様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

平成　２９　年　　５　月　２６　日現在

機関番号：　８２４０１
研究種目：　挑戦的萌芽研究
研究期間：　2015～2016
課題番号：　１５Ｋ１３５２６

研究課題名（和文）Dynamical screening effects in pump-probe Hard X-ray Photoelectron Spectroscopy

研究課題名（英文）Dynamical screening effects in pump-probe Hard X-ray Photoelectron Spectroscopy

研究代表者

Ｃｈａｉｎａｎｉ　Ａｓｈｉｓｈ（Chainani, Ashish）

国立研究開発法人理化学研究所・放射光科学総合研究センター・専任研究員

研究者番号：８０４２５６３６

交付決定額（研究期間全体）：（直接経費）　　1,300,000円

研究成果の概要（和文）：我々は、微小焦点X線自由電子レーザー（XFEL、hnu = 8keV）パルスをプローブとして、赤外線レーザーパルス（hnu = 1：55eV）をポンプとする時間分解硬X線光電子分光法（trHAXPES）開発した．我々は、XFEL誘発真空空間電荷効果を研究するために実験とシミュレーションの組み合わせを使用した。この結果は、La：SrTi03の固有電荷キャリア再結合ダイナミクスから真空空間電荷効果を分離する方法を提供し、マイクロメータスケールでの空間分解能を備えたピコ秒時間スケールでの固有電荷キャリアダイナミクスの研究への道を開く 。

研究成果の概要（英文）：We have carried out Time-resolved hard X-ray photoelectron spectroscopy (trHAXPES) using microfocused X-ray free-electron laser (XFEL, hnu =8 keV) pulses as a probe and infrared laser pulses (hnu = 1:55 eV) as a pump to determine space-charge effects and separate out intrinsic charge-carrier recombination dynamics in La:SrTi03. We have used a combination of experiments and numerical N-body simulations for developing a simple approach to characterize and decrease XFEL-induced vacuum space-charge effects. We then show that, using an analytical mean-field model, vacuum space-charge effects can be compensated by pump laser-induced photoholes at high excitation densities. This provides us a method to separate vacuum space-charge effects from the intrinsic charge-carrier recombination dynamics in the time domain. Our trHAXPES results thus open a route to studies of intrinsic charge-carrier dynamics on picosecond time scales with lateral spatial resolution on the micrometer scale.

研究分野：　Condensed Matter Physics

キーワード：　time-resolved　pump-probe　HAXPES

１．研究開始当初の背景

In this project, we proposed to carry out and establish the method of time-resolved Hard X-ray Photoelectron Spectroscopy (tr-HAXPES) using an infra-red laser pump and a hard-x-ray probe. We proposed to study the transition metal compounds $SrTiO_3$, Nb-doped $SrTiO_3$ and La-doped $SrTiO_3$ which are important materials for oxide electronics. Typically, these experiments were proposed to span the important time scales from nanosecond to picosecond range, with a step-size of about 50 picoseconds in the time delay. In our recent studies carried out at SACLA XFEL facility at SPring-8, we had found that at zero time delay, the HAXPES spectra show a maximum shift and broadening due to space charge effects[1-3]. Thus it is an important challenge to separate out space charge effects from intrinsic charge carrier dynamics using an element specific bulk sensitive technique and that was the main motivation of the research project

We proposed to investigate the difference in the time dependence at negative and positive delays in detail for $SrTiO_3$ based samples. From careful studies, we wanted to quantify and elucidate the role of space charge effects. Having done this, it would be possible to separate out and address the quantification of electron-hole recombination time-scales. Since it is known that the optical spectroscopy results indicate nanosecond scale dynamics associated with electron-hole recombination, it is hoped that we can identify the corresponding changes in the time resolved HAXPES spectra in the nanosecond to picoseconds range.

２．研究の目的

The purpose of the research is to carry out tr-HAXPES using an infra-red pump and a hard x-ray synchrotron probe as to be able to separate out space charge effects from intrinsic charge carrier dynamics. The project aims to describe element-specific dynamical time scales associated with electron-hole recombination in the series of oxides $SrTiO_3$, Nb-doped $SrTiO_3$ and La-doped $SrTiO_3$. The results will provide us intrinsic charge carrier lifetimes for designing electronic devices based on these oxides. The range of interest is nanosecond to picosecond scale electron dynamics.

The method can then be applied to a series of isostructural compounds in the future. The obtained information would help to design materials with appropriate metal-ligand (cation-anion) character for improving the properties of transition metal oxides for electronic, thermal and magnetic applications. In particular, the aim will be to determine the recombination lifetimes and this will also help to improve synthesis protocols for increasing the electron-hole recombination lifetime in transition metal compounds.

３．研究の方法

(1) Experimental techniques : Time-resolved HAXPES experiments were performed at beamline 2 (experimental hutch 3 providing a microfocused beam) of the SACLA XFEL facility at SPring-8. We used ultrashort ($\Delta t \approx 10$ fs), quasi-monochromatic ($\Delta E \approx 1$ eV) XFEL pulses with a photon energy of ~8 keV at a repetition rate of 30 Hz. The XFEL pulse timing jitter was at maximum ~250 fs. The average XFEL fluence was about 175 Jcm^{-2}, corresponding to ~4.1×10^9 photons per pulse, with 10% fluctuation over 30 shots. The pulse energy at the sample was adjusted by inserting Si and Al attenuators of varying thickness into the beam. Typical attenuation factors were in the range of up to 1000–2500. All photoemission spectra were recorded using a Scienta R4000-10 kV electron analyzer. For the (tr)HAXPES experiments the pass energy was set to 200 eV at an entrance slit width of 1.5 mm resulting in a nominal analyzer energy resolution of 0.75 eV and thus a total experimental energy resolution of about 1.25 eV.

The typical data acquisition time for one spectrum was about 40–60 minutes. For the time-resolved pump-probe photoemission studies, the XFEL probe pulses were complemented by synchronized optical pump pulses delivered by a Ti:Sapphire amplifier system with a photon energy of 1.55 eV, a pulse length of $\Delta t \approx 40$ fs, and incident fluences of up to 30 $mJcm^{-2}$. The effective probe and pump beam spot sizes on the sample (full width at half maximum: FWHM) were about $2.5 \times (40–145)$ μm^2 and $190 \times (2300–5000)$ μm^2, respectively, depending on the photon incidence angle, which was chosen in a range of 3.5° to 1° (relative to the sample surface). In this scheme, the horizontal pump spot diameter was limited by the sample size. Pump and probe beam hit the sample quasi-collinearly with an angle of 1° between the beams. In this experimental geometry, the relative delays between pump and probe pulses are maintained when measuring in a grazing photon incidence geometry. However, the optical path for the photon pulses increases along the major axis of the spot profiles and the photoelectron excitation process is thus spread in time (by < 2 ps along the footprint of the XFEL beam). The temporal overlap of the pulses was determined using an ultrafast photodiode with a rise time of 30 ps and the pump-probe time delay was adjusted by using an optical delay line. As single crystal samples, 5% La-doped $SrTiO_3$ as well as undoped Si were chosen. The equilibrium sample temperature

during all experiments was set to 300 K

Complementary soft X-ray PES experiments were conducted on a polycrystalline gold sample at the undulator beamline BL17SU of SPring-8 using a photon energy of 600 eV at a total energy resolution of 200 meV. Soft X-ray PES and (tr)HAXPES experiments were carried out using the same experimental setup with the photoelectron emission direction being perpendicular to the direction of photon incidence.

(2) Mean-field model : To reproduce the measured pump-probe delay dependence of the pump laser-induced spectral shift, we extended a simple mean-field model, which was successfully used to describe pump laser-induced space-charge effects in trHAXPES experiments in our earlier study[2,3]. The basic assumption of this model is to approximate the electron cloud excited by the pump pulse as a Gaussian charge distribution moving at the average pump-electron velocity *v*pump in the direction normal to the surface (*z* direction). To account for long-living photoholes at the surface ($z = 0$) arising from multiphoton electron emission or separation of photoexcited electron-hole pairs in a surface space-charge layer, an additional positive charge distribution is introduced, equaling the shape of the pump electron charge distribution directly after its birth. Electron-hole recombination mechanisms inside the sample, such as nonlinear Auger recombination, single-carrier trapping, or other microscopic carrier recombination processes, are included by phenomenologically assuming a bi-exponential decay of the number of positive charge carriers, based on known results of time-resolved photoluminescence studies of $SrTiO_3$ in the high excitation density regime, as is also relevant for our case.

４．研究成果

(1) Fundamental limitations to XFEL-based tr-HAXPES : There are two general limitations of solid-state photoelectron spectroscopy arising from the use of a microfocused, ultrashort-pulsed photon source with high peak intensities: sample ablation and (probe-induced) vacuum space-charge effects[1-3].

When using the unattenuated microfocused SACLA XFEL photon beam, fluences, i.e., pulse energies per

area, of approximately 175 Jcm^{-2} are reached, which are well above the ablation threshold of the samples used, e.g., 80 Jcm^{-2} in the case of silicon, resulting in severe sample damage. The magnitude of the ablation threshold fluence, F_{abl}, for the single crystal La:$SrTiO_3$ sample used in the present study can be estimated as 90 $Jcm^{-2} < F_{abl} < 175$ Jcm^{-2}. This type of radiation damage typically does not arise in experiments with an unfocussed XFEL beam (spot diameter ~700 μm)[1-3]. However, in order to perform photoelectron spectroscopy experiments, the average pulse energy has to be reduced further than just below the sample ablation threshold. This is because of vacuum space-charge effects, which can result in severe distortions of the recorded energy distribution curves. Figure 1(a) shows the evolution of the measured Ti 1 *s* HAXPES spectra of La:$SrTiO_3$ as a function of the average XFEL pulse energy. These data were recorded at a photon incidence angle of about 1° relative to the sample surface. The applied mean fluencies ranged from 0.06 Jcm^{-2} up to 90.83 Jcm^{-2}. The latter value corresponds to a beam attenuation of 52%. With increasing XFEL pulse energies, the spectral distributions become broadened and shifted towards higher kinetic energies, until at the highest applied pulse energies no spectral features can be recognized anymore.

For a quantification of the observed space-charge effects, we have fitted the experimental data using Voigt profiles after subtraction of a Shirley-type background [Fig. 1(a)]. The extracted spectral shift and broadening are shown in Fig. 1(b,c). The space-charge broadenings were calculated from the measured, broadened (Gaussian) FWHM of the respective energy distribution curve and the ‘intrinsic’ linewidth as determined by high-resolution HAXPES experiments at the same photon energy[1], convoluted with the instrumental energy resolution (~1.25 eV FWHM). The data reveal the behavior known from previous XFEL photoemission experiments6 and predicted by numerical *N*-body simulations[3] : near-to-linear dependencies of the spectral shift and broadening as a function of the average fluence or, equivalently, the number of excited photoelectrons *N*. The fitted linear slopes are (1.98 ± 0.26) eV/(Jcm^{-2}) and (17.48 ± 0.96) eV/(Jcm^{-2}) for the spectral shift and broadening, respectively. Thus, to perform photoelectron spectroscopy experiments with a microfocused XFEL beam, or more precisely, to obtain spectral widths where the spectral broadening is smaller than the intrinsic linewidth, the available photon intensity has to be reduced by at least 3 orders of magnitude resulting in prolonged acquisition times of 40 to 60 minutes in comparison to measurements with a less attenuated beam operating at a repetition rate of 30 Hz.

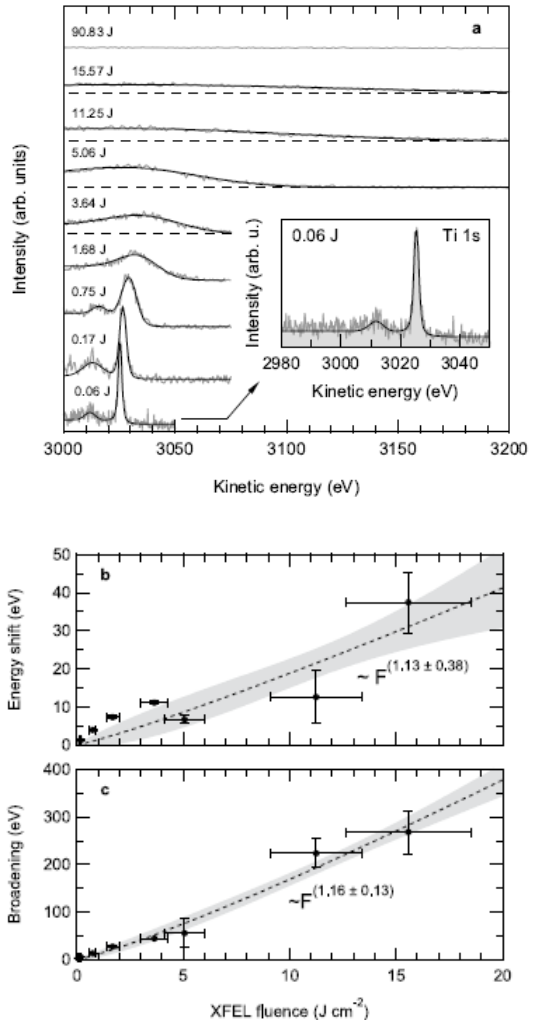

Figure 1. Space-charge effects in XFEL-based micro-HAXPES. (**a**) Evolution of the Ti 1 *s* core-level photoemission spectrum of La-doped $SrTiO_3$ as a function of XFEL fluence ($h\nu \approx 8$ keV). All fluences are given in units of pulse energies per cm^2. (**b**) Spectral shift and (**c**) spectral broadening of the Ti 1 *s* core-level emission of $SrTiO_3$ as a function of XFEL fluence. The filled symbols are experimental data. The dashed line is a power-law fit to the data, 68.3% confidence bands are indicated by gray filling.

(2) Space-charge and charge-carrier recombination dynamics in trHAXPES. Finally, we exploit the novel approach and investigate the 1.55-eV-pump laser-induced dynamics of the Ti 1 *s* emission of La-doped $SrTiO_3$ as probed by the 8 keV XFEL radiation. The pump laser was set to a fluence of 30 $mJcm^{-2}$ and the XFEL probe fluence on the sample was 0.17 Jcm^{-2}. Importantly, we note that in comparison to our previous trHAXPES experiments on La:SrTiO3, in which an unfocused XFEL photon beam was used at a pump and probe photon incidence angle of $\vartheta \approx 15°$ (relative to the sample surface)[3], the reduced photon incidence angle of $\vartheta \approx 1°–1.5°$ leads to an up to 15-fold reduction of the effective XFEL penetration depth, $L\text{eff}=L\times\sin\vartheta$, where L(8 keV, $\vartheta = 90°$) ≈ 5.5 nm. By contrast, the pump laser penetration depth, which is assumed to be in the order of ~50 nm is not expected to change significantly upon reduction of the incidence angle. Hence, whereas similar incident pump laser fluences and thus similar excitation densities were used in the two experiments, the present grazing-incidence measurements enable us to be more sensitive to surface effects due to the drastically decreased effective XFEL probing depth.

Figure 2(a) shows the experimental spectra for various pump-probe delays together with the best fits using Voigt profiles on a Shirley-type background. The zero of the energy axis is defined by the position of the Ti 1 *s* emission at a blocked pump beam. The maximum positive kinetic energy shift and broadening are observed at time zero, when pump and probe pulses overlap in time[2,3]. The relaxation dynamics of the extracted shift in kinetic energy as well as the spectral width show a distinctly different character for positive and negative delays [Fig. 2(b,c)]. For negative delays both decay on a 100 picosecond time scale, whereas for positive delays three-staged dynamics can be observed. The measured spectral shift and broadening, first, decrease within a few tens of picoseconds toward a minimum at kinetic energies and spectral widths, respectively, lower than the mean values of the unpumped spectrum, before, second, recovering toward positive shift and broadening values and, finally, relaxing back into equilibrium on a nanosecond time scale.

To understand the origin of this dynamics, we first present the results of mean-field model calculations neglecting the possible presence of (quasi-)stationary photoholes at the surface ($p = 0$ photoholes per pump electron). Figure 2(b) shows the time dependence of the Ti 1 *s* shift extracted from the experimental data in comparison to the calculated results. To reproduce the maximum positive kinetic energy shift as well as the negative delay dynamics, the number of pump electrons had to be set to $3.5 * 10^6$. The beam spot diameters as well as the mean pump- and probe-electron velocities, on the other hand, were taken from the experiment. When neglecting any possible influence of pump laser-induced photohole effects at the surface ($p = 0$) and only accounting for pump laser-induced space-charge effects in vacuum, the model cannot reproduce the observed three-staged dynamics for positive time delays [Fig. 2(b)]. However, when we take into account stationary photohole states ($p > 0$) as well as possible bi-exponential electron-hole recombination inside the strongly electron-doped $SrTiO_3$ sample (with time constants $\tau 1$ and $\tau 2$), the model can qualitatively

describe the observed delay dependence of the spectral shift. In fact, the calculations give a successively better agreement with the experimental data for an increasing number of photoholes at the surface [Fig. 2(b)]. The best agreement can be found if p = 0.9 stationary photoholes per excited pump electron are assumed. We note that in our simple 1D model the position of the minimum at kinetic energies lower than the mean value of the unpumped spectrum is mainly determined by the time constant $\tau 1$, which, however, at the same time defines the recovery rate toward positive kinetic energy shift values. The chosen value of the time constant $\tau 1$ appears to be the best fit between both stages. The subsequent relaxation into equilibrium is mainly governed by the value of the time constant $\tau 2$. The charge-carrier recombination time constants of $\tau 1$ = (150 ± 20) ps and $\tau 2$ = (5 ± 0.5) ns chosen to reproduce the observed dynamics [Fig. 2(d)] as well as the assumed charge population ratio $N_1^+ : N_2^+$ of (9 ± 0.5) : 1 are in good agreement with the findings of time-resolved photoluminescence experiments in the high excitation density regime on undoped $SrTiO_3$ samples reported in the literature. The microscopic origin of these recombination processes, however, remains an interesting subject for further investigations. We note that similar effects, i.e., negative shifts in kinetic energy due to the influence of photoholes in the high excitation density regime, have recently also been observed in time-resolved extreme ultraviolet photoelectron spectroscopy of solutions[4]. In view of the simplicity of the model, the agreement between calculated and measured results is remarkable.

Thus, our tr-HAXPES experiments in combination with a simple mean-field model can be used to deconvolve pump laser-induced extrinsic space-charge dynamics and intrinsic charge-carrier recombination dynamics in La:$SrTiO_3$. The combined experimental and theoretical approach thus establishes trHAXPES as a novel spectroscopic tool for determining electron recombination dynamics with bulk sensitivity.

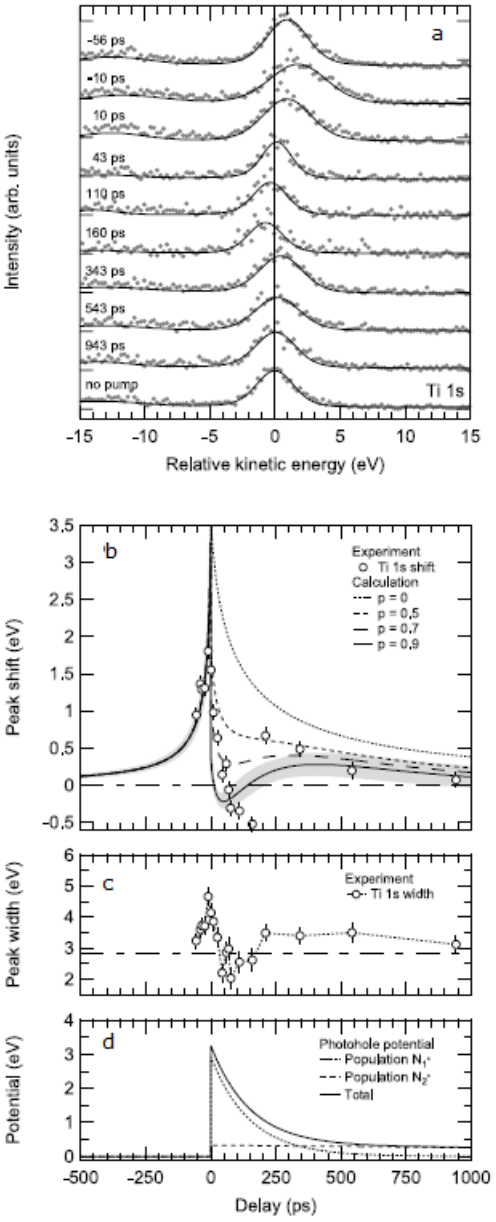

Figure 2. Tracking pump laser-induced dynamics in La:$SrTiO_3$. (**a**) Evolution of Ti 1 *s* core-level photoemission spectra of La:$SrTiO_3$ as a function of pump-probe delay at a pump fluence of 30 mJcm^{-2} ($h\nu \approx 8$ keV). (**b**) Spectral shift of the Ti 1 *s* emission as a function of pump-probe delay. The open circles are experimental data; the lines are from an analytical model considering different fractions of stationary photoholes p inside the sample. Gray shadings represent error bars for p = 0.9. (**c**) Measured Gaussian width of the Ti 1 *s* emission as a function of pump-probe delay. The dashed horizontal line marks the peak width for a blocked pump beam.(**d**) Photohole recombination dynamics inside the sample extracted from the mean-field calculations (p = 0.9 photoholes per pump electron included). The photohole population (N_1^++N_2^+) as well as the related electrostatic potential are assumed to decay bi-exponentially as a function of time with time constants $\tau 1$ = 150 ps and $\tau 2$ = 5 ns.

References :
[1] Oura, M. *et al.* Development of a single-shot CCD-based data acquisition system for time-resolved x-ray photoelectron spectroscopy at an x-ray free-electron laser facility. *J. Synchrotron Rad.* **21,** 183 (2014).
[2] Oura, M. *et al.* Electron dynamics probed by time-resolved hard x-ray photoelectron spectroscopy. *Trans. Mat. Res. Soc. Jpn*. **39,** 469 (2014).
[3] Oloff, L.-P. *et al.* Time-resolved HAXPES at SACLA: probe and pump pulse-induced space-charge effects. *New J. Phys.* **16,** 123045 (2014).
[4] Al-Obaidi, R. *et al.* Ultrafast photoelectron spectroscopy of solutions: space-charge effect. *New J. Phys.* **17,** 093016 (2015).

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計　2　件）

① Time-resolved HAXPES using a microfocused XFEL beam: From vacuum space-charge effects to intrinsic charge-carrier recombination dynamics, L.-P. Oloff, A. Chainani, M. Matsunami, K. Takahashi, T. Togashi, H. Osawa, K. Hanff, A. Quer, R. Matsushita, R. Shiraishi, M. Nagashima, A. Kimura, K. Matsuishi, M. Yabashi, Y. Tanaka, G. Rossi, T. Ishikawa, K. Rossnagel and M. Oura, Scientific Reports, **6**, 35087; doi:10.1038/srep35087 (2016).(peer reviewed)

② Hard x-ray photoelectron spectroscopy experiment at SACLA ~ towards femtosecond time-resolved measurement, M. Oura, L.-P. Oloff. K Rossnagel, A. Chainani and M. Matsunami, Journal of Japanese Society for Synchrotron Radiation Research, Vol. 29, pg. 14-22 (2016). (peer reviewed).

〔図書〕（計　1　件）

① Femtosecond Time-Resolved HAXPES, L.-P. Oloff, M. Oura, A. Chainani and K Rossnagel, in the book entitled “Hard X-ray Photoelectron Spectroscopy (HAXPES)”, Springer Series in Surface Sciences, Ed. J. Woicik, Vol. 59, pg. 555-568 (2016).

６．研究組織
(1)研究代表者
Chainani Ashish（CHAINANI ASHISH）
国立研究開発法人理化学研究所・放射光科学総合研究センター・専任研究員
研究者番号：80425636