(BL5A)

Photo-induced change in GaAs (100) surface

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In recent years, photo-induced phenomena such as color-transition, magnetic-transition, and structural-transition have attracted much interest. The transition or change in electronic structures is closely related to these photo-induced transitions. However, most of works have been carried out using optical spectroscopy, but few have been conducted using photoelectron spectroscopy. As it is well known, the photoelectron spectroscopy is so surface sensitive that it may be powerful to investigate small change or transition on the photo-irradiated surfaces. Laser-induced change in photoelectron spectra has been reported by Long *et al.*, who have first observed the transient surface photo-voltage on Si (111) using synchrotron radiation (SR) and laser pulses.1) They used a high-power laser in the experiments, for examples, the repetition rate and time-width of their laser was 6 kHz and 0.1 mJ/cm^2, respectively. The average power of the laser was 0.6 W in 20 ns. They have also reported the laser-induced photochemical decomposition of GaAs(110), where metallic Ga was observed on the surface irradiated by laser pulses of 3.9 mJ/cm^2.2) In this case the average power was 23.4 W. This means that the photo-induced phenomena have much variety depending on the laser power within two-orders of magnitude. The purpose of the present study is to know good experimental condition when we use powerful lasers to investigate photo-induced phenomena on GaAs(100).

Experiments have been carried out at BL5A, UVSOR facility. A high-resolution monochromator SGM-TRAN, which was recently constructed,3) was used to excite samples at 100 eV. The OMICRON electron energy analyzer (EA-125HR) was used to measure the angle-resolved photoelectron spectra. The p-type GaAs (100) doped with Zn was installed in a liquid-nitrogen type cryostat without Ne-sputtering. Low-repetition and high-power Q-switched Nd:YAG laser was used. Second-harmonic light of the laser (photon energy 2.33 eV) was introduced on the sample in a vacuum chamber with a set of mirrors. The repetition rate and time-width were 20 Hz and 5 ns, respectively. We used the average power of 0.2-1 W without focusing in the present experiments. These conditions correspond to the pulse energy of 10-50 mJ/cm^2.

Figure 1 shows photoelectron spectra with 0.2-W laser excitation at 90 K. It is clearly observed that the photoelectron spectra were changed drastically by laser irradiation, for examples, the As-3d peak of oxide As around 55 eV disappeared after laser irradiation. This indicates that laser irradiation is useful to get clean surface of GaAs.

Figure 2 shows the photoelectron spectra with 1-W laser excitation at room temperature. The spectrum before laser irradiation has been already irradiated due to the experimental alignment. The As-*3d* peak increases after laser irradiation. This indicates that GaAs surface is easily decomposed by laser irradiation. We have carefully checked the threshold power to avoid the decomposition, and obtained the value of 0.28 W.

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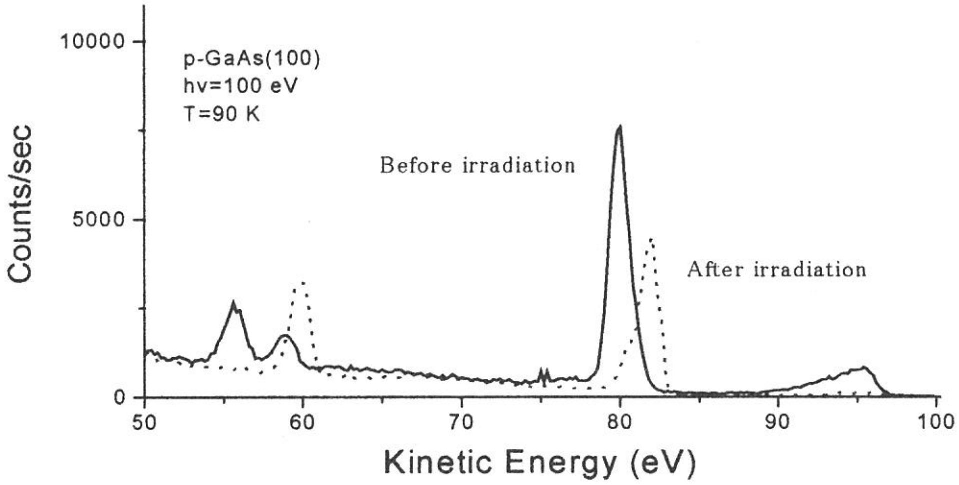

Fig. 1. Photoelectron spectra of GaAs with 0.2- W laser excitation at 90 K.

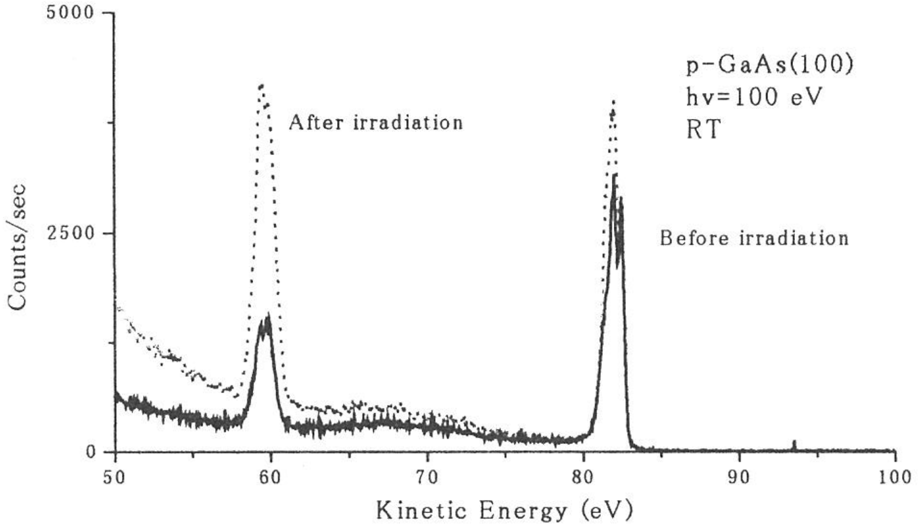

Fig. 2. Photoelectron spectra of GaAs with 1-W laser excitation at RT.

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Photoelectron Spectra of $Zn_{60}Mg_{30}Ho_{10}$ Icosahedral Quasicrystal

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The small electrical conductivity and its negative temperature dependence of quasicrystals (QCs) have been considered to partly arise from the existence of a pseudo-gap near the Fermi level as the Hume-Rothery phases [1]. The Al-based QCs composed of the Mackay icosahedron clusters seems to be stabilized near the electron per atom ratio $e/a \approx 1.75$, and some of them reveal the spectroscopic evidence of the pseudo-gap. On the other hand, icosahedral Zn-Mg-R (R = heavy rare earth element) QCs have attracted much interest because of the possibility to show the magnetic property intrinsic in the quasiperiodicity [2]. They also show the relatively high electrical conductivity [3] and the quasiperiodic structure consisting of the rhombic triacontahedron clusters with $e/a \approx 2.1$. These are somewhat different from the Al-based Mackay-icosahedron-type QCs. Thus, we have measured the photoelectron spectra of an icosahedral Zn-Mg-Ho QC for clarifying its electronic structure.

Ingots of poly-grain F-type icosahedral $Zn_{60}Mg_{30}Ho_{10}$ QCs were synthesized with use of a programmable electric furnace. The detailed sample preparation and its structural characterization are described elsewhere [4]. Specimens were cut from the ingot into a typical size of 5 x 5 x 3 mm^3 and attached on a copper plate by conductive epoxy glue. Clean surfaces for the photoelectron measurement were prepared by *in situ* scraping the specimen with a diamond file. Photoelectron spectra were taken under an ultrahigh vacuum of 2 x 10^{-8} Pa at room temperature with a hemispherical energy analyzer at BL5A. Total energy resolution including the thermal broadening was estimated to be 0.2 eV at the photon energy $h\nu$ of 45 eV from the measurement of the Fermi edge of gold. The origin of the binding energy E_B was also determined by the Fermi edge of Au.

Figure 1 shows typical photoelectron spectra near the valence band region. The excitation photon energies $h\nu$ are indicated in the figure. The spectra are enlarged below $E_B = 8$ eV by a factor of 20. The large peak with a shoulder around $E_B = 9$ eV is attributed mainly to the Zn $3d$ states. The structures seen in the binding energy region between 5 and 7 eV are ascribed to a part of the Ho $4f^9$ final state multiplets, the rest of which probably overlap with the Zn $3d$ peaks [5]. These $4f^9$ multiplets indicate the $4f^{10}$ configuration of Ho, *i.e.* Ho^{3+}. This is consistent with the magnetization measurement reported for the Zn-Mg-Ho QC [3].

Detailed spectral profiles near the Fermi level (close circles) are shown in Fig.2 in comparison with the spectrum of Au (open circles). The obtained valence band spectrum of the $Zn_{60}Mg_{30}Ho_{10}$ QC is peaked around $E_B = 0.6$ eV. However, its edge profile resembles much that of Au. This suggests no or weak pseudo-gap in this QC, although the unoccupied states cannot be probed in the photoelectron spectroscopy. Absence or weakness of the pseudo-gap may be related to the above-mentioned relatively high conductivity and the fact that the electron diffraction patterns show no intense spots near the wavevector of 0.470 $Å^{-1}$, which is double the Fermi wavevector, $2k_F$, estimated on the assumption of the density of 5.4 ± 0.1 g/cm^3 and the valence of Zn^{2+}, Mg^{2+} and Ho^{3+} with the nominal composition of $Zn_{60}Mg_{30}Ho_{10}$. This seems to be in contrast to the Al-based Mackay- icosahedron-type QCs.

Further studies are intended with the higher energy resolution at the low temperature. Inverse photoelectron spectroscopy and soft X-ray emission spectroscopy of the $Zn_{60}Mg_{30}Ho_{10}$ QC are also in progress now, and their results will be reported elsewhere.

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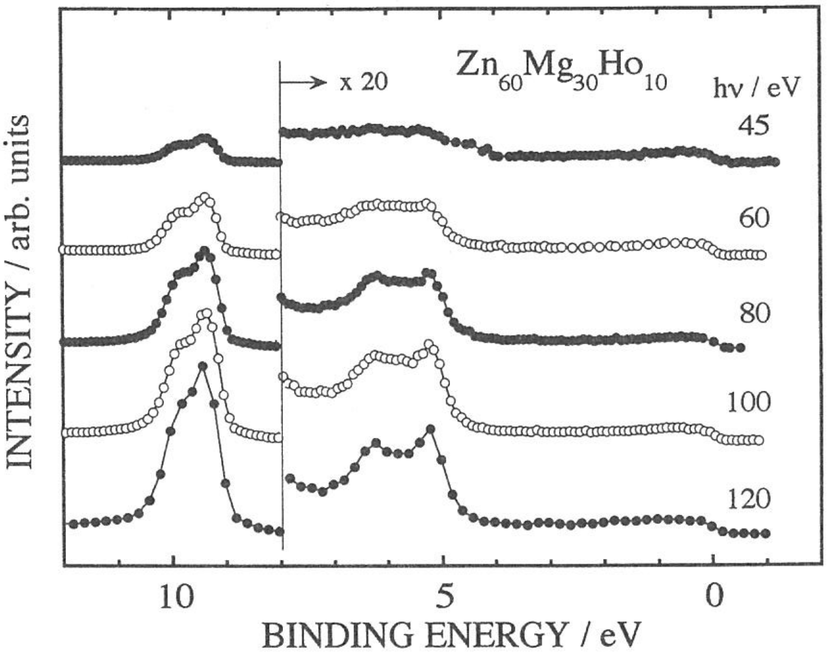

Fig.1 Photoelectron spectra of an icosahedral $Zn_{60}Mg_{30}Ho_{10}$ quasicrystal.

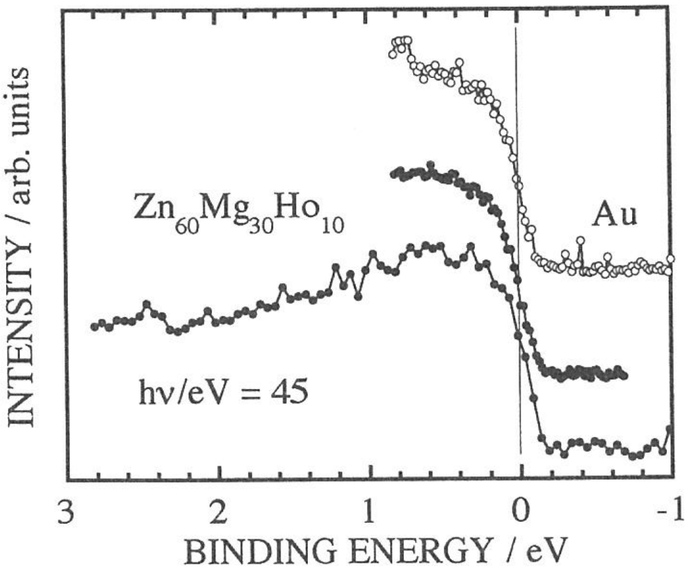

Fig.2 Photoelectron spectra of an icosahedral $Zn_{60}Mg_{30}Ho_{10}$ quasicrystal near the Fermi level (closed circles) in comparison with that of Au (open circles).

(BL5A)

High-Resolution Photoemission Study of Si(111)-$\sqrt{3}$x$\sqrt{3}$-Ag Surface

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Recent progress of the high-resolution photoelectron measurement is bringing one of the powerful techniques which elucidate the chemical bonding and local atomic arrangement of the complicated Si surface layers [1]. The structure of the Si(111)-$\sqrt{3}$x$\sqrt{3}$-Ag surface has been already studied by various techniques in surface science, and the honeycomb chained triangle (HCT) model proposed by Takahashi *et al.* [2] has been widely accepted. In the HCT model, the top layer is occupied by three Ag atoms in the $\sqrt{3}$x$\sqrt{3}$ unit cell, and the underlying Si atoms form a Si trimer layer as the missing-top layer model. According to the analysis of surface X-ray diffraction, the third and forth Si layers have large bucklings in the normal direction and the reconstruction ranges up to the seventh Si layer. In this report, we present the results of the high-resolution measurement of the Si(111)-$\sqrt{3}$x$\sqrt{3}$-Ag surface at temperatures T of 100 and 300 K.

Measurements were performed at the BL-5A of UVSOR. Silicon specimens used were mirror-polished n-type Si(111) wafers with a size of 5x9x0.5mm^3. The specimen was placed on a manipulator in a conventional ultrahigh vacuum chamber equipped with a hemispherical analyzer, a LEED optics, an AES one, and a Ag evaporation source. The Si(111)-$\sqrt{3}$x$\sqrt{3}$-Ag surface was produced by about 1 monolayer deposition of Ag onto the Si(111)-7x7 surface, prepared by repeated direct-current heating, and subsequent annealing at 700 K for 300 s. Clear $\sqrt{3}$x$\sqrt{3}$ LEED spots were obtained, and no contamination was observed by AES. The amount of deposited Ag was also checked by AES. The total energy resolution was estimated to be less than 70 meV.

Figure 1 shows Si2*p* core-level spectra taken at T=100 and 300 K with the photon energy $h\nu$ of 130 eV at the emission angles θe of (a) 60° and (b) 0°. The normal emission spectrum obtained at 300 K agrees well with the results reported by Herman *et al.* [3]. They have explained the spectrum by three surface components and a bulk one. However, we have found that another surface component (S2 in our notation), at least for the low-temperature, is needed to consistently explain all the low-temperature spectra taken at θe=0° and 60° with $h\nu$=110 and 130 eV. The decomposition into a bulk component B and four surface components S1-S4 is also shown in the figure, and the fitting parameters are summarized in Table 1, where the surface core-level shifts are referred to the bulk position. The relative intensities of the components are listed in Table 2.

The S1 component is assigned to the top-most Si layer bonding to the Ag atoms, since it is the most intense in the surface-sensitive spectra taken with $h\nu$=130 eV, in particular, at θe=60°. Because of its large intensity, comparable to the S1 component in the normal emission spectra, the new component S2 may be also attributed to another Si in the Si top layer, which is inconsistent with the HCT model. Recent theoretical calculation [4] suggests that an asymmetric structure might have lower total energy than the HCT arrangement. However, this structure appears to be incompatible with the observed intensity ratio of the components. Another possible interpretation within the HCT framework is that the large S2 peak might be caused by the diffraction of the photoelectron emerging from Si atoms in the deeper Si layer. Thus, further investigation on the low-temperature surface phase is necessary to solve this problem. The S3 and S4 components, whose chemical shifts of –0.25 and +0.51 eV are in accordance with the result reported by Herman *et al.* [3], are tentatively ascribed to Si atoms in the domain walls and those below the second Si layer.

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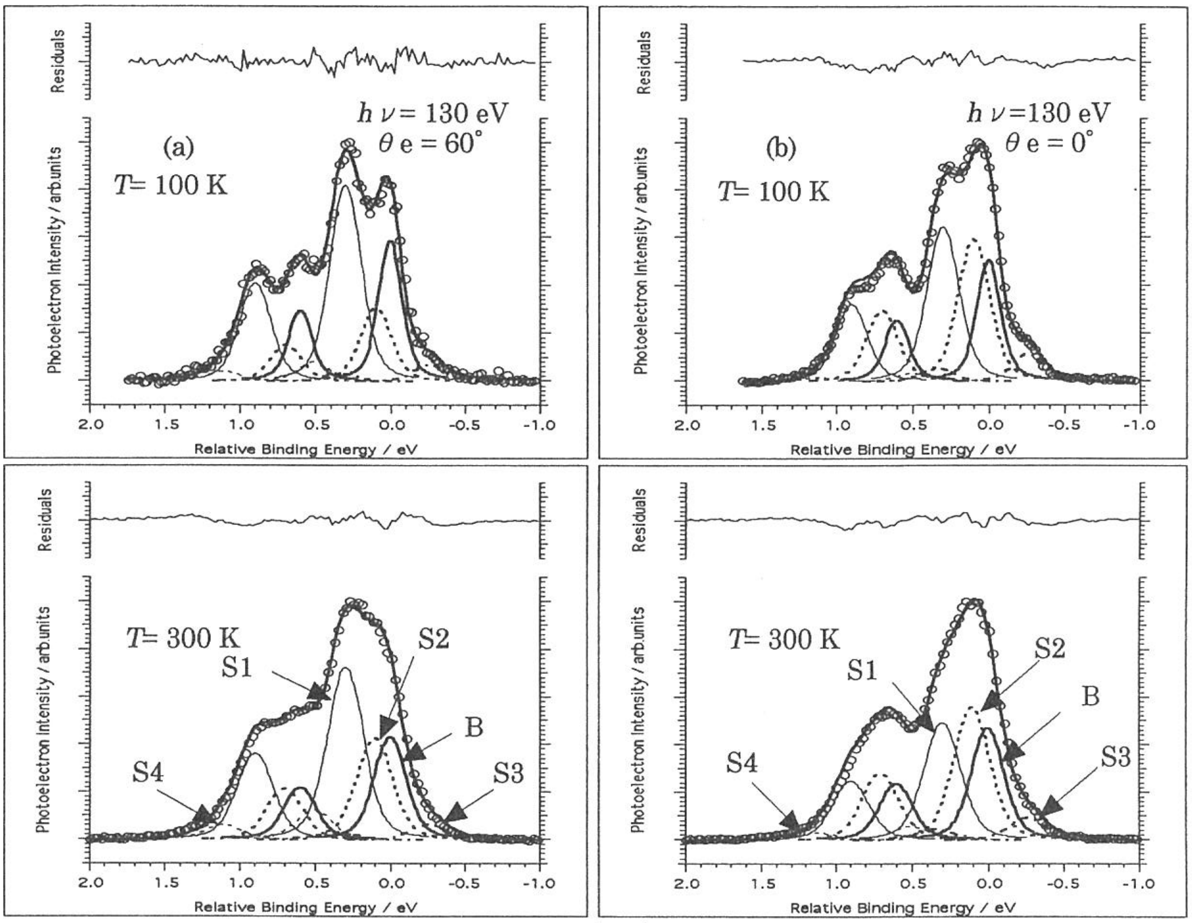

Fig. 1 Si2*p* core-level spectra of the Si(111)-√3x√3-Ag surface taken at the emission angle θe of (a) 60° and (b) 0° with a photon energy $h\nu$ of 130 eV at temperatures *T* of 100 K (top) and 300 K (bottom). The relative binding energy scale is referenced to the 2*p*3/2 line of the bulk component B. The decomposition of the spectra is also shown.

Table 1 Fitting parameters for the Si2*p* spectra. All energies are in eV. The Lorentzian and Gaussian widths refer to the full width at half maximum.

Spin-orbit splitting	0.600
Branching ratio	0.5
Lorentzian width	0.083
Gaussian width of a bulk compnent	0.136 (100 K) 0.204 (300 K)
Gaussian widths of surface components	0.199 (100 K) 0.235 (300 K)
Surface core-level shifts	S1: +0.301 S2: +0.104 (100 K) +0.112 (300 K) S3: −0.251 S4: +0.510

Table 2 Fraction of integrated intensity for the decomposed components measured at 100 K.

	$h\nu$=130 eV θe=60°	$h\nu$=130 eV θe=0°	$h\nu$=110 eV θe=0°
B	0.32	0.27	0.82
S1	0.44	0.34	0.09
S2	0.16	0.31	0.03
S3	0.04	0.06	0.06
S4	0.04	0.02	0

(BL5A) Photoemission Study of Initial Growth of Cu Layers on Si(111)-√3x√3-Ag Surface

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The epitaxial growth of a Cu film on Si substrates has received intensive attention from the points of view of fundamentals and technology for epitaxial metallization in Si microdevices. Adsorbate Cu atoms have been considered to be reactive with the substrate Si ; a LEED pattern at the coverage higher than 10 monolayers (ML) suggests an fcc (111) lattice of Cu metal or α-phase Cu-Si alloy [1], and an η-Cu3Si interface between Cu layers and the Si substrate at the 100℃-deposition is proposed from X-ray diffraction measurements [2]. In addition to the research on the single adsorbate system, a binary adsorbate system has interest due to the possible modification of surface structure, which may assist the epitaxial growth. Ishikawa *et al.* studied the room-temperature Cu deposition onto the Si(111)-√3x√3-Ag surface by AES and RBS techniques, and proposed that Cu3Si is formed with Ag atoms kept at the top-most surface [3]. Here, we have measured the Si2*p* core-level spectra of Cu-deposited Si(111)-7x7 (Cu/Si(111)-7x7) and Si(111)-√3x√3-Ag (Cu/Si(111)-√3x√3-Ag) surfaces in order to clarify change in the chemical bond on the initial growth of Cu layers on the Si(111)-√3x√3-Ag surface.

Measurements were performed at the BL-5A of UVSOR. The silicon specimen was placed on a manipulator in a conventional ultrahigh vacuum chamber equipped with a hemispherical analyzer, a LEED optics, an AES one, and evaporation sources of Ag and Cu. After the preparation of the Si(111)-√3x√3-Ag and Si(111)-7x7 surfaces, Cu was deposited onto these surfaces at room temperature. The amount of deposited Cu was monitored by AES.

Figure 1 shows typical Si2*p* core-level spectra on the Cu deposition onto the Si(111)-7x7 and Si(111)-√3x√3-Ag surfaces, and their decomposed components. The decomposition was performed with use of measured bulk- and surface-sensitive spectra and Voigt functions representing a bulk and several surface components with the 2*p*1/2-2*p*3/2 branching ratio of 0.5 and the appropriate fitting energy parameters. The surface components S1-S5 obtained for the Si(111)-7x7 surface (a) are consistent with the result of Karlsson *et al.* [4], and S1*-S4* for the Si(111)-√3x√3-Ag surface (d) are referred to the spectrum measured at low temperature [5]. Spectra with increasing Cu desorption onto the Si(111)-7x7 and Si(111)-√3x√3-Ag surfaces are shown in (b)-(c), and (e)-(f), respectively. The abscissa is the relative binding energy whose origin is the energy position of the bulk component B, in order to cancel out the shift due to the band-bending.

As seen in the figure, the main peak of the Si2*p* spectra is shifted to the low relative binding-energy side for both surfaces, and the low-binding energy tail is enhanced with the Cu deposition increasing. For the Cu/Si(111)-7x7 surface, the spectral change is ascribed to decrease of the initial surface components S1-S5 and increase of the S3' and S4' components, which indicates that new Cu-Si bonds are formed on the Cu deposition. The increase of the Cu-Si bonds is also recognized in the panels (e) and (f) for the Cu/Si(111)-√3x√3-Ag surface. Furthermore, the S1* component corresponding to the Ag-Si bond is much reduced on the Cu deposition. These findings are consistent with the growth model proposed by Ishikawa *et al.* On the other hand, the S1 component persists in the panel (c), in accordance with its assignment of the pedestal atoms in the Si(111)-7x7 surface. The S2* component may be attributed to Si atoms in the third and forth layers rather than another type of Si in the first Si layer [5], because of its less sensitivity to the deposition and its small chemical shift from the bulk.

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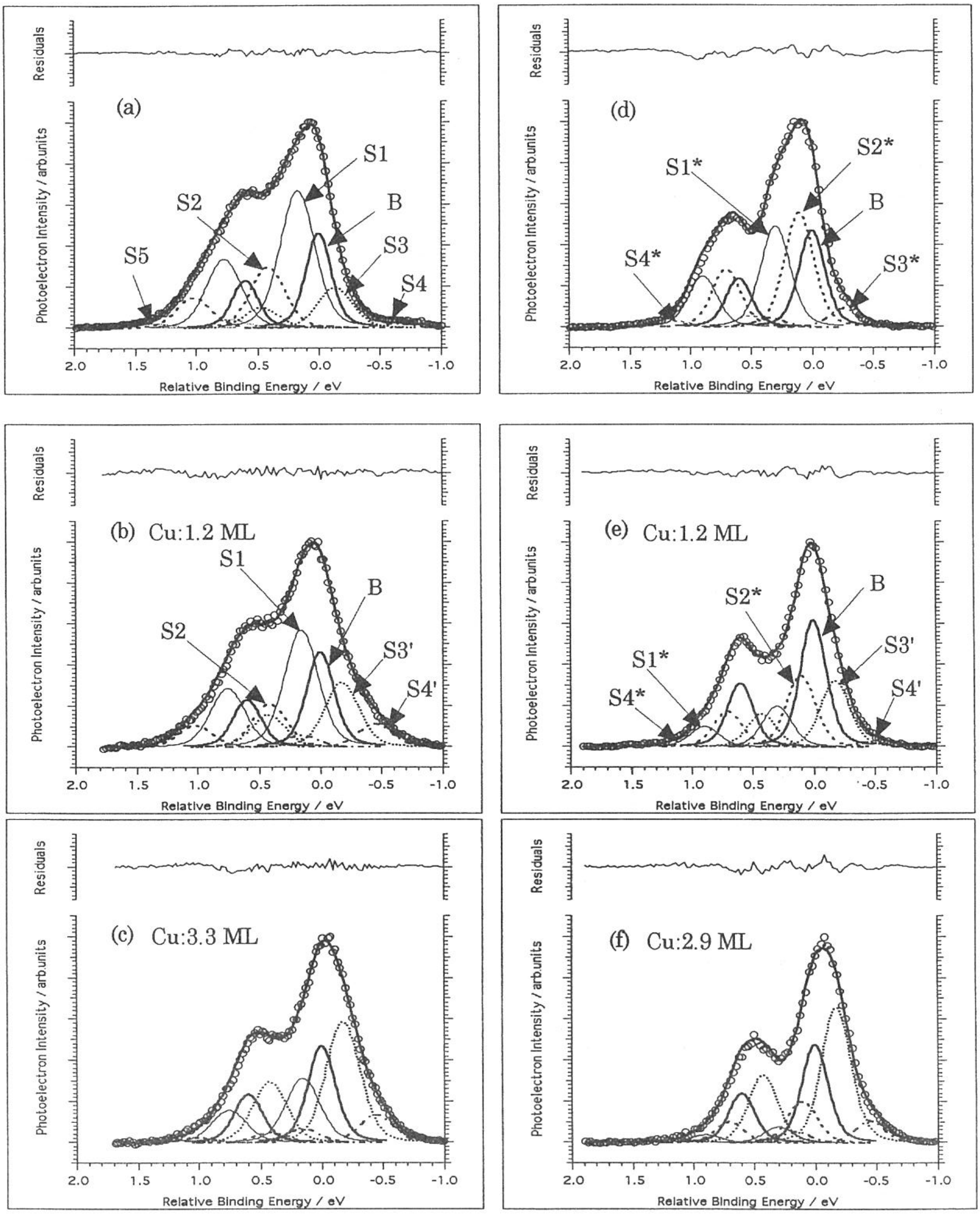

Fig. 1 Si2*p* core-level spectra and their decomposed components of Cu/Si(111)-7x7 surfaces (left panels) and Cu/Si(111)-√3x√3-Ag ones (right panels). These spectra were taken at the normal emission with a photon energy of 130 eV at room temperature. The initial Si(111)-7x7 and Si(111)-√3x√3-Ag surfaces are shown in the panels (a) and (d), respectively. The Cu coverages are indicated in the figure. The abscissa is the relative binding energy referenced to the 2*p* 3/2 line of the bulk component B.

(BL5A)

Core-level excitation and decay of multi-layered Xe film

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The core-level excitation and decay of solids and solid surfaces has been extensively studied for these decades. The measurements of photo-absorption spectrum near the core-level edge and the Auger electron spectra taken at the photons of which energies corresponds to a specific excitation allow us to insight the detailed mechanism of excitation and decay. The Auger decay of the excited state created by the photons at the core-threshold is different from the Auger decay of normally ionized state created by the photons or electrons far beyond from the threshold energy. In the former situation, excited electrons stays during the Auger decay ("spectator" case) or take part in the Auger decay ("participator" case), so that the final state of the Auger decay contains 2 holes 1 electron (spectator) or 1 hole only (participant). Meanwhile, the final state of the normal Auger decay contains 2 holes. In the case of the isolated molecule or atoms, an excited electron can stay near the core hole long enough to survive during the Auger decay, and therefore, resonant Auger electron spectra, like the spectator or participant Auger described above, are observed usually. However, in the case of the metallic solid, the excited electron has only a short lifetime due to the charge transfer in the crystal, and the excited state decays to be ionized state before the Auger decay. Therefore, only the normal Auger electron spectra are observed taken at the photon energy of the threshold of the core excitation for the metallic solid. In this report, we made an investigation of the absorption spectroscopy and resonant Auger electron spectroscopy, at the 4d level of Xe layers produced on the Si(111) surface at 30K. We observed the surface core exciton, and observed the resonant Auger spectra of the surface and bulk core exciton of Xe film.

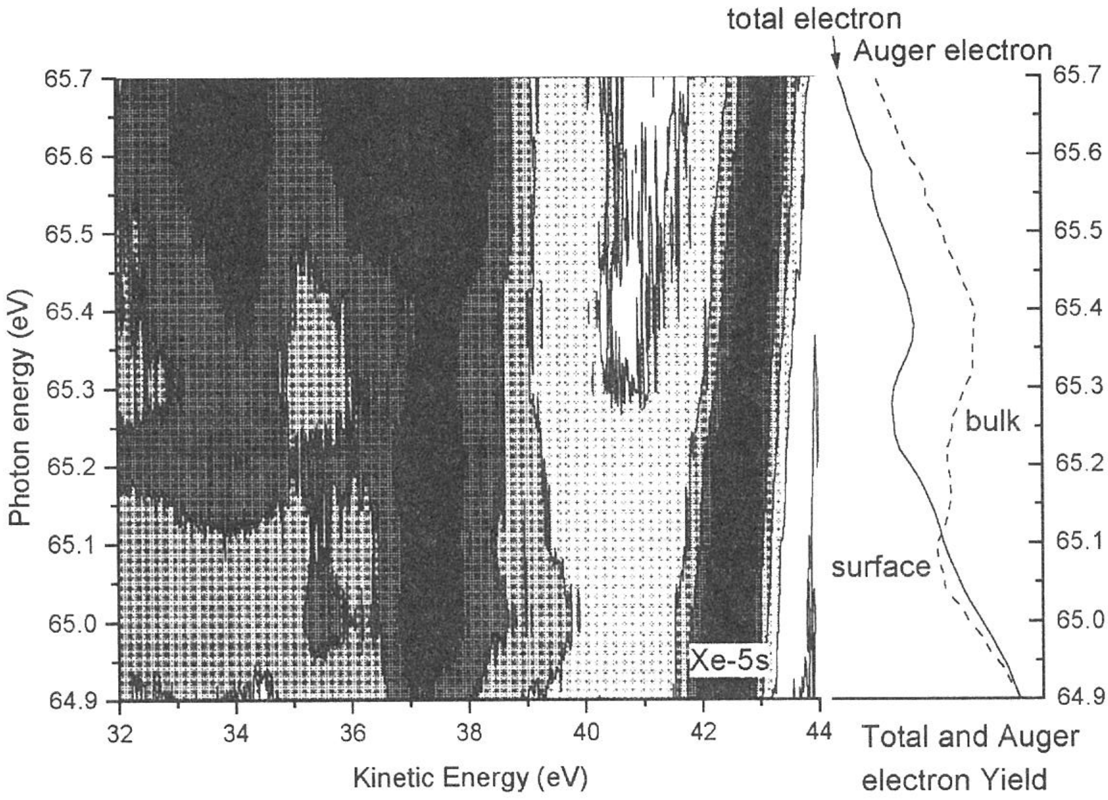

Figure 1

The right panel of the figure 1 shows the total electron yield (bulk sensitive) and Auger electron yield (surface sensitive). The kinetic energy of the electron was set to be corresponding to the Xe-NOO Auger emission. The bulk core exciton is observed at 65.28 eV, and the surface core exciton is observed at 65.08 eV. The left panel of the figure 1 shows the contour plot of the series of photoelectrons obtained by changing the photon energy in steps of 0.1 eV across the surface and bulk core exciton. Peaks observed near E_K=42 eV

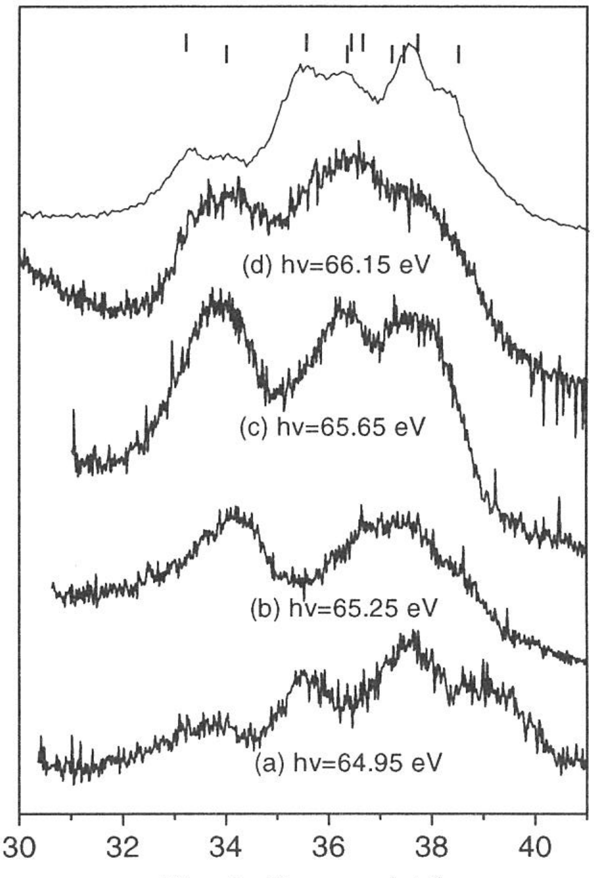

Figure 2

(hv=64.9eV) is the direct emission from the Xe-5s level, and is shifted as a linear function of the photon energy. The structures observed in 32-40 eV is attributed to the Xe-NOO Auger electron and the shake-up satellite of the Xe valence peaks. It is obvious that contour plot can be separated into 3 regions correspoiding to the surface core exciton (near hv=65.0 eV), to the bulk core exciton (near hv=65.2 eV), and to the higher photon energies (hv>65.5 eV). The spectra at hv>65.5 eV is considered to be mostly contributed by the normal Auger emission, which result in the 2 hole as the final state. The decay spectra of the surface and bulk core exciton were different from the normal Auger, which may mean that the resonant Auger spectra are observed. In order to investigate the resonant behavior of the decay spectra of the surface and bulk core exciton, we eliminate the contribution of the satellite peaks of the Xe valence level from the raw spectra. Results are shown in the figure 2.

Spectra (a) and (b) of the fig. 2 correspond to the decay spectra of the surface and bulk core exciton, respectively. Spectra (c) and (d) were taken at higher photon energies, and do not show significant differences from a top curve which is the normal Auger electron spectrum obtained at hv=90 eV. A shift to higher kinetic energies in the Auger electron spectrum is clearly observed for the decay of the surface core exciton [Fig.2 (a)]. Thus, it is considered that the lifetime of the surface core-exciton is long enough to survive during the Auger decay. The resonant behavior of the bulk core-exciton is not so clear as observed in the case of the surface core exciton [fig2.(b)]. The investigation of the system in detail is now under progress.