Development of Electron-Ion Coincidence Spectroscopy for the Study of Surface Dynamics

Kazuhiko Mase,* Mitsuru Nagasono, Tsuneo Urisu, and Yoshitada Murata†

Institute for Molecular Science, Okazaki 444

†Institute for Solid State Physics, Minato-ku, Tokyo 106

(Received November 1, 1995)

Electron-ion coincidence (EICO) spectroscopy for studying surface dynamics has been developed. The apparatus consists of an electron gun, a cylindrical mirror analyzer (CMA), and a time-of-flight ion mass spectrometer (TOF-MS). A sample surface is excited with an electron beam, and the energy of the emitted electrons is analyzed by the CMA. The TOF spectra of desorbed ions are measured with the TOF-MS and a multichannel scaler, taking the energy-analyzed electron signal as the starting trigger. Those ions coincidently desorbed with electrons give a characteristic peak in the TOF spectrum. The apparatus has been evaluated on the basis of electron-ion coincidence measurements of an F/$SrTiO_3$ (100) surface. The F^+ coincidence signal was observed to be enhanced at electron kinetic energies of 650—655 eV, corresponding to the $F(KL_{23}L_{23})$ Auger transition. The result provides direct evidence of the Auger-stimulated ion-desorption mechanism for an ionically bonded surface (the Knotek–Feibelman (KF) mechanism).

Surface dynamics has developed into one of the most active fields of fundamental as well as applied science. The desorption induced by electronic transitions (DIET) has been an important topic in surface dynamics.[1] Until now, the mechanism of DIET has been discussed mainly on the basis of the incident photon (or electron) energy dependence of the desorption yield. In those studies the electronic transitions which correspond to the thresholds or the characteristic peaks in the yield spectra were inferred to induce desorption. For ion desorption induced by electron emissions, coincidence measurements of energy-selected electrons and mass-selected ions represent another powerful approach, because the intermediate electronic states leading to ion desorption is directly identified by an energy analysis of the emitted electron.[2]

Knotek and Rabalais have developed an electron-ion coincidence (EICO) spectrometer for surface studies, and presented some preliminary results of EICO measurements for a fluorinated oxidized Ti (100) surface in 1985.[3] After this pioneering work, however, EICO spectroscopy was not applied to surface studies at all, bacause of several problems characteristic of a surface, such as abundant secondary electrons, ions produced by secondary electrons, a difficulty to collect electrons and ions efficiently, and the high probability for the recapture or neutralization of ions. Lately, however, we have developed a new EICO apparatus, and have succeeded to improve this technique to the level of practical use. In the present article we describe details concerning the apparatus and some results of EICO measurements of an F/$SrTiO_3$ (100) surface around the electron kinetic energies corresponding to the $F(KL_{23}L_{23})$ Auger transition.

Experimental

The apparatus consists of an ultra-high vacuum (UHV) chamber with a mu-metal magnetic shield (base pressure: 2×10^{-10} Torr, 1 Torr = 133.322 Pa), an EICO spectrometer, low-energy electron diffraction (LEED) optics, and a sample-preparation system. The EICO spectrometer consists of an electron gun of 20-mm-diameter and 57-mm-length, a coaxial cylindrical mirror electron energy analyzer (CMA) with retarding grids,[4] a time-of-flight ion mass spectrometer (TOF-MS), a power supply, and an electronic system for measuurements, as schematically shown in Fig. 1. The electron gun consists of a thoriated tungsten hairpin filament, three electrodes for focusing, and two pairs of deflection plates. The electron gun axis is directed at 45° from the CMA axis. The CMA consists of a mu-metal magnetic shield, semicylinders of 58- and 120-mm diameter with apertures of 10°-angular-width and 120°-azimuthal-width (solid angle: 0.24 sr), three sets of electrodes for maintaining a radial electric field at the ends of semicylinders, retarding grids of 22- and 25-mm radii, a cylindrical slit of 2-mm-diameter and 1.5-mm-length, and tandem microchannel plates (MCP) (Hamamatsu Photonics, F4655). The CMA has a resolving power of 1.2% without a retarding field. The TOF-MS consists of an ion-extraction grid spot-welded on the top of a drift tube (T1), a 35-mm-drift tube (T2), and MCP (Hamamatsu Photonics, F4655).

The metallic parts of the electron gun, the CMA, and the TOF-MS are mainly made of SUS 316L, whose residual magnetism is diminished through annealing to 950 °C. The electron gun, the CMA, the TOF-MS, and a 75-mm-retraction mechanism are mounted on a 203-mm-diameter flange, as a bolt-on instrument. The sample surface is excited by an electron beam, and emitted electrons are analyzed by the CMA, while the desorbed ions are accelerated with an extraction electric field towards the TOF-MS. The voltage supplies for the CMA are controlled by a computer (NEC, PC-9801FA) via a D-A converter board (CONTEC, DA16-

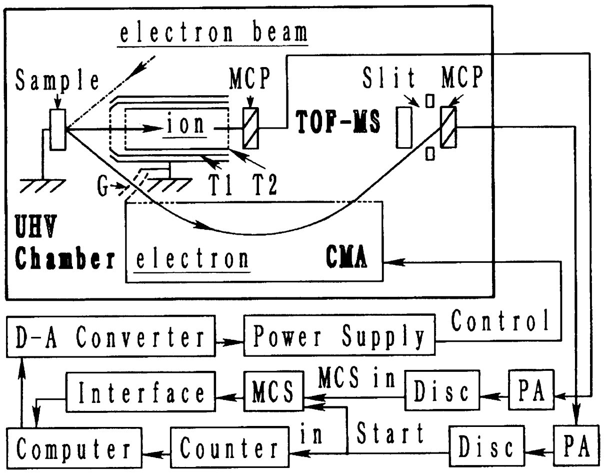

Fig. 1. Schematic diagram of the apparatus for electron-ion coincidence spectroscopy and non-derivative Auger electron spectroscopy. The abbreviations used are as follows: PA, preamplifier; Disc, discriminator; T1, drift tube with an extraction grid; T2, 35-mm-drift tube; G, retarding grids (see the text for other abbreviations). The typical distances between sample and T1 grid, and T1 grid and T2 grid are 5 and 6 mm, respectively.

2D(98)H). Electron and ion signals are transformed to the nagative NIM pulses via preamplifiers (Phillips Scientific, 6954, Gain 100 and 10, respectively) and discriminators (Phillips Scientific, 6904 and 6908, respectively, 300 MHz). The ion counts are recorded as a function of the TOF difference between the electrons and ions with a multichannel scaler (MCS) (Laboratory Equipment Corporation, LN-6500, pulse pair resolution = 10 ns), taking the energy-analyzed electron signal as the starting trigger. The MCS is also controlled by the computer via an interface board (Laboratory Equipment Corporation, MCA/PC98). The ion desorbed from the same excited molecule which had emitted the electron gives a true coincidence signal at a specific TOF, while the ion irrelevant to the electron increase the background level as a chance coincidence signal. Hence, this technique is called electron-ion coincidence spectroscopy.[2] The software for the CMA control and data acquisition is coded with Quick BASIC ver. 4.5. Non-derivative Auger spectra are also measured with the present instrument and counter (ORTEC, 996).

The present apparatus has been improved as compared with that reported by Knotek and Rabalais[3] regarding the following points: (1) The ion collection efficiency has been improved, because the ion extraction voltage at T1 is increased to −638 V, which is −110 V for the apparatus by Knotek and Rabalais. (2) The dead time for ion counting has been reduced, bacause an MCS is used instead of a system comprising a time to pulse-height converter and a pulse-height analyzer. (3) The efficiency of the conditioning and measurements has been improved due to the computer-controlled measurement system. (4) The efficiency of the instrumentation and geometric setting has been improved because of the simple bolt-on structure.

Results and Discussion

Fluorine absorbed on an $SrTiO_3$ (100) surface at room temperature ($F/SrTiO_3$ (100)) is used as the test sample. Although this surface is expected to be similar to the fluorinated oxidized Ti (100) surface studied by Knotek and Rabalais,[3] $F/SrTiO_3$ (100) is more advantageous than fluorinated oxidized Ti (100) for an EICO study around the F Auger region, because F does not exist in the bulk which is not responsible for the ion desorption, and because the surface structure and composition are relatively defined. An Nb : $SrTiO_3$ (100) single crystal (Nb: 0.5%, 0.0065 Ω cm, Shinkosha Co.) was washed with acetone and annealed in UHV to 300 °C by direct-current heating. The surface exhibited a diffuse (1×1) LEED pattern after the cleaning. The surface was then dosed with fluorine to saturation at room temperature using a $Pt/CaF_2/Pt$ electrochemical cell.[5] A typical non-derivative Auger-electron spectrum for $F/SrTiO_3$ (100) is shown in Fig. 2(a). In addition to Sr, Ti, O, and F Auger peaks, a C Auger peak due to contamination was also observed. A trace of $F(KL_{23}L_{23})$ Auger electron peak was observed around a kinetic energy of 655 eV. When an ion-extraction electric field of $128\ \mathrm{V\,mm^{-1}}$ was applied, the electron count for kinetic energies of > 330 eV was enhanced, while that for < 330 eV was suppressed; also, the Auger peaks above 330 eV shifted to a higher kinetic energy by a few eV (Fig. 2(b)), because the electron trajectory was distorted by the electric field. Usually the angular distribution of emitted electrons has a lobe towards the surface normal direction ($\alpha = 0°$), while the aperture of the CMA is located at $\alpha = 42\pm5°$. The ion-extraction field deflects the electron trajectory towards the off-normal direction. Therefore, the detection efficiency of the CMA for those electrons with higher kinetic energies is enhanced, while that with lower kinetic energies is suppressed.

Figure 3 shows typical EICO spectra for the $F/SrTiO_3$ (100) around an electron kinetic energy of 655 eV, which corresponds to the $F(KL_{23}L_{23})$ Auger transition. The relatively large ion-extraction field of $128\ \mathrm{V\,mm^{-1}}$ is advantageous for EICO measurements, because both the electron and ion-detection efficiencies are enhanced, and because the width of the coincidence ion peak is reduced. The coincidence ion peak superimposed on the background was observed at 970, 840, 790, and 760 ns for the T2 voltages of −400, −646,

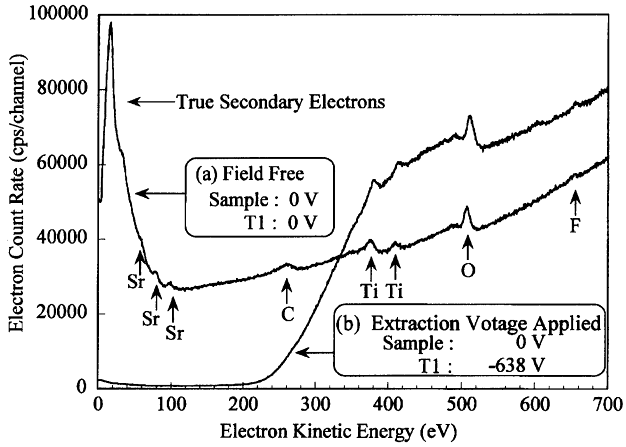

Fig. 2. Typical non-derivative Auger electron spectra for $F/SrTiO_3$ (100) (a) without and (b) with an ion-extraction electric field of $128\ \mathrm{V\,mm^{-1}}$. The primary electron energy is 2300 eV. Each channel is measured for 1 s at the step of 0.5 eV.

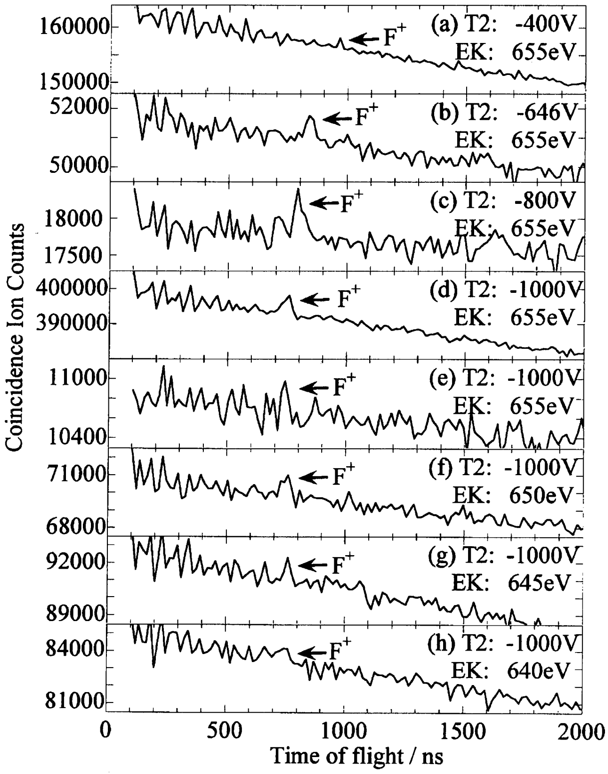

Fig. 3. Typical coincidence spectra of F/$SrTiO_3$ (100). The primary electron energy is 2300 eV. The dwell time of the MCS is 16 ns/channel. The voltages at the sample and T1 are 0 and −642 V, respectively. The T2 voltages (T2) are (a) −400, (b) −646, (c) −800, (d)—(h) −1000 V. The electron kinetic energies (EK) are (a)—(e) 655, (f) 650, (g) 645, and (h) 640 eV. The accumulation times are (a) 10000, (b) 6909, (c) 10000, (d) 20528, (e) 1255, and (f)—(h) 10000 s. The ion and electron count rates are approximately (a) 29 and 53, (b) 30 and 26, (c) 16 and 16, (d) 37 and 27, (e) 28 and 26, (f) 26 and 28, (g) 27 and 31, and (h) 26 and 30 kcps, respectively. The F^+ coincidence peak for T2 of −400 V is small, because the ion detection efficiency is reduced due to the deceleration electric field between T1 and T2.

−800, and −1000 V, respectively (Fig. 3(a)—(d)). On the basis of the T2 voltage dependence of the TOF, the mass number of the ion was estimated to be 19±2. We therefore assigned the ion to F^+. Figure 3(e) shows the EICO spectrum measured under the same condition with Fig. 3(d), except for the accumulation time. The true coincidence signal intensities observed in 728—776 ns superimposed on the background in Fig. 3(d) and (e) were estimated to be 12600±1900 and 600±300, respectively, where the errors were estimated based on the fluctuation of the background over the range of 600—728 and 776—1200 ns. The true coincidence signal intensity is proportional to the background level (N), while the error is proportional to $\sqrt{N}$, because the background is derived from the statistical fluctuations of the chance coincidence signal.[3] Therefore, the ratio of the true coincidence signal to the error is improved in proportion to $\sqrt{N}$ as the accumulation time increases. The true coincidence-signal intensities normalized to N (I_N) for Fig. 3(d) and (e) at an electron kinetic energy of 655 eV are 0.032±0.005, and 0.056±0.030, respectively. The true coincidence signal count per measured ion count is $1.6\pm0.3\times10^{-5}$, which is of a similar order with that for the fluorinated oxidized Ti (100) reported by Knotek and Rabalais.[3]

Figure 3 (f)—(h) show the EICO spectra at electron kinetic energies of 650, 645, and 640 eV. The true coincidence signal intensities estimated for Fig. 3(f)—(h) are 2980±810, 1820±920, and 1840±880, respectively. I_N at 650, 645, and 640 eV are 0.043±0.012, 0.020±0.010, and 0.022±0.011, respectively. That is, I_N at 655 and 650 eV is larger than those at 645 and 640 eV by a factor of 2. Since the $F(KL_{23}L_{23})$ Auger electrons have been reported to have peaks at 653 and 656 eV,[6] these results show that the F^+ coincidence signal is enhanced at electron kinetic energies corresponding to the $F(KL_{23}L_{23})$ Auger transition.

The zigzag peaks in 100—600 ns are caused by an artifactual signal, because these are not reduced even when the accumulation time is increased. Figure 4 shows the coincidence spectra of an amorphous multilayer H_2O condensed on an oxidized Si (111) surface at 80 K ($H_2O/SiO_2/Si$ (111)) for different ion and electron count rates at an electron kinetic energy of 505 eV, which corresponds to O (KVV) Auger transitions. When the product of the ion and electron count rates exceeds 1×10^8 s^{-2}, the artifactual peaks are again observed in 0—600 ns, which is attributed to the characteristics of the MCS. The optimum condition is attained for ion and electron count rates of 10 and 10 kcps, respectively. Details concerning an EICO study of $H_2O/SiO_2/Si$ (111) are reported elsewhere.[7]

The $SrTiO_3$ (100) surface is reported to consist of an SrO-

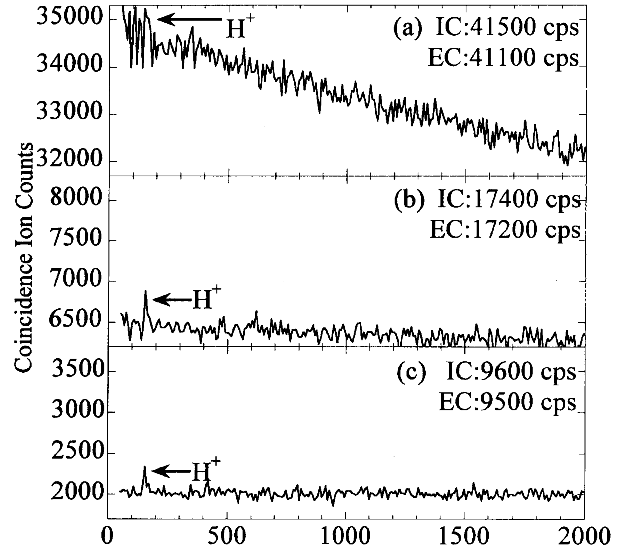

Fig. 4. Typical coincidence spectra for $H_2O/SiO_2/Si$ (111) at the electron kinetic energy of 505 eV, which corresponds to O (KVV) Auger transitions. The primary electron energy is 1900 eV. The voltages at the sample, T1, and T2 are 0, −500, and −700 V, respectively. the dwell time of the MCS is 8 ns/channel. The accumulation time is 3600 s. IC and EC represent the ion and electron count rates, respectively.

terminated surface, a TiO_2-terminated surface, or mixture of these surfaces.[8)] Therefore, the fluorine atoms on the $SrTiO_3$ (100) are supposed to be bonded as an anion on the cationic Ti and Sr site. The most probable model for F^+ desorption is the Auger-stimulated ion-desorption mechanism for an ionically bonded surface (the Knotek–Feibelman (KF) mechanism), which is described approximately by a sequence of three steps: The first step is a core-level excitation of an anion adsorbed on a cation, the second is an Auger transition leaving a multiply ionized anion, and the final is ion desorption induced by a Coulomb repulsion between the cation and the multiply ionized anion.[9)] The enhancement of the F^+ coincidence signal at electron energies corresponding to the $F(KL_{23}L_{23})$ Auger transition indicates that the KF mechanism is responsible for the F^+ desorption.

An EICO study of F/$SrTiO_3$ (100) around the Ti and Sr Auger transition regions is another interest topic, because F is supposed to be bonded on the Ti and Sr site. However, such measurements are more difficult than those for the F Auger region, because the collection efficiency for the Ti and Sr Auger electron is reduced by the ion extraction field, as shown in Fig. 2(b). An EICO study of F/$SrTiO_3$ (100) around the O Auger transition region is another important topic, because O^+ desorption is reported to be induced by the KF model.[9)] However, the desorption probability for O^+ is expected to be smaller than F^+, because the emission of three electrons is required to convert O^{2-} to O^+, while the emission of two electrons is sufficient for the conversion of F^- to F^+. Furthermore, the Ti, Sr, and O Auger peaks are derived not only from the topmost layer, but also from the bulk which is not responsible for the ion desorption. These topics will be treated in the future.

The authors wish to thank Prof. Masao Kamada for fruitful discussions. The authors are deeply grateful to Mr. Shin-ichiro Yamamoto and Mr. Rin Yamamoto for their valuable supports in developing the electron-ion coincidence spectrometer. The authors acknowledge Dr. Shin-ichiro Tanaka for his constructive support in developing the software for the measurements. This work was partly defrayed by a Grant-in-Aid for Scientific Research (Nos. 04740183, 05740211, 07740268) and a Grant-in-Aid on Priority-Area-Research "Photoreaction Dynamics" (Nos. 06239264 and 07228267) from the Ministry of Education, Science, Sports and Culture.

References

1) T. E. Madey, *Surf. Sci.*, **299/300**, 824 (1994), and references therein; R. D. Ramsier and J. T. Yates, Jr., *Surf. Sci. Rep.*, **12**, 243 (1991), and references therein.

2) W. Eberhardt and R. Murphy, "Desorption Induced by Electronic Transitions, DIET-III," Vol. 13 of Springer Series in Surface Sciences, ed by R. H. Stulen and M. L. Knotek, Springer-Verlag, Berlin (1988), p. 32.

3) M. L. Knotek and J. W. Rabalais, "Desorption Induced by Electronic Transitions, DIET-II," Vol. 4 of Springer Series in Surface Sciences, ed by W. Brenig and D. Menzel, Springer-Verlag, Berlin (1985), p. 77.

4) R. L. Gerlach, *J. Vac. Sci. Technol.*, **10**, 122 (1973).

5) B. Bechtold, *Appl. Surf. Sci.*, **7**, 231 (1981).

6) R. G. Albridge, K. Hamrin, G. Johansson, and A. Fahlman, *Z. Phys.*, **209**, 419 (1968).

7) M. Nagasono, K. Mase, and T. Urisu, *Surf. Sci.*, in press.

8) Y. Tanaka, H. Morishita, M. Watamori, K. Oura, and I. Katayama, *Appl. Surf. Sci.*, **82/83**, 528 (1994).

9) M. L. Knotek and P. J. Feibelman, *Phys. Rev. Lett.*, **40**, 964 (1978); P. J. Feibelman and M. L. Knotek, *Phys. Rev.*, **B18**, 6531 (1978); M. L. Knotek and P. J. Feibelman, *Surf. Sci.*, **90**, 78 (1979).