# ANGLE RESOLVED PHOTOEMISSION STUDIES OF PALLADIUM : Pd(110) CLEAN AND OXYGEN ADSORBED c(2×4)-O/Pd(110) SURFACES

YAGI KAZUTOSHI

ANGLE RESOLVED PHOTOEMISSION STUDIES OF PALLADIUM

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Submitted in partial fulfillment of the requirements
for the degree of Doctor of Science in Doctoral
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function of the polar emission angle $\theta_e$ along the <110> azimuth ($\overline{\Gamma}\,\overline{H}'\,\overline{N}'$).

Fig. 5-7: The AREDC's measured using HeI radiation as a function of the polar emission angle $\theta_e$ along the <001> azimuth ($\overline{\Gamma}\,\overline{N}'$).

Fig. 5-8: Normal emission AREDC's with $h\nu$ =28 eV on different polarized light. (A) $\theta_I$=65° and $A_{//}$ along <110>, (B) $\theta_I$=30° and $A_{//}$ along <110>, (C) $\theta_I$=30° and $A_{//}$ along <001>. For comparison, a normal emission AREDC for the clean Pd(110) taken at $\theta_I$=30° and $A_{//}$ along <110> is also shown at the bottom.

Fig. 5-9: The off-normal emission AREDC's at N′ of SBZ measured at (A) $\theta_I$=65° and (B) $\theta_I$=30°. The photon energy is $h\nu$ =29 eV and $A_{//}$ is along <001> direction. For comparison, the AREDC for the clean Pd(110) taken at $\theta_I$=30° is also shown at the bottom.

Fig. 5-10: The off-normal emission AREDC's at N′ of SBZ measured in two sets of geometries; (A) the light is p polarized in the collection plane, (B) the light is p polarized in the plane perpendicular to the collection plane. The photon energy is $h\nu$ =25 eV and $\theta_I$=30°.

Fig. 5-11: Two sets of collection geometries of angle resolved photoemission. (A) the light is p polarized in the collection plane. Only initial states of even symmetry with respect to the collection plane can be observed. (B) the light is p polarized in the plane perpendicular to the collection plane. Even and odd initial state with respect to the collection plane can be observed.

Fig. 5-12: Measured energy vs $k_{//}$ dispersion of oxygen induced state along the symmetry lines of SBZ.

Fig. 5-13: Bandwidth of the O-2p-derived state vs O-O nearest-neighbor distance for ordered oxygen layers on various substrate in a semilog plot (Ref. 10). The line corresponds to an exponential

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Contents

1 Introduction
1-1 General background 1
1-2 Experimental background 4
1-3 Typical experimental applications 5
1-4 Palladium 7
1-5 Oxygen adsorption of Pd(110) surface 10

2 Theory
2-1 Photoemission 12
2-2 Two-dimensional energy bands 15
2-3 Three-dimensional energy bands 17
2-4 Umklapp process 19
2-5 Band symmetry and polarization selection rules 21

3 Experiment
3-1 Preface 22
3-2 Angular distributions electron spectrometer model 400 (ADES-400) 23
3-2-1 Spectrometer chamber
3-2-2 Vacuum system
3-2-3 Analyzer
3-2-4 UV lamp
3-3-5 X-ray source
3-2-6 Ion gun
3-2-7 LEED
3-2-8 Spectrometer control and pulse counting
3-3 Experiments using synchrotron radiation 29
3-4 Sample preparation 30
3-4-1 Sample
3-4-2 Sample holder
3-4-3 Sample cleaning
3-4-4 Checking the surface cleanliness
The oxygen adsorption on Pd(110)surface
3-5 Measurements 34
3-5-1 Angle-resolved photoemission measurements
3-5-2 Work-function measurements

3-5-3 Constant initial energy (CEI) curve measurements

4 Angle-resolved photoemission study of Pd(110) clean surface
4-1 Normal emission spectra from Pd(110) 35
4-2 Experimental energy band dispersion for Pd(110) 36
4-3 Band symmetry 37
4-4 Other discussions 39

5 Angle-resolved photoemission study of Oxygen adsorbed Pd(110) surface
5-1 LEED observation 42
5-2 Work function change 43
5-3 Coverage dependent normal emission 45
5-4 Angle-resolved photoemission from Pd(110)c(2× 4)-O 46
5-5 Isolated oxygen monolayer models 49
5-5 Tight binding calculations involving the d electrons of substrate 53

6 Conclusion 56

Acknowledgenents 57

References 58

Figure captions 61

# 1 Introduction

## 1-1 General background

A solid surface has different properties from the bulk material and there are many technologically significant processes; for example, adsorption, catalysis, and corrosion etc.. Especially, catalysis plays an important role in the chemical industry and it will be useful in solving the resources and environmental problems. The transition metal surfaces and with and without adsorbed species thereon have been of great interest because of their important roles as catalyst. It is well known that a catalyst composed mainly of ion is used in synthesis of ammonia. Another example is oxidation of carbon monoxide by the use of platinum catalyst. However, the catalysis is the subject of a largely empirical literature and details on mechanism of catalysis are not well known; especially it is one of the main theme of the surface studies. Detailed studies of typical gas-metal systems in terms of microscopic parameters representing adsorbate-adsorbate and adsorbate-substrate interactions are highly needed. Usually, several of the electron spectroscopic technique have been effectively employed for such investigations.[1] The angle-resolved photoelectron spectroscopy (ARPES) is most useful to investigate the electronic structure of atomic and molecular chemisorption for several gas-metal adsorption systems.[2,3]

Photoelectron spectroscopy[4,5] is an experimental technique that measures the kinetic energy of photoemitted electrons. An electron with the initial energy $E_i$ absorbs the photon of energy $h\nu$, and is lifted into an unoccupied state with a final energy $E_f$, which then emerges from solid with a kinetic energy $E_{kin}=E_f-E_{vac}$ (Figure 1-1). The vacuum level $E_{vac}$ is the energy of the electron resting at infinity. Thus, the final energy $E_f$ of the electron is measured and the initial energy $E_i$ as well; subtracting the photon energy $h\nu$ from final energy $E_f$. In the simplest

case, therefore, the energy distribution of photoemitted electrons should simply give the energy distribution of electron state in the solid shifted up in energy by an amount $h\nu$ (Figure 1-2).

Photoelectron spectroscopy has been generally divided into two techniques by the two types of conventional light sources available in the laboratory; inert gas discharge lamps ($h\nu \sim 10$-$40$ eV) leading to Ultraviolet Photoelectron Spectroscopy (UPS), and soft X-ray sources (typically $\sim$ 1200-1400 eV) which are used for X-ray Photoelectron Spectroscopy (XPS) (alternatively called electron spectroscopy for chemical analysis (ESCA)).[5] Characteristics of inert gas vacuum ultraviolet sources most widely used are summarized in table 1-1. UPS is most commonly performed with HeI resonance line. The He radiation is used mostly to study the electrons in the valence band of the solid. The X-rays have sufficient energy for ionization of core levels in many elements and can be used to study electrons in both band and core states. The two most important X-ray sources are the Al $K\alpha$ and Mg $K\alpha$ X-ray emission at 1486.6 eV and 1253.6 eV respectively. The line width of the Al $K\alpha$ line is 0.9 eV and that of Mg $K\alpha$ is 0.8 eV.

Synchrotron radiation opened a new field in the photoelectron spectroscopy; continuous tunability of the synchrotron radiation makes it possible to do measurements such as energy band mapping and constant final or initial spectroscopy; polarization of the synchrotron radiation makes it easy to assign the symmetry of the initial state.

The photoelectron spectroscopy has an advantage for the investigation of the surface. It is a surface sensitive spectroscopy. The surface sensitivity[1] of the photoelectron spectroscopic methods does not depend upon the penetrating depth of the incident radiation but rather upon the probability that a photoelectron will be able to escape to the surface without further energy loss. An electron of energy $\sim$ 5-2000 eV passing through a solid can lose energy in a number of ways. The main processes of electron energy

losses are plasmon scattering, single particle electron excitation involving valence electrons and ionization of core levels of the atoms which composed the solid. The mean free path of an electron prior to inelastic scattering will vary with its kinetic energy. At very low energies, the electron will be unable to excite any of above losses and the mean free path will be long. At very high energies, the cross-sections for exciting the losses decrease, and again the mean free path will be long. Figure 1-3 shows experimental values of electron inelastic mean free path lengths as a function of electron energy. The mean free path is of the order of, or less than, a few tens of Å and certainly in the optimum energy range (20~ 100 eV) is typically less than 10 Å (a few atomic monolayers). Thus the surface sensitivity of the photoelectron methods will vary with the kinetic energy of the ejected electron but is best on the range 20-100 eV.

Angle-resolved detection of the photoemitted electrons adds a new dimension to photoelectron spectroscopy.[6,7] The intensity and energy dependence can be measured as a function of the collection angle with respect to some fixed axes. Energy and momentum of electrons in a solid are probed by measuring energy and momentum of photoelectrons. Thus, energy versus momentum band dispersions can be measured. Especially, angle-resolved photoelectron spectroscopy utilizing polarized light has been used to investigate the nature of the chemical bond of an adsorbate with the substrate, i.e., bonding geometry, electronic struc ture and wave function symmetry.

In particular, using tunability of the synchrotron radiation, energy dispersion for occupied valence bands have been determined in various metals.[2,3] In order to determine the valence band dispersion from the photoemission data, it is necessary to know the final state band dispersion. The final state is often assumed to be a free-electron band shifted only by a constant inner potential. The free-electron approximation for the final state has been successfully applied to Cu and has yielded

rather accurate valence band dispersions.

## 1-2 Experimental background

The development of ultra-high vacuum (UHV) techniques enabled preparation and preservation of well defined surfaces, which could be characterized in a reproducible way.[1] This level of vacuum is one in which the rate of impingement upon the surface being studied of molecules from the ambient residual atmosphere in the vacuum chamber is negligible in the time required for the observation. The kinetic theory of gases shows that the amount of gas hitting unit area of a surface per unit time is given by:

$$N = 3.51 \times 10^{22} p(M \cdot T)^{-1/2} \quad [\mathrm{cm^{-2}sec^{-1}}] \qquad (1\text{-}1)$$

where $p$ (torr) is the ambient gas pressure above the surface, $M$ is the relative molecular mass of the gas, and $T$ (K) is thermodynamic temperature. In the pressure of $10^{-6}$ torr, Eq. (1-1) shows that approximately $3.0 \times 10^{14}$ molecules of nitrogen arrive each second on each square centimeter of a surface at room temperature. Since an atomic monolayer corresponds to about $10^{15}$ atoms/cm$^2$ (inter-atomic distances being about 3 Å) such conditions result in nitrogen arrival rates of a monolayer every 3 second assuming that every molecules stick to the surface. Eq. (1-1) shows that $10^{-10}$ Torr corresponds to nitrogen arrival rates of $3.8 \times 10^{10}$ molecules/sec, or about 1 monolayer in about 8 hours. Thus, experiment must be carried out in an UHV environment of below $10^{-10}$ Torr so as to minimize surface contamination by ambient residual gases.

A surface destined for photoemission studies must be prepared in UHV chamber. The surface preparation consists of a series of cleaning procedures aimed at eliminating all foreign atoms from the surface while maintaining appropriate crystallinety. The problem of achieving the clean surface is not only the elimination of surface impurities but also the depletion of the bulk impurities from which prevent precipitating from the bulk onto the

surface. The most common techniques used for surface preparation *in situ* are: ion bombardment cycles followed by appropriate annealing treatment, heating to high temperatures to evaporate surface impurities away, gas reactions at elevated temperatures or cleavage along favorable crystallographic planes. Each crystal face of each material presents its own individual cleaning difficulties, and many man-months of effort must be expended in discovering how to produce a clean surface upon which to start study. The criteria for deciding if a clean surface had been realized in practice is usually *in situ* assessment based upon Auger electron spectroscopy (AES), XPS, UPS, low energy electron diffraction (LEED) etc.. The experiments are often designed to allow several *in situ* operations on the sample surface and several *in situ* types of measurement. The sample itself is mounted on some kind of manipulator which may allow various combinations of transition and rotation of the sample in the experimental geometry, electrical isolation, heating and cooling as a means of preparing a clean single-crystal surface.

Synchrotron radiation sources provide a continuous wavelength beam of polarized photons over an energy range starting at about 10 eV and going up easily to 1000 eV. The radiation emitted from charged particle beams accelerated around a synchrotron is in the form of an intense polarized continuum narrowly defined in the plane of the accelerator. The output curve from this type of machine is shown in Figure 1-4 and clearly demonstrates the broad continuum; the exact range of this is machine dependent but most machines are capable of high emission throughout the range relevant to photoemission i.e. from photon energies of a few eV to a few keV. If the output is passed through a monochrometor, a tunable photon source results. The photoemission measurements have attempted to choose the photon energy to optimize the mean free path of the outgoing photoelectron and hence enhance surface sensitivity. It is also in these studies that the plane polarized nature of the radiation has been exploited.

## 1-3 Typical experimental applications

Until recently, angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) studies utilizing synchrotron radiation has been used to study the band structures of certain ordered gas-metal systems.[2,3] Indeed, many gas-metal systems, especially dissociative chemisorption of electronegative diatomic gases on transition metals, have been studied by this method. The gases most widely studied are hydrogen, oxygen and carbon monoxide. The metal surfaces most extensively studied are nickel and copper.[2,3]

An ordered overlayer of an adsorbate presents a two-dimensional system interacting with a three-dimensional substrate.[8] When the adsorbate concentration on the surface is increased to form an ordered overlayer, there is interaction between the adsorbates. This interaction occurs if there is direct overlap of the adsorbates wave functions, or by way of indirect interaction through the substrate. The discrete electronic energy levels of isolated adsorbate become energy bands for an ordered overlayer. ARUPS can determine the dispersion of such adsorbate bands i.e., the dependence of energy levels on the wave vector $k_{//}$ of the two-dimensional surface Brillouin zone (SBZ), and give information on the nature of the adsorbate-substrate and adsorbate-adsorbate interaction. Detailed discussions of the valence electronic properties for some gas-metal systems of oxygen on Fe(110),[9] oxygen on Ni(110)[10] and hydrogen on Ni(110)[11] surface have been reported in previous papers. The major trends and essential features of the O-2p-derived band of Fe(110)c(2× 4)-O, Fe(110)c(3× 1)-O, Ni(110)(3× 1)-O, Ni(110)(2× 1)-O can qualitatively be reproduced by a simple tight binding model for two-dimensional isolated oxygen monolayer. However, the indirect O-O interaction via substrate is important for the band formation of the oxygen adsorbed structures where the oxygen strongly interact with the substrate.

## 1-4 Palladium

In this thesis, ARUPS studies on clean and oxygen adsorbed palladium surface are reported. Palladium is of great interest because of its catalytic properties. Oxidation of the carbon monoxide on palladium surface has been studied as one of the best model system of catalyst. The present thesis describes the results of the most open Pd(110) surface. The most open fcc(110) face is rough compared to the more close-packed smooth fcc(111) and (110) faces, cf. Figure 1-5. This roughness means that surface atoms stick out of the surface to some extent, producing a lumpy or ridged appearance and such surface is rather chemically active. The oxygen adsorption can be considered to be important and to be well suited for fundamental investigation of adsorption phenomena. The interaction of oxygen with well-defined clean palladium surface is important to understand the elementary mechanism of oxidation processes.

The studies of the electronic structure of clean palladium surface is essential as the first step for investigating its catalytic and chemisorptive properties. Several investigations of the electronic structure of palladium, theoretical[12-14] and experimental,[15-18] have been performed. The electronic energy band calculation of palladium has been reported previously by several authors. Mueller et al.[12] have calculated in terms of two different band models: the *ab initio* non-relativistic augmented plane wave (APW) method and semiempirical combined interpolation scheme augmented by inclusion of relativistic corrections. Figure 1-6 shows non-relativistic electronic band structure of palladium calculated by Mueller et al.. The relativistic palladium band structure is presented in Figure 1-7. The addition of relativistic effect splits band which are degenerate at high symmetry points of the Brillouin zone in the non-relativistic augmented plane wave method. Christensen's calculation[14] of the electronic

energy band structure of palladium by means of relativistic augmented plane wave (RAPW) method is shown in Figure 1-8.

De Hass-van Alphen experiment gives direct information on Fermi surface.[17,18] Indirect information about electronic state has been gathered by optical[19] and angle-integrated photoemission[20-22] experiments. Using angle-resolved photoemission with synchrotron radiation, Himpsel and Eastman[16] have determined accurate energy versus momentum dispersion relation along the <111> direction using Pd(111) crystal.

As for the Pd(110) surface, no detailed ARUPS study has been reported yet. The only observation of the ARUPS from Pd(110) surface has been reported by Lloyd et al.[15] However, their observations are limited in normal emission using HeI and NeI radiations and their data might be considered to arise from contaminated surface. We measured the normal emission ARUPS utilizing synchrotron radiation for the Pd(110) clean surface at the extended photon energy range of 21~88 eV. The special attention has been paid upon the surface preparation because the Pd(110) clean surface is rather active and is easily degrade even in the UHV condition. Measured normal emission ARUPS from clean Pd(110) surface have been analyzed by one-electron direct transition model and determined the experimental energy band dispersions E(k) along $\Gamma$ K X symmetry line. Our studies for Pd(110) show that the normal emission spectra can be mainly interpreted using free-electron primary cone emission and show fairly good agreement with the existing theories. The details are presented in Ch. 4.

## 1-5 Oxygen adsorption on Pd(110) surface

In resent years, many techniques for surface analysis such as low energy electron diffraction (LEED),[23-25] electron energy loss spectroscopy (EELS),[24,25] thermal desorption spectroscopy (TDS),[26-28] work function change ($\Delta\phi$)[25,28] and nuclear reaction analyses (NRA) have been applied to the investigation of the interaction of oxygen with a Pd(110) surface.

The surface phases of oxygen on Pd(110) exhibit considerable complexity. Many surface phases induced by oxygen adsorption upon exposure and heating have been reported. Ertl and Rau[23] observed five LEED patterns which were identified as the (1×3), (1×2), c(2×4), c(2×6) and "complex" patterns. Nishijima et al.[24] have studied the adsorption of oxygen on a Pd(110) surface using LEED and EELS. They observed a sequence of superstructures of "complex", c(2×6), c(2×4) and (2×3)-1D, as the Pd(110) clean surface was exposed 3L (1L= $10^{-6}$ torr·sec) oxygen at 100 K and subsequently heated to ~400-800 K. Jo et al.[25] also observed the exposure dependent changes in the LEED pattern formed by exposure at 300 K and subsequent heating to ~450 K, which were identified as the "streak", (2×3)-1D and c(2×4) patterns. By the exposure of oxygen on the clean Pd(110) surface, they observed only a single EELS peak in the specular mode. An oxygen induced peak was observed at 56 meV, which grows with increasing exposure. Thus, they proposed that there is only one kind of binding site for oxygen adatoms on the Pd(110) surface and the 56 meV loss is tentatively ascribed to the oxygen adatoms located in the long-bridge sites.

J.-W. He and P. R. Norton[27,28] have reported TDS and the corresponding work function changed measurements for desorption of oxygen from a Pd(110) surface. They observed three main peaks in the TDS labeled $\alpha$ peak (130 K), $\beta_1$ peak (744 K) and $\beta_2$ peak (816 K), respectively. They also carried out isotope exchange experiments using $^{16}O_2$ and

$^{18}O_2$, and they identified these three peaks as being from molecular oxygen ($\alpha$ Peak) and from atomic oxygen ($\beta_1$ and $\beta_2$ peaks) respectively. After exposure to 5L oxygen at 475 K, TDS exhibit only the $\beta_1$ state and surface structure is c(2× 4). The assignment of c(2× 4) phase seem to be the least controversial. Goschnick et al.[26] reported the sticking coefficient of oxygen on Pd(110) as a function of substrate temperature and oxygen coverage ~0.48 ML for the c(2× 4) phase using two mass spectrometers. He et al.[27] have measured the absolute surface coverage of oxygen by NRA using the $^{16}O(d,p_1)^{17}O^*$ reaction. They reported that oxygen coverage in the c(2× 4) phase is 0.50± 0.05 ML. This value agrees with the value reported by Goschnik et al..

However, no ARUPS study of Pd(110)c(2× 4)-O surface has been reported yet. Moreover, no detailed structural analysis of Pd(110)c(2× 4)-O surface has been carried out and the geometry of this surface has not yet been deduced. In this thesis, we applied ARUPS technique to Pd(110)c(2× 4)-O surface and studied the band structure of its ordered layer. This is the first ARUPS investigation of Pd(110)c(2× 4)-O surface. The O-2$p_z$-derived state of Pd(110)c(2× 4)-O structure exhibits considerable dispersion of about 1 eV with $k_{//}$, while the O-2p states of the Ni(110)c(2× 4)-O structure do not exhibit dispersion.[10] Our experimental band dispersion is inconsistent with the dispersion predicted for isolated oxygen monolayer. The oxygen strongly interact with the palladium and the adatom-substrate interaction is responsible for the band formation. In order to give agreement with experiment and to yield better description, the model must to be improved by considering the change in the adsorbate wave functions caused by mixing with the substrate electron. Detailed discussion is presented in Ch. 5.

## 2 Theory

### 2-1 Photoemission[29]

Within the independent electron model, the Hamiltonian for a system in the presence of an external electromagnetic field is

$$H = \frac{1}{2m}(P + \frac{e}{c}A)^2 + V(r) - e\Phi$$

$$= \frac{1}{2m}P^2 + V(r) + \frac{e}{2mc}(P\cdot A + A\cdot P) - e\Phi + \frac{e^2}{2mc^2}A^2 \qquad (2.1)$$

where A and $\Phi$ are the vector and scalar potentials of external electromagnetic field, P is momentum operator. It is always possible to chose a gauge where $\Phi = 0$. The Hamiltonian of the system can be separated into two basic parts,

$$H = H_0 + H' \qquad (2.2)$$

$$H_0 = \frac{1}{2m}P^2 + V(r) \qquad (2.3)$$

$$H' = \frac{e}{2mc}(P\cdot A + A\cdot P) + \frac{e^2}{2mc^2}A^2 \qquad (2.4)$$

Here $H_0$ describes the system in the absence of any applied radiation fields. The Hamiltonian H' contains the interaction between the electron and the radiation field. The term $e^2A^2/2mc^2$ can be neglected because we are interested in the linear response of the system to weak field. In general,

$$P\cdot A - A\cdot P = -i\hbar\nabla\cdot A \qquad (2.5)$$

so that $P\cdot A \neq A\cdot P$. However, since we have chosen to work on Coulomb gauge, $\nabla\cdot A = 0$, and hence $P\cdot A = A\cdot P$.
Thus, we have

$$H' = \frac{e}{mc} A \cdot P = \frac{ie\hbar}{mc} A \cdot \nabla \tag{2.6}$$

The vector potential A(r, t) can be represented by a plane wave,

$$A(r, t) = A_0 \exp[i(q \cdot r - \omega t)] \tag{2.7}$$

The transition rate between two eigenfunction of the same Hamiltonian $H_0$ denoted by $\psi_i$ and $\psi_f$ is given Fermi's golden rule,

$$W = \frac{2\pi}{\hbar} |H_{fi}|^2 \delta (E_f - E_i - \hbar\omega) \tag{2.8}$$

$$H_{fi} = \frac{e}{mc} < \psi_f | A \cdot P | \psi_i >$$

$$= \frac{ie\hbar}{mc} \int \psi_f^* \exp(-iq \cdot r) A_0 \cdot \nabla \psi_i dr \tag{2.9}$$

The initial and final states must both be Bloch states.

$$\psi_f \propto \exp(ik_f \cdot r) u_f(k_f \cdot r) \tag{2.10}$$

$$\psi_i \propto \exp(ik_i \cdot r) u_i(k_i \cdot r) \tag{2.11}$$

Putting these into Eq.(2.9) gives

$$H_{fi} = \frac{ie\hbar}{mc} \int \exp[-i(k_f - q) \cdot r] u_f^*(k_f \cdot r) \cdot A_0$$

$$\nabla \exp(ik_i \cdot r) u_i(k_i \cdot r) dr$$

$$= \frac{ie\hbar}{mc} \int \exp[-i(k_f - q - k_i) \cdot r] u_f^*(k_f \cdot r) \cdot A_0$$

$$\exp(ik_i \cdot r) \nabla u_i(k_i \cdot r) dr \tag{2.12}$$

Because of periodicity of lattice, we have

$$\exp[-i(k_f - q - k_i) \cdot R] = 1 \tag{2.13}$$

The $\exp[-i(\mathbf{k}_f - \mathbf{q} - \mathbf{k}_i)\cdot \mathbf{R}]$ is equal to zero unless $\mathbf{k}_f - \mathbf{q} - \mathbf{k}_i = \mathbf{G}$, where G is a reciprocal lattice vector. The momentum of UV photons, q, is negligible compared to the electron momentum.

An electron of initial energy $E_i(\mathbf{k}_i)$ is excited in a final state of energy $E_f(\mathbf{k}_f)$ by photon (The energy $E_f$ and $E_i$ are referenced to the Fermi energy). Energy and momentum conservation of photoexcitation gives,

$$E_f = E_i + \hbar\omega \tag{2.14}$$

$$\mathbf{k}_f = \mathbf{k}_i + \mathbf{G} \tag{2.15}$$

In the reduced zone scheme, we take G= 0, so that $\mathbf{k}_f = \mathbf{k}_i$. Transition of this kind are called direct transition. This direct transition picture is schematically shown in Figure 2-1.

If we arbitrarily define the zero of energy as the Fermi energy, the kinetic energy $E_{kin}$ measured in the vacuum (referenced to the vacuum level) is

$$\begin{aligned} E_{kin} &= E_f - \Phi \\ &= E_i + \hbar\omega - \Phi \end{aligned} \tag{2.16}$$

where $\Phi$ is the work function.

## 2-2 Two-Dimensional Energy Bands[2, 3]

When the photoelectron transverse the crystal surface, there is a momentum transfer to the crystal that complicate the relation between the momentum k measured in the vacuum and the momentum $k_f$, $k_i$ of the Bloch states in the crystal. All that we know about the momentum of the final state inside the solid is the component parallel to the surface. When the excited electrons cross the "perfect" two-dimensional interface between the solid and vacuum, the parallel component of momentum is conserved.

$$k_{i//} = k_{f//} = k_{//} + g_{//} \tag{2.17}$$

where $k_{//}$ is the parallel component of momentum in vacuum, $g_{//}$ is a reciprocal surface lattice vector.

When $k_{//}$ in vacuum is measured, we know the parallel component of momentum inside the solid. The kinetic energy and the momentum of the emitted electron are determined by the angle resolved analyzer;

$$E_{kin} = \frac{\hbar^2}{2m}(k_{//}^2 + k_{\perp}^2) \tag{2.18}$$

The parallel component of momentum is given by a simple projection (assuming $g_{//} = 0$);

$$\begin{aligned} |k_{f//}| &= \frac{1}{\hbar}\sqrt{2mE_{kin}}\,\sin\theta \\ &= \frac{1}{\hbar}\sqrt{2m(E_i + \hbar\omega - \Phi)}\,\sin\theta \end{aligned} \tag{2.19}$$

where $\theta$ is the emission angle in the collection plane measured from the surface normal. Thus, based on a direct transition model, it is possible to determine the relation $E_i(k_{i//})$ experimentally which describes an two-dimensional energy bands.

The classic example of two-dimensional energy band is

graphite. An ordered surface of a adsorbate presents a two-dimensional system interacting with a three-dimensional substrate. The angle-resolved photoelectron spectroscopy of two-dimensional system such as surface is a particularly rich area of study. It is now widely used for determining the electric band structure of solids or studying surface and adsorbate states.

## 2-3 Three-Dimensional Energy Bands[2,3]

The electronic structure of a surface is closely related to the bulk electronic structure. Therefore it is important to measure the bulk band structure in studies of surface properties. Indeed, energy dispersions ($E$ vs k) for occupied valence bands have been obtained for metals: Cu,[30-32] Ni,[33] Al,[34] Fe,[35] Pd,[16] and semiconductors GaAs.[36] However, introducing the third dimension into the energy band picture complicates the data analysis considerably because there is no simple conservation law such as Eq. (2.17) for the third momentum quantum number $k_\perp$. The momentum perpendicular to the surface $k_\perp$ is not conserved since the electron transfers a certain perpendicular momentum to the crystal when escaping through the surface barrier. The perpendicular component $k_\perp$ inside the solid is undetermined experimentally. The value of $k_\perp$ could be anywhere on a rod in k-space with fixed $k_{//}$. This is illustrated in Figure 2-2 (a), where the bulk Brillouin zone is shown at the bottom for a face-centered cubic (fcc) solid and the surface Brillouin zone (SBZ) for the (110) surface is shown at the top.

To determine the complete momentum vector directly from an angle resolved experiment, the momentum transfer perpendicular to the surface must be found. If we know the final state band dispersion $E_f(k_{f\perp})$, by inverting the relation $E_f(k_{f\perp})$, the momentum $k_{f\perp}$ can be obtained from the energy $E$ measured in the vacuum which is equal to $E_f$ in the solid (see Fig. 2-1).

$$k_{i\perp} = k_{f\perp} = k_{f\perp}(E_f) = k_{f\perp}(E) \tag{2.20}$$

In ordre to determine the valence band dispersion, it is necessary to know the final state band dispersion. The final state is often assumed to be a prabolic free-electron-like band in a constant inner potential $U_0$ (Figure 2-3 (a)).

$$E_f(\mathbf{k}_f) = \frac{\hbar^2}{2m}\mathbf{k}_f^2 + E_0$$

$$= \frac{\hbar^2}{2m}(\mathbf{k}_{f//}^2 + \mathbf{k}_{f\perp}^2) + E_0 \qquad (2.21)$$

$$U_0 = \Phi - E_0 \qquad (2.22)$$

where $E_0$ is the bottom energy of the muffin tin ($E_0$ is referenced to the Fermi energy). By inverting Eq. (2.21), we obtain

$$\mathbf{k}_{i\perp} = \mathbf{k}_{f\perp} = \frac{1}{\hbar}\sqrt{2m(E_f - E_0) - \hbar^2\mathbf{k}_{//}^2}$$

$$= \frac{1}{\hbar}\sqrt{2m(E_{kin} + U_0) - \hbar^2\mathbf{k}_{//}^2} \qquad (2.23)$$

$\mathbf{k}_{//}$ is given by Eq. (2.19). Since $\mathbf{k}_{//}$ is known from the emitted electron energy and angle, $\mathbf{k}_\perp$ can be uniquely determined. Eq. (2.22) describes the refraction of the outgoing photoelectron when it crosses the potential step $U_0$ at the surface.

Normal emission from low index surface simplifies the analysis. The component of momentum parallel to the surface is zero. The final state lies in a high-symmetry direction of the bulk. For example, for fcc structure the $\Delta_1$ ($\Sigma_1$ and $\Lambda_1$) band is the only detectable final band for (100) ((110) and (111)) surface in the normal emission collection geometry. In this case the momentum is easy to show from Eq. (2.23) that

$$\mathbf{k}_{i\perp} = \mathbf{k}_{f\perp} = \frac{1}{\hbar}\sqrt{2m(E_{kin} + U_0)}$$

$$= \frac{1}{\hbar}\sqrt{2m(E_i + \hbar\omega - \Phi + U_0)} \qquad (2.24)$$

In normal emission from (100) ((110) and (111)) surface of fcc structure, the $\Gamma\Delta X$ ($\Gamma\Sigma KSX$ and $\Gamma\Lambda L$) line is sampled when $\mathbf{k}_\perp$ is varied by tuning the photon energy.

## 2-4 Umklapp Process

Eqs. (2.14) and (2.15) bring out the fact that the direct interband optical transition involve not only the absorption of photon $\hbar\omega$, but also diffraction against the crystal lattice through a reciprocal lattice vector G (Umklapp process). In this case, the final states in the crystal are described by the empty lattice solution (Figure 2-3):

$$E_f(\mathbf{k}_f) = \frac{\hbar^2}{2m}(\mathbf{k}_f + \mathbf{G})^2 + E_0 \qquad (2.25)$$

Emissions with G perpendicular to the surface are called primary cone emission. Emissions from extra bands with G not perpendicular to the surface (dashed lines in Fig. 2-3) are much weaker in intensity (typically an order of less than primary cone emission),[32, 38, 39] and are called secondary cone emission.[37]

Figure 2-4 shows empty-lattice band along $\Sigma$ line of fcc. The final states can be written as a sum of plane waves

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} C_{\mathbf{G}}^{(n)}(\mathbf{k}) e^{i\mathbf{G}\cdot\mathbf{r}} \qquad (2\text{-}25)$$

k is the reduced-zone crystal momentum and n is the band index. The partial wave

$$e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \qquad (2\text{-}26)$$

is a plane wave propagating in the k+G direction and it's amplitude is given by the coefficient $C_{\mathbf{G}}^{(n)}(\mathbf{k})$. Consider the empty-lattice final band structure shown in Fig. 2-4, if the initial state characterized by k=(k, k, 0) ($0 \leqq k \leqq 1$ on units of $2\pi/a$) is excited into the final band associated with the reciprocal-lattice vector (-2, -2, 0), then the extended zone K is (k-2, k-2, 0), which comes out of the

crystal in the normal direction. But if the excitation is to the final band formed by any of the reciprocal-lattice vectors $(-1,-1,\pm 1)$ then the extended zone K is $(k-1, k-1, \pm 1)$. This wave comes out of crystal with surface reciprocal-lattice vector $g_{//}=(0,\pm 1)$ which is the $\overline{\Gamma}$ point in the second surface Brillouin zone (see Figure 2-5). This excitation will not be seen in normal emission. However, this discussion above has ignored the problem of matching the bulk Bloch states with plane waves on the vacuum. An internal partial wave propagating in the direction of detection is reflected from the surface or as internal wave propagation in the wrong direction is elastically scattered at the surface via an surface umklapp process in the correct direction. In principle, the coupling of a final band in the bulk to a plane wave on the vacuum can be calculated using a standard LEED calculation, since the photoemission final state is related to a time-reversed LEED state.[40]

## 2-5 Band Symmetry and Polarization Selection Rules[41, 42]

Electron wave function in a crystal have extra quantum numbers which are related to the crystal symmetry operations. Those symmetries can be found by using polarization selection rules. Direct transition are described by dipole matrix element $\langle \psi_f | A \cdot P | \psi_i \rangle$ (see Eq. (2-9)). In order to find out whether this matrix element describes a dipole allowed transition, we can apply the rules of group theory. For nonvanishing matrix element, the direct product of the representation of the initial state and the final state contains or is equal to the representation of the dipole operator.

The wave functions with k in a mirror plane containing surface normal have to be either even or odd parity under reflection with respect to the mirror plane. The mirror plane emission should contain even parity final states since the emitted electron is a plane wave with momentum vector lying in the mirror plane. The operator $A \cdot P$ is of even parity if the polarization vector A is parallel to the mirror plane and odd if A is perpendicular to the mirror plane. A non-zero matrix element is therefore obtained with either A perpendicular and $\psi_i$ odd, or A parallel and $\psi_i$ even.

For normal emission the final state is totally symmetric under point group operations about the surface normal.[41] Using the known final state symmetry, dipole allowed initial states for normal emission from low index face of cubic crystals are listed in Table 2-1. Spin-orbit coupling is omitted for simplicity so that the single group notations are appropriate.

# 3 EXPERIMENT

## 3-1 Preface

The experiments were carried out in two separate ultra high vacuum (UHV) chambers. One was a model ADES-400 (VG Scientific Ltd.). Sample preparation and angle-resolved photoemission measurements using He I resonance radiation were performed in this chamber. Measurements using synchrotron radiation were carried out in another chamber with a constant deviation monochrometor[43] at BL11-D, Photon Factory, National Laboratory for High Energy Physics.

## 3-2 Angular Distributions Electron Spectrometer Model 400 (ADES-400)

### 3-2-1 Spectrometer Chamber

This UHV chamber is equipped with a 150° spherical type electron energy analyzer, UV lamp, X-ray source, ion gun, LEED, quadrupole mass spectrometer and manipulator. Detailed positions of all apparatuses are drawn in Figure 3-1 and Figure 3-2. Fig. 3-1 and 3-2 show the upper level and lower level of experimental vessel respectively. The sample is generally prepared in the upper level of vessel. This spectrometer vessel is made of mu-metal to optimize magnetic shielding.

### 3-2-2 Vacuum System

The valve layout for the system is shown in Figure 3-3. The spectrometer vessel is pumped by a titanium subrimation pump and turbomolecular pump (BALZERS TPU2200) with a pump speed of 2200 l/s. The turbomolecular pump is backed by an rotary pump (Edowards E2M40). Pressure measurement is by means of an ionization gauge which is located directly on the chamber.

Backout at a temperature of 150° C was done for about 24 hours. The ion gauges, sublimation pump filaments and any other hot filament devices were outgassed after the backout while the system was still warm. Those procedure permitted UHV condition in the $10^{-11}$ mbar range. Figure 3-4 shows the mass spectrum of residual gas in the spectrometer vessel at the pressure of $1\times 10^{-10}$ torr. The composition of residual gas are mainly hydrogen and small amount of water, carbon monoxide and carbon dioxide.

### 3-2-3 Analyzer

An electron energy analyzer is a 150° spherical type analyzer with a 50mm mean radius. The analyzer can be

operated in either of two mode. The first is the constant analyzer energy (CAE) mode where the pass energy of the electrons transmitted through the analyzer is fixed during a spectrum. The second is the constant retard ratio (CRR) mode where the ratio of kinetic energy to pass energy is constant during a spectrum. In the CAE mode, energy resolution $\Delta E$ is fixed during a spectrum and is determined by the analyzer pass energy setting. Using the Mg K$\alpha$ source (line width is approximately 0.8 eV) the following observation are given for Au 4f.

| Analyzer energy (eV) | FWHM (ev) |
|---|---|
| 20 | 1.03 |
| 50 | 1.38 |
| 100 | 1.94 |

At 20 eV pass energy the largest contribution is from the Mg K$\alpha$ line width. Using He I resonance line, the total experimental resolution was $\Delta E$=0.12 eV at 20 eV pass energy.

The inlet and exit slits width of the analyzer are 1 mm. An angular resolution is 2°. The analyzer is mounted on a rotatable table so that it can be moved in one plane around a specimen (both vertically and horizontally). The electron passed through the analyzer are detected by a channel electron multiplier (channeltron) mounted over the exit slit.

### 3-2-4 UV Lamp

The UV source is a gas discharge lamp in which the discharge is confined by quartz capillary tube. Two stage differential pumping is provided from a roughing pump (Edowards E2M5) via V15 and to the sample preparation turbomolecular pump (BALZERS TPU170) via V16 so that the spectrometer vessel can operate in the $1\times 10^{-10}$ mbar with the lamp on. The gas inlet system comprises automatic pressure controller (APC) and servo driven valve assembly

(GRANVILLE-PHILLIRS Ltd.) and a modified MSS50 sorption pump which can be liquid nitrogen cooled for gas purification purposes.

The gas pressure in the lamp for operating as a He I source via controlled in 2nd stage pumping line at $1\times 10^{-7}$ mbar by APC. The lamp as He I source is operated with an applied voltage of 0.6 kV and a current of 60 mA.

### 3-2-5 X-Ray Source

The X-ray source is operated with the filament near earth potential and the anode at a positive potential of up to 15 kV. The twin anode source has magnesium on one side and aluminum on the other. This gives the facility of two independent X-ray lines at 1253.6 eV and 1486.6 eV respectively.

### 3-2-6 Ion Gun

An ion gun (ANELVA Ltd., 981-9201) is fitted for sputter etching specimens with inert gas ions at energy up to 3 kV. Beam current depends on the accelerating electrode potential and the gas pressure. The gas inlet is controlled by a variable leak valve.

### 3-2-7 LEED

We made a LEED apparatus. Figure 3-5 schematically shows our LEED optics and electrical connections. The optics are the spherically symmetric type consisting of a concave phosphor screen and four mesh grids centered on the specimen position. The usable area of the phosphor screen subtends an angle of 122° at the specimen. The meshes and screen are electrically isolated from the surrounding shields.

The LEED assembly is mounted on a table which provide linear movement of 100 mm so that the optics assembly can be retractable (Figure 3-6).

Technical specification of our LEED is following

| | |
|---|---|
| Subtended Angle | 122° (measured at phosphor screen) |
| Screen Radius | 56 mm |
| Screen Material | SUS 310 |
| Phosphor | P-7 ZnS:Ag Blue |
| Grid Radii | G1:42 mm |
| | G2:45 mm |
| | :48 mm |
| | G3:51 mm |
| Grid Material | Tungsten mesh plated with gold |
| | 10l/mm 30μ |
| | 49% transparency |
| Electron Gun | Lux Electronics Ltd. |
| Filament | 0～4 A |
| Anode Voltage | A1:-250～-300 V |
| | A2:-300～0 V |
| | A3:earth |
| Screen Voltage | 0～5 kV |
| Retard Grid Voltage | 0～300 V |

## 3-2-8 Spectrometer Control and Pulse Counting

The spectrometer control system is drawn in Figure 3-7. The spectrometer control unit (SCU) type 362 provides operating voltage for the analyzer. It supplies positive and negative hemisphere voltages and retard potential. The SCU 362 include providing programming outputs for multiplier supply and external inputs for computer control of the spectrometer. Table 3-1 shows the computer controlled socket connection of SCU 362.

The SCU 362 is controlled by 16-bit computer (NEC, PC9801). We made peripheral interface adapter (PIA) board for interface between CPU and SCU 362. The circuits of PIA board and counter board are drawn in Figure 3-8 and 3-9 respectively. Table 3-2 shows extended slot bus of PC9801.[44] We use the LSI of 8255-A for interface between computer and SCU 362.

◆ Programmable Peripheral Interface (PPI) 8255-A

8255-A is generally called the programmable peripheral interface (PPI).[45,46] Pin configuration and block diagram are drawn in Figure 3-10. PPI has a bi-directional 8-bit data bus ($D_0 \sim D_7$) and reads and/or writes control bus ($A_0$, $A_1$, RD, WR and RESET) for CPU side terminals. Peripheral side terminals are I/O port of $PA_0 \sim PA_7$, $PB_0 \sim PB_7$, $PC_0 \sim PC_3$ and $PC_4 \sim PC_7$. The table 3-3 shows read/write control ward and I/O relation between data bus and peripheral bus.

The PPI can be operated in three modes. Each mode is following.

MODE0 : peripheral bus for I/O port
MODE1 : 8-bit hand shake mode
MODE2 : bi-directional hand shake mode

Each mode can be selected with writing control ward onto command register of PPI. Table 3-4 shows the format for mode selection.

◆ PIA board[47]

The PIA board consists of two 8255-A for 16 bit notation (Fig. 3-8). Each port address are decorded as shown in table 3-5. Port A (lower $PA_0 \sim PA_7$ and upper $PA_0 \sim PA_7$) are used as the output of data.

Figure 3-11 shows timing chart of PIA. $1/16384 \times 1/N$ frequency demultiplication of 307 kHz internal clocking of PC9801 provides gate signal. N is decided from input signal into the synchronous up down binary counter LS193 and it can be selected for N=1, 2, ··· 10 by dip switches. Then the gate open time can be selected from 0.05337 second up to 0.5337 second.

◆ Pulse counting

Pulses from the channeltron are fed via a DC isolating capacitor to the pulse counting circuits. They first encounter pulse sharping and amplifying circuits and then

encounter a discriminator which allows only those pulses whose height is sufficiently large to pass. Those pulses, which are approximately 5 volts in amplitude and of 500 nano-second duration, are fed to the 16-bit binary counter. The data from counter is fed via the port B of 8255-A to computer.

## 3-3 Experiments Using Synchrotron Radiation

Experiments using synchrotron radiation were carried out at Photon Factory (PF). The Photon Factory is a national synchrotron radiation (SR) research facility affiliated with the National Laboratory for High Energy Physics. It consists of a 2.5 GeV electron linear accelerator, 2.5 GeV electron storage ring as a dedicated light source, and beam-lines and experimental stations for exploiting SR. A view of the experimental hall is shown in Figure 3-12.[48]

We used a constant deviation monochomator (CDM)[43] which was attached to one of the beam line, BL-11D. The CDM equipped with three interchangeable concave gratings (600, 1200 and 2400 grooves/mm) of 2 m radius of curvature to cover the photon energy range of 23～160 eV. A synchrotron radiation was polarized in the horizontal plan.

The UHV chamber for ARPES experiment was connected to the CDM. This chamber was equipped with electron energy analyzer, AES, ion gun, LEED, quadrupole mass spectrometer. The experimental vessel was pumped by a titanium subrimation pump, turbomolecular pump (300 l/s) and ion pump with a pump speed of 500 l/s. Pressure measurement was by means of an ionization gauge which was located directly on the chamber. The base pressure in this system was $1\times 10^{-10}$ torr. An electron energy analyzer was a 150° spherical type analyzer with a 50 mm mean radius. The total experimental resolution was 0.2～0.3 eV at 20 eV pass energy. An acceptance angle of analyzer was ± 1 °. The analyzer was mounted on a two axis rotation mechanism. Other equipments of ion gun, AES and LEED were for sample preparation and characterization.

The CDM and analyzer were controlled by a 8-bit computer (NEC, PC8801).

## 3-4 Sample Preparation

### 3-4-1 Sample

Sample was of 99.999 % purity palladium single crystal (Johnson Massay Ltd.). The Pd(110) surface was cut within 0.5°. It's dimension was 8 mm diameter and 2 mm thickness. The crystal surface was mechanically polished with alumina past (Baiokalox) down to 0.05 $\mu$m particle size and then chemically etched by 5 % nitric acid diluted with alcohol. The sample was washed clean with alcohol and distilled water before mounting to the sample holder.

### 3-4-2 Sample Holder

Figure 3-13 shows sample holder. The sample holder consists of tantalum ring (the inside diameter 8 mm, thickness 1.8 mm) and 0.05 mm thickness tantalum foil. Sample was inlaid in the tantalum ring and held with tantalum ribbons as shown in Fig. 3-13. This sample holder was mounted on the rotatable table of manipulator. The manipulater allows linear motion in three directions and axial rotation of the sample. The sample could be rotated about the crystal normal (azimuth $\phi$) and about an axis in the surface plane (polar angle $\theta$). The crystal surface normal was adjusted to the rotation axis within 0.2° using laser.

Sample was electronically isolated by ceramic insulators. A Chromel-Alumel thermocouple was attached to the end of the holder. In order to cool the sample, the holder was connected to the liquid nitrogen reservoir by copper wire bundle. Cooling could be achieved down to about 150 K. Filament (1 % thoriated tungsten wire of 0.3 mm$\phi$) was installed behind the sample for the purpose of sample heating.

### 3-4-3 Sample Cleaning

Sample cleaning was done in the ADES-400 chamber. The Pd(110) sample was initially cleaned by extended cycles of argon ion bombardment and annealing at 600°C to deplete the surface and bulk of impurities. High purity Argon (99.999 %) was induced to the spectrometer vessel via gas inlet variable leak valve. The sample was heated indirectly by bombardment of electrons emitted from a thoriated tungsten wire filament mounted behind. Temperature of the sample was measured by radiation thermometer (CHINO, IR-AH1S). The pressure in the spectrometer vessel rose to $10^{-9}$ mbar range during sample anneal. An argon ion bombardment of 30 minutes and annealing of 10 minutes were done for one cycle of cleaning.

The following conditions were used:

| | |
|---|---|
| Argon Ion Bombardment | |
| Target Current | ~ 3 μA |
| Beam Energy | 1.2 kV |
| Incident to angle | 65 ° |
| Inlet Gas Pressure | ~ $4 \times 10^{-5}$ mbar (argon was induced from gas inlet variable leak valve) |
| Emission Current | 20 mA |
| Annealing | |
| Temperature | 600 °C |
| Emission Current | ~ 4 mA |
| Sample Voltage | 300 V |
| Filament Current | ~ 5 A |

### 3-4-4 Checking the Surface Cleanliness

The cleanliness was monitored by X-ray photoelectron spectroscopy (XPS) in ADES-400. Figure 3-14 shows typical wide-scan XPS performance on palladium related to the

operation of Al K$\alpha$ X-ray source. An intense Pd $3p_{3/2}$ peak at 534 eV overlaps with O 1s peak at 531 eV. The impurities were mainly carbon. Figure 3-15 shows XPS with Al K$\alpha$ in the binding energy range between 400 and 200 eV. Pd $3d_{3/2}$ peak at 342 eV and Pd $3d_{5/2}$ peak at 337 eV are observed with C 1s peak at 287 eV. Repeated cycles of $Ar^+$ bombardment and annealing was very efficient method of depleting carbon from surface and bulk. Figure 3-16 shows XPS after cleaning. This cleaning procedure produce an extremely clean surface as judged by XPS. Low energy electron diffraction (LEED) pattern was observed to have sharp 1×1 spots and a low background intensity[49,50] after cleaning procedure.

ARPES chamber at PF was equipped with Auger electron spectroscopy (AES) apparatus. The surface cleanliness was checked by AES in this chamber. Figure 3-17 shows AES spectrum with 2 kV excitation. Sulphur Auger signal (LMM) at 152 eV was observed. Two or three cycles of $Ar^+$ bombardment and annealing depleted sulphur from the surface region as shown in Figure 3-18. However, AES are not conclusive about the presence of residual carbon due to overlap of the Pd $M_{4,5}N_{2,3}N_{4,5}$ signal at 279 eV with the carbon Auger signal at 271 eV. We used LEED observation and UPS as indicator for the cleanliness of the surface. LEED studies on contaminated Pd(110) surface[49] was reported and a diffuse LEED background with weak extra diffraction structure was expected to the carbon contaminated surface. Sharp 1×1 LEED spots and a low background intensity was obtained for our sample. Figure 3-19 shows the LEED pattern of clean Pd(110). The UPS spectrum with HeI radiation was also used as reference of checking the cleanliness of the surface. The spectrum shows prominent peak at -0.3 eV and weak peaks at -1.2 eV and -2.8 eV. This spectral feature was rather sensitive to surface contamination. The prominent peak at -0.3 eV was reduced slightly in one hour after cleaning at a total background pressure of $1\times10^{-10}$ torr. Heating to only 250°C for 5 min was sufficient to regenerate the earlier spectrum. Therefore, the sample was

cleaned by heating up to 250°C every one hour during measurements.

### 3-4-5 The Oxygen Adsorption on Pd(110) Surface

LEED pattern observed after oxygen adsorption at room-temperature were diffuse and faint.
The Pd(110)c(2× 4)-0 ordered surface can be formed by either an oxygen exposure at high temperature[26-28] or annealing a surface exposed at low temperature.[24,25] We produced the c(2× 4) surface by exposing the clean Pd(110) surface to 3L oxygen (1L=1× $10^{-6}$ torr·sec) at a sample temperature 473 K.

Oxygen was induced 3× $10^{-8}$ mbar to spectrometer vessel via gas inlet variable leak valve. Sample was heated indirectly by thermal radiation from a filament mounted behind the sample. Temperature was monitored by thermocouple. At room-temperature, c(2× 4) LEED pattern was lost within 30 minutes and transformed to (1× 1) LEED pattern. Figure 3-20 shows the AES from oxygen induced Pd(110) surface. Oxygen Auger signal (KLL) at 503 eV was observed. This Auger signal of oxygen was vanished within 30 minutes at room-temperature. The oxygen on the Pd(110) surface may diffuse back to the vacuum at room-temperature. Therefore, sample was cooled to about 200 K after exposed to oxygen in order to maintain the ordered c(2× 4) surface. When sample was cooled to ~ 200 K, the contamination of CO from ambient vacuum was recognized in UPS after 3 hours from sample preparation. Therefore, the sample was cleaned every 3 hours during measurements.

## 3-5 Measurements

### 3-5-1 Angle-Resolved Photoemission Measurements

Schematic illustration of the experimental arrangement is drawn in Figure 3-21. The sample was mounted vertically and the polarization vector of incident light was in the horizontal plane. The sample could be rotated about vertical axis to change an incident angle of the light. The sample also could be rotated around the crystal surface normal, then the measurements were capable in the $(1\bar{1}0)$ or (001) mirror plane. A synchrotron radiation was linearly polarized in the horizontal plane of incidence so that the surface component of the electric field vector of the light was in either the $\langle 1\bar{1}0 \rangle$ or $\langle 001 \rangle$ axis. The orientation of the crystal with respect to the analyzer was first checked with LEED and finally adjusted using symmetry-related angle-resolved photoemission measurements.

### 3-5-2 Work-function measurements

Work-function were measured by the Fermi edge and the cutoff of the secondary electrons in the photoemission energy distribution. For these work-function measurements the sample was biased by several volts to avoid any problems originating from work-function difference between the sample and analyzer.

### 3-5-3 Constant initial energy (CIE) curve measurements

CIE curves are the plotting of the photoemission intensity of one special initial state versus photon energy. The measurements were made by simultaneously sweeping $h\nu$ and retardation voltage of analyzer to keep $h\nu - E_{kin}$ constant. Data were normalized to the relative flux of incident photons.

## 4 Angle-resolved photoemission study of Pd(110) clean surface

### 4-1 Normal emission spectra from Pd(110)

We obtained angle-resolved energy distribution curves (AREDC) for normal emission from Pd(110) surface at room temperature as a function of photon energy $h\nu$. The light source for these measurements was synchrotron radiation of photon energy range of $23 \leqq h\nu \leqq 88$ eV and was linearly polarized in horizontal plane. Figure 4-1 shows example of normal emission AREDC's of the polarization vector of incident light, A, parallel to the (001) mirror plane (the mirror plane which involves <110> and the normal axes), plotted versus binding energy below the Fermi level $E_F$. Figure 4-2 shows normal emission AREDC's of A parallel to the (110) mirror plane (the mirror plane which involves <001> and the normal axes). The incident angle of the light was 25°. The peaks labeled 1-4 and A-D are observed in spectra. The peaks 1-4 show significant dispersion with changing of photon energy as indicated dashed curves. The peaks A-D do not show distinct dispersion with changing of photon energy. Figure 4-3 shows bulk Brillouin zone of a face-centered cubic (fcc) solid. The momentum $k_\perp$ of electron is on a $\Sigma$ axis in k-space in the case of normal emission from (110) surface of fcc crystal.

## 4-2 Experimental energy band dispersion for Pd(110)

Figure 4-4 presents our experimental energy band mapping along $\Gamma$-K-X symmetry line ($\Sigma$ axis) in the bulk Brillouin zone. The experimental point indicated by circles are measurements in A parallel to the (110) mirror plane, and diamonds correspond to the spectrum with A parallel to the (001) mirror plane. The hexagons correspond to measurements using unpolarizied HeI resonance radiation. The open symbols are weak peaks or shoulders and closed symbols are well defined peaks in spectra.

In order to plot the photoemission peaks, we suppose primary cone emission and a free-electron final band in constant inner potential. Figure 4-5(A) shows Christensen's band structure[14] of palladium along $\Sigma$-K-X symmetry line as calculated by the relativistic augmented plane wave (RAPW) method. Dashed curve is a free-electron band shifted by an inner potential. As can be seen from Fig. 4-5(A), the free-electron final band with an adjusted inner potential agrees fairly well with the calculated band, except near the zone edge where a gap is formed. The bottom of the free-electron final band is determined to -2.7 eV as fit to the calculated $\Sigma_1$ conduction band of Christensen. Our experimental work function, which was determined from photothreshold is $\Phi$ =5.13 eV. Thus, inner potential $V_0=E_0-\Phi$ is -7.83 eV.

The solid curves in Fig. 4-4 are Christensen's calculated band dispersions. Data points obtained from peaks 1-4 correspond to transitions from valence band 1-4, respectively. Especially, our experimental band plots for peak 3 agree well with the dispersion of calculated band 3 of Christensen. The behavior of the peaks 1-4 can be understood in termes of the free-electron dispersion for the final states.

## 4-3 Band symmetry

The electronic states in crystal are classified according to their symmetries in single-group representations in a non-relativistic treatment; the spin-orbit interaction in palladium is relatively weak ($\sim$ 0.3 eV),[14] so that hybridization of bands with single-group representations will be small except for the band crossing region. In the <110> direction ($\Sigma$ axis), there are four different single-group representations of $\Sigma_1$, $\Sigma_2$, $\Sigma_3$ and $\Sigma_4$. The dipole selection rules for normal emission can be used to determine the symmetry in single-group representations of initial state band.[41] When A is oriented parallel to the (001) mirror plane, only initial states of symmetry $\Sigma_4$ and $\Sigma_1$ are allowed. If A is oriented parallel to the (110) mirror plane, only states of $\Sigma_3$ and $\Sigma_1$ symmetry are allowed. The state of symmetry $\Sigma_1$ is excited by the component perpendicular to the surface. The initial state of symmetry $\Sigma_2$ is not allowed for normal emission collection.

Our normal emission AREDC's show those polarization dependence as can be seen from Fig. 4-1 and 4-2. The intensity of peak 3 is dominant in $\Sigma_3$ allowed collection geometry (see Fig. 4-2). In $\Sigma_4$ allowed geometry (Fig. 4-1), the intensity of peak 3 reduced but the intensity of peak 4 increases. Therefore we can conclude that peak 3 (peak 4) has $\Sigma_3$ ($\Sigma_4$) symmetry. This symmetry assignments of band 3 and 4 are consistent with non-relativistic APW calculation of Mueller et al.[12] (see Fig. 1-4). Symmetry of band 1 and 2 can be identified from non-relativistic calculation as $\Sigma_1$ symmetry. Actually, peak 1 and 2 can be observed on both A parallel to (001) and (110) mirror plane collection (Figs. 4-1 and 4-2). Figure 4-6 shows the normal emission AREDC's at two angles of incidence of the light: $\theta_I$=55° (both $A_{//}$ and $A_{\perp}$ components, parallel and perpendicular to the surface) and $\theta_I$=25° (predominant $A_{//}$ and small $A_{\perp}$ components). The photon energy of incident light was $h\nu$ =34 eV. The peaks 2, 3, 4 and C are observed at -3.5,

-2.5, -1.3 and -0.3 eV, respectively. For $\theta_I=25^\circ$, peak at -3.5 eV is reduced in intensity as compared with $\theta_I=55^\circ$. The polarization vector perpendicular to the surface, $A_\perp$, can excite only $\Sigma_1$ symmetry initial state in normal emission collection. This indicates that peak 2 has $\Sigma_1$ symmetry; the polarization vector perpendicular to the surface, $A_\perp$, can excite only $\Sigma_1$ symmetry initial state in normal emission collection. Thus, symmetry of bands can be described by approximate non-relativistic representations as given in Fig. 4-4. However, this dose not mean that the relativistic effect is always negligible for the band structure of palladium. Figure 4-7 shows more detailed normal emission AREDC'S measured at (A) $A_{//}$ oriented parallel to the <001> axis ($\Sigma_3$ allowed) and (B) $A_{//}$ oriented parallel to the $\langle 1\bar{1}0\rangle$ axis ($\Sigma_4$ allowed) for $h\nu = 24\sim 29$ eV of $\theta_I = 30^\circ$. Two dashed curves connecting peaks correspond to transition from $\Sigma_3$ and $\Sigma_4$ bands, respectively. The $\Sigma_3$ and $\Sigma_4$ bands cross at photon energy between $h\nu = 25$ and 24 eV (Fig. 4-7(A)). Peak 4 ($\Sigma_4$ band) can be seen as well as peak 3 ($\Sigma_3$ band) in the $\Sigma_3$ allowed collection, especially the intensity of peak 4 is rather intense as compared with peak 3 at the band crossing region (Fig. 4-7(A)). Therefore the hybridization of $\Sigma_3$ and $\Sigma_4$ bands due to spin-orbit interaction is expected at this point; the spin-orbit coupling yields hybridization of electronic states with other single-group representations. This band crossing is prevented in the relativistic band structure.[14] In Fig. 4-1, since the hybridization of $\Sigma_3$ and $\Sigma_4$, the peak 3 which is assigned to $\Sigma_3$ symmetry dose not vanish in $\Sigma_4$ allowed geometry.

## 4-4 Other discussions

Our experimental band plots in terms of free-electron final state deviate from actual band dispersion near zone boundary. The $\Sigma_3$ band crosses the Fermi level at $h\nu = 24$ eV (Fig. 4-7(A)). The Fermi energy crossing of $\Sigma_3$ band can be observed at $h\nu$ 24 eV. The Fermi energy crossing k position of $\Sigma_3$ band is marked by triangle in Fig. 4-4. De Hass van Alphen (dHvA) experiments[17,18] found hole pocket whose center is located X point. The arrow in Fig. 4-4 shows the hole surface's k point given by dHvA data.[18] Our observed Fermi energy crossing k position dose not agree with that determined from dHvA data. This deviation of $k_\perp$ value means that the free-electron final band is not accurate enough to represent final band near X point where the band gap produced.

The information about conduction band critical points can be seen as structures in the AREDC's of secondary electron emission (SEE). In Figure 4-8, the low kinetic energy portion of normal emission AREDC with $h\nu$ =50 eV are plotted versus final energy above $E_F$. These portion of AREDC is due to SEE, and is expected to reflect structure in the one-dimensional density of final states along $\Sigma$. In Fig. 4-8 SEE curve shows two distinct structures at 13.4 eV and 22.3 eV final energy, which are projected out high density critical points. These final states energy correspond to the calculated high density critical points $X_5'$ and $X_1$, their energies are shown by dots in Fig. 4-5(A) and compared to Christensen's calculation.[14]

Very weak structures labeled A and B are seen in Fig. 4-1 and 4-2. They can not be ascribed to primary cone emission. They agree well with the expected behavior of umklapp processes.[37] Figure. 4-5(B) shows the empty-lattice band with corresponding reciprocal-lattice vectors indicated. We assigned these weak features A and B to direct transition from flat bands around $\Gamma_{12}$ and $\Gamma_{25}'$ points into the final state with a $(-1,-1,\pm1)$ or $(1,1,\pm1)$ reciprocal-lattice vector. With one-step model calculation

of Lindroos[51] predicted the secondary cone emission feature at the energy of peak B, which corresponds to the final state band with (1,-1,1) reciprocal-lattice vector. Generally, the intensities of peaks due to secondary cone emission are an order of magnitude less than those due to the primary cones.[33,38,39]

The feature at -0.34 eV labeled C in Fig.4-4 lies on the Christensen's calculated band 5.[14] However, symmetry of the band 5 is $\Sigma_2$, which is not allowed in normal emission. Peak C is excited with the light of $A_{//}$ parallel to the ⟨110⟩ axis (Fig.4-1). Thus, it can be identified as $\Sigma_4$ symmetry. This peak dose not show dispersion when the photon energy is changed. This non-dispersive feature may be attributed to surface related state or the final state effect. Due to final state broadening, the normal emission spectra should lose the photon energy variations. The constant binding energy of the peak C may indicated that it corresponds to a transition from a critical point with high state density into broad final electron state. The satisfactory candidate of the high density critical point at -0.34 eV is $X_2$ point ($\Sigma_4$ band). Detailed information about the corresponding final state can be obtained from constant-initial-energy (CIE) curves which plot the photoemission intensity of one special initial state versus photon energy. Figure 4-9 shows the CIE curve of peak C at -0.34 eV. This spectrum is closely related to the spectral distribution of final states. The spectrum can be fitted by Lorentzian function[30,52] as indicated by dashed curved in Figure 4-9. The broadening energy of final states can be directly extracted as the width of Lorentzian, also shown in Fig.4-9. Lifetime broadening of the excited state contribute to the final states broadening. Another interpretation of the final state broadening is $k_\perp$ broadening due to surface disorder.[53] Francis and Richardson[54] reported possible existence of surface disorder at room-temperature. However, there still remains some problems: transition from other high density critical points to broad final states can not be observed, existence

of surface order-disorder transition of Pd(110) is ambiguous.[55]

Peak C may also be attributed to the transition from $X_2$ level to evanescent final states located near the surface. The energy of this state dose not show $k_\perp$ dependence. Indeed peak C is rather sensitive to the surface contamination. The adsorption of oxygen and hydrogen on the surface caused the drastic reduction in intensity of the peak C.

Above $h\nu \sim 50$ eV, spectral profiles have less variations with photon energy changing. Peak D can not be described using three-step direct transition model. A one-electron theory would fail to explain the experimental photoemission data. Many body interaction in the final state seem to be important above $h\nu \sim 50$ eV.[56]

## 5 Angle-resolved photoemission study of Oxygen adsorbed Pd(110) surface

### 5-1 LEED observation

The LEED patterns for oxygen covered Pd(110) surface formed by the exposure at 473 K are shown in Figure 5-1 together with their schematic representations. Below ~ 0.1 L exposure, in the integral-order positions, the streaks oriented along <001> direction are visible which indicate one-dimensional disorder (Fig. 5-1(a)). The first clearly distinguishable structure of (2× 3)-1D appears after an exposure of ~ 0.1 L (Fig. 5-1(b)). It is characterized by relatively sharp 1/3-order spots between the integral-order spots along the <001> direction, while on the half-order positions streaks are visible. Upon increasing the exposure, the 1/3-order spots continuously move together and coalesce to streaks and simultaneously the streaks in the half-order positions are contracted as shown in Fig. 5-1(c). Finally a c(2× 4) superstructure is formed after ~ 0.4 L exposure (Fig. 5-1(d)). Our observed LEED patterns agree well with those observed by Jo et al.. However, Ertl and Rau[23] observed five LEED patterns which were identified as the (1× 3), (1× 2), c(2× 4), c(2× 6) and "complex" patterns. We can not observed the c(2× 6) and "complex" patterns.

## 5-2 Work function change

Work function were measured by the photothreshold position referred to the Fermi level. Figure 5-2 shows the photothreshold of the secondary electrons in the AREDC as the clean Pd(110) surface is exposed to an increasing amount of oxygen. The photothreshold shifts as increasing oxygen exposure. The energy position of photothreshold was determined as a midpoint of the ascending slope. Figure 5-3 shows the plots of the work function as a function of oxygen exposure; it is given by subtructing the photothreshold energy from $h\nu$ (21.22 eV) . The work function increases monotonically up to ~ 0.3 L exposure and saturates. This work function behavior agrees well with that reported by Jo et al..[25]

The change of the work function of a surface upon adsorption can be ascribed to a electric dipole layer resulting from charge transfer between substrate and adsorbate atoms.[8,53] The work function change, $\Delta\phi$, can be obtained from estimate of the amount of charge transfer induced by the adsorption:

$$\Delta\phi = \frac{e\sigma d}{\varepsilon_0} \qquad (5\text{-}1)$$

where $e$ is the electronic charge, $\sigma$ the surface charge density and $d$ the effective dipole length perpendicular to the surface. The $d$ is related to the properties of surface chemical bond and adsorbate geometry in complicated manner. The $\sigma$ is related to the adsorption coverage.

The work function increase by oxygen exposure can be interpreted as the electronegative oxygen adsorption i.e. negative charge surface layer. The monotonic increase of work function suggests that the oxygen adatom sits on the same binding site on Pd(110) surface irrespective of different surface superstructure. The surface dipole momentum essentially depends on oxygen adatom site. Then, the monotonically work function change with oxygen exposure

corresponds to the increase of adsorption coverage i.e. dipole density.

## 5-3 Coverage dependent normal emission

Figure 5-4 shows the variations on the normal emission AREDC's of Pd(110) surface measured with HeI radiation as a function of oxygen exposure. The binding energy is referred to the Fermi energy $E_F$ of the clean Pd(110) substrate. The normal emission spectrum from clean surface shows three peaks at -0.3, -1.4 and -2.8 eV. As discussed in Ch.4, the -0.3 eV peak is ascribed to emission from the Pd-4d like $\Sigma_4$ bulk band. The -1.4 and -2.8 eV feature is due to secondary cone emission. By small amount of oxygen exposure of 0.15 L, the -0.3 eV peak is weakened and the -1.4 and -2.8 eV features are taken the place of the -1.8 and -2.4 eV features. A new peak is also seen at about -4.8 eV. From detailed inspection of the spectra, this perk is divided in two features at -4.5 and -4.9 eV. These peaks at are attributed to emission from the O-2p-derived levels which are characteristic of dissociatively chemisorbed oxygen on Pd(110). The O-2p-derived peak grows in intensity with increasing exposure and nearly saturated by 0.5 L exposure. However, the binding energy of O-2p-derived levels does not depend on oxygen exposure. It is understood that the O-2p-derived level is attributed to a localized oxygen chemisorption bond and the chemisorbed oxygens are essentially in the same site on the Pd(110) sruface irrespective of the surface superstructures. This is consistent with the discussion of work function change.

After 0.5 L exposure, the -1.8 and -2.4 eV peaks appeared in spectrum for 0.15 L exposure are shifted to -1.5 and -2.5 eV, respectively. This binding energy change is associated with the surface superstructure.

## 5-4 Angle-resolved photoemission from Pd(110)c(2× 4)-O

We measured the sequence of AREDC's at various emission angles for Pd(110)c(2× 4)-O surface in the two symmetry directions of the surface Brillouin zone (SBZ). The SBZ of Pd(110)c(2× 4)-O is shown in Figure 5-5. Figure 5-6 shows example of AREDC's measured using HeI radiation as a function of the polar emission angle, $\theta_e$, along the $\langle 1\bar{1}0 \rangle$ azimuth ($\bar{\Gamma}\bar{H}'\bar{N}'$). Figure 5-7 shows the similar AREDC's along the $\langle 001 \rangle$ azimuth ($\bar{\Gamma}\bar{N}'$). The solid curved in Fig. 5-6 and 5-7 indicate the corresponding AREDC's of Pd(110) clean surface. The shaded area in those figures indicate the new features appeared in c(2× 4)-O spectra.

If the properties of the adsorbate induced features are discussed in terms of a metal-adsorbate surface molecule, the oxygen induced states are to be expressed as molecular orbitals formed with O-2p orbitals as well as Pd-4d, 5s orbitals. For the clean surface, the Pd-4d state density at the energy near -5 eV is small, so that the O-2p-derived state have essentially p character. Thus, the O-2p derived states are classified in $p_x$, $p_y$ and $p_z$ states (see the coordinate system of Fig. 5-5). The $p_x$, $p_y$ and $p_z$ states can be identified using polarization selection rule. The polarization vector perpendicular to the surface, $A_\perp$, can excite only $p_z$ initial state. When A is oriented parallel to the $\langle 1\bar{1}0 \rangle$ azimuth ($\langle 001 \rangle$ azimuth), only initial state of $p_x$ ($p_y$) is allowed. The O-2p-derived states show those polarization dependence. Figure 5-8 shows the normal emission spectra on different polarized light. The photon energy is $h\nu$ =26 eV. The spectra are taken at several arrangements; (A) $\theta_I$=65° (both $A_{//}$ and $A_\perp$ components) and $A_{//}$ oriented along $\langle 1\bar{1}0 \rangle$, (B) $\theta_I$=30° (predominant $A_{//}$ and $A_\perp$) and $A_{//}$ along $\langle 1\bar{1}0 \rangle$ and (C) $\theta_I$=30° and $A_{//}$ along $\langle 001 \rangle$. For comparison, a normal emission spectrum for the clean Pd(110) taken at $\theta_I$=30° and $A_{//}$ along $\langle 1\bar{1}0 \rangle$ is also shown in the figure. We can confirme that the O-2p-derived peak consists of two features at -4.9 and -4.5 eV. The peak at -4.9 eV is predominant in $\theta_I$=65° spectrum, while in

$\theta_i$=30° (B), its intensity is reduced and the peak at -4.5 eV grows. The -4.5 eV peak is observed for both $A_{//}$ oriented along $\langle 1\bar{1}0 \rangle$ and $\langle 001 \rangle$ arrangements. Therefore, it can be concluded that the $p_z$ level is at ~ -4.9 eV and the $p_x$, $p_y$ levels are at ~-4.5 eV at $\bar{\Gamma}$. The $p_z$ level lies below the $p_x$, $p_y$ states at $\bar{\Gamma}$, which indicates that the O-Pd bond is primarily through the O-$p_z$ orbital.

In the $\langle 001 \rangle$ direction ($\bar{\Gamma}\bar{N}'$), the O-2p-derived peak is considerably broad; it exhibits a width of about 1 eV at $\bar{N}'$ ($k_{//}$=0.4Å$^{-1}$). This peak can be divided in two features using polarized light. Figure 5-9 shows the off-normal emission AREDC's at $\bar{N}'$ of SBZ measured at (A) $\theta_i$=65° and (B) $\theta_i$=30°. The photon energy is $h\nu$=29 eV and $A_{//}$ is along $\langle 001 \rangle$ direction. The O-2p-derived peak at -4.9 eV is observed for $\theta_i$=65°, while the -4.9 eV peak is reduced in intensity and the -4.5 eV peak is observed for $\theta_i$=30°. Therefore, the $p_z$ level is at -4.9 eV at $\bar{N}'$ of SBZ. Figure 5-10 also shows the off-normal emission AREDC's at $\bar{N}'$ measured in two sets of geometries; (A) the light is p polarized in the collection plane (illustrated in Figure 5-11 (A)) and (B) the light is p polarized in the plane perpendicular to the collection plane (illustrated in Figure 5-11 (B)). The photon energy is $h\nu$=25 eV and $\theta_i$=30°. In both geometries the detector is in a mirror plane formed by the surface normal and $\bar{\Gamma}\bar{N}'$ direction, so the final state must have even symmetry with respect to reflection about this mirror plane. Thus, only initial states that can be observed in Fig. 5-10 (A) are even with respect to reflection abort the $\bar{\Gamma}\bar{N}'$ mirror plane i.e. the $p_y$ and $p_z$ states. On the other hand, in Fig. 5-10 (B), odd initial states as well as even states can be observed i.e. the $p_x$ and $p_z$ states. However, such polarization dependence of -4.5 eV peak dose not distinctly observed. So the -4.5 eV feature has $p_x$ as well as $p_y$ character. The other oxygen induced peaks observed between -3~-1 eV do not clearly show the polarization dependence.

Figure 5-12 present our experimental energy versus $k_{//}$ dispersion of oxygen induced state along the symmetry lines

of SBZ. The $k_{//}$ can be obtained directly from the measured kinetic energy and its direction using Eq. (2.19). The experimental points are presented by dots. In the $\langle 1\bar{1}0 \rangle$ direction ($\bar{\Gamma}\bar{H}'\bar{N}'$), the O-2p derived state exhibits considerable dispersion; the lower band (-4.9 eV at $\bar{\Gamma}$), which is ascribed to $p_z$ state, disperse to higher binding energy (downward) by $\sim$0.9 eV with increase of $k_{//}$ up to 0.57 $Å^{-1}$ (i.e. 8/9k($\bar{H}'$)) and then disperse weakly downward by $\sim$0.1 eV from $k_{//}=0.57Å^{-1}$ to $k_{//}=1.14Å^{-1}$ (i.e. 16/8k($\bar{H}'$)). The dispersion of upper band (-4.5 eV at $\bar{\Gamma}$) are ambiguous because this peak is weakened in intensity with increasing $k_{//}$ and then disappeared. The -2.2 eV state at $\bar{H}'$ has a symmetric dispersion in the $\bar{\Gamma}\bar{H}'\bar{N}'$ direction as compared to that of the O-2$p_z$ band. This band can be assigned as the antibonding partner of the O-2$p_z$ band.

In $\langle 001 \rangle$ direction ($\bar{\Gamma}\bar{N}'$), the O-2p-derived levels do not exhibit definite dispersion. The upper band (-4.5 eV at $\bar{\Gamma}$) shows very small dispersion. This band is related to the O-2$p_x$ and/or $p_y$ state as discussed above, while it can not be clearly distinguished whether it is $p_x$ or $p_y$ bands. The dispersion of the $p_z$ level in $\langle 001 \rangle$ direction was not observed. The -2.5 eV level disperse upward by $\sim$0.3 eV with increase $k_{//}$ up to 0.4$Å^{-1}$ (i.e. $\bar{N}'$)

The solid line in Fig. 5-2 representa the possible dispersion curve of $p_z$ band which connect experinental points. This dispersion curve does not show an expected periodicity of c(2$\times$4) surface lattice. The wave functions at 16/9k(H$'$), i.e. at $\bar{N}'$ in the second zone must be same as at $\bar{N}'$ in the first zone, while our observed $p_z$ level at $k_{//}$=16/9k($\bar{H}'$) does not agree with that at N$'$. We surveyed the -6 eV state at $\bar{N}'$ in the first zone as well as -5 eV state at $\bar{N}'$ in the second zone under all possible geometries using polarized light of $h\nu$ =23$\sim$35 eV and unpolarzed HeI resonant radiation. However, we could not observe such states.

## 5-5 Isolated oxygen monolayer model

In order to achieve a qualitative understanding of the electronic properties of oxygen adsorbed Pd(110) surface, we discuss band dispersions of adsorbate levels for several structural models. The discrete electronic energy levels of an isolated adsorbate become energy bands for an ordered surface as a result of the direct overlap of the adsorbate wave functions and/or the indirect interaction through the substrate. Some of previous studies[9,10,58,59] of chemisorption were made with the tight binding calculations because of its mathematical simplicity and because it was believed to be a useful approximation for transition metal d-bands. For oxygen overlayer on Fe(110)[9] and Ni(110)[10] surface, the essential features of the measured dispersion are reproduced well by the dispersion predicted in a qualitative way for isolated oxygen monolayer. Based on a simple tight binding model argument for an isolated monolayer, dispersion effects in adsorbate layers depend on orbital overlap and thus on inter-adsorbate spacing, i.e., the bandwidth depends exponentially on the inter-adsorbate distance. Figure 5-13 shows the bandwidth of the O-2p-derived state versus O-O nearest neighbor distance for ordered oxygen layers on various substrates.[10] The line corresponds to an exponential decay constant of ~0.6 Å.

The surface structure of the Pd(110)c(2×4)-O has not yet been known. The most simple case is c(2×4) oxygen overlayer with a coverage (Θ) of 0.25, i.e., only one oxygen atom exists in a unit cell. In this case, the O-O nearest neighbor distance is 5.5 Å and this spacing exceed the generally accepted covalent diameter (~1.5 Å) or Van der Waals diameter (~2.8 Å) of oxygen atom. As can be seen from Fig. 5-13, within the tight binding approximation for isolated monolayer picture, the dispersion can not be expected. For Ni(110)c(2×4)-O, the O-p states do not exhibit dispersion. However, our experimental result of Pd(110)c(2×4)-O exhibits considerable band dispersion of ~1.0 eV for $p_z$ band.

We discuss more detailed about a two-dimensional isolated c(2× 4) oxygen monolayer on the basis of a simple tight binding picture. The matrix elements of the Hamiltonian H can be written as

$$H_{ij}(k) = N\sum_{n} \exp(ik\cdot t_n)\cdot A_{ij}(t_n) \qquad (5.2)$$

where

$$A_{ij}(t_n) = \langle \psi_i(r-t_n)|H|\psi_j(r)\rangle \qquad (5.3)$$

using atomic orbital wave functions $\psi$ (r) of oxygen as basis function.

Some investigators reported[26-28] that the oxygen coverage for Pd(110)c(2× 4)-O surface is 0.5, however we consider at first the most simple case of $\Theta$ =0.25. Figure 5-14(a) shows the real and reciprocal space unit cells being considered. Each oxygen atom is surrounded by six neighboring oxygen atoms: two nearest neighbors (5.5Å distance) and four second neighbors (8.25 Å distance). The inclusion of only nearest neighbor interactions seems to be insufficient in this case and therefore the second neighbor interaction are also considered. The electronic states are given as

$$E = E_p + 2W_1\cos\sqrt{2}ak_x + 4W_2\cos\frac{\sqrt{2}}{2}ak_x\cos 2ak_y \qquad (5.4)$$

Here $E_p$ is the orbital energy of the oxygen 2p, $W_1$ and $W_2$ are the O-O interaction integral between the nearest and second neighbor atoms, respectively. We consider the $\pi$ -type bond for $p_z$ orbitals, the $p_z$-$p_z$ interaction integral W(pp$\pi$ ) is negative. Figure 5-14(b) illustrates the schematic dispersion curve of $p_z$ band. The $p_z$ band disperses upward with $k_{//}$ increasing from zero at $\overline{\Gamma}$ to $\pi/\sqrt{2}a$ at 8/9$\overline{H}'$ and then downward to $\sqrt{2}\pi/a$ at 16/8H′ (i.e. $\overline{N}'$ point in the second zone. We can easily illustrate the qualitative features of the dispersion by plotting schematically the real parts of the tight binding wave functions in real space for values of $k_{//}$

corresponding to high symmetry points in reciprocal space. Figure 5-15 shows the phases of $p_z$, $p_x$ and $p_y$ states at three different values of $k_{//}$. The sites with zero phase are represented by small dots. At $\overline{\Gamma}$ ($k_{//}=0$), all the wave functions at the neighboring lattice sites are in phase. Therefore, the $p_z$ state has a complete bonding configuration. At $\overline{N}'$, the $p_z$ state is antibonding because each atom is surrounded by four atoms of opposite phase (antibonding) and two bonding atoms. At $8/9\overline{H}'$, the $p_z$ state is strongly antibonding. Therefore, the $p_z$ state should disperse upward from $\overline{\Gamma}$ to $\overline{N}'$ as well as to $\overline{H}'$. Therefore, our experimental band dispersion can not be explained qualitatively and also quantitatively by isolated oxygen overlayer model of $\Theta=0.25$.

In the next place, we make similar argument of tight binding approximation for two-dimensional isolated oxygen monolayer of $\Theta=0.5$ as $\Theta=0.25$ model above mentioned. When we assume that the oxygen atoms are located at high symmetry site of unreconstructed clean Pd(110) surface, the possible oxygen atom configuration is confined as illustrated in Figure 5-16. In this case, the O-O nearest neighbor distance is 3.89 Å, and the expected O-2p bandwidth by simple tight binding picture is about 0.5 eV (see Fig. 5-13). Figure 5-17(a) shows the real and reciprocal unit cells being considered. Each oxygen atom surrounded by three neighboring oxygen atoms: one nearest neighbor (3.89Å distance) and two second neighbors (6.74Å distance). The electronic states of O-2p are given as

$$E=E_p \pm |W_1 \cos ak_y + 2W_2 \cos \frac{\sqrt{2}}{2} ak_x \cos ak_y| \qquad (5.5)$$

Figure 5-17(b) illustrates the schematic dispersion curve of $p_z$ band. The $p_z$ band disperses upward from $\Gamma$ to the zone boundary. The experimental results of downward dispersion of $p_z$ band for Pd(110)c(2×4)-O is inconsistent with the dispersion predicted for isolated oxygen monolayer. Therefore, it can be concluded that indirect O-O

interaction via substrate is important for the band formation for Pd(110)c(2× 4)-O where the oxygen strongly interacts with the palladium. In order to understand experimental band dispersion, we should consider the system including the Pd 4d electrons.

## 5-5 Tight binding calculations involving the d electrons of substrate

We calculated the two-dimensional band dispersion for several surface structure model of Pd(110)c(2× 4)-O system by a simple tight binding approach[60] including the Pd 4d electrons. For adsorption of oxygen on the surface, the Pd layers are assumed to be unreconstructed. The adsorbate species on the unreconstructed metal surfaces usually choose the high-symmetry sites preserving the symmetry of substrate, i.e., 2-fold long-bridge site, 4-fold hollow site, 2-fold short-bridge site, etc., cf. Figure 5-18. The O adsorption sites considered in the present work are the long-bridge and hollow sites. In calculation, we assume the oxygen coverage of 0.5 ML, since several experiments[26,27] of Pd(110)c(2× 4)-O surface have suggested that $\Theta$ =0.5 ML.

Recent EELS measurements[25] claimed that the oxygen atoms are located at the long-bridge adsorption site. Therefore, we try to calculate the band dispersion for the long-bridge adsorption site model. Figure 5-19 shows the top view of the geometrical arrangement of long-bridge site model. For simplicity, we assume that the oxygen atoms are placed in the plane of the first Pd layer and neglect the second and deeper substrate layers. With the choice of axis indicated in Fig 5-19, the primitive lattice vectors are

$$t_1 = a\left(\frac{\sqrt{2}}{2},\ 2\right)$$

$$t_2 = a\left(-\frac{\sqrt{2}}{2},\ 2\right)$$

In this model, there are two O atoms and four Pd atoms per unit cell. The O atoms are in the positions (0, a/2, 0), (0, 7a/2, 0) and Pd atoms in the positions (0, 0, 0), (0, a, 0), (0, 2a, 0), (0, 3a, 0). The Pd-O bond length is 1.95Å. We considered Bloch functions formed with O 2p and Pd 4d atomic orbitals. Interaction between nearest neighbor Pd and O atoms is predominant, however the inclusion of

only nearest neighbor interactions is insufficient in this case and the second nearest neighbor interactions of Pd-Pd along <001> direction also have to be considered. Numerical values of the tight binding parameters we used are given in Table 5-1. These tow center integrals have been calculated for Pd-Pd distance of 2.751Å and Pd-O of 2.04Å by Boudeville et.al..[61]

Figure 5-20 shows the plots of our calculated energy levels of the long-bridge site model along symmetry directions. For comparison, we also calculated the two-dimensional band in the absence of oxygen adsorption, where only Pd-Pd interaction contained. This is illustrated in Figure 5-20. The Pd-O bonding band extends approximately from -5.5 eV to -8.5 eV and the Pd 4d bands from 1 to -4.5 eV. Since the $\overline{\Gamma}$ and $\overline{N}'$ points have $C_{2v}$ symmetry, the electronic states at $\overline{\Gamma}$ and $\overline{N}'$ are classified according to their representations in $C_{2v}$ symmetry, $A_1$, $A_2$, $B_1$ and $B_2$. Those representations also shown in Fig.20. The polarization vector perpendicular to the surface can excite only an $A_1$ symmetry initial state. The solid curves in Fig.5-20 correspond to the p-derived band with $A_1$ symmetry. The lower $A_1$ symmetry band (-8.3 eV at $\overline{\Gamma}$ point) disperses weakly upward with increasing k. The upper $A_1$ symmetry band (-6.0 eV at $\overline{\Gamma}$ point) disperses downward. However, these p-derived band exhibit a relatively small dispersion of ~ 0.2 eV in the $\overline{\Gamma}\,\overline{H}'\,\overline{N}'$ direction. When the O atom is placed in long bridge site, O and Pd atoms mainly interact along the <001> ($\overline{\Gamma}\,\overline{N}'$) direction and the interaction along the $\langle 1\bar{1}0\rangle$ direction seems to be small. This is inconsistent with our experimental result; the $p_z$ band has about 1 eV dispersion. Therefore, the long-bridge adsorption site model could not reproduce our experimental results of ARUPS.

The adatom tend to choose its adsorption site to maximize the number of nearest neighbors and/or to smoothen the surface on an atomic scale. In the light of this maximization principle, the oxygen atoms appear to favor the 4-fold hollow-adsorption site. Figure 5-22 shows the

top view of the adsorption geometry for the hollow adsorption site model. Each oxygen atom is surrounded by four neighboring Pd atoms. When the oxygen atoms are placed in the same plane of the first Pd layer, the bond length between Pd and O is 2.38Å. Figure 5-23 shows the tight binding two dimensional band dispersions for hollow-adsorption site model. In calculation, we considered Bloch functions formed with O-2p and Pd-4d atomic orbitals and the interactions between nearest neighbor Pd and O atoms as well as the second nearest neighbor interactions of Pd-Pd along <001> direction.

At $\overline{\Gamma}$ point, the O-$2p_z$-derived levels exist at -7.0 and -9.3 eV. The solid curves in Fig. 5-23 connect the $p_z$ levels as a function of k in the two symmetry direction of Brillouin zone. In the $\overline{\Gamma}\overline{H}'\overline{N}'$ direction, the lower $p_z$ band (-9.3 eV at $\overline{\Gamma}$ point) disperses to upward by ~ 2 eV with increasing $k_x$ up to 1.14Å$^{-1}$ (i.e. N′). This band has $B_2$ symmetry at $\overline{\Gamma}$ as well as $\overline{N}'$ points. The $B_2$ state is odd with respect to reflection about the $\overline{\Gamma}\overline{H}'\overline{N}'$ mirror plane (the mirror plane formed by the surface normal and $\overline{\Gamma}\overline{H}'\overline{N}'$ direction). The upper $p_z$ band (-7.0 eV at $\overline{\Gamma}$ point) disperses to downward by ~ 2 eV with increasing $k_x$ up to 1.14Å$^{-1}$ (i.e. N′). This band has $A_1$ symmetry, which is even with respect to the collection plane. When the light is p polarized in the collection plane, only even initial states can be observed. Therefore, the $p_z$ band with $B_2$ symmetry can not be observed in the $\overline{\Gamma}\overline{H}'\overline{N}'$ direction with p polarized light. The experimental result of downward dispersion of $p_z$ state in the $\overline{\Gamma}\overline{H}'\overline{N}'$ direction can be explained qualitatively by the behavior of the p-derived band with $A_1$ symmetry, whereas the bandwidth of about 2 eV of the $A_1$ band is somewhat large. The bandwidth depends on the two center integrals of $pd\sigma$ and $pd\pi$ and thus on O-Pd distance. From a viewpoint of simple tight binding approximation, the hollow adsorption site is probable for the surface structure model of Pd(110)c(2×4)-O.

## 6 Conclusion

### 6-1 Pd(110) clean surface

Angle-resolved photoemission studies have been made on the Pd(110) clean surface. We measured the normal emission ARUPS utilizing polarized synchrotron radiation at the extended photon energy range of 21～88 eV. Measured normal emission ARUPS have been analyzed by one-electron direct transition model. The energy band dispersion along the $\Gamma$-K-X symmetry line in the Brillouin zone assuming the free-electron final band with adjusted constant inner potential. We assigned the band symmetry using the dipole selection rule. Fairly good agreement between experiment and theory has been obtained for the $\Sigma_1$, $\Sigma_3$ and $\Sigma_4$ bands.

### 6-2 Pd(110)c(2×4)-O

ARUPS measurements have been made on Pd(110)c(2×4)-O surface in the two symmetry direction of SBZ. The O-$2p_z$-derived state of c(2×4)-O structure show considerable dispersion of about 1 eV with $k_{//}$ in the $\overline{\Gamma}\,\overline{H}'\,\overline{N}'$ symmetry line. The antibonding partner of the O-$2p_z$ band was also observed, which has a symmetric dispersion as compared to that of the O-$2p_z$ band. The experimental results were compared with the dispersion predicted in a qualitative way for two-dimensional isolated c(2×4)-O oxygen monolayer in a simple tight binding model. Our experimental band dispersion was inconsistent with the dispersion predicted for isolated oxygen monolayer model. The indirect O-O interaction via substrate is important for the Pd(110)c(2×4)-O structure where the oxygen strongly interacts with the palladium.

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Figure captions

Fig. 1-1: Energy balance in the photoemission process.

Fig. 1-2: Energtics of photoemission from the surface of a metallic solid, showing schematically the electronic potential, core levels, an adsorbate level, valence band (cross hatched). On the right is typical photoelectron energy distribution curve.

Fig. 1-3: Experimental values of electron inelastic mean free path lengths as a function of electron energy from UPS, XPS, and AES studies. Schematic comparison of the synchrotron radiation (SR) continuum with VUV and X-ray line sources: NeI (16.65, 16.85 eV), HeI (21.2 eV), NeII (26.8 eV), HeII (40.8 eV), Mg Kα (1253.6 eV), and Al Kα (1496.6 eV). (Ref. 8)

Fig. 1-4: Spectral curve for synchrotron radiation. The photon flux is normalized to 1 mA of circulating electron current at 2.5 GeV in the accelerator and measured in 1 mradian of horizontal divergence.

Fig. 1-5: (a) fcc (111), (b) fcc (001), (c) fcc (110) faces, each in top view (top diagrams) and side view (bottom diagrams)

Fig. 1-6: Electronic band structure of palladium. Open circles are non-relativistic APW energy levels. (Mueller et al. Ref. 12).

Fig. 1-7: Relativistic bands of palladium. (Mueller et al. Ref. 12).

Fig. 1-8: Band structure of palladium as calculated by the RAPW method. (Christensen, Ref. 14)

Fig. 2-1: Schematic representation of the direct transition model. (Ref. 7)

Fig. 2-2: Surface Brillouin zone for the (110) surface of fcc crystal compared to the bulk Brillouin zone. (a) Projection of bulk Brillouin zone onto SBZ. (b) and (c) Cuts through the bulk Brillouin zone in two directions of the SBZ. (ref. 2)

Fig. 2-3: Schematic representation of various approximations for final state bands. Left hand side shows the

band dispersion, right hand side shows the corresponding crystal potential. (Ref. 7)
Fig. 2-4: Empty-lattice band structure of fcc crystal along Γ K X line.
Fig. 2-5: Surface Brillouin zone (SBZ) for the (110) surface of fcc crystal. The Γ (1) represents Γ point for the first zone and Γ (2) for the second zone.
Fig. 3-1: Upper level of experimental vessel (VG Ltd. ADES-400).
Fig. 3-2: Lower level of experimental vessel.
Fig. 3-3: The valve layout for the experimental system
Fig. 3-4: The mass spectrum of residual gas in the spectrometer vessel at the pressure of $1\times 10^{-10}$ torr.
Fig. 3-5: LEED optics and electrical connections
Fig. 3-6: LEED mounting assembly and electrical connections.
Fig. 3-7: Block diagram of spectrometer control system
Fig. 3-8: Circuit diagram of counter board
Fig. 3-9: Circuit diagram of peripheral interface adapter (PIA).
Fig. 3-10: Pin configuration and block diagram of programmable peripheral interface (PPI) 8255-A.
Fig. 3-11: Timing chart.
Fig. 3-12: A view of the experimental hall at PF.
Fig. 3-13: Sample holder. Sample holder is mounted on the rotatable table of manipulator. The manipulator allows linear motion in three direction and axial rotation about crystal normal and about an axis in the sample surface plane.
Fig. 3-14: XPS spectrum of palladium before cleaning.
Fig. 3-15: XPS spectrum of palladium before cleaning in the binding energy range between 400 and 200 eV. The C 1s peak at 278 eV is observed.
Fig. 3-16: XPS spectrum after cleaning. The C 1s peak vanished in the spectrum.
Fig. 3-17: AES spectrum of palladium before cleaning. S(LMM) signal at 152 eV is observed. AES is not conclusive about the presence of carbon due to

overlap of Pd(MNN) signal at 297 eV with C(KLL) signal at 271 eV.

Fig. 3-18: AES spectrum after cleaning.

Fig. 3-19: The LEED pattern of the clean Pd(110) surface.

Fig. 3-20: AES spectrum from oxygen induced Pd(110) surface.

Fig. 3-21: Experimental geometry of the angle resolved photoemission measurements.

Fig. 4-1: Normal emission spectra from Pd(110) as a function of photon energy $h\nu$. The incident angle of the light, $\theta_I$, is 25° with polarization vector A in the (110) mirror plane. Only initial states of symmetry $\Sigma_1$ and $\Sigma_4$ are allowed. Dashed curved connect peaks.

Fig. 4-2: Normal emission spectra from Pd(110) as a function of photon energy $h\nu$. The incident angle of the light, $\theta_I$, is 25° with polarization vector A in the (001) mirror plane. Only initial states of symmetry $\Sigma_1$ and $\Sigma_3$ are allowed. Dashed curved connect peaks.

Fig. 4-3: Bulk Brillouin zone for fcc crystal

Fig. 4-4: Experimental valence band dispersions (E vs k) for Pd along $\Gamma$ K X symmetry line. Circles correspond to polarization vector A in the (110) mirror plane, diamonds to A in the (001) mirror plane, hexagons to measurement using HeI resonance radiation, The open symbols are weak peaks or shoulder and solid symbols are well-defined peaks in spectra. Solid curves correspond to Christensen's band calculation.

Fig. 4-5: (A) The Christensen's band structure of Pd along $\Gamma$ K X symmetry line as calculated by the RAPW method. Dashed curve is a free-electron bend shifted by an inner potential. Dots are conduction band points determined from secondary electron energy distribution curve. (B) Empty lattice band along $\Gamma$ K X symmetry line of fcc crystal.

Fig. 4-6: Normal emission spectra from Pd(110) clean surface at two angle of incidence of the light ($\theta_I$=25°

and 55°). The photon energy is $h\nu$ =34 eV.

Fig. 4-7: Normal emission spectra from Pd(110) clean surface as a function of photon energy $h\nu$. The incident angle of the light is 30°. (A) $A_{//}$ oriented parallel to the ⟨001⟩ axis. (B) $A_{//}$ oriented parallel to the ⟨110⟩ axis.

Fig. 4-8: Low energy portion of normal emission AREDC from Pd(110) obtained at $h\nu$ =50 eV.

Fig. 4-9: Constant initial energy (CIE) curve for -0.34 eV peak. The spectrum can be fitted by Lorentzian function as indicated by the dashed curves.

Fig. 5-1: The LEED patterns for oxygen covered Pd(110) surface formed by the exposure at 473 K together with their schematic representations (● ; integral order spots, ○ ; fractional order spots). (a) ~0.1 L exposure; (b) (2×3)-1D; (c) diffuse c(2×4); (d) c(2×4) (after 0.5 L exposure).

Fig. 5-2: The photothreshold of the secondary electrons in the AREDC as the clean Pd(110) surface is exposed to an increasing amount of oxygen at 473 K.

Fig. 5-3: The plots of the work function as a function of oxygen exposure.

Fig. 5-4: The variation on the normal emission AREDC's of Pd(110) surface measured with HeI radiation as a function of oxygen exposure. The binding energy is referred to the Fermi energy of the clean Pd substrate.

Fig. 5-5: Two-dimensional lattice points (real space) and reciprocal lattice points (momentum space) of Pd(110)c(2×4)-O. Surface Brillouin zone for clean Pd(110) is indicated by dashed line and for Pd(110)c(2×4)-O by solid line. The coordinate system is chosen such that the z axis is normal to the surface, and the x and y axis coincide with crystallographic ⟨$\bar{1}$10⟩ and ⟨001⟩ azimuth, respectively.

Fig. 5-6: The AREDC's measured using HeI radiation as a

function of the polar emission angle $\theta_e$ along the <110> azimuth ($\overline{\Gamma}\,\overline{H}'\,\overline{N}'$).

Fig. 5-7: The AREDC's measured using HeI radiation as a function of the polar emission angle $\theta_e$ along the <001> azimuth ($\overline{\Gamma}\,\overline{N}'$).

Fig. 5-8: Normal emission AREDC's with $h\nu$ =28 eV on different polarized light. (A) $\theta_I$=65° and $A_{//}$ along <110>, (B) $\theta_I$=30° and $A_{//}$ along <110>, (C) $\theta_I$=30° and $A_{//}$ along <001>. For comparison, a normal emission AREDC for the clean Pd(110) taken at $\theta_I$=30° and $A_{//}$ along <110> is also shown at the bottom.

Fig. 5-9: The off-normal emission AREDC's at N´ of SBZ measured at (A) $\theta_I$=65° and (B) $\theta_I$=30°. The photon energy is $h\nu$ =29 eV and $A_{//}$ is along <001> direction. For comparison, the AREDC for the clean Pd(110) taken at $\theta_I$=30° is also shown at the bottom.

Fig. 5-10: The off-normal emission AREDC's at N´ of SBZ measured in two sets of geometries; (A) the light is p polarized in the collection plane, (B) the light is p polarized in the plane perpendicular to the collection plane. The photon energy is $h\nu$ =25 eV and $\theta_I$=30°.

Fig. 5-11: Two sets of collection geometries of angle resolved photoemission. (A) the light is p polarized in the collection plane. Only initial states of even symmetry with respect to the collection plane can be observed. (B) the light is p polarized in the plane perpendicular to the collection plane. Even and odd initial state with respect to the collection plane can be observed.

Fig. 5-12: Measured energy vs $k_{//}$ dispersion of oxygen induced state along the symmetry lines of SBZ.

Fig. 5-13: Bandwidth of the O-2p-derived state vs O-O nearest-neighbor distance for ordered oxygen layers on various substrate in a semilog plot (Ref. 10). The line corresponds to an exponential

decay constant of ~0.6 Å.

Fig. 5-14: The band dispersion of an isolated c(2×4) oxygen ordered monolayer model ($\Theta$ =1/4). (a) Two dimensional atomic geometry and Brillouin zone. (b) Schematic representation of energy vs $k_{//}$ dispersion for $p_z$ state.

Fig. 5-15: Schematic representation of the $p_z$, $p_x$ and $p_y$ wave function (real part) for isolated c(2×4) oxygen monolayer at three different values of $k_{//}$ along $\Gamma H' N'$ and $\Gamma N'$ directions in the SBZ. The arrows indicate the direction of $k_{//}$.

Fig. 5-16: Atomic configuration of an isolated c(2×4) oxygen ordered monolayer model ($\Theta$ =1/2).

Fig. 5-17: The band dispersion of an isolated c(2×4) oxygen ordered monolayer model ($\Theta$ =1/2). (a) Two dimensional atomic geometry and Brillouin zone. (b) Schematic representation of energy vs $k_{//}$ dispersion for $p_z$ state.

Fig. 5-18: Adsorption geometry for fcc (110) surface. Adatoms are hatched.

Fig. 5-19: The top view of the geometrical arrangement of long-bridge site model.

Fig. 5-20: The plots of calculated energy levels of the long-bridge site model along symmetry directions in terms of tight binding approximation.

Fig. 5-21: The calculated two-demindional band in the absence of oxygen adsorption.

Fig. 5-22: The top view of the geometrical arrangement of hollow site model.

Fig. 5-23: The plots of calculated energy levels of the hollow site model along symmetry directions in terms of tight binding approximation.

$E_f$
$E_{kin}$
$E_{vac}$
$h\nu$
$E_i$

Fig. 1-1

PHOTOELECTRON
ENERGY
SPECTRUM
E
$\hbar\omega$
VACUUM
LEVEL
FERMI
LEVEL
$\Phi$
W
ADSORBATE
LEVEL
CORE
LEVEL

Fig. 1-2

(c)
BULK BAND STRUCTURE
SURFACE EFFECTS
INITIAL BULK DOS
(b)
NeI NeII
H HeI HeII
MgKα AlKα
SR
10 32 150
SN TG
800
GI
(a)
ℓ(E), MEAN FREE PATH (Å)
E, ELECTRON ENERGY (eV)

Fig. 1-3

Photon energy (eV)
100,000
10,000
1,000
100
10
Light output (Photons/s/mrad/mA/1% band width)
$10^{12}$
$10^{11}$
$10^{10}$
$10^{9}$
2.5 GeV
0.1
1
10
100
1,000
10,000
Wavelength (Å)

Fig. 1-4

(a) fcc (111) (b) fcc (001) (c) fcc (110)

Fig. 1-5

PALLADIUM
∘ AUGMENTED PLANE WAVE METHOD
— COMBINED INTERPOLATION SCHEME
ENERGY (RYDBERGS)
k VECTOR
Γ Δ X Z W Q L Λ Γ Σ K X
$E_F$

Fig. 1-6

PALLADIUM
WITH SPIN-ORBIT
ENERGY (RYDBERGS)
k VECTOR
Γ X W L Γ K X

Fig. 1-7

RAPW
Pd
$E_F$ = 0.558 Ry
Energy E (Ry)
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Δ
Z
Q
Λ
Σ
S
Γ
X
W
L
Γ
KU
X

Fig. 1-8

BULK PHOTOEMISSION
CRYSTAL
VACUUM
ENERGY E
$E_f, k_f$
$h\nu$
$E_i, k_i$
E, k
0
$k_{BZ}$
0
$k_{BZ}$
MOMENTUM k

Fig. 2-1

SURFACE NORMAL
SURFACE BRILLOUIN ZONE (110)
BULK BRILLOUIN ZONE
Q LINES
(a)
(b)
(c)

Fig. 2-2

(a)
(b)
(c)
$-V_0$
$-V_0$
0
$k_{BZ}$
$2k_{BZ}$
$k_f^{\perp}$
0
$-V_0$
0
$-V_0$
0
$-V_0$
SURFACE
z
ENERGY
BANDS
POTENTIAL

Fig. 2-3

(200)
(020)
(00±2)
(11±1)
(1-1±1)
(-11±1)
(-2-20)
(-200)
(0-20)
$X_1, X_3, X_5'$
(110)
ENERGY
(-1-1±1)
$X_1, X_4'$
(001)
(000)
$\Gamma_1$
(000)
(110)
(2π/a) unit
MOMENTUM

Fig. 2-4

<001>
$\bar{\Gamma}(2)$
$\bar{\Gamma}(1)$
<110>
SBZ

Fig. 2-5

Q-MASS
ANALYZER
LEED
GAS INLET
(Ar, O2)
VARIABLE
LEAK VALVE
SAMPLE
x,y,z,θ,φ
ION GUN
UPPER LEVEL

Fig. 3-1

LOWER LEVEL

Fig. 3-2

BAKEOUT ZONE
VARIABLE LEAK VALVE
X RAY SOURCE
LEED
V4
PVG2
V3
SPECTROMETER
SAMPLE PREP CHAMBER
ROTARY HOUSING
ION PUMP
UV SOURCE
VIG17
V16
H2
O2
Ar
GAS AMPUL
AUTOMATIC PRESSURE CONTROLLER (APC)
VIG17
ST22
ST22
V17
V1
V2
TPH 2200
TPH 170
V45
V15
PVG2
VENT VALVES
PVG1
PVG1
PVG1
RT2
V12
E2M40
RT1
V19
MSS50HELIUM PURIFIER
V11
E2M5
V20
ROTARY HOUSING
RT1
V13
E2M5
V18

Fig. 3-3

Total Pressure = 1 x 10^-10 Torr
MASS SPECTROMETER INTENSITY (ARB. UNITS)
H2
H2O
CO
CO2
0
20
40
60
80
100
MASS

Fig. 3-4

G1 G2 G3 SCREEN
0~5kV
A3 A2 A1 FILAMENT
SAMPLE
0~4A
0~15V
100k
100k
100k
-300V

Fig. 3-5

A2
FILAMENT
FILAMENT
A1
ELECTRON GUN CONNECTIONS
G3
G2
ELECTRON GUN
SCREEN

Fig. 3-6

VACUUM WALL
SAMPLE
DPM
16 BIT
COMPUTER
PC 9801
SPECTROMETER
CONTROL
UNIT
TYPE 362
+Ve HEMI
RETARD
-Ve HEMI
PROG
MULT
SUPPLY
+
PRE. AMP
COUNTER
DISCRIMINATOR

Fig. 3-7

8255-A
8255-A
LS241
LS241
LS32
LS32
LS32
LS30
LS14
LS14
LS08
LS221
LS221
LS221
LS107
LS107
LS161
LS161
LS161
LS04
LS193
0.033μ
47k
0.022μ
39k
3300p
39k
1k x 4
10k x 4
307kHz
D15 B20
D14 B19
D13 B18
D12 B17
D11 B16
D10 B15
D9 B14
D8 B13
D7 B12
D6 B10
D5 B9
D4 B8
D3 B7
D2 B6
D1 B5
D0 B4
BHE A44
CPUENB A42
A7 A12
A6 A10
A5 A9
A4 A8
A3 A7
A2 A6
A1 A5
A0 A4
ICW A34
IOR A33
RESET B34
CLK A47

Fig. 3-8

2SC2000
1k
6.8k
LS293
QA QB QC QD
A
B
RO(1) RO(2)
LS00
GATE
RESET
SIGNAL

Fig. 3-9

PIN CONFIGURATION

PIN NAMES

| | |
|---|---|
| $D_0$–$D_7$ | DATA BUS (BI-DIRECTIONAL) |
| RESET | RESET INPUT |
| $\overline{CS}$ | CHIP SELECT |
| $\overline{RD}$ | READ INPUT |
| $\overline{WR}$ | WRITE INPUT |
| A0.A1 | PORT ADDRESS |
| PA7-PA0 | PORT A(BIT) |
| PB7-PB0 | PORT B(BIT) |
| PC7-PC0 | PORT C(BIT) |
| Vcc | -5 VOLTS |
| GND | 0 VOLTS |

8255 BLOCK DIAGRAM

Fig. 3-10

START
STOP
A RUN
B CLOCK
GATE OPEN
CLOSES
C GATE
1mS
D
E
53.37mS
F
G
0.6mS
H RESET
0.1mS
I
J SIGNAL
K COUNT
EOC

Fig. 3-11

0
25M
1A
1C
1B1
2A
1B2
2B2
2B1
4A
4B
4C
6A1
6A2
6B
7B
6C1
6C2
7C
7A
8C1
8A
8B
8C2
9C
10A
9B
9A
10B
10C
11C
11D
12B
11A
12A
11B
12C
13A
13B1
13B2
14B
14A
14C
15A
15C
15B
16C
16A1
16A2
17B
17C
17A
19B
19A
21

Fig. 3-12

LN2 Reservior
Cu
Cu
Pd
Ta
Heater Leads
Heater (Thoriated Tungsten Wire ø0.3)
Insulator
Thermocouples

Fig. 3-13

PALLADIUM
XPS Al Kα
Pd3d
Pd3p3/2
Pd3p1/2
Pd3s
Pd4p
Pd4s
C1s
INTENSITY (ARB.UNITS)
-1000
-800
-600
-400
-200
0
BINDING ENERGY (eV)

Fig. 3-14

PALLADIUM
XPS Al Kα
Pd 3d3/2
Pd3d5/2
C1s
INTENSITY (ARB. UNITS)
-400
-350
-300
-250
-200
BINDING ENERGY (eV)

Fig. 3-15

Pd3d3/2
Pd3d5/2
PALLADIUM
XPS Al Kα
INTENSITY (ARB.UNITS)
-400
-350
-300
-250
-200
BINDING ENERGY (eV)

Fig. 3-16

PALLADIUM
AES $E_p$=2keV
dN/dE
S(LMM)
152
Pd
Pd 78
43
Pd
190
Pd
243
Pd
279
Pd(MNN)330
0
100
200
300
400
500
600
700
800
900
ELECTRON ENERGY (eV)

Fig. 3-17

PALLADIUM
AES Ep= 2keV
dN/dE
Pd 78
Pd 43
Pd 190
Pd 243
Pd 279
Pd(MNN) 330
0
100
200
300
400
500
600
700
800
900
ELECTRON ENERGY (eV)

Fig. 3-18

Fig. 3-19

Pd(110) surface
exposed to 3L $O_2$
AES $E_p$=1.5 keV
dN/dE
O(KLL)
503
Pd
78
Pd
190
Pd
243
Pd
279
Pd(MNN) 330
0
100
200
300
400
500
600
700
800
900
ELECTRON ENERGY (eV)

Fig. 3-20

Fig. 3-21

Pd(110) NORMAL EMISSION
θI = 25°
A// along ⟨1$\bar{1}$0⟩
A
B
C
D
1
2
3
4
hν (eV)
24
26
28
30
31
32
33
34
35
36
37
40
42
44
46
48
50
52
56
60
68
PHOTOELECTRON INTENSITY (ARB.UNITS)
-7 -6 -5 -4 -3 -2 -1 EF
BINDING ENERGY (eV)

Fig. 4-1

Pd(110) NORMAL EMISSION
θ = 25°
A// along ⟨001⟩
A
hν (eV)
24
26
28
30
32
34
36
38
40
42
44
46
48
52
56
60
68
2
C
4
1
2
3
D
PHOTOELECTORON INTENSITY (ARB.UNITS)
-7 -6 -5 -4 -3 -2 -1 E_F
BINDING ENERGY (eV)

Fig. 4-2

Fig. 4-3

hν (eV) 20 25 30 35 40 50 60 70 80
X
K
Γ
E_F
-1
-2
-3
-4
-5
-6
-7
ENERGY (eV)
A
B
C
D
1
2
3
4
5
6
Σ1
Σ1
Σ3
Σ4
2.5
3.0
3.5
4.0
4.5
WAVE VECTOR k⊥ (Å⁻¹)
25 30 35 40 50 60 70 80 90 hν(eV)

Fig. 4-4

Fig. 4-5 (A)

Fig. 4-5 (B)

Pd(110) CLEAN
NORMAL EMISSION
hν = 34 eV A// ⟨1$\bar{1}$0⟩
C
4
2
3
θI = 55°
θI = 25°
INTENSITY (arb. units)
-7
-6
-5
-4
-3
-2
-1
EF
BINDING ENERGY (eV)

Fig. 4-6

Pd(110) CLEAN
NORMAL EMISSION
θI=30°
A// along ⟨001⟩
A// along ⟨1$\bar{1}$0⟩
Σ4
Σ3
hν(eV)
24
25
27
29
3
4
C
(A)
(B)
-3
-2
-1
EF
BINDING ENERGY (eV)

Fig. 4-7

Pd(110)
SEE
hν = 50 eV
INTENSITY
10
20
30
40
FINAL ENERGY ABOVE $E_F$ (eV)

Fig. 4-8

Pd (110)
CIE
$E_i$ = -0.34 eV
INTENSITY
Γ=8.7eV
Γ=5.2eV
25
30
35
40
45
50
55
60
Photon energy (eV)

Fig. 4-9

Fig. 5-1

Photothreshold O/Pd(110)
hν = 21.22 eV (HeI)
Clean
0.06 L
0.13 L
0.25 L
0.50 L
1.00 L
3.00 L
PHOTOELECTRON INTENSITY (ARB. UNITS)
-16.5
-16.0
-15.5
-15.0
-14.5
ENERGY BELOW $E_F$ (eV)

Fig. 5-2

Pd(110)-O
(2x3)-1D
c(2x4)
WORK FUNCTION φ (eV)
6.0
5.5
5.0
0
0.5
1.0
3.0
EXPOSURE (L)

Fig. 5-3

O/Pd(110)
NORMAL EMISSION
hν = 21.22 eV (He I)
θI = 65°
3.0 L
1.0 L
0.7 L
0.5 L
0.2 L
0.15 L
clean
INTENSITY (ARB.UNITS)
-6
-5
-4
-3
-2
-1
EF
BINDING ENERGY (eV)

Fig. 5-4

Pd(110)c(2x4)-O

Fig. 5-5

Pd(110)c(2x4)-O hυ=21.22 eV (HeI)
k// along ⟨1$\bar{1}$0⟩ ($\bar{\Gamma}$-$\bar{H}'$-$\bar{N}'$)
θe
44°($\bar{N}'$)
40°
36°
32°
28°
24°($\bar{H}'$)
20°
16°
12°
8°
4°
0°($\bar{\Gamma}$)
INTENSITY
-8 -7 -6 -5 -4 -3 -2 -1 $E_F$
BINDING ENERGY (eV)

Fig. 5-6

Pd(110)c(2x4)-O hν=21.22 eV (HeI)
k// along ⟨001⟩ (Γ̄-N̄')
θe
20°
16°
14°(N̄')
12°
8°
4°
0°(Γ̄)
INTENSITY
-8 -7 -6 -5 -4 -3 -2 -1 EF
BINDING ENERGY (eV)

Fig. 5-7

NORMAL EMISSION
hν = 28 eV
Pd(110)c(2x4)-O
A// ⟨1$\bar{1}$0⟩
θI = 65°
Pz
A// ⟨1$\bar{1}$0⟩
θI = 30°
Px
A// ⟨001⟩
θI = 30°
Py
Pd(110) clean
A// ⟨1$\bar{1}$0⟩
θI = 30°
INTENSITY (ARB. UNITS)
-7
-6
-5
-4
-3
-2
-1
EF
BINDING ENERGY (eV)

Fig. 5-8

N' θe = 10.4°
hυ = 29 eV
A// ⟨001⟩
Pd(110)c(2x4)-O
(A) θI = 65°
pz
(B) θI = 30°
py
Pd(110)clean
θI = 30°
INTENSITY (ARB. UNITS)
-7 -6 -5 -4 -3 -2 -1 E
BINDING ENERGY (eV)

Fig. 5-9

N̄'  θe = 11.5°
hν = 25 eV
θ = 30°
Pd(110)c(2x4)-O
(A) A// ⟨001⟩
even
Py
(B) A// ⟨1$\bar{1}$0⟩
even + odd
Pz Px
Pd(110)clean
A// ⟨1$\bar{1}$0⟩
INTENSITY (ARB. UNITS)
-7 -6 -5 -4 -3 -2 -1 EF
BINDING ENERGY (eV)

Fig. 5-10

x ⟨110⟩
hν
A⊥
A
A//
Pd(110)
θI
z
⟨110⟩
θe
e⁻
y
⟨001⟩
(A)

y ⟨001⟩
hν
A⊥
A
A//
Pd(110)
θI
z
⟨110⟩
θe
e⁻
x
⟨1$\bar{1}$0⟩
(B)

Fig. 5-11

(N̄'2nd)
16/9 H̄'
H̄'
8/9 H̄'
Γ̄
N̄'
Γ̄2nd
-2
-3
-4
-5
-6
ENERGY
Px Py
Pz
1.0
0.5
0
0.5
← ⟨1 1̄ 0⟩
⟨001⟩ →
MOMENTUM k// (Å-1)

Fig. 5-12

Ni ● 1—7
Fe ▲ 8—11
Cr ▼ 12, 13
Cu ■ 14, 15
Ag ◆ 16
Al ⬢ 17
Cr(100)(1x1)
Ni(110)(2x1)
Cu(110)(2x1)
Fe(100)(1x1)
Fe(110)c(3x1)
Al(111)(1x1)
FeO(111) on Fe(110)
Ag(110)(3x1)
Cu(100)c(2x2)
NiO(100) on Ni(110)
Ni(100)c(2x2)
Ni(110)(3x1)
Cr(100)c(2x2)
Fe(110)c(2x2)
Ni(111)(√3 x √3)R30°
Ni(100)(2x2)
Ni(110)c(2x4)
O 2p Bandwidth (eV)
O nearest-neighbor distance (Å)

Fig. 5-13

(a)
Real space
Reciprocal space
2a
√2a
H̄'
N̄'
Γ̄
(b)
N̄'2nd
H̄'8/9H̄'
Γ̄
N̄'
ENERGY
√2/a π
π/√2a
0
π/2a
MOMENTUM k//

Fig. 5-14

⟨1$\bar{1}$0⟩
c(2x4)-O
⟨001⟩
$k_{//} = \frac{8}{9}\bar{H}' = \frac{\pi}{\sqrt{2}a}$
$k_{//} = \bar{\Gamma} = 0$
$k_{//} = \bar{N}' = \frac{\pi}{2a}$
$p_z$
$p_x$
$p_y$

Fig. 5-15

Fig. 5-16

(a)
Real space
Reciprocal space
H̄'
N̄'
Γ̄
(b)
N̄'2nd
H̄'
8/9 H̄'
Γ̄
N̄'
ENERGY
√2/a π
π/√2a
0
π/2a
MOMENTUM k//

Fig. 5-17

fcc(110): long-bridge site

fcc(110): hollow site

fcc(110):
short-bridge site

Fig. 5-18

Fig. 5-19

N'
H'
Γ
N'
ENERGY (eV)
E_F
4
3
2
1
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
1.14
0.64
0
0.4
← k_x
k_y →
WAVE VECTOR (Å^-1)

Fig. 5-20

N̄'
H̄'
Γ̄
N̄'
4
3
2
1
EF
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
ENERGY (eV)
1.14
0.64
0
0.4
←kx
ky→
WAVE VECTOR (Å⁻¹)

Fig. 5-21

Fig. 5-22

Fig. 5-23

Table 1-1

| Source | Energy (eV) | λ (Å) |
|---|---|---|
| He II | 40.8 | 303.8 |
| He I | 21.22 | 584.8 |
| Ne I | 16.85 | 735.9 |
| | 16.65 | 743.7 |
| Ar I | 11.83 | 1048.2 |
| | 11.62 | 1066.7 |
| H(Ly α) | 10.20 | 1215.7 |

Table 2-1

| Crystal Face | Coordinate Axes x | y | z | Irreducible Representations | Allowed Initial Symmetris E//x | E//y | E//z |
|---|---|---|---|---|---|---|---|
| (001) | ⟨100⟩ | ⟨010⟩ | ⟨001⟩ | $\Delta_1$ $\Delta_1'$ $\Delta_2$ $\Delta_2'$ $\Delta_5$ | $\Delta_5$ | $\Delta_5$ | $\Delta_1$ |
| (110) | ⟨001⟩ | ⟨1$\bar{1}$0⟩ | ⟨110⟩ | $\Sigma_1$ $\Sigma_2$ $\Sigma_3$ $\Sigma_4$ | $\Sigma_3$ | $\Sigma_4$ | $\Sigma_1$ |
| (111) | ⟨$\bar{1}$10⟩ | ⟨$\bar{1}\bar{1}$2⟩ | ⟨111⟩ | $\Lambda_1$ $\Lambda_2$ $\Lambda_3$ | $\Lambda_3$ | $\Lambda_3$ | $\Lambda_1$ |

Table 3-1

| COMPUTER CONTROLLED SOCKET SK3 ON REAR OF 362 UNIT | | |
|---|---|---|
| PIN | FUNCTION | CLOSE TO ENABLE OPEN=0, CLOSE=1 |
| 1 | X-RAY SHUTDOWN (LINKED TO PINS 1 & 2 ON PL21) | 10v 200mA D.C. |
| 2 | | |
| 3 | DIVIDE R + HV BY 20 FOR UV OPERATION | 5v 100mA 4,12,13,14 |
| 4 | LINKED TO PINS 12,13,14 INSIDE 362 | SEE PINS 3, 8, 16 TO 19, 20 TO 35 |
| 5 | 0V | SEE PINS 21 TO 35 |
| 6 | LINK TO PL2/9 | |
| 7 | LINK TO PL2/10 | |
| 8 | MULTIPLY R + HV BY 2 | 5v 30mA 4,12,13,14 |
| 9 | N.C. | |
| 10 | LINK TO PL2/11 | |
| 11 | N.C. | |
| 12 | LINKED TOGETHER & TO PIN 4 INSIDE 362 RETURN PATH FOR PINS 3, 8, 16 TO 19, 20 TO 35 | SEE PINS 3, 8, 16 TO 19, 20 TO 35 LINK TO PL2/5 |
| 13 | | |
| 14 | | |
| 15 | N.C. | |
| 16 | SELECTS 'CAC' MODE (DEFAULT 'CRR') | 5v 30mA 4,12,13,14 |
| 17 | 200 1, 100 1, 50 1, 20 0, 10 0, 5 0, 2 0, 1 1, CAC; PASS ENERGY 'CAC' OR RETARD RATIO 'CRR' SELECTED BY PIN 15 | " |
| 18 | 0 0, 1 1, 0 0, 0 0, 1 1, 0 0, 1 1 | " |
| 19 | 0 1, 0 2, 1 4, 0 10, 0 20, 1 50, 1 100, CRR | " |
| 20 | ION GUN RELAY (CONTACTS 6 & 4 PL 21) | 15v 30mA 4,12,13,14 |
| 21 | -819 2v | 5v 2mA (4,12,13,14) or 5 |
| 22 | -409 6v | " |
| 23 | -204 8v | " |
| 24 | -102 4v | " |
| 25 | -51 2v | " |
| 26 | -25 6v | " |
| 27 | -12 8v | " |
| 28 | -6 4v | " |
| 29 | -3 2v | " |
| 30 | -1 6v | " |
| 31 | -800mv | " |
| 32 | -400mv | " |
| 33 | -200mv | " |
| 34 | -100mv | " |
| 35 | -50mv | " |

R + HV (MODIFIED BY PINS 8 OR 31)

Table 3-2

| PIN | SYMBOL | I O | FUNCTION | PIN | SYMBOL | I O | FUNCTION |
|---|---|---|---|---|---|---|---|
| A 1 | GND | | | B 1 | GND | | |
| A 2 | V 1 | | | B 2 | V 1 | | |
| A 3 | V 2 | | | B 3 | V 2 | | |
| A 4 | AB001 | I/O | ADDRESS | B 4 | DB001 | I/O | DATA |
| A 5 | AB011 | 〃 | 〃 | B 5 | DB011 | 〃 | 〃 |
| A 6 | AB021 | 〃 | 〃 | B 6 | DB021 | 〃 | 〃 |
| A 7 | AB031 | 〃 | 〃 | B 7 | DB031 | 〃 | 〃 |
| A 8 | AB041 | 〃 | 〃 | B 8 | DB041 | 〃 | 〃 |
| A 9 | AB051 | 〃 | 〃 | B 9 | DB051 | 〃 | 〃 |
| A10 | AB061 | 〃 | 〃 | B10 | DB061 | 〃 | 〃 |
| A11 | GND | | | B11 | GND | | |
| A12 | AB071 | I/O | ADDRESS | B12 | DB071 | I/O | DATA |
| A13 | AB081 | 〃 | 〃 | B13 | DB081 | 〃 | 〃 |
| A14 | AB091 | 〃 | 〃 | B14 | DB091 | 〃 | 〃 |
| A15 | AB101 | 〃 | 〃 | B15 | DB101 | 〃 | 〃 |
| A16 | AB111 | 〃 | 〃 | B16 | DB111 | 〃 | 〃 |
| A17 | AB121 | 〃 | 〃 | B17 | DB121 | 〃 | 〃 |
| A18 | AB131 | 〃 | 〃 | B18 | DB131 | 〃 | 〃 |
| A19 | AB141 | 〃 | 〃 | B19 | DB141 | 〃 | 〃 |
| A20 | AB151 | 〃 | 〃 | B20 | DB151 | 〃 | 〃 |
| A21 | GND | | | B21 | GND | | |
| A22 | AB161 | I/O | ADDRESS | B22 | +12V | | |
| A23 | AB171 | 〃 | 〃 | B23 | +12V | | |
| A24 | AB181 | 〃 | 〃 | B24 | IR31 | I | INT 0 |
| A25 | AB191 | 〃 | 〃 | B25 | IR51 | I | INT 1 |
| A26 | AB201 | 〃 | 〃 | B26 | IR61 | I | INT 2 |
| A27 | AB211 | 〃 | 〃 | B27 | IR91 | I | INT3(5"HD) |
| A28 | AB221 | 〃 | 〃 | B28 | IR101/IR111 | I | INT41/INT42(1) |
| A29 | AB231 | 〃 | 〃 | B29 | IR121 | I | INT 5 |
| A30 | INT0 | O | | B30 | IR131 | I | INT 6 |
| A31 | GND | | | B31 | GND | | |
| A32 | IOCHK 0 | I | ex NMI | B32 | −12V | | |
| A33 | IOR 0 | I/O | COMMAND | B33 | −12V | | |
| A34 | IOW 0 | I/O | 〃 | B34 | RESET 0 | O | $\overline{\text{RESET}}$ |
| A35 | MRC 0 | I/O | 〃 | B35 | DACK00 | O | 5"HD |
| A36 | MWC 0 | I/O | 〃 | B36 | DACK30/DACK20 | O | AUX(1) |
| A37 | S00 | I/O | S 0 | B37 | DRQ00 | I | 5"HD |
| A38 | S10 | I/O | S 1 | B38 | DRQ30/DRQ20 | I | AUX(1) |
| A39 | S20 | I/O | S 2 | B39 | WORD 0 | I | |
| A40 | LOCK0 | I/O | | B40 | CPKILL 0 | I | |
| A41 | GND | | | B41 | GND | | |
| A42 | CPUENB10 | O | | B42 | RQGT0 | I | |
| A43 | RFSH 0 | O | | B43 | DMATC 0 | O | END OF PROCESS |
| A44 | BHE 0 | I/O | | B44 | NMI0 | O | |
| A45 | IORDY 1 | I | | B45 | MWE 0 | O | |
| A46 | SCLK 1 | O | 7.9872/4.9152MH,(2) | B46 | HLDA00 | O | |
| A47 | S18CLK 1 | O | 307.2KHz | B47 | HRQ00 | I | |
| A48 | POWER 0 | O | | B48 | DMAHLD 0 | I | |
| A49 | + 5 V | | | B49 | + 5 V | | |
| A50 | + 5 V | | | B50 | + 5 V | | |

Table 3-3

| $A_1$ | $A_0$ | RD | WR | CS | function | |
|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 1 | 0 | PA → Data Bas | CPU ← PPI |
| 0 | 1 | 0 | 1 | 0 | PB → Data Bas | (read) |
| 1 | 0 | 0 | 1 | 0 | PC → Data Bas | |
| 0 | 0 | 1 | 0 | 0 | Data Bas → PA | CPU → PPI |
| 0 | 1 | 1 | 0 | 0 | Data Bas → PB | (write) |
| 1 | 0 | 1 | 0 | 0 | Data Bas → PC | |
| 1 | 1 | 1 | 0 | 0 | Data Bas → COMMAND | CPU → PPI |
| 1 | 1 | 0 | 1 | 0 | forbidden | |

Table 3-4

| $CR_7$ | $CR_6$ | $CR_5$ | $CR_4$ | $CR_3$ | $CR_2$ | $CR_1$ | $CR_0$ |
|---|---|---|---|---|---|---|---|
| MODE SELECTION 1 | PA GROUP | | $PA_{0-7}$ | $PC_{4-7}$ | PB GROUP | $PB_{0-7}$ | $PC_{0-3}$ |
| | 0 0 ·····MODE 0 | | | | | | |
| | 0 1 ·····MODE 1 | | 1····INPUT | 1····INPUT | 1····MODE 1 | 1····INPUT | 1····INPUT |
| | 1 0 , 1 1 | ····MODE 2 | 0····OUTPUT | 0····OUTPUT | 0····MODE 0 | 0····OUTPUT | 0····OUTPUT |

Table 3-5

| Port | Upper | Lower |
|---|---|---|
| PA | D8 | D9 |
| PB | DA | DB |
| PB | DC | DD |
| COMMAND | DE | DF |

Table 5-1 tight binding paramaters

| | |
|---|---|
| $Ep_x$ | -4.5 eV |
| $Ep_y$ | -4.5 |
| $Ep_z$ | -5.0 |
| $Ed\gamma$ | -2.7 |
| $Ed\varepsilon$ | -1.0 |
| $(pd\sigma)$ | -3 |
| $(pd\pi)$ | 2 |
| $(dd\sigma)$ | -1.1 |
| $(dd\pi)$ | 0.85 |
| $(dd\delta)$ | -0.21 |

inches
cm
Kodak Color Control Patches
© Kodak, 2007 TM: Kodak
Blue
Cyan
Green
Yellow
Red
Magenta
White
3/Color
Black
Kodak Gray Scale
C
Y
M
© Kodak, 2007 TM: Kodak
A 1 2 3 4 5 6 M 8 9 10 11 12 13 14 15 B 17 18 19