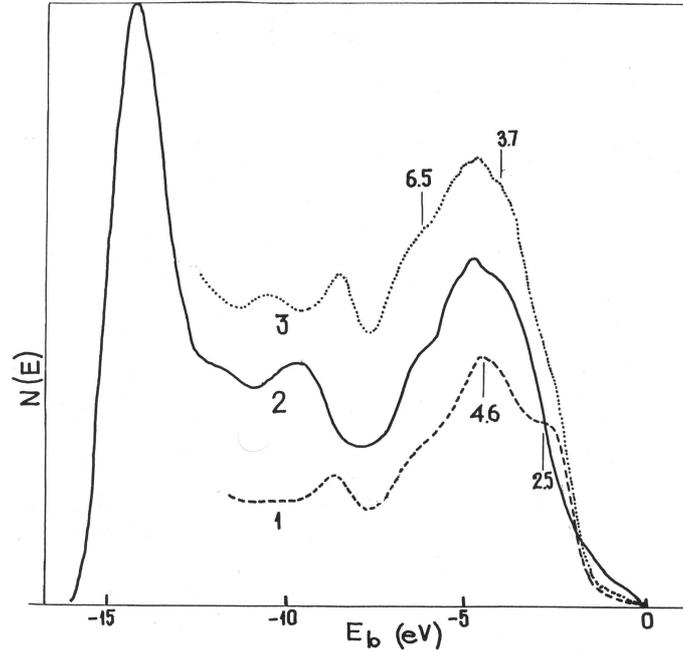It should be noted that some surfaces of Nd214 (001) crystals show the recon-

Figure 4. UPS photoemission spectra (He I, $h\nu = 21.1$ eV) of "as grown" surfaces of $(LnM)_2CuO_4(001)$: 1) $(NdCe)_2CuO_4(001)$ 2) $La_{1.85}Sr_{0.15}CuO_4(001)$ 3) $(NdCe)_2CuO_4(001)$ after annealing ($T = 1000$ K, 2 min UHV).

struction related to the coexistence of the 6-fold and 4-fold symmetries (Fig.3). This superstructure is stable in UHV and as compared with the $3\sqrt{2} \times 1$ superstructure is stable under electron beam and did not changes during annealing up to 1000 K). Similar to the pattern described in Ref. [7] for the Ni+O system, the superposition of this new 6-fold and 4-fold patterns of Nd_2CuO_4 forms a new complex structure. Estimation of the lattice parameter of the 6-fold pattern on the LEED picture yields the value of 6 Å close to the (111) lattice parameter of a hypothetical cubic crystal with $a = 4.26$ Å (for example, Cu_2O).

4. Possible model of reconstruction and spectroscopic data

Now let us briefly discuss a possible model of the reconstruction and spectroscopic data.

According to the data reported in Ref. [6] by Cox and Shultz for the Cu_2O surface, (001) "as grown" surfaces of Nd and Pr cuprates can be described as O-terminated and Cu-terminated (after growth process) surfaces with $3\sqrt{2} \times 1$
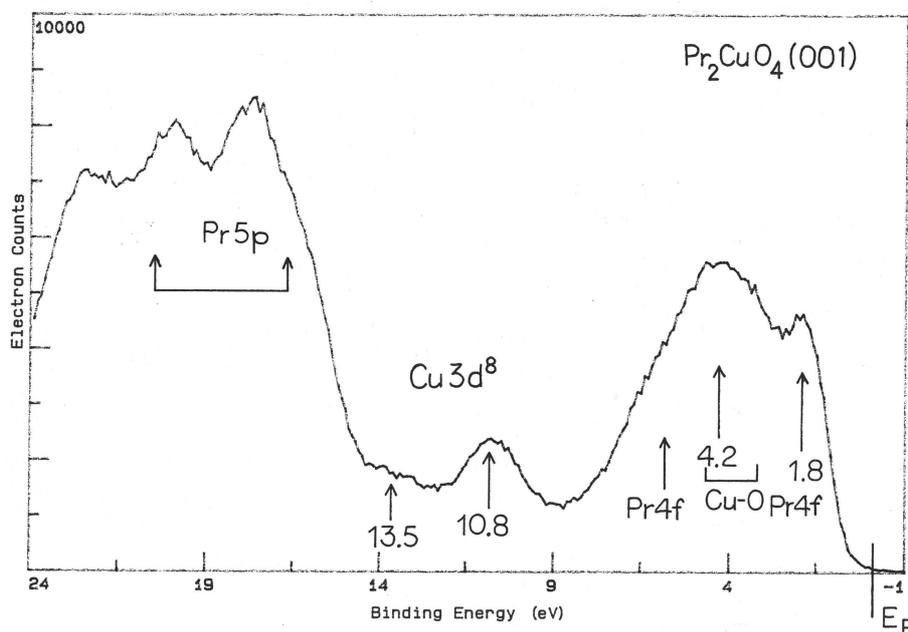
Figure 5. XPS (Al K_α) valence band spectrum of $Pr_2CuO_4(001)$.

and a composite superstructure, respectively. In our first case the topmost layer of "as grown" surface of Nd214 can be described in terms of the sensitive to the electron beam oxygen-terminated labile $3\sqrt{2} \times 1$ reconstructed copper-oxygen surfaces similar to $Cu_2O(001)$ [6] transformed to 1×1 under electron beam due to oxygen diffusion and partial disordering on the surface. In the second case, "as grown" topmost layer of (001) Nd_2CuO_4 (of copper-oxygen origin) was terminated by Cu-derived stable surface of the (111) plane of cubic copper oxide with the lattice parameter equal to 4.26 Å.

In the case of La cuprates, both unreconstructed and reconstructed surfaces terminated by a stable copper-oxygen surface. It should be noted for comparison that we only observed this type of superstructural reconstruction on the high symmetry surfaces of tetragonal cuprates while no superstructure and reconstruction was observed on the (001) surfaces of low symmetry cuprate $La_2Cu_2O_5$ [8].

Crystal morphology and possible relaxation and reconstruction of the low index surfaces of La_2CuO_4 and Nd_2CuO_4 have been investigated by Kenway, Parker and Mackrodt [9] using static lattice simulation. It was shown that an important difference between the two structures is that copper is six-fold coordinated in La_2CuO_4 but only four-fold coordinated in Nd_2CuO_4 (and isostructural

Pr_2CuO_4). So plane stacking differs in these two compounds. In La_2CuO_4, termination with a La_2O_2 layer leads to stable non-dipolar stacking, while termination with a CuO_2 plane leads to dipolar stacking sequence so that the surface must be reconstructed to lower surface energy. In Nd_2CuO_4 there are three possible terminations, all of which lead to dipolar stacking and necessitate reconstruction for stability. The two simplest reconstructions are oxygen-terminated and CuO_2-terminated surface [9].

So based on our LEED results, data from Ref. [6], and calculation of Ref. [9] one can argue that the most reasonable explanation of morphology of "as grown" surface is that during the growth procedure the surface of $Nd_{1.8}Ce_{0.2}CuO_4$, Nd_2CuO_4, and $Pr_2CuO_4(001)$ terminated similar to the (001) surface of Cu_2O in the first case and (111) surface of Cu_2O in the second case.

But let us first discuss the results obtained by UPS and XPS techniques.

Photoemission studies of "as grown" surfaces of $(LnM)_2CuO_4$ show a rather similar structure of the valence band and core levels for the whole family of cuprates both for the hole and electron-carrier compounds. The UPS spectra of $(LaM)_2 CuO_4$, Nd214 and $Nd_{1.8}Ce_{0.2}CuO_4(001)$ (see Fig. 4) were found to be practically identical and well agree with the literature data [10] (except for a noticeable shoulder at 6.5 eV in our UPS spectra). We have also found that UPS spectra taken at 300 K and 20 K coincide as well. Annealing in UHV at $T = 700$ K did not produce any detectable changes in the UPS spectrum. However, annealing at $T > 1050$ K shifts the peak at 4.6 eV towards the higher binding energy by 0.2–0.3 eV. The same tendency was observed for the 6.5 eV peak. The performed analysis of the electronic structure of the studied cuprates and the literature data allows to undoubtedly identify the peaks at 2.5, 4.6, and 3.7 eV as the Cu $3d$ – O $2p$ hybridized states.

Exposure of "as grown" $La_{1.85}Sr_{0.15}CuO_4$ (001) surfaces to electron beam in UHV was accompanied by a slight increase (5–10%) of oxygen content (see Auger data). This behavior is also accompanied by the growth of a shoulder at 2.5 eV in UPS spectra (see Fig. 4) and the center of gravity of the entire feature moves to the Fermi level, E_F, so the photoemission intensity in the vicinity of E_F proves to be slightly increased, although it is still small. This fact supports the idea that oxygen essentially contributes to the electron density of states in the vicinity of E_F and forms the 2.5 eV feature. It is important that electron beam irradiation ($E_p = 100$ eV) which gives rise to the surface extra ordering and improved sharpness of the LEED picture is accompanied by the growth of the 2.5 eV shoulder in UPS spectra. The nature of the 6.5 eV peak in our UPS spectra of VB is left unclear so far and apparently can also be associated with the superstructural reordering on the such "as grown" surfaces of rare-earth

cuprates.

The rare earth elements Nd an Pr induce small changes in UPS spectra as compared to La cuprate due to the existence of $4f$ states although in XPS spectra of these cuprates the $4f$ states are clearly observed as shown in Fig. 5.

It should be noted that XPS spectra of such "as grown" surfaces of the studied La, Nd, and Pr cuprates demonstrate the Cu $2p$ states typical of divalent copper (with remarkable Cu $2p$ satellite characteristic of divalent Cu [10]) that means that during the final stages of the crystal growth procedure in oxidized atmosphere the crystal topmost layers can be terminated by the copper-oxygen planes forming a cuprate layer with the lattice parameter of about 4.26–4.28 Å (similarly to cubic Cu$_2$O) of metastable CuO but with cubic (NaCl) structure. A possible model of formation of CuO with the NaCl structure was also discussed in Refs. [11,12]. We should also mention a possibility of formation, in principle, of the quite rare Cu$_4$O$_3$ mixed valence phase (paramelaconite) on the surface, although according to Ref. [13] Cu$_4$O$_3$ cannot be obtained thermally (oxidation of Cu$_2$O or reduction of CuO) and only exists as a metastable phase in ion-beam sputtered CuO thin films.

Taking into account all the above mentioned arguments, we arrive at the conclusion that for such clean "as grown" surfaces, the proposed possible model of the topmost layer can probably explain the superstructural ordering (oxygen-derived and copper-derived) on "as grown" surfaces of the studied La, Nd, and Pr cuprates and some unclear features in the valence band spectra as well as some anomalies in several studies of physical properties of polycrystalline CuO and rare earth cuprates. Of course, additional experimental investigations and numerical calculations of such metastable structures are needed.

5. Conclusions

1. "As grown" surfaces of (LnM)$_2$CuO$_4$ are terminated by Cu-O planes. Annealing of these surfaces in UHV or O$_2$ allows to obtain clean surfaces.

2. "As grown" surfaces of cuprates demonstrate a number of superstructural reconstructions: $\sqrt{2} \times \sqrt{2}$, 1×5, 1×8, $(3\sqrt{2} \times 1)$, as well as the existence of Cu-O terminated surfaces. Cu-O surfaces with a labile oxygen subsystem are sensitive to electron beam irradiation (LEED gun) due to electron stimulated diffusion of oxygen and extra ordering on the surface.

3. Soft ion bombardment and annealing results in the growth of the copper content on the surface and leads to irreversible changes of the superstructures to 3×1 and 3×3 on the surface of (LnM)$_2$CuO$_4$. Chemical polishing restores only the original 1×1 structure of the surface.

4. Electronic structures of all the studied rare earth cuprates are quite similar (except 4f-states), and the similarity of electronic structure for hole-doped and electron-doped compounds was also observed.

5. LEED patterns and UPS spectra do not qualitatively depend on temperature in the range of 20–400 K.

6. Superstructural ordering on the surfaces of La, Nd, and Pr cuprates and some unclear features in the valence band electronic structure can be explained by the formation of a metastable CuO topmost layer with the NaCl structure during the final stage of the crystal growth.

Acknowledgements

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