

Chapter 1

Introduction

A detailed understanding of electronic structures of materials is very important from the view points of fundamental science as well as application. Among various means to probe electronic structures, the photon-in and electron-out measurements seem to be very useful since the energies, wave vectors numbers, polarizations and time structures are well defined for photons and electrons. Historically speaking, the photoelectric effects were first observed more than a century ago [1] when the spark between two electrodes was facilitated by illumination of the negative electrode by ultraviolet light. Electrons were discovered in 1897 [2] and the above mentioned photoelectric effect was found to be associated with the emission of electrons from the metal under ultraviolet light irradiation [3]. From the dependence of the emitted electron current on the light intensity and the electron velocity on the light frequency, Einstein proposed in 1905 the concept of photons [4]. The concept of the work function was also recognized around this time. Many metals were later carefully studied and the validity of the Einstein's photoelectric equation was confirmed.

The question of whether the photoelectric effect is a pure surface effect or due to a bulk effect was raised and unsettled for a long time because of poor vacuum condition. Considerable efforts were made to determine the work functions of many materials. It was then found that the work function of tungsten was significantly lowered by Cs coverage. From the application point of view, the lowering of the work function by means of Cs deposition was applied in Ag–O–Cs cathodes to detect infrared radiation. A similar technique is now often used for negative electron affinity cathodes to have sensitivity for infrared radiation down to $h\nu \sim 0.9$ eV or to prepare the spin polarized electron source from GaAs by circularly polarized laser light excitation. The photoelectric effect is now used for photomultipliers in a wide $h\nu$ region.

By the late 1950s the understanding of electronic structures of simple solids was noticeably advanced. For example, the photoelectron spectrum of Si was compared with the experimentally obtained optical spectra and band structures obtained by band structure calculations. Then a lot of experimental works were made on tetrahedral semiconductors. Correspondingly, development of theoretical

works followed. The concept of k -conserving direct transitions and non-conserving transitions was intensively discussed in the early 1960s [5] in photoelectron spectroscopy (PES).

The very early PES was performed below $h\nu \sim 6$ eV limited by the absorption by air. The PES in higher $h\nu$ was performed in the vacuum ultraviolet (VUV) with use of hydrogen lamps separated from the experimental chamber by LiF windows with a cut off at $h\nu \sim 11.8$ eV in the mid 1960s [6, 7]. The use of synchrotron radiation (SR) for PES became a reality in late 1960s at Deutsches Elektronen-Synchrotron (DESY) in Hamburg, Germany. The use of the SR from electron or positron storage rings instead of electron synchrotrons became a major stream after the mid 1970s due to the beam stability (with respect to the intensity and the time dependence of the beam position) in storage rings. Even in the case of VUV lamp sources, the extension of the $h\nu$ toward higher energies became feasible by He discharge lamps, which provide a strong discrete line at $h\nu = 21.2$ eV (HeI) and a weaker line at $h\nu = 40.8$ eV (HeII) under low pressures. Due to the narrow line width of the strong HeI line source, even the molecular vibration levels were studied in the case of gaseous samples. Rare gas lamps using Xe, Kr, Ar and Ne were also used for VUV PES.

On the other hand, photoelectron spectroscopy with X-ray sources later called XPS was also widely used. The origin of XPS can be traced back to the early 1910s. However, the energy resolution around that time was very poor ($> \text{few eV}$) due to the broad X-ray lines and inadequate resolution of the analyzers. When X-ray absorption and emission spectroscopy became popular, XPS became less used. Four decades later, Siegbahn and collaborators started to realize a high resolution photoelectron spectrometer for XPS in 1951 [8]. It was soon found that sharp peaks were observed at the high kinetic energy end of several broad bands or inelastic backgrounds. The sharp peaks observed in XPS were corresponding to core levels and often much sharper than absorption and emission spectra. Consequently such a new applications as the electron spectroscopy for chemical analysis (ESCA) was opened [9]. The $K\alpha$ lines of Al and Mg are nowadays most often used for conventional XPS. However, the width of these characteristic lines is ~ 1 eV. By use of bent quartz crystals, a resolution down to 0.2 eV was achieved for the Al $K\alpha$ line at the sacrifice of intensity. Nowadays XPS in the valence band region is thought to provide information on the density of states modified by the photoionization cross sections (PICS) of the constituent electronic states. Fine structures and satellites of core levels accessible by high resolution XPS are also useful to discuss the final state interactions and screening processes besides obtaining chemical information as discussed in [Chaps. 5, 6, 7 and 8](#).

Later conventional PES systems in laboratories became often equipped with both He lamp and X-ray tube to study valence band as well as core levels with as good resolution as possible. The ultra high vacuum (UHV) conditions were satisfied to some extent and various surface cleaning techniques became available. The large $h\nu$ gap between the He lamp and the X-ray tube became gradually covered by SR source. SR has various useful properties compared with the radiation from the X-ray tubes and VUV radiation from the He, Ne and other rare gas

lamps as discussed later in [Sect. 3.1](#). First of all, the high brilliance of SR due to its low emittance enables one to focus high photon flux in a small spot ($\ll 1$ mm) on the sample, facilitating the measurement of small-size samples. Tunability of $h\nu$ by use of the photon monochromators is another advantage, which enables the efficient excitation of some particular core levels. The polarization, either linear (horizontal or vertical) or circular (left or right helicity), enables one to probe the specific symmetry of the orbitals due to the selection rules and also enables one the measurements of dichroism in PES. Moreover, the pulsed feature of SR facilitates the time-of-flight PES measurements.

From the mid 1970s the angle resolved photoelectron spectroscopy (ARPES) became feasible to study band dispersions utilizing the energy and momentum conservation, where the momentum parallel to the specular surface was thought to be conserved during the electron escape from the surface. The momentum perpendicular to the surface was thought not to be conserved in this case. For quasi-two-dimensional (2D) or one-dimensional (1D) systems with negligible dispersion to the perpendicular direction, the ARPES at one $h\nu$ could provide information on 2D or 1D band dispersions when the sample was properly rotated and/or the detection angle was scanned. For three-dimensional (3D) materials, the band dispersions depend on the momenta along three directions. In this case, the dispersion perpendicular to the surface was evaluated by normal emission measurements with changing the $h\nu$ if the final state dispersion was already known or approximated by a parabolic band. ARPES measurements could be performed by (1) rotating a small analyzer with enough angular resolution around the sample or (2) rotating the sample in front of the analyzer entrance slit or (3) using a 2D detector installed on a hemispherical analyzer. One example of (3) was to use a microchannel plate just behind the exit of the hemispherical analyzer, where the energy corresponds to one axis on the detector and the emission angle corresponds to the other axis parallel to the exit slit of the hemispherical analyzer. In addition to these approaches, (4) really two dimensional detectors are now used which can detect the full angular distribution simultaneously. Development of this technique is explained in [Sects. 3.4, 3.6, Chaps. 11 and 12](#).

The use of SR made it possible to do the resonance photoemission (RPES) with tuning $h\nu$ in a particular core absorption edge region, thereby enhancing the intensity of the state with a particular orbital character as a result of quantum interference between the direct photoemission and the direct recombination following the core absorption. Such states as f and d outer shell states buried in the valence band can be effectively enhanced and probed by this technique. The resonance enhancement seems to be strongly related to the degree of the localization of the electronic states.

Besides the energies and momenta, the spin is another important physical quantity to be probed by PES. In accordance with the development of spin detectors, spin-polarized and angle-integrated and -resolved PES measurements became feasible. In the case of ferromagnetic materials, the essence of the long range and short range spin exchange interactions is gradually clarified. The spin polarization of the emitted photoelectron is also observed for nonmagnetic materials when they are

excited by the circularly polarized light as a result of spin-orbit interaction. In addition, spin polarization is observed in the cases of Rashba effects and topological insulators in non-magnetic materials as explained in [Sect. 11.3](#).

While abundant information was obtained on occupied electronic states by PES, less is known for the unoccupied states. The inverse photoemission spectroscopy (IPES) became available for the study of unoccupied states in the early 1980s, where monochromatic electrons impinged onto the sample and relaxed to the lower unoccupied states above the Fermi level with the emission of photons. Angle resolved IPES could provide information on the band dispersion of the unoccupied states. When spin polarized electrons were used, the spin polarized and angle resolved IPES is feasible. These subjects are handled in [Chap. 10](#) and [Sect. 11.5](#).

In the PES studies the concept of the inelastic mean free path (λ_{mp}) of photoelectrons is very important. The electron-electron interaction induces the finite and rather short inelastic mean free path, which is often in the range of 3–5 Å between ~ 15 and ~ 200 eV of kinetic energies (E_K). Therefore PES in this energy region is generally surface sensitive. Although this quantity depends upon the individual materials, it is widely accepted that the λ_{mp} increases above $E_K \sim 200$ eV. On the other hand its increase below ~ 10 eV is known to be much more material specific. Therefore caution is required to discuss the bulk electronic structures based on the PES data for $E_K < 10$ eV.

In the case of strongly correlated electron systems, the surface electronic structures are noticeably different from the bulk electronic structures. In order to overcome this difficulty, high resolution PES above a few hundred eV is strongly favored. Such experiments are now progressing on several beam lines of SR facilities in the world by using bright undulator light sources, high transmittance and high resolution photon monochromators and high performance electron analyzers.

As for low energy high resolution PES, the resolution better than 1 meV has been already achieved by use of a quasi-CW high repetition pulsed lasers. Microwave-excited electron cyclotron resonance Xe, Kr and Ar lamps have comparable $h\nu$ resolution and are nowadays employed for high resolution low energy PES and ARPES for $E_K < 12$ eV. Many examples of the soft X-ray, hard X-ray and low energy bulk sensitive high resolution PES are explained in [Chaps. 7, 8 and 9](#). As for electron analyzers, performance of hemispherical analyzers has been amazingly improved in the last two decades, realizing the resolution better than 1 meV in the low energies and ≤ 50 meV in the region up to a few keV as explained in [Sect. 3.4](#).

There are a lot of ARPES results for band mapping in the E_K range below 200 eV ([Sect. 3.6](#) and [Chap. 6](#)), providing useful information on the momentum dependence of the electron energies. As is well known the momentum resolution is in proportion to the square root of E_K . Therefore ARPES is feasible even in the soft X-ray region of a few hundred eV as discussed in [Sect. 7.2](#). However, still the λ_{mp} is at most of the order of 10 to 20 Å (1–2 nm) and some contribution from the surface is not fully negligible. Although higher bulk sensitivity is achieved at a few keV, ARPES becomes more difficult due to the worse momentum resolution

and low photoelectron count rate. In addition, recoil effects on photoelectron emission have recently been recognized in various solid materials composed of non-heavy elements even though such effects are not observed in some solids. Therefore ARPES in the hard X-ray region (Sect. 8.7) is not so popular yet. In the case of extremely low energy ARPES for $E_K < 10$ eV, on the other hand, the matrix element effects are very strong and the measurement in a wide region of the Brillouin zone (BZ) is not so simple. One must be very careful to check whether the extremely-low-energy-ARPES and -PES are really bulk sensitive in the individual materials (Chap. 9).

In order to realize an extreme bulk sensitivity for the study of the momentum dependence of electronic structure, resonance inelastic X-ray scattering (RIXS) experiment can be employed as very simply explained in Sect. 13.3. In this case the probing depth can be easily >10 μm and one can cover a few BZ by slightly and properly rotating the sample. One of the advantages of RIXS is that even insulators could be studied without the problem of charging up. Therefore RIXS is a powerful complementary tool to PES to study, for example, metal–insulator transition (MIT) systems.

In accordance with the development of nanotechnology, PES of micro- and nano-materials is of strong interest. By focusing the high brilliance synchrotron radiation and scanning the sample, such materials can be studied by scanning photoelectron microscopy (SPEM) with the lateral resolution better than 100 nm. If only the secondary electrons are detected, photoelectron emission microscopy (PEEM) is applicable to nano-materials with the lateral resolution down to 10 nm. Such techniques are explained in Sects. 3.6.4 and 3.6.5. In the case of magnetic materials, magnetic circular and/or linear dichroism is utilized to realize the contrast of the magnetic domains. In the case of quantum well states (QWS) in thin films on substrate materials, the confinement is perpendicular to the surface and the dispersion parallel to the surface can be observed by angle resolved measurements as discussed in Sect. 6.7 in the case of ARPES and in Chaps. 10 and Chap. 11 in the case of IPES. PES utilizing standing waves is also a powerful means to study such systems and also interface systems as explained in Sect. 7.3. Further the time resolution is now utilized for PES experiments as explained in Sect. 3.4.4. The aspects of high resolutions in energy, momentum, space and time are treated as much as possible in this book to overview the state of the art technologies.

Although the $h\nu$ resolution was much improved in the last two decades in the wide $h\nu$ region from a few eV up to 10 keV, the efforts for realizing higher total resolution and higher bulk sensitivity are still going on. To clarify the difference between the surface and bulk properties is one of the urgent subjects in materials sciences. Combination of not only PES and ARPES in wide $h\nu$ regions but also various complementary techniques are thought to provide fruitful information on electronic and atomic structures of materials attracting wide interest from both fundamental science and application.

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