TWO-PHOTON PHOTOEMISSION OF METAL OXIDE

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Two-photon photoemission (2PPE) spectroscopy has been applied to metal oxides. Light source for 2PPE has been designed to cover the wavelength region from near-IR ($2\mu m$) to deep-UV ($0.2\mu m$). This tunability over wide wavelength range is essential to detect the resonant excitations of unoccupied states. The capability of 2PPE method achieved by our apparatus is demonstrated by the observation of adsorption-induced excited states. 2PPE measurements on Bi2212 crystal have revealed an excited state 2.6 eV above the Fermi level (E_F). Polarization dependent 2PPE spectrum indicates that the excited state is localized in a plane parallel to the surface.

Key words: Laser method, two-photon photoemission, time-resolved phenomena, Bi2212

1. INTRODUCTION

Two-photon photoemission (2PPE) spectroscopy is a relatively new method to probe electronic structure and its dynamical properties [1-3]. In 2PPE, pulsed laser light is used to excite a normally unoccupied state and a second light is used to stimulate photoemission from the excited state. By analyzing energy distribution of photoelectrons, we can determine the initial occupied state and the intermediate unoccupied state simultaneously with energy resolution comparable to that of conventional ultraviolet photoemission spectroscopy (UPS). 2PPE spectroscopy provides unique information that is not available with UPS and/or inverse photoemission spectroscopy (IPES). Energy difference between an occupied state and an unoccupied state is directly probed in 2PPE. This is advantageous to investigating photon-induced processes due to the valence excitation by VIS/UV photons. IPES probes negatively charged states above the Fermi level (E_F), while 2PPE can probe neutral excited states. Thus 2PPE spectroscopy is useful to investigate electron correlation effects. Another important advantage of 2PPE is its high time resolution. Owing to the recent development of ultrafast lasers, 2PPE has been applied to investigating dynamical processes in a time region as fast as 10^{-15} s (fs) [3,4]. For example, the hot electron lifetimes of high-Tc cuprate $Bi_2Sr_2CaCu_2O_8$ (Bi2212) were measured with time resolution better than fs [5]. Except for ref.5, 2PPE spectroscopy has not been applied to electronic structures of metal oxide despite its inherent high capability. Here, we constructed a 2PPE apparatus for the study of metal oxides. Particular effort has been paid to achieve wide wavelength tunability of pump and probe laser lights. This is important to search for the resonant valence excitation processes. Capability of the present apparatus is demonstrated on the study of benzene adsorbed Cu(111). Preliminary result on Bi2212 is also described.

2. EXPERIMENT

In order to stimulate photoemission through two-photon process, the light source should be pulsed lasers whose peak power is higher than 10^4 W. Beside the peak power, specifications of lasers required for 2PPE spectroscopy is to be settled in terms of wavelength tunability, repetition rate, and pulse width. Wavelength of pump and probe light should be tunable from near-IR (2 μm, 0.6 eV) to deep-UV (0.2 μm, 6.0 eV). The near-IR light is required for pumping the unoccupied states close to E_F. The deep-UV light is for probing the excited electrons slightly above E_F. The light should be continuously wavelength tunable, because we should detect sharp resonance features whose widths are frequently narrower than 0.3 eV. Such a wide wavelength tunable light source is available with optical parametric amplifier (OPA) excited by regeneratively amplified titanium sapphire (Ti:Sa) laser.

Repetition rate of the light pulses is also an important parameter. In order to record a photoelectron spectrum within a few 10 minutes, electron count rate higher than 10^4 per second is typically required. With light pulses of 1KHz repetition rate and 100fs pulse duration, for example, this count rate is achieved when 10 electrons pass through the energy analyzer within time duration of the light pulse of 100 fs. This

electron flux is equivalent to electron burst of 10^{14} electrons/s. The high electron flux causes severe space charge effect in the energy analyzer leading to broadening and deformation of the spectrum. It is also impossible to count 10 electrons within 100 fs time duration, because response of an electron multiplier is not linear to such high input current. Thus the repetition rate of the laser should be sufficiently higher than 10^4 Hz. Repetition rate as high as 10^8 Hz brings about another problem. Intensity of 2PPE is proportional to the square of the peak power multiplied by repetition rate, while the energy to heat the sample is proportional to the laser peak power multiplied by the repetition rate. Thus light pulse of high peak power and low repetition rate is advantageous to avoiding sample
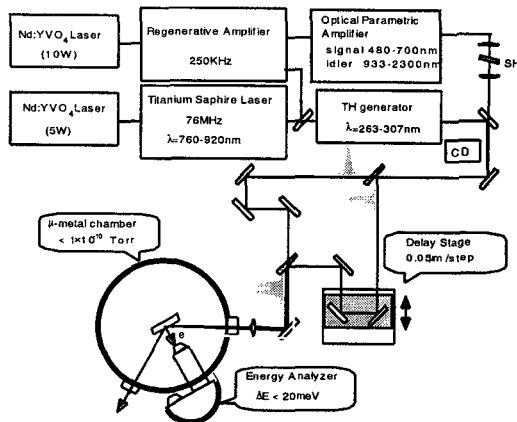

Fig.1 Experimental set up of two-photon photoemission. The delay line, not described in the text, is used for time-resolved experiment.

heating while keeping 2PPE intensity. Optimum repetition rate can be estimated from the relaxation lifetime of electron and phonon. The relaxation time of electron near the conduction band minimum of semiconductor can be as long as several hundred pico-second. Lifetime of phonon scattering is longer than nano-second [2]. When the time separation between laser pulses is comparable to the relaxation lifetime, effect of light irradiation is piled-up pulse by pulse causing electronic or vibrational heating. Thus the optimum repetition rate of the laser is estimated to be inverse of hundred times of the relaxation lifetime, that is, about MHz.

Figure 1 shows the optical system of the present experiment designed considering the above described specifications. A titanium sapphire laser (Mira 900F) pumped by a solid state green laser (Verdi-5) generates mode-locked pulse train of 100fs pulse duration and 76 MHz repetition rate. The wavelength is tunable from 790 to 920 nm.

Output of the laser is further frequency upconverted to the second, third and fourth harmonics. When 2PPE spectrum of weakly adsorbed molecule is measured, the repetition rate should be reduced in order to avoid desorption of molecules [6]. The repetition rate can be reduced to less than 3.6 MHz by a pulse picker (CD). Part of the Ti:Sa output is used for seeding a regenerative amplifier (RegA 9000) pumped by an another solid state green laser (Verdi-10). Maximum repetition rate of the amplifier is 300KHz. Though the repetition rate is the highest among commercially available regenerative amplifiers, it is still lower than the optimum value of a few MHz. The amplified output, typically 3-4 μJ/pulse at 800 nm wavelength, is fed to an optical parametric amplifier (OPA9400). In OPA, visible white light is parametrically amplified by the second harmonic of RegA output to generate visible signal light of 150-200 fs pulse duration. The signal light is tunable in the wavelength region 700-480nm, and the idler light, 922-2300nm. The signal light is then frequency doubled and used for 2PPE measurement. The power was typically 20nJ/pulse, which is sufficiently intense for one-color 2PPE.

The laser light is then coupled to the UHV chamber. The chamber is magnetically shielded and is equipped with a hemispherical electron energy analyzer (VG, CLAM 2).

In Fig.2, one-photon photoemission of Cu(111) is shown. The copper sample surface is slightly roughened by Ar ion sputtering. The light source is the fourth harmonic of Ti:Sa at 5.51 eV photon energy. Judging from the width of the stepwise feature at E_F, resolution of the present system is better than 22 meV. The Fourier transform limited energy resolution of 100 fs pulse duration laser light is about 18 meV, and the width of Fermi distribution at 30K is about 10 meV. Taking account of these values, the energy

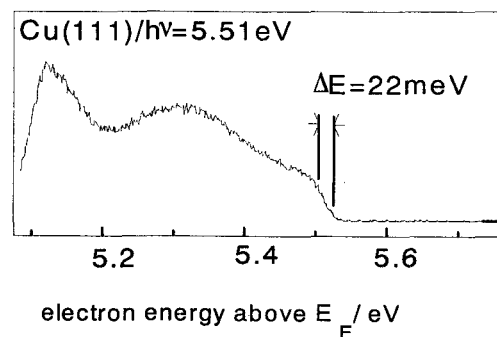electron energy above E_F / eV

Fig.2 One-photon photoemission from copper measured at 30K. The width of the Fermi edge is about 22 meV. The sample surface is roughened by ion sputtering. Peak at 5.12 eV is due to the occupied surface state.

resolution of the present analyzer is better than 20 meV. This confirms that the present system achieves purely transform limited energy and time resolution. This is important for time resolved experiment. If the energy resolution of the analyzer is wider than the laser light, it is difficult to distinguish the coherently excited feature from incoherent ones [3,4]. If one requires energy resolution higher than 20meV, a laser of longer pulse width should be used in sacrifice of time resolution.

3.RESULTS AND DISCUSSIONS

3.1 Benzene adsorbed Cu(111)

The capability of the present system has been tested with 2PPE spectrum of benzene adsorbed Cu(111) [6-8]. Temperature of the sample was 100K. Coverage of benzene was about 0.6 monolayer. The 2PPE spectra are recorded at the electron emission angle normal to the sample surface. Spectra measured with p-polarized light at several photon energies are shown in Fig.3 for benzene adsorbed Cu(111) surfaces. Two structures A and B are observed at low-energy side of E_F. Structure A aligns at constant initial energy of 0.3 eV, and structure B shifts with the photon energy. We have ascribed structure A to the adsorption-induced bonding state formed between benzene and copper. The lowest unoccupied $\pi^*(e_{2u})$ orbital may largely contribute to the formation of the bonding state [6,7]. Structure B arises from the normally unoccupied image potential state at the surface [6]. This is confirmed by putting the spectra on the intermediate energy

scale, (initial energy) + (photon energy). Note the remarkable variation of the intensities and peak shapes caused by a small change of photon energy by 0.3 eV.

The peak heights of the bonding state feature and the image state feature are plotted in Fig.4 as a function of photon energy. The wavelength dependence of the bonding feature intensity clearly shows a resonance effect [8]. The smooth curve in Fig.4 is a Lorentzian fit to the bonding feature intensity. The peak of the fitted curve is at 4.07 eV and the full width at half maximum (FWHM) is less than 0.12eV. The enhancement of the 2PPE intensity is due to the resonance between the bonding state and the first image state on a benzene-covered area. The present results demonstrate the importance of fine wavelength tunability and high-energy resolution in 2PPE measurement.
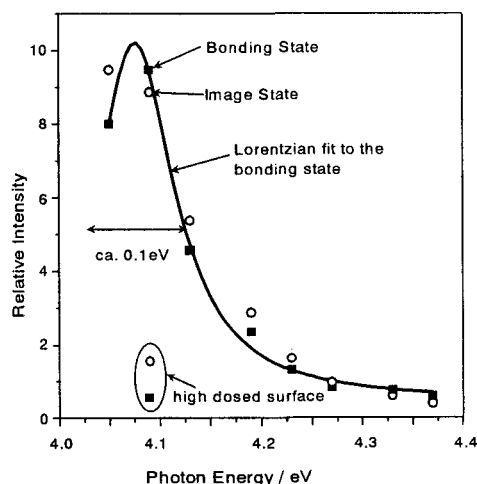
Fig.4 Photon energy dependence of the bonding state feature (filled square) and the image potential structure (open circle).

3.2 Bi2212

2PPE spectra of Bi2212 are shown in Fig.5. The sample, supplied by Prof. K. Kadowaki of Tsukuba Univ., was cleaved by scotch tape in vacuum and transferred to the 2PPE apparatus. Photoelectrons emitted normal to the surface are detected. The light is p- and s-polarized for the top and bottom traces, respectively. Three features labeled A, B and C are observed. Structures A and B show clear polarization dependence. Structure A becomes weak and peak B completely disappears at s-polarization, while structure C is only weakly dependent on the polarization. The width of peak B is as narrow as 0.3 eV. The work function is estimated to be 4.7 eV from the right hand cutoff at 0.5 eV.   Similar 2PPE spectra have been measured for photon energies in the range between
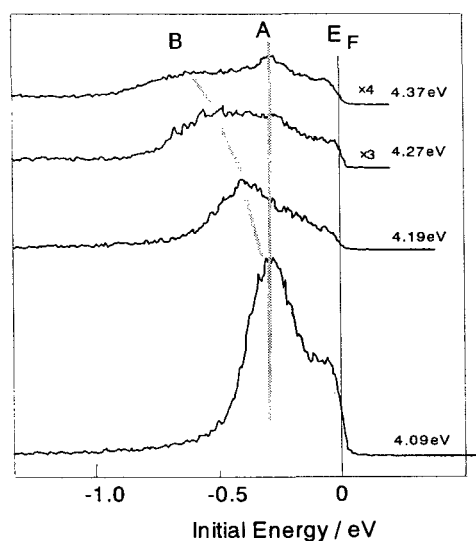

Fig.3 2PPE spectra of benzene covered Cu(111). Structure A arises from the benzene-copper bonding state. Structure B is due to the image state. Note the strong photon energy dependence.

4.07 and 4.74 eV. The photon energy dependence indicates that B and C structures arise from fixed intermediate states at 2.6 and 1.6 eV above E_F, respectively. The intermediate state causing structure C is related to the O-$2p$ dominant normally unoccupied state [9]. The narrow width of peak B is surprising for the electronic states of solids. The polarization dependence indicates that the wavefunction of the intermediate state causing peak B is localized in a plane parallel to the surface. It is not clear at the present stage whether the state is localized at the surface or in the layered planes in bulk. Similar structure was reported in inverse photoemission work [9]. In the IPES result, a structure at 3.0 eV above E_F showed a dispersive feature and was ascribed to the surface image potential state. Image potential states on metal surfaces have been extensively studied by 2PPE experiments [1,2,4]. The image state peaks in 2PPE spectra are very narrow (<0.1 eV) and can be observed only with p-polarization due to their two-dimensional free electron nature. The narrow peak width and the polarization dependence of peak B support the assignment of peak B to the image potential state. The assignment, however, requires further discussions. The image potential at the surface forms Rydberg-like bound states converging to the vacuum level. The lowest state is at 0.85 eV below the vacuum level. From the work function of 4.7 eV, the intermediate state causing B structure is estimated to be 2.1 eV below the vacuum level. Such high binding energy cannot be ascribed for the image potential state. Thus we cannot fix the origin of peak B at the present stage. The states causing structure A are also localized in the parallel plane. We expect that the localized states play some role in the functionality of Bi2212. It is interesting to note that structures A, B and C were not identified in 2PPE spectrum of ref.5 measured at 3.1 eV photon energy. These structures should exhibit resonance feature at some photon energies. The resonance will be detected with our wide wavelength tunable laser system.

We demonstrate the capability of 2PPE to detect unknown electronic states of metal oxide. Another advantage of 2PPE is its ultrafast time resolution. Together with the time-resolution, 2PPE will open up new experimental aspect to investigating electronic structure and its dynamics of metal oxides.
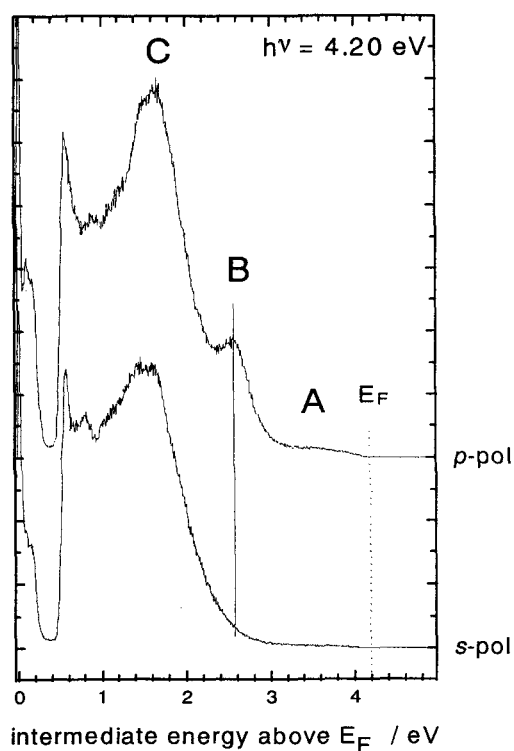
4. Acknowledgement

Fig.5 Polarization dependent 2PPE spectra of Bi2212 measured at room temperature.

REFERENCES
[1] W. Steinmann, Appl.Phys., A49, 365 (1989).
[2] "Laser Spectroscopy and Photochemistry on Metal Surfaces" Ed. By H. L. Dai and W. Ho, World Scientific, Singapole, 1995.
[3] H.Petek and S. Ogawa, Prog. Surf. Sci. 56, 239 (1997).
[4] papers in Chem. Phys., 251,1 (2000), special issue on "Electron Dynamics in Metals".
[5] W.Nessler, S.Ogawa, H.Petek, J.Shimoyama, Y.Nakayama, and K.Kino, Phys. Rev. Lett., 81, 4480 (1998).
[6] T. Munakata and K.Shudo, Surf. Sci., 433-435, 184 (1999).
[7] T.Munakata, J.Chem. Phys. 110, 2736 (1999).
[8] T.Munakata, Surf. Sci., 454-456, 118 (2000).
[9] T.Takahashi, T. Watanabe, T.Kusunoki and H. Katayama-Yoshida, J. Phys. Chem. Solids, 52, 1427 (1991).