

# SAMPLE PREPARATION OF SINGLE CRYSTAL (100) AND (111) SURFACES OF COBALT MONO-OXIDE AND STUDIES ON THEIR SURFACE PROPERTIES BY USING LEED AND EELFS

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## Abstract

Clean CoO(100) and (111) surfaces were prepared by controlling the oxygen pressure and the temperature during surface cleaning to hold stoichiometric composition. The LEED pattern of CoO(100) was (1×1), and that of the CoO(111) plane showed a superstructure of ( $\sqrt{3} \times \sqrt{3} - R30^\circ$ ). ELNES, the near edge structure in EELFS (electron energy loss fine structure) was measured for these specimens to obtain information on the electronic states and it was found that the ELNES of the CoO(100) surface was similar to that of a NiO(100), however, the CoO(111) showed a slightly different feature from the former, for which some discussion was given.

Keywords: EELFS, LEED, single crystal, cobalt monoxide

## 1. Introduction

It is usually not easy for a surface of compound materials to hold stoichiometric composition when a cleaning process is applied to a specimen in a vacuum. Since the surface properties of oxides are usually rather sensitive to a small variation of chemical composition near the surface, as observed in the case of oxide superconductors, it is important to prepare well defined surfaces of oxides. So far, studies on surface properties of oxides have been carried out with the use of limited kinds of surface planes which can be obtained by cleavage, or epitaxially grown films on crystalline metal or semiconductor surfaces [1,2].

In this study, it was attempted first to grow bulk single crystals of cobalt mono-oxide, then to investigate surface structures and electronic states of clean CoO(100) and CoO(111) surfaces, which are impossible to be prepared by cleavage. A (100) oriented surface of NiO was also measured in order to compare with the CoO surfaces in the same manner.

## 2. Experimental

In order to prepare specimens for the surface study, single crystals of cobalt mono-oxide were grown by the Verneuil method to obtain bulk crystals of good quality large enough to be cut accurately along a desired direction. The crystals were confirmed to have the crystal structure of only cobalt mono-oxide by the X-ray diffraction and it also was found that the electric resistance of prepared crystals was more than  $10^4 \Omega \cdot \text{m}$  at room temperature, which is much

The cleanliness of the specimen surface was examined by using of the EELFS spectrometer which was used as an Auger electron analyser. As seen in Fig. 2, the spectrum of the clean surface obtained in the above manner showed no traces of carbon, except for the occasional appearance of a small peak of calcium although the origin was uncertain.

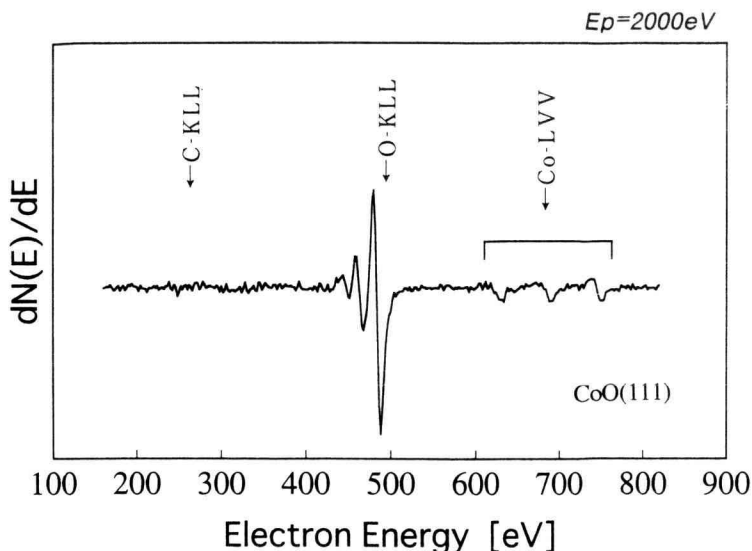


Fig. 2. The Auger electron spectrum of the CoO(111) plane after thermal cleaning process.

The LEED optics was of a conventional reverse-view type, while the EELFS spectrometer has been developed in our research project to measure the electron energy loss fine structure at a low scattering angle. It provides us equivalent data to those of XAFS, which are usually obtained with the use of a strong X-ray source like an SR facility. It is theoretically proved that the electron energy loss excitation of a core shell gives rise to the identical fine structures which appear in the photon absorption spectrum on the approximation of dipole selection rule under the condition of small momentum transfer[3]. The near edge structure is specially called as ELNES (electron energy loss near edge structure) which reflects the local electronic states of surface atoms.

### 3. Results and discussion

#### 3.1 LEED

The LEED measurements on CoO(100) and (111) surfaces were carried out with a primary electron current of  $1 \mu A$  at the energy of around 100 eV. The observed LEED patterns of CoO(110) and CoO(111) were shown in Fig. 3 (a) and (b). The former is a primitive ( $1 \times 1$ ), however, the latter showed a super-structure of  $(\sqrt{3} \times \sqrt{3}-R30^\circ)$ . The samples were almost non-conductive, however, the observation was free from the disturbance of electronic charging.

The crystal structure of CoO as well as NiO is of the NaCl type, so each (100) plane should be constructed with equal number of oxygen anions and metal cations, holding charge neutrality in the plane. On the other hand, there are two different sheets of (111) planes, one of which is composed of only oxygen atoms but another kind of sheets has only metal atoms and they are stacked each other alternately. Therefore, the outermost layer should ideally be occupied either by only oxygen or by only metal atoms. In relation to such (111) surfaces of transition metal compounds, a previous report on a TiC (111) surface is suggestive [7], which describes that the outermost layer of a clean TiC (111) plane is formed by only Ti atoms. In our case, the cleaning process was always given prior to the measurement, so if it would be the case, the top layer is expected to be presumably covered by oxygen atoms which were chemisorbed or chemically bonded on the cobalt layer underneath. This situation may be qualitatively supported by the AES measurement performed at a grazing incident angle for the CoO(111) as seen in Fig. 2, which displays a large peak of oxygen-KLL compared to Co-LVV.

higher than that of sintered polycrystals.

The crystals were cut in parallel to a plane of (111) orientation within the accuracy of  $0.5^\circ$ . Cleaved planes were used as specimens for CoO(100) and NiO(100) surfaces. Both (111) and (100) surfaces of CoO were polished by mechanical machining with diamond paste to accomplish mirror finish, and also to remove cleavage-induced steps from the CoO(100) surface.

Thus prepared specimens were mounted on a manipulator in an UHV chamber of the background pressure at  $10^{-8}$  Pa, where two units of equipment were installed: a LEED optics and an electron energy loss spectrometer for the observation of EELFS (electron energy loss fine structure). The latter was operated in the reflective mode at a small scattering angle [3~5]. The cleaning procedure was carried out chiefly by heating a specimen in the oxygen atmosphere, although the ion sputtering process was supplementarily employed.

It is known that there exist principally two kinds of cobalt oxides: CoO and  $\text{Co}_2\text{O}_3$ . In addition, there are their mixed compounds, depending on the oxygen pressure as well as on the sample temperature during thermal cleaning. Therefore, when the cleaning procedure is performed by thermal heating of samples, it is necessary to control the oxygen pressure of ambient atmosphere and the temperature of a specimen to hold the desired composition of the oxide. Thus, on the basis of the phase diagram of cobalt-oxygen system [6], thermal cleaning was carefully practiced so as to permit only a single phase of  $\text{CoO}_x$  ( $x=1.0$ ). A typical example of the temperature-control program for thermal cleaning is shown in Fig. 1. This process for cleaning was also useful for annealing an ion-sputtered surface.

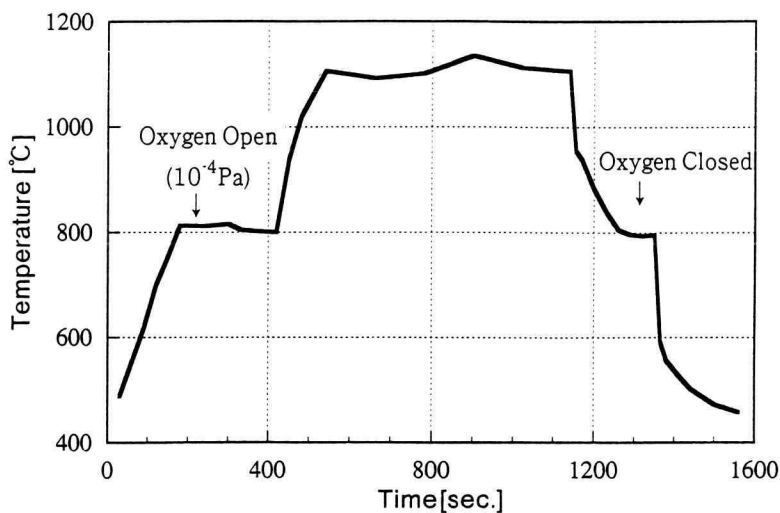


Fig. 1. A typical scheme for controlling the partial pressure of oxygen and temperatures to clean a surface of specimen.

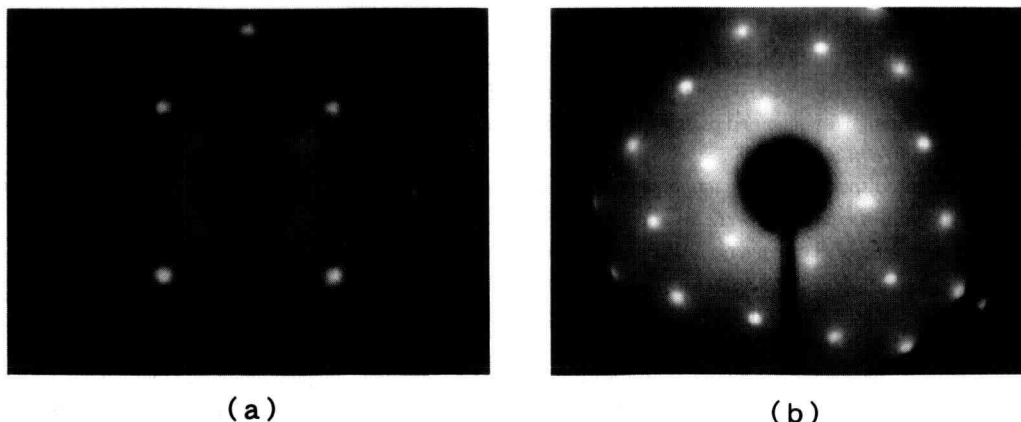


Fig. 3. LEED patterns (a) and (b) for CoO(100) and CoO(111) planes, respectively at the electron energy of 100 eV using an optics of reverse-view type.

### 3.2 ELNES

The ELNES spectra were observed with the resolving power of 0.8 eV under the following conditions. The beam current of primary electrons at the energy of 2 keV was 130 nA. An incident angle was  $4^\circ$  and forward-scattered electrons were detected at an angle of  $6^\circ$  on the surface, hence yielding a scattering angle of  $10^\circ$ . As mentioned earlier, the EELFS spectrometer was able to be used in the AES mode under the same condition as in the EELFS mode with a reduced size of an electron beam to one fifth.

Figure 4 shows the oxygen K-edge ELNES of the CoO(100) surface, which can be compared with that of NiO(100).

Kurata et al. measured the ELNES of several transition metal oxides and compared their results with a theoretically derived relationship[8,9],

$$\Delta E \cdot R^2 = \text{const.} \quad (1)$$

,where  $\Delta E$  means the energy difference between a peak labeled B and the threshold, and  $R$  is a lattice constant of an oxide under consideration. The lattice constant of CoO is larger than that of NiO by 1.02 %, and the ratio of  $\Delta E$  for these oxides was obtained to be 1.07 from the experiment, when the threshold is assumed to be 530 eV. The above relation (1), therefore, seems to be consistent with our results shown in Fig.4. Figure 4 also represents the oxygen K-edge ELNES of the CoO (111) oriented plane, which is rather different from that of the CoO (100), which suggests the different local environment of the nearest metal and oxygen atoms according to the theoretical analyses cited above [9]. It is noticed that a large peak A is almost remained at a fixed energy position, even though metal atoms or surface orientations are different. This feature is also interpreted by the above mentioned theoretical point of view.

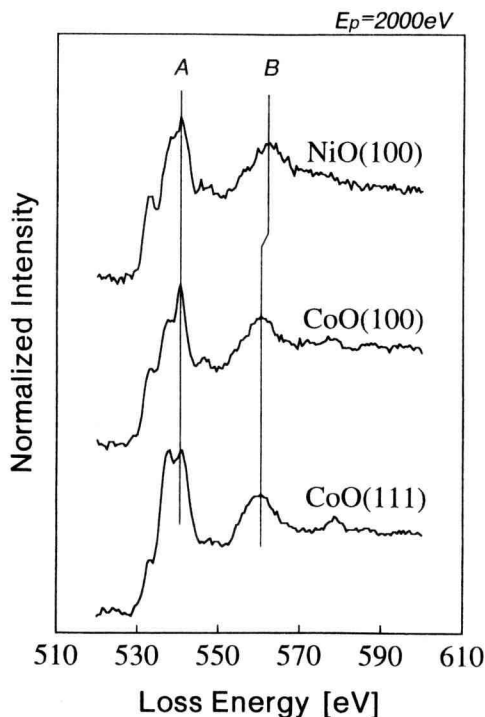


Fig. 4. Oxygen K-edge ELNES spectra of the CoO(100), CoO(111) and NiO(100) surfaces. The incident electron beam was focussed in the shape of an elongated spot (due to the grazing irradiation) of  $100 \times 1500 \mu\text{m}$  at 2 kV with a current of 130 nA. The grazing angle of primary beam was  $4^\circ$  and the forward-scattered electrons were detected at  $6^\circ$  on the surface.

#### 4. Summary

Clean surfaces of stoichiometric cobalt mono-oxides were able to be prepared by controlling the oxygen pressure and the sample temperature.

The CoO(100) showed similar properties to those of NiO(100) on the surface structure and the electronic state, however, the (111) oriented surface of CoO indicates rather different features of EELFS, reflecting considerable differences in the local configuration near the top layer.

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