論文内容の要旨

論文題目　Photoemission Study of Perovskite-Type
Transition-Metal Oxide Thin Films and Multilayers
(ペロブスカイト型遷移金属酸化物薄膜および多層膜の光電子分光
による研究)

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　　　　Perovskite-type transition-metal oxides have been attracting great interest in these decades because of their intriguing physical properties such as high-temperature superconductivity, giant magneto-resistance, charge-spin-orbital ordering and metal-insulator transition. Photoemission spectroscopy (PES) has greatly contributed to the understanding of the electronic structures of these materials. The intrinsic bulk electronic structure, however, has been difficult to study by PES measurements, because PES measurements are very sensitive to the surface conditions due to the relatively short mean-free path of photoelectron (several to several tenth Å).

　　　　Nowadays, high-quality single-crystal thin films grown by the pulsed laser deposition technique have become available for perovskite-type oxides and the above mentioned difficulty has been considerably overcome. Moreover, thin films have further advantages that bulk samples do not have. In the present thesis, by utilizing characteristic features of high-quality single-crystal epitaxial thin films, the electronic structures of perovskite-type transition-metal oxides thin films and multilayers have been investigated.

Electronic structure of single-crystal thin films
　　　　The well-defined atomically flat surfaces enabled us to study the intrinsic electronic states in strongly correlated electron systems. First, we have made a detailed

angel-resolved photoemission spectroscopy (ARPES) study of *in-situ* prepared $SrVO_3$ thin films. The well-defined atomically flat surfaces of the thin films dramatically reduced contributions from surface states at ~ -1.5 eV overlapping the incoherent peak, and enabled us to study the intrinsic behavior of the incoherent part. We have observed a clear momentum dispersion not only in the coherent quasiparticle peak but also in the incoherent part as well as the momentum-dependence of the spectral weight in the incoherent part, as shown in Fig. 1. We have precisely determined the band dispersion including the band minimum so that the mass renormalization factor can be discussed in detail.

Second, we have performed *in-situ* soft x-ray ARPES measurements on the ferromagnetic metallic oxide $SrRuO_3$ (SRO) thin films. The observed O $2p$ band dispersions are well explained by those from local spin-density-approximation (LSDA) calculation as shown in Fig. 2. Near the Fermi level along Γ (0, 0, 0) - X (π/a, 0, 0) direction, small and large electron-like pockets were observed. The Ru $4d$ conduction bands are found to be narrow compared with the LSDA calculation, which we attribute to electron correlation effects.
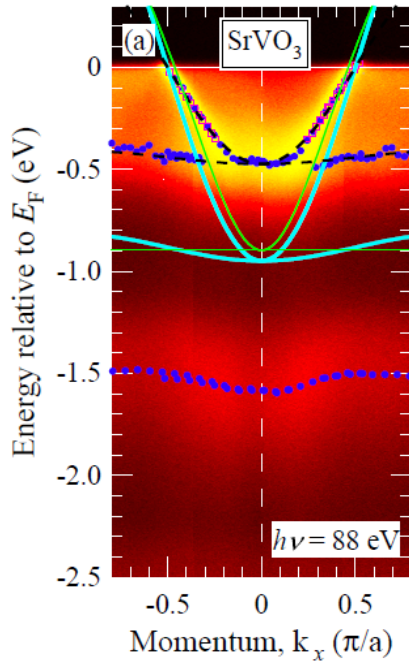

Figure 1: Energy- and momentum-dependent intensity plot of $SrVO_3$ thin films near the Fermi level. The V $3d$ bands from LDA and TB calculations are also shown.
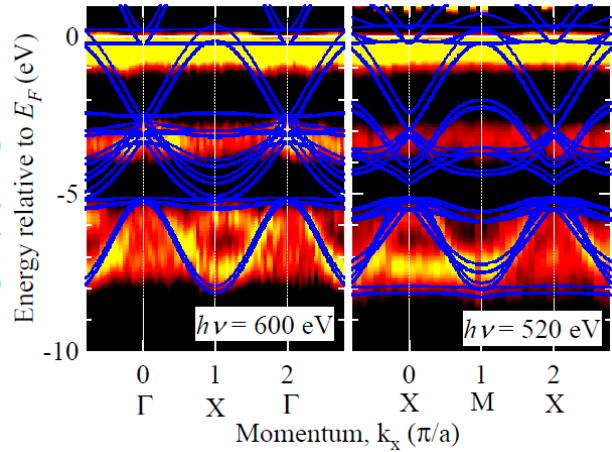

Figure 2: Valence-band dispersions of $SrRuO_3$ thin film. The grey-scale plot has been obtained by taking the second derivatives of EDCs. Bright parts correspond to energy bands. The band dispersions from the LSDA calculation are also plotted as blue curves.

Thickness-dependent evolution of magnetic and electronic states

       Thickness-controlled ultra thin films with atomic-level precision challenged us to criticalness about low dimension. We have performed x-ray magnetic circular dichroism (XMCD) measurements on ferromagnetic metallic SRO thin films with various thickness. With decreasing film thickness, the intensity of XMCD spectra, corresponding to a magnetic signal, decreased and below about 3 unit cells, the magnetic signal disappeared (Fig. 3). The appearance of the XMCD signal is well correlated with the appearance of the Ru $4d$-derived coherent peak near Fermi level in the photoemission spectra. The ferromagnetism in the SRO films is caused by the metallic conductivity.
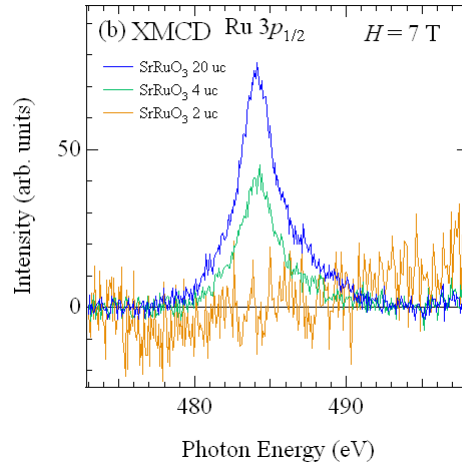

Figure 3: XMCD spectra of SrRuO$_3$ thin films with various thickness.

Electronic structure reconstruction in multilayers

       The complex artificial oxide heterostructures led us to new physics world. We have studied the valence redistribution of transition-metal ion B in LaAlO$_3$/LaBO$_3$/LaAlO$_3$ trilayers (B = Ti, V), which are composed of only polar layers grown on SrTiO$_3$ (001) substrates, by core-level PES measurements. We have found that the average B valence is intermediate between B^{3+} and B^{4+} for thin LaAlO$_3$ cap layers, decreases with increasing cap layer thickness, and finally recovers the bulk value of B^{3+} at ~ 6 unit-cell thickness (Fig. 4). These results indicate that the atomic reconstruction of the polar LaAlO$_3$ surface competes with a purely electronic transition-metal ion (B) valence change so that the ``polar catastrophe'' is avoided at the cost of minimum energy.
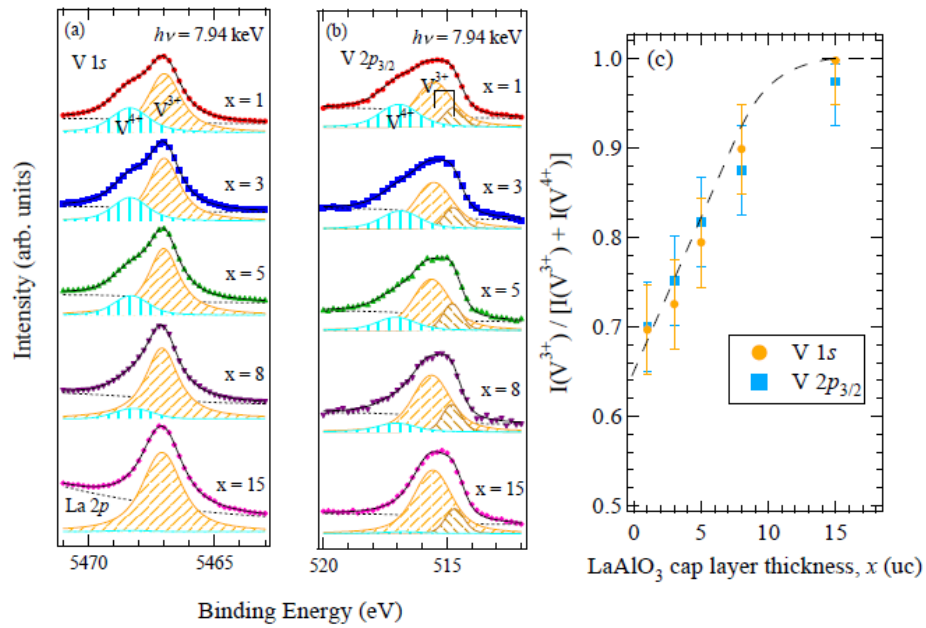
Figure 4: LaAlO₃ cap layer thickness dependence of the V $1s$ (a) and V $2p_{3/2}$ (b) core-level spectra of LaAlO₃(x uc)/LaVO₃(3 uc)/LaAlO₃(30 uc) trilayers grown on SrTiO₃ substrates. Fitting results are also shown. Panel (c) shows the LaAlO₃ cap layer thickness dependence of the V^{3+} ratio to the total number of V atoms in the V $1s$ and $2p_{3/2}$ core-level spectra. The dashed curve is a guide to the eye.