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Electronic structures in unoccupied states of Bi thin film studied with two-photon photoemission spectroscopy

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ABSTRACT

We have performed synchrotron-radiation angle-resolved photoemission and angle-resolved two-photon photoemission (2PPE) study of Bi(1 1 1) films with the thickness of 12 bilayers grown on Si(1 1 1) – 7 × 7. From the detailed analysis of the excitation energy dependence of angle-resolved 2PPE spectra, we have determined the electronic structures in the occupied and unoccupied regions. The observed electronic structures in the unoccupied states above the Fermi-energy were attributed to the quantum-well states originate from the quantization of the *6p*-derived bulk bands.

1. Introduction

Metallic thin films have been widely investigated for the purpose of the investigations of fundamental physics and developing many electronic devices [1–4]. In metallic thin film, the electronic bulk-band structure evolves into the discrete electronic states in the direction perpendicular to the surface by reducing the film thickness to comparable to the Fermi wavelength. The quantization arises from the standing electron-wave pattern supported by the film and depends critically on film thickness. From the view point of developing the technological applications, the quantum size effect in metallic thin-film system is considered to be suitable to control their static-physical properties. Among the various metals, Bi is prospected material for the investigation of the quantum confinement effects and for the thin-film-based electronic devices due to its small effective mass and long Fermi-length. To date the study on the quantum well states in Bi have been mainly focused on the occupied states below the Fermi-level [5–7]. In contrast to an understanding of the quantum well state in the occupied state in Bi, the reports of the quantum well state in the unoccupied state are very few to date. The scanning tunneling spectroscopy (STS) technique has been applied to observe the unoccupied electronic structure of semi metallic surface. Previously, the unoccupied electronic structures of Bi thin film studied by the STS and first-principle calculations have been reported by Yaginuma et al. [8]. They have observed the density of states around the $\bar{\Gamma}$ point, and assigned these states as the surface states. Since the quantum well states of Bi is buried in the surface-derived electronic states at $\bar{\Gamma}$ point, the unoccupied quantum well states could not be observed with STS. From their result, in order to exploit the unoccupied quantum-well-states of Bi thin film experimentally, the observation of the electronic states near the $\bar{M}$ point is required. On the other hand, two-photon photoemission (2PPE) spectroscopy has been also used as a powerful tool for investigating the unoccupied electronic structures. In 2PPE spectroscopy, the photoelectrons are excited with the lower photon-energy than work function, and are emitted through the unoccupied regions. Therefore, the measured 2PPE spectrum contains the information both of the occupied and unoccupied regions. Furthermore, by varying the detection angle of the photoelectron, we can experimentally observe the unoccupied electronic structures that locate away from the Γ point.

In this article, we have prepared the thin Bi (1 1 1) film with the thickness of the 12 bilayers (BL) grown on Si(1 1 1) – 7 × 7 by the evaporation, and performed the synchrotron-radiation angle-resolved photoemission in the valence-band region and the angle-resolved 2PPE measurement. From the detailed analysis of photoemission spectra, the electronic structures observed in the occupied and unoccupied regions are discussed.

2. Experiment

All the experiments were carried out at the Saga University beamline BL13 in the Saga Light Source (Saga-LS). The Bi films used

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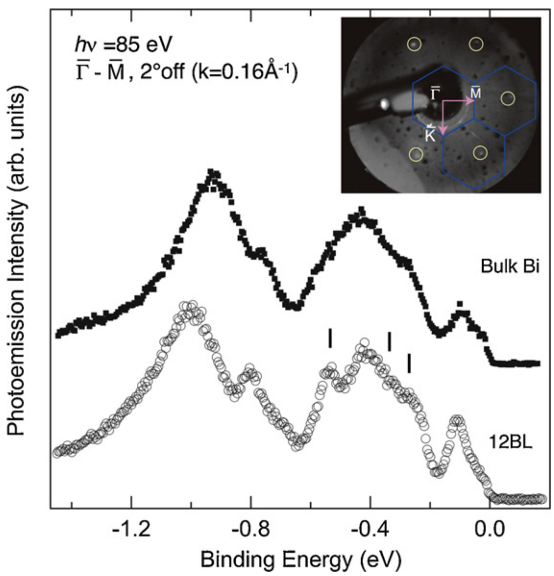

Fig. 1. Synchrotron-radiation angle-resolved photoemission spectrum in the valence-band region at 2° off from the normal emission for the thin Bi film with the thickness of 12 BL at 20 K. The excitation energy is 85 eV. The detection angle corresponds to the wavenumber of $k_{||} = 0.16$ Å^{-1} along the $\bar{\Gamma}$–$\bar{M}$ line in the surface Brillouin zone. As a reference, the photoemission spectrum of bulk Bi with the same experimental set up is also shown. The spectral features derived from the quantum confinement are indicated with the markers. Inset shows LEED image of Bi thin film with the thickness of 12 BL. Open circles highlight the LEED spots from the Bi film. High symmetry lines in the surface Brillouin zone are also indicated.

in this work were prepared in the following procedure. In a vacuum chamber, a p-type Si (1 1 1) wafer was outgassed at about 800 °C for more than 10 h. Then the Si substrate was flashed up to 1200 °C repeatedly by the direct current heating to yield a 7 × 7 reconstructed surface. Then Bi was deposited onto a Si substrate at room temperature. The deposition rates of Bi films were monitored by the quartz micro-balance. The pressure of the chamber during the deposition was kept less than 8.0×10^{-8} Pa. The deposition rate was 0.6 BL/min. In this paper, 1 BL is defined as the density of the Bi atoms in a Bi (1 1 1) plane (1 BL = 1.12×10^{15} atoms/cm^2, 3.9 Å thick) [9]. We have prepared the Bi film with the thickness of 12 BL for the photoemission measurements. As a reference, we also prepared the bulk Bi film with the thickness of about 200 BL. The crystallinity of the prepared films was checked by the low-energy electron diffraction (LEED). Fig. 1(inset) shows the LEED pattern obtained from Bi thin film with the thickness of 12 BL. High symmetry line along the $\bar{\Gamma}$–$\bar{M}$ direction in the surface Brillouin zone is also shown by the arrows. The obtained LEED image for Bi films show the sixfold patterns those indicate the growth of the (1 1 1) plane of a rhombohedral lattice.

For the photoemission measurements, we used a hemispherical electron-energy analyzer (MB Scientific, A-1) to observe the photoemission spectra with high energy resolution. The angle-resolved photoemission measurements with synchrotron radiation and angle-resolved 2PPE experiments were employed to elucidate the occupied and unoccupied electronic structures of Bi film. The synchrotron-radiation photoemission measurements for the characterization of occupied electronic structure were carried out with the photon energy of 85 eV. The 2PPE studies were performed with the second harmonic generation of the broadly energy tunable Ti:Sapphire laser (Chameleon, Coherent Inc.). The excitation energy was tuned from 2.8 to 3.6 eV. The repetition rate of laser pulse was 80 MHz. For the 2PPE measurement, the intensity of the laser pulse was limited below 0.15 nJ to avoid the space charge effect. The polarization of the light on the sample surface was p-polarized. All the photoemission measurements were carried out at 20 K to minimize the phonon derived broadening in the spectra (Debye temperature of Bi is 120 K).

3. Results and discussion

Fig. 1 shows the angle-resolved synchrotron-radiation photoemission spectra for Bi films with the thickness of 12 BL grown on Si (1 1 1) – 7 × 7 in the valence-band region excited with the photon energy of 85 eV. The detection angle was 2° off from the normal emission that corresponds to the wavenumber of $k_{||} = 0.16$ Å^{-1} along the $\bar{\Gamma}$–$\bar{M}$ direction in the surface Brillouin zone. As a reference, photoemission spectrum of bulk Bi measured at the same experimental set up is also shown. The spectral features of angle-resolved photoemission spectrum for Bi (1 1 1) with the thickness of about 200 BL was identical with the previously reported ones for the Bi (1 1 1) clean surface [10]. Therefore, the thickness of bulk Bi is large enough that the quantum-confinement effects are ignored. The photoemission spectra of bulk Bi and Bi film with the thickness of 12 BL show similar spectral features at the binding energy of 0.1, 0.4, 0.8, and 1.0 eV. From a comparison with the previous reports of the photoemission measurements for the bulk Bi, the peaks at the binding energy of 0.1 eV are assigned as the surface state, and the peaks at the binding energy of 0.8, and 1.0 eV are assigned as the *6p*-derived bulk-band states [6,10–12]. The spectral features at 0.4 eV are attributed to the surface states that located in the spin–orbit gap. On the other hand, the spectral features in the photoemission spectrum of Bi film located at the binding energy of 0.2–0.6 eV (indicated by the vertical lines) were different from those of bulk Bi. Previously, the angle-resolved photoemission measurements of Bi films with the thickness of 6.8–40 BL using He I radiation (21.2 eV) have been reported by Hirahara et al. [5,6]. They have reported the thickness-dependent spectral features in the binding energy between 0.2 and 0.6 eV at the wavenumber of $k_{||} = 0.14$ Å^{-1} along the $\bar{\Gamma}$–$\bar{M}$ direction, and have assigned these features as a quantum-well states resulting from the quantization of the bulk-band perpendicular to the surface. These quantum-well states are clearly observed at off-normal emission, while these states are difficult to discriminate from the other band structures at the $\bar{\Gamma}$ point. The spectral features of the present photoemission spectrum measured at the wavenumber of $k_{||} = 0.16$ Å^{-1} along the $\bar{\Gamma}$–$\bar{M}$ direction for the Bi films with the thickness of 12 BL in Fig. 1 are consistent with the corresponding spectra that has similar film thickness in the previous report. Therefore, the specific spectral features at the binding energy of 0.2–0.6 eV for the present Bi films are attributed to the quantum well states. The good agreement in the energy position of the quantum well states for the corresponding thickness with the previous report indicates a confirmation of the correct characterization of the thickness for the present Bi film with the thickness of 12 BL.

Fig. 2 shows the angle-resolved 2PPE spectra of Bi film with the thickness of 12 BL excited with the photon energy of 2.8–3.5 eV measured at 20 K. The excitation energies and detection angles of the emitted photoelectron are also indicated. The photoemission measurements were performed along the $\bar{\Gamma}$–$\bar{M}$ direction symmetry line in the surface Brillouin zone. The photoemission intensities were plotted as a function of intermediate energy above the Fermi-energy. In order to compensate the band bending and a laser-power dependent photo-voltage effects at the Bi–Si interface, the apparent shifts in electron energies observed in the 2PPE spectra are corrected by comparing spectra with the reference spectra measured on the bulk Bi. The intensity of each spectrum is normalized by the laser intensity. As shown in Fig. 2, the spectral features of the Bi film with the thickness of 12 BL changed with the excitation photon-energies and the detection angles of emitted photoelectron. In order to analyze the 2PPE spectra in detail, all the 2PPE