Background-Free Auger Spectra from the Surface Top-Layer Measured by Positron-Annihilation Induced Auger-Electron Spectroscopy

Toshiyuki Ohdaira, Ryoichi Suzuki, and Tomohisa Mikado

Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305-8568, Japan

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We developed an apparatus for time-of-flight positron-annihilation induced Auger-electron spectroscopy with an intense slow positron beam produced with an electron linear accelerator. With this apparatus, we measured background-free Si-$L_{2,3}VV$ Auger lineshapes from the top layer of clean and oxygen-adsorbed Si(100) surfaces.

1. Introduction

Core-valence-valence (CVV) Auger lineshapes provides information about a local valence density of states of the Auger emitting atoms [1]. However, the Auger lineshapes measured by the conventional electron-excited Auger electron spectroscopy (EAES) are distorted by the large background of the secondary electrons and the energy losses in the surface layers. In Positron-annihilation induced Auger-electron spectroscopy (PAES) [2], Auger spectra from with no background of secondary electrons can be obtained by using a low energy (~10 eV) positron beam. In PAES, core hoes are created by annihilations of positrons with the core electrons. The background can be eliminated by using the positron beam with an energy lower than the Auger energies. In addition, the PAES signals originate exclusively from the top layer of surfaces, because most of the positrons implanted at low energies are trapped by the image potential outside the surface before annihilation. Therefore, the Auger lineshape obtained by PAES could provide information about chemical states of the top-layer atoms. However, Auger lineshape analysis by PAES has been difficult, because the intensity of the slow positron beam (usually < 10^6 e^+/s) is much lower than the intensities of electrons or photons used for EAES or XPS. So far, PAES Auger lineshapes have been measured for only a few materials [3,4].

At the Electrotechnical Laboratory, a slow positron beam with an intensity of 10^8 e^+/s is produced with an electron linear accelerator (linac) [5]. At this beam-line, we constructed a new apparatus for PAES [6]. The apparatus uses a magnetic parallelisation technique and a time-of-flight (TOF) method with a pulsed beam, which enable high angular acceptance ($\sim 2\pi$) and high collection efficiency. An energy resolution better than 3% is achieved by the use of a retarding flight tube. In the present study, we measured Si $L_{2,3}VV$ Auger lineshapes from clean and oxygen-adsorbed Si(100) surfaces with this apparatus.

2. Experimental

Figure 1 shows the schematic of the TOF-PAES apparatus [6]. The base pressure of the system is 1×10^{-10} Torr. An axial magnetic field (40 G) was applied to the whole system as a beam guide. A slow positron beam with an intensity of 10^8 e^+/s produced by the electron linac [5] was pulsed with a chopper and a buncher to a pulse width of 7 ns (FWHM), and was incident on the sample with an energy of 45 eV. The electrons emitted from the sample over 2π were parallelised to the axial direction by a magnetic field gradation [7] produced with a Nd-Fe-B magnet (2500 G) mounted behind the sample. The parallelisation took place

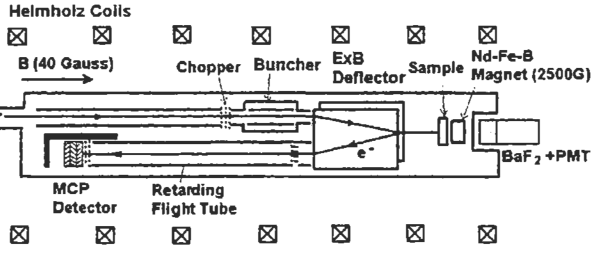

Figure 1. The schematic of the TOF-PAES apparatus.

within a few cm of the sample. Then, the electrons were separated from the incident beam with an $E\times B$ deflector, and were detected with a micro-channel-plate (MCP) detector which was placed 1 m away from the sample. The energy distributions of the electrons were determined by measuring the time of flight of the electrons. To improve the energy resolution, the electrons were retarded in a negatively-biased flight tube (0.6 m) installed between the $E\times B$ and the MCP. In the present study, Si-$L_{2,3}VV$ Auger spectra (60–90 eV) were measured at a retarding voltage Vr = -50 V. Figure 2 shows the calculated resolution functions at Vr = -50 V. For analyzing energies below 90 eV, the energy resolution (the FWHM of the resolution function) is expected to be better than 3 eV.

The sample was a Cz-Si(100) wafer (n type, P doped, 0.01 Ωcm). The surface was cleaned by repeated annealing up to 1100 °C followed by slow cooling. After the annealing, no Auger signals from contaminants such as C or O were detected by PAES. The data were taken within 1 h while the pressure was less than 2×10^{-10} Torr.

3. Results

The Si-$L_{2,3}VV$ Auger spectrum obtained with the TOF-PAES for the clean Si(100) surface is shown in Fig. 3. The count rate at the $L_{2,3}VV$ peak was ~30 cps. The spectrum showed a sharp peak at 88 eV with a smooth tail on the low-energy side. It should be noted that the measured Auger lineshape has no background of secondary electrons, because the incident positron energy (45 eV) is lower than the Auger energies. The absence of background was confirmed by measuring the PAES spectrum for the Si(100) whose surface was covered with one-monolayer of K (shown in Fig. 3). The deposition of K was done at room temperature with an alkali dispenser (SAES getters). It is known that the adsorption of alkali metals eliminates PAES signals, because almost all the surface-state positrons are desorbed from the surface as positronium [8]. The PAES spectrum for the K-covered surface clearly showed no background at energies above ~50 eV. It is also noted that the Auger lineshape obtained by PAES shows no bulk-plasmon-loss feature which is clearly seen in EAES spectra at ~70 eV [9]. This fact indicates that Auger electrons emitted from the top layer have a low probability of exciting bulk plasmons.

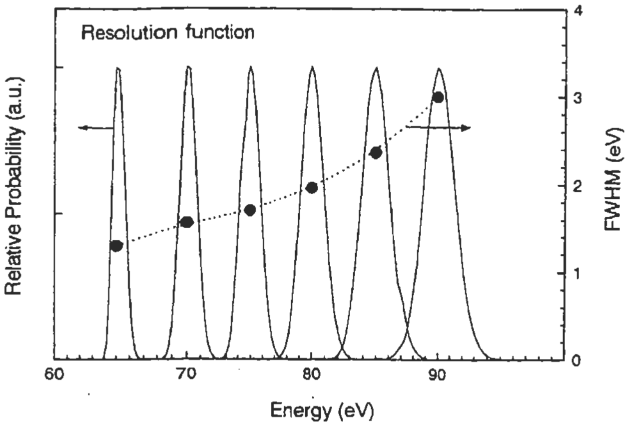

Figure 2. The calculated resolution functions at Vr = -50 V. The FWHM of the resolution functions are also plotted.

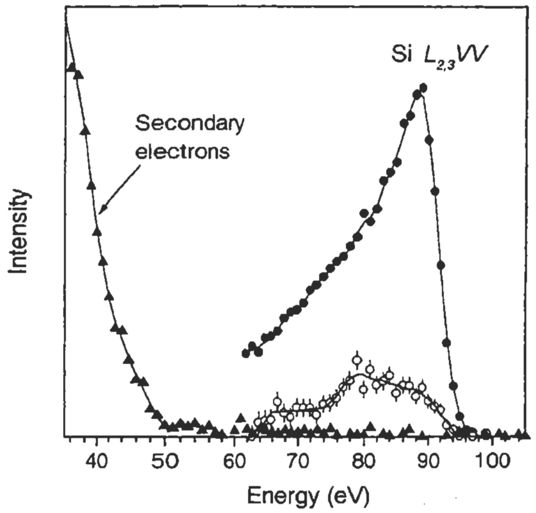

Figure 3. PAES Si $L_{2,3}VV$ Auger spectra for clean Si(100) (solid circles), Si(100) exposed to 5-L O_2 at -80 °C (open circles), and 1-ML K covered Si(100) (solid triangles).

For demonstration of the chemical analysis by PAES, we measured a PAES spectrum for oxygen-adsorbed Si(100) surface. In this measurement, the clean Si(100) surface at -80°C was exposed to O_2 gas at a pressure of 1×10^{-8} Torr for 500 sec (5 Langmuir). As can be seen in Fig.3, the intensity of the $L_{2,3}VV$ peak was attenuated significantly by the exposure. Furthermore, a large chemical shift to lower energy was observed. It is established that the peak at ~78 eV is the $L_{2,3}VV$ Auger transition associated with the valence electrons of Si-O bonds [10]. Since the PAES signal originates exclusively from the top layer as mentioned above, the chemical shift observed in the Si-$L_{2,3}VV$ peak indicates that the adsorbed oxygen has a bond with the top-layer Si atoms. The result demonstrates that the TOF-PAES could be a useful tool to study chemical bonding of the top-layer atoms.

Figure 4 compares the PAES Si-$L_{2,3}VV$ Auger lineshape with those obtained by EAES [11] and theoretical calculation [12]. The EAES spectrum shown in Fig. 4 was corrected by subtracting the background and the energy-loss contributions. For direct comparison with the present PAES spectrum, the EAES and theoretical Auger spectra were convoluted with the resolution function of the PAES apparatus (Fig. 2). The comparison clearly shows that the PAES spectrum has a large tail on the low-energy side of the main peak. In the conventional picture of CVV Auger transitions, the width of the CVV Auger peak is twice the valence-band width. For Si(100)2×1 surface, the valence-band width is ~12 eV [13]. Thus, the maximum width of the $L_{2,3}VV$ peak is expected to be ~24 eV, and Auger emission at energies below ~70 eV is forbidden. However, the PAES spectrum showed a significant intensity even at energies below 70 eV. This result indicates that Auger spectra from the top surface atomic layer cannot be explained only by a simple two-hole Auger decay process, and that some inelastic energy-loss process must occur at the surface. It is noted that the low-energy tail (LET) was reported also in the PAES Cu $M_{2,3}VV$ [3] and Ag $N_{2,3}VV$ [4] Auger spectra. Similar LET features were observed also in Auger-photoelectron coincidence spectroscopy [14]. However, the detailed mechanism of the LET has not yet been understood. Further experimental and theoretical studies are needed to clarify the origin of the LET.

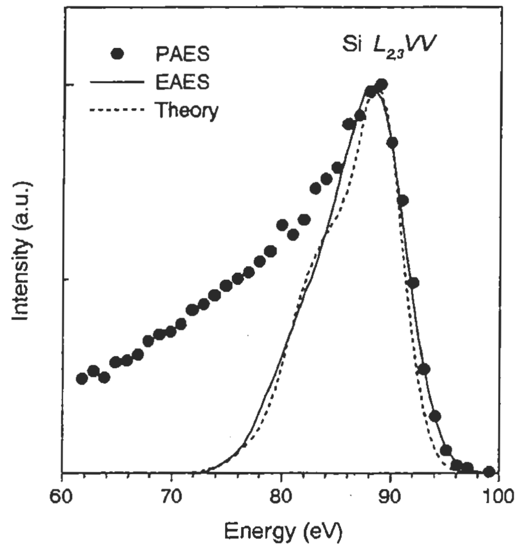

Figure 4. Comparison of the PAES Si $L_{2,3}VV$ Auger lineshape (solid circles) with loss-corrected EAES lineshape of Ref. 11 (solid line), and theoretical calculation of Ref. 12 (dotted line).

4. References

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