Mem. SR Center Ritsumeikan Univ. No. 26, 16-17 (2024)

Electronic Structure of $NdGaO_3$ (001) Probed by Soft and Hard X-Ray Photoemission

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The electronic structures of $NdGaO_3$ (001) single crystal have been investigated by high-energy photoemission spectroscopy using soft and hard X-ray utilizing both sputtering and neutralizer. The Nd 3*d* core level spectra show the shoulder structures in the lower binding energy side than the main peak due to the screening effects from the ligand sites, suggesting that the Nd 4*f* states are strongly hybridized with O 2*p* states.

1. Introduction

$NdGaO_3$ is one of typical insulating oxides at room temperature, and it is often used for the substrate of the perovskite oxides [1], such as colossal magnetoresistance manganites and ferroelectric materials [2,3,4]. From the viewpoint of the rare-earth compounds, hybridization between the 4*f* electrons and valence electrons is also interesting in the sense of the strongly correlated electron systems. Thus, it is worth studying the electronic structures using the photoemission spectroscopy (PES). However, PES measurement is usually difficult for the insulating samples because of the charging problem.

In this study, we have successfully investigated the bulk electronic structure of $NdGaO_3$ (001) by using neutralizer to compensate the charging effect. The strong hybridization between the valence electrons and Nd 4*f* electrons are observed in the hard-x-ray PES (HAXPES) spectra.

2. Experimental

Photoemission experiments were performed at SR Center SA-1 station by the scanning soft- and hard-x-ray photoemission system (ULVAC-PHI Quantes). The photon energy was set to Al Kα (hν = 1486.7 eV) and Cr Kα (hν = 5414.7 eV) lines for soft and hard-x-ray PES measurements, respectively. The single crystalline $NdGaO_3$ (001) with semi-transparent color as shown in Fig.1 was mounted by using a carbon tape. The strong charging effect giving the energy shift over 600 eV is observed for the survey scan (wide energy scan) of soft-X-ray PES (SXPES) as shown in Fig. 2 (top). This charging effect was compensated by utilizing a neutralizer [Fig. 2 (middle)]. To remove the contamination, the sample surface was sputtered by Ar ions with energy of 500 V for one minute before the PES experiments [Fig. 2 (bottom)]. The measurement temperature was set to 300 K.

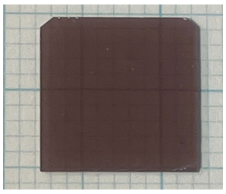

Fig. 1 Photograph of $NdGaO_3$(001) single crystal.

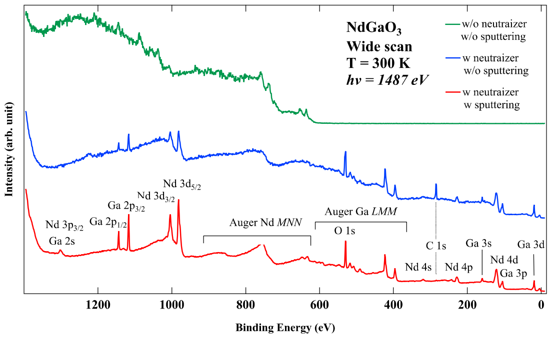

Fig. 2 Survey scans of $NdGaO_3$ (hv = 1486.7 eV)

3. Results and Discussion

Figure 3(a) shows the O 1*s* core level spectra obtained by SXPES and HAXPES. In the SXPES spectrum, the shoulder structure labeled as A is observed in addition to the main peak. This shoulder structure is strongly suppressed in the HAXPES spectrum due to the longer inelastic mean free path of photoelectrons excited in the HAXPES measurements with higher kinetic energy than those in the SXPES [5]. Therefore, the satellite structures obtained in the SXPES are possibly due to the surface contribution, having the different chemical states induced by the Ar sputtering. The single peak structure of the O 1*s* peak in the HAXPES data suggests that the bulk sensitivity is high enough to avoid the effect of the Ar sputtering.

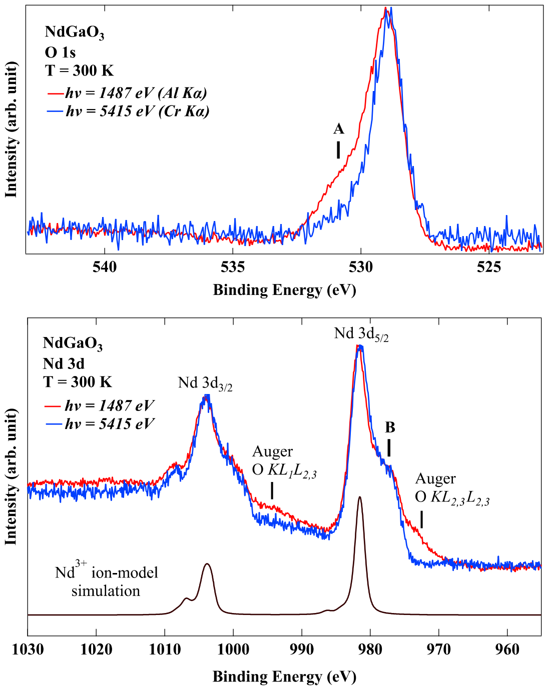

Fig. 3 (a) O 1*s* and (b) Nd 3*d* spectra obtained by soft and hard x-ray PES on NdGaO$_3$ (001) with Nd $^{3+}$ ionic model simulation.

Figure 3(b) shows the Nd 3*d* spectra recorded by SXPES and HAXPES. The main peak structures are almost identical, although the additional low-energy tails for both $3d_{5/2}$ and $3d_{3/2}$ peaks, originating from the O *KLL* Auger components [6], are observed in the SXPES spectrum. This suggests that the 4*f* mean valence does not change by Ar sputtering for both surface and bulk electronic states. To check the local electronic structures of Nd ions, we have conducted ionic model calculation, which is a localized limit of the 4*f* electrons in the Nd^{3+} ions. The calculation was implemented by the Xtls 9.0 program [7]. The spectral line shape of the main peak and multiplet-structures located at higher binding energy side than the Nd $3d_{3/2}$ peak are well explained by the ionic model simulation. However, the shoulder structures observed at the lower binding energy side labelled as B is not reproduced by the Nd^{3+} ionic simulation, which is due to $3d^9 4f^4 \underline{L}$ components originating from the charge transfer from the ligand (*L*) sites as discussed in the high-T_c cuprate superconductor NdCuO$_4$ [8,9]. This can be explained by the strong hybridization between the Nd 4*f* and O 2*p* states in the oxides.

The valence band spectra for NdGaO$_3$ (001) were also probed by using soft-X-ray as shown in Fig. 4. The valence band spectra of NdGaO$_3$ are mutually similar for (001) and (110) planes [6]. The O 2*p* components are dominant in the regime from the top of valence band to 10 eV [6,10,11], and the band gap opens over 2.5 eV, which explains the insulating state of this material.

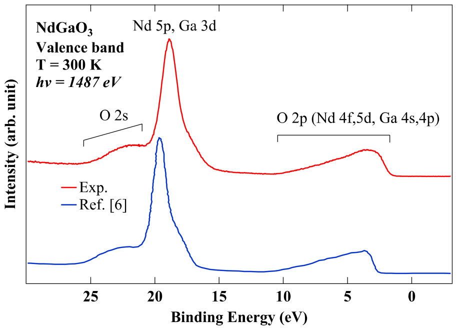

Fig. 4 Valence band spectra of NdGaO$_3$(001) and (110) planes [6] by using soft x-ray.

Summary

The electronic structures of NdGaO$_3$ (001) are investigated by SXPES and HAXPES utilizing the neutralizer. The satellite structures located at the lower binding energy side of the Nd 3*d* HAXPES spectrum indicate the strong hybridization effects in the bulk Nd 4*f* states with the valence electrons originating from ligand oxygen sites.

Acknowledgement

We thank K. Yamagami for fruitful discussions. This work was supported by a Grant-in-Aid for Scientific Research (Grant No. JP22K03527) and a Grant-in-Aid for Transformative Research Areas (Grant No. JP23H04867) from MEXT and JSPS, Japan.

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