論文の内容の要旨

論文題目　Electronic Structures and Carrier Dynamics at Metal Oxide Surfaces

(金属酸化物の表面電子構造と表面におけるキャリアダイナミクス)

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Surface physics has in these decades become a fundamental branch of condensed matter research. In the field of the surface science, the surfaces of metal-oxide semiconductors such as ZnO and $SrTiO_3$ (STO) have nowadays been attracting great interest not only for their technological applications in future electronic devices and optoelectronic applications e.g., high-electron-mobility transistor (HEMT), photovoltaics, and photocatalyst, but also for their intriguing physical properties such as the Rashba effect, many-body effects, and photocatalystic properties. Electronic structures and carrier dynamics at semiconductor surfaces are strongly related to their band-bending structures. Because of the charge transfer between the bulk and the surface, band bends downward or upward and a charged layer a so-called space-charge layer (SCL) is formed [1]. Surface donors at an *n*-type semiconductor surface form an accumulation layer where electron carriers are accumulated at the surface and the band is bent downward. With a large number of surface donors, a conduction-band minimum (CBM) crosses the Fermi level and a two-dimensional electron gas (2DEG) is formed at the surface. On the other hand, surface acceptors from a depletion layer where the band is bent upward and few electron carriers exist. Above the various experimental methods, photoelectron spectroscopy (PES) is the most powerful method to obtain band-bending and electronic structures.

In this thesis, the electronic structures and carrier dynamics related with their band-bending structures of metal-oxide-semiconductor surfaces have been studied by angle-resolved PES

(ARPES) measurements and time-resolved PES measurements. The band-bending structures of the surfaces have been obtained by calculations with a theoretical model proposed in this thesis.

In Chapter 4, a simplified but reasonable solution for calculations of band bending and subband structures of accumulation layers at wide-gap-semiconductor surfaces is proposed. Chapter 5 describes the experimental probes of hydrogen-induced metallization of a STO(001) surface. The electronic structures of the 2DEG formed at the surface have been obtained with polarization-dependent ARPES studies. In Chapter 6, high-resolution ARPES results on hydrogen-adsorbed ZnO($10\bar{1}0$) and STO(001) surfaces are presented. Spectral weights at the lower energy sides of the 2DEG are observed at both of the surfaces, indicating the many-body interactions at the surfaces. Time-resolved PES results on ZnO(0001) surface are presented in Chapter 7. PES and Hall measurements have revealed an upward depletion-layer-type band-bending structure at the surface. An electron-hole recombination process and carrier lifetime are discussed.

Theoretical approach for multiple band structures at wide-gap semiconductors

Conduction bands of ZnO and STO are made of isotropic *s*-orbitals and anisotropic Ti 3*d*-t_{2g} orbitals, respectively. Recent ARPES studies showed that complicated subband structures are formed at STO(001) surfaces by the oxygen vacancies [2]. Since *ab initio* approach is lacking in feasibly, much simpler approach is required to evaluate the electronic structure at the surface.

A simplified theoretical model for multiple-subband structures at wide-gap-semiconductor surfaces is proposed, and the model well-reproduces the experimental results of 2DEG taken at a STO(001) surface (Fig. 1) [2].

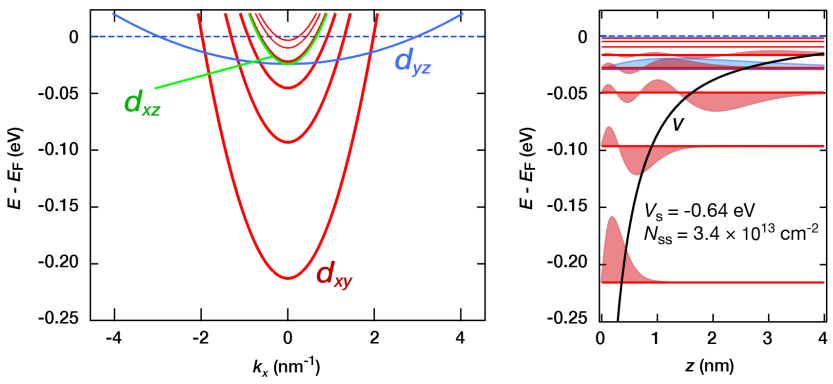

FIG. 1 The calculated subband structures of an accumulation layer at a STO (001) surface. The subband dispersion curves (left), potential variation and wavefunctions (right) for Ti-3d_{xy} (red), 3d_{xz} (green), and 3d_{yz} (blue) bands are displayed.

Moreover, the calculated results indicate the existence of a high electron density, exceeding 2×10^{21} cm^{-3} and a high electric field of 20 MVcm^{-1} at the STO(001) surface.

Hydrogen-induced metal-insulator transitions of the STO(001) surface

Hydrogen-induced metal-insulator transitions at STO(001) surface have been experimentally proved by ARPES and surface conductivity measurements with four-point probes (4PP) methods. Figure 2(a) shows the surface conductivity change associated with the hydrogen adsorption on the STO(001) surface. The increase of the surface conductivity indicates H-induced metallization at the surface. Surface metallization was also confirmed by the PES spectra showing metallic peaks near the Fermi level (E_F) shown in Fig. 2(b). A core-level peak shift toward the lower energy side revealed that metallization was induced by the formation of an accumulation layer. Figure 2(c) shows the PES intensity ratio taken by *p*- and *s*-polarized light. The large intensity ratio at the binding energy (E_B) of $E_B \sim 10$ eV is assigned to the σ(O-H) states. The small intensity ratio near the E_F indicates that the origin of 2DEG is mainly electrons of Ti $3d_{xy}$ bands. The spectra also show the peak structure in the band gap [in-gap states (IGSs)]. Since the intensity ratio at $E_B \sim 1.5$ eV shows no polarization dependency, the origin of IGSs can be assigned to the O 2*p* derived states.

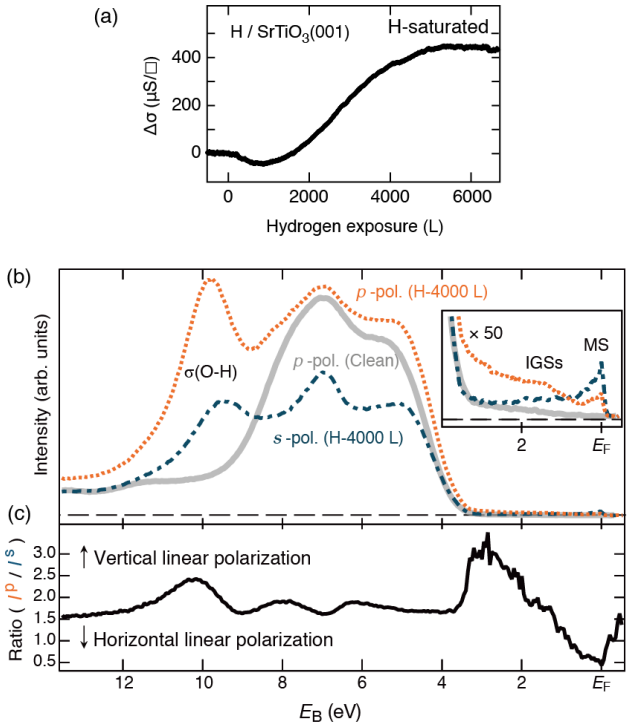

FIG. 2 (a) Surface conductivity change by the hydrogen adsorption at the $SrTiO_3$(001) surface. (b) The PES spectra taken at the H-STO surface with *p*- (orange) and *s*- (blue) polarized light and their intensity ratio (c).

High-resolution ARPES studies of the hydrogen-adsorbed ZnO($10\bar{1}0$) and STO(001) surfaces

Electronic and band-bending structures of the hydrogen-adsorbed STO(001) and ZnO($10\bar{1}0$) surfaces have been obtained by high-resolution ARPES measurements. The band-bending structures of the surfaces are theoretically calculated with the model presented in Chapter 4. We found non-vanishing spectral weights at the lower energy sides of the MS peaks of both the ZnO($10\bar{1}0$) and STO(001) surfaces. The spectral weights indicate the enhanced many-body interactions inherent to the 2DEGs.

Carrier dynamics at the ZnO(0001) surface

Relaxation of the surface photovoltage (SPV) shift generated at the ZnO(0001) surface has been investigated by time-resolved PES measurements with a laser pump and soft-x-ray probe system. The flat-band carrier lifetime at the surface was determined to be about one picosecond, which is the order of magnitude as those reported by the former time-resolved optical experiments. Potential variation at the ZnO(0001) surface was determined by self-consistent calculations with a bulk donor density and valence band maximum obtained by the Hall and PES measurements, respectively. From pumping-laser-power dependences of the SPV shifts, we found that the electron-hole recombination process can be described by a thermionic relaxation model, where photoexcited electrons thermally transport the potential barrier to the surface and recombine with holes trapped at the surface-recombination center (inset of Fig. 3).

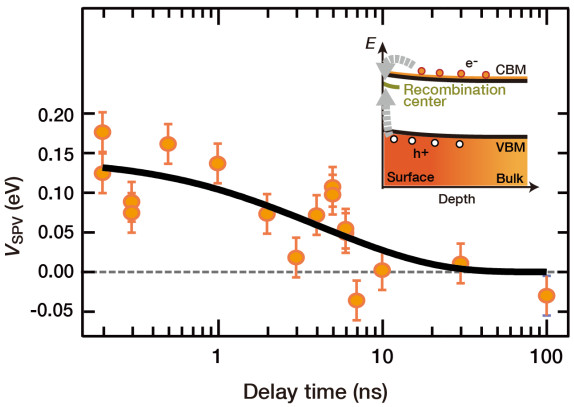

FIG. 3 Time dependencies of SPV shifts observed at the ZnO(0001) surface. The inset shows a schematic image of the potential variation and electron-hole recombination process.

Conclusion

The simple and effective anisotropic approach to self-consistently solve the Poisson-Schrödinger equations to obtain band-bending and subband structures of *n*-type wide-gap semiconductors is proposed. We found metallization of a well-defend STO(001) surface by hydrogen adsorption and obtained the band structures of the 2DEG. The evidences of many-body interactions at both the hydrogen-terminated ZnO($10\bar{1}0$) and STO(001) surfaces were found by high-resolution ARPES studies. The depletion-layer-type band-bending structures and carrier recombination time are obtained at the ZnO(0001) surface. We found that the recombination process is described by the thermionic relaxation model.

[1] H. Lüth, Surfaces and Interfaces of Solid Materials (Springer-Verlag, 1995).

[2] P. D. C. King *et al*. Nat. Commun. **5**, 3414 (2014).