Image-potential states on the metallic (111) surface of bismuth

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Abstract. An extended series (up to \( n = 6 \), in quantum beats) of image-potential states (IPS) is observed in time-resolved two-photon photoelectron (TR-2PPE) spectroscopy of the Bi(111) surface. Although mainly located in the vacuum, these states probe various properties of the electronic structure of the surface as reflected in their energetics and dynamics. Based on the observation of IPS a projected gap in the surface normal direction is inferred in the region from 3.57 to 4.27 eV above the Fermi level. Despite this band gap, the lifetimes of the IPS are shorter than on comparable metals, which is an indication of the metallic character of the Bi(111) surface.

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1. Introduction

Bismuth and its low-energy surfaces have received increasing attention recently for their unique electronic properties near the Fermi level which to a great extent are defined by strong spin–orbit interaction. While bulk bismuth, having a very low density of states (DOS) at the Fermi level, is a semimetal, its surfaces support electronic bands which cross the Fermi level, thereby rendering the surface metallic [1]. These properties were observed with angle-resolved photoemission [2], explained using first-principles calculations [3], and, recently, confirmed with surface conductivity measurements [4].

In this paper, we report time-resolved two-photon photoelectron (TR-2PPE) spectroscopy measurements of the Bi(111) surface. Over the last decade, TR-2PPE has evolved into a widely used tool for the study of the energetics and dynamics of unoccupied electronic states. As for many metal surfaces, the 2PPE spectrum of Bi(111) exhibits distinct features due to image-potential states (IPS), i.e. electronic states due to the attraction of an electron to the surface of a polarizable medium [5]. Owing to their omnipresence and conceptual simplicity, IPS have been successfully used as probes of electron dynamics on a variety of metal surfaces and adsorbate systems [6]. Because their properties depend also on the coupling to electronic bands in the metal substrate, electronic material properties such as gaps in the projected band structure in the surface normal direction can be inferred. Furthermore, their binding energies depend on the polarizability of the material, which was first demonstrated by Cole and Cohen on condensed rare gas layers [7]. Correspondingly, for a semimetallic substrate such as bismuth which has a dielectric constant $\epsilon \approx 100$ [8, 9], a reduction of the binding energies should be expected. With respect to dynamics, the low DOS at the Fermi level of a semimetal restricts scattering with valence electrons, which is the major decay channel of IPS on atomically flat surfaces [6]. However, the measured lifetimes of IPS on Bi(111) are shorter than one would expect based on these considerations.

IPS on a polarizable medium are characterized by the following equations [7, 10]: the potential $V(z)$ at a distance $z > 0$ in front of the surface has the form of a Coulomb potential

$$V(z) = E_{\text{vac}} - \frac{e^2}{4\pi \epsilon_0} \frac{\beta}{4z},$$

(1)
where $E_{\text{vac}}$ denotes the vacuum level, $e$ the charge of the electron, and $\epsilon_0$ the vacuum permittivity. The factor

$$\beta = \frac{\epsilon - 1}{\epsilon + 1}$$

(2)
takes into account the finite polarizability of a non-metallic medium based on its dielectric constant $\epsilon$. For pure metals $\beta$ approaches 1. Bound states occur if the potential $V$ is combined with a potential barrier at $z = 0$. They form a hydrogen atom-like series of states with energies

$$E_n = E_{\text{vac}} - \beta^2 \frac{0.85 \text{eV}}{(n + a)^2}, \quad n = 1, 2, 3, \ldots$$

(3)

where $n$ is the quantum number, and the 0.85 eV corresponds to $1/16$ of the Rydberg energy. $a$ is the ‘quantum defect’ parameter which accounts for an energy shift due to the wave matching condition at the solid–vacuum interface, or, in other words, for the crystal potential $V(z)$ at $z < 0$. Like other surface states, IPS are typically supported by a gap in the projected band structure in the direction of the surface normal.

Whereas on many metals only the lowest one or two states are observed in 2PPE, we find an extended series of IPS up to $n = 6$ on Bi(111). While the lower three states are resolved directly in the energy domain, the three higher states which are located closely together are inferred from oscillations of the 2PPE signal due to coherent excitation of multiple states. Such quantum beats were first observed on the Cu(001) surface by Höfer et al [11].

2. Experimental

2.1. Sample preparation and characterization

Clean, crystalline and atomically flat Bi(111) samples are grown epitaxially in situ under ultrahigh vacuum (UHV; base pressure $\leq 5 \times 10^{-10}$ mbar) by following the method of Nagao et al [12]. Briefly, a Si(111)-7 × 7 surface is first prepared by thermal desorption of the native oxide layer from a p-type ($\rho \leq 0.5 \Omega \text{cm}$) Si(111) surface at 1400 K. An epitaxial Bi(111) thin film is formed by vapor deposition of $>10$ monolayers of Bi from a Ta crucible at a substrate temperature of 298 K, followed by annealing at 410 K. For the 2PPE experiments, the sample is cooled down to 120 K to reduce single-photon photoemission from thermally occupied states.

We verify the crystallinity of the surface by low-energy electron diffraction (LEED). Our Bi(111) samples give a sharp sixfold LEED pattern [12] (the surface can be referred to both as the (111)-plane of a rhombohedral Bravais lattice or the trigonal (0001) plane of a hexagonal lattice). Bismuth is chemically inert, and, once prepared, the surface remains clean under UHV conditions for several days. The purity is checked with Auger electron spectroscopy which does not detect any contamination. A more sensitive measure, however, is the work function as measured in 2PPE by equation (3) as described later. The average work function measured on a series of different samples is $4.27 \pm 0.05$ eV which is compatible with ultraviolet photoemission results [13].

Using epitaxial bismuth is one important factor for ensuring good surface morphology, i.e. atomic flatness over distances of the order of 100 nm [12]. On a sample cut from a single crystal, we find that the intensity and lifetimes of the IPS are significantly reduced, and the higher lying states $n \geq 3$ are below the detection limit. A complication of epitaxial Bi on Si(111) is band bending and a laser power-dependent photovoltage at the Bi–Si interface. The resulting
Figure 1. Normal emission 2PPE spectrum of the clean Bi(111) surface measured with photon energies $h\nu_1 = 4.28\text{ eV}$ (pump) and $h\nu_2 = 1.42\text{ eV}$ (probe). The bottom scale refers to the energy of the transient state with respect to the Fermi level $E_F$, whereas the top scale represents the binding energy with respect to the vacuum level (4.257 eV on this sample). The three IPS peaks are labeled with their quantum number $n$ according to equation (3).

apparent shift in electron energy is corrected for by comparing spectra with reference spectra measured on the single crystal sample.

2.2. 2PPE spectroscopy

A Ti:sapphire femtosecond laser system as described elsewhere [14] is used to generate laser pulses with a center wavelength of 870 nm, pulse duration 86 fs full-width at half maximum (FWHM), and pulse energy of 9 nJ. The output is split into two beams, one of which is frequency-tripled. Each beam passes through a pair of prisms to compensate for group velocity dispersion in the optical elements. The beams are recombined and directed collinearly and p-polarized at the sample at an angle of incidence of $\approx 60^\circ$. Photoelectrons are detected using a 100 mm hemispherical electron analyzer with an energy resolution of 35 meV and an angular resolution of 0.5°.

3. Results

3.1. Spectrum

Figure 1 displays the 2PPE spectrum of the Bi(111) surface measured with two laser pulses of photon energies $h\nu_1 = 4.28\text{ eV}$ (pump) and $h\nu_2 = h\nu_1/3 = 1.42\text{ eV}$ (probe) in coincidence. Three well-resolved peaks above 3.6 eV originate from the lowest three IPS. Their peak positions follow the typical $1/n^2$ progression of energy levels of equation (3). Peak positions obtained from Gaussian fits are summarized in table 1. Binding energies are referenced to

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Table 1. Measured and extrapolated intermediate state energies $E - E_F$ and binding energies $E_B$ of the IPS on Bi(111). Values in parentheses are extrapolated from $\Delta E_n$ fits discussed in the text. $\Delta E_n = E_{n+1} - E_n$ is the difference between two subsequent energy levels, determined from beat frequencies. The quoted error values are $1\sigma$ limits of the fit parameters. The work function is $4.257 \pm 0.003$ eV.

| $n$ | $E - E_F$ (eV) | $E_B$ (meV) | $\Delta E_n$ (meV) |
|-----|----------------|-------------|-------------------|
| 1   | $3.571 \pm 0.001$ | $685 \pm 3$ |                    |
| 2   | $4.052 \pm 0.006$ | $205 \pm 7$ |                    |
| 3   | $4.170 \pm 0.006$ | $87 \pm 7$  |                    |
| 4   | $(4.205)$        | $(51.1)$    | $18.2 \pm 0.1$   |
| 5   | $(4.224)$        | $(32.8)$    | $10.1 \pm 0.1$   |
| 6   | $(4.234)$        | $(22.8)$    |                    |

$E_{\text{vac}} - E_F = 4.257$ eV which is obtained from fitting of equation (3) as will be discussed later. The significant single-photon peak at low kinetic energy (originating from occupied as well as thermally activated states at the Fermi level) indicates that the work function is close to the UV photon energy $h\nu_1$. Since single-photon photoemission poses the risk of space charge-related distortions of the spectrum, we have compared the spectrum shown here with spectra measured at lower photon energies. The differences in binding energy for $n = 1, 2$ are negligible, whereas the higher lying states ($n \geq 3$, see below) are out of resonance with the pump pulse, and thus do not show up in the low-energy spectrum.

### 3.2. Lifetimes

In order to study the dynamics of the transient states, cross-correlation curves (intensity versus delay between pump and probe pulses at fixed kinetic energy) are measured, as shown in figure 2. The signal corresponds to the intensity cross-correlation of the two laser pulses if the lifetime of the transient state is significantly shorter than the duration of the laser pulses. This is the case for the $n = 1$ state, the correlation curve of which fits a Gaussian with a width of $161$ fs FWHM. In this curve, a slight deviation from a pure Gaussian at $t < 100$ fs arises from hot electrons in the conduction band, which will be discussed in a separate paper. The intensity of that component is small compared with the intensity of the image state, and thus does not significantly broaden the correlation curve. For the $n = 2$ and 3 peaks, the signal contains the response from the long-lived population of the intermediate state. The curves show a clear single-exponential decay after the cross-correlation peak. The decay constants indicate the lifetimes of the respective transient populations, $\tau_2 = 91 \pm 5$ fs and $\tau_3 = 212 \pm 20$ fs, where the uncertainties are estimated based on variations between different samples.

### 3.3. Quantum beats

At a kinetic energy slightly higher than that of the $n = 3$ peak (labeled $n > 3$ in figure 2) the correlation trace does not show a simple exponential decay, but it features oscillations on top of an exponentially decaying background. These oscillations reflect the beating of the
wave function between multiple image states which are coherently excited by the pump pulse. As shown in the inset of figure 3, the spectral width of the laser pulse (19 meV FWHM) is comparable with the energetic spacing between two image states, and excites a wavepacket

\[ \psi(z, t) = \sum_n a_n(t) \phi_n(z) e^{-i\omega_n t} \tag{4} \]

as the coherent superposition of the individual IPS. Here, \( \phi_n \) denotes the stationary part of the wave function of the individual IPS, and the time-dependent part oscillates at a frequency \( \omega_n \) given by the energy eigenvalue \( E_n = \hbar \omega_n \) of the stationary Schrödinger equation. The coefficients \( a_n \) define the amplitude and phase of each component of the wavepacket. Their time dependence \( a_n(t) = A_n e^{-t/\tau_n} \) models the exponential decay of the transient population due to inelastic scattering. The effect was first observed on Cu(001) and described in detail by Höfer et al [11]. In the case of Bi(111), the three-state system with \( n = 4, 5 \) and 6 sufficiently describes the observed temporal evolution, and the time dependence of the 2PPE intensity after the pump
Figure 3. Least-squares fit of the $n = 5$ correlation trace including quantum beats between the $n = 4$, 5 and 6 image states (black line). The dashed–dotted lines and the lower panel show the decaying populations $a_n^2$ of the individual states, and the contributions of the three oscillation terms, respectively. The inset compares the spectral width of the pump pulse to the energy levels of the three coherently excited image states.

Thus, the 2PPE intensity oscillates at the beat frequencies $\hbar \omega_{n,m} = E_m - E_n$ which correspond to the energy differences between the levels. Here, the coefficients $A_n$ are used as fit parameters for all time-independent coefficients such as the photoemission matrix element, and the phases are accounted for separately by the $\alpha_{n,m}$ parameters.

$I(t; \mathbf{p})$ of equation (5) with parameter vector $\mathbf{p} = (a_4, a_5, a_6, \omega_{4.5}, \omega_{5.6}, \alpha_{4.5}, \alpha_{5.6}, \alpha_{4.6})$ and $\omega_{4.6} = \omega_{4.5} + \omega_{5.6}$ is fit to the raw data using a least-squares fit in a genetic optimization scheme [15], where the $\chi^2$ function

$$
\chi^2(\mathbf{p}) = \sum_{i=1}^{N} \frac{(I_i - I(t_i; \mathbf{p}))^2}{\sigma_i^2}
$$

(6)
is minimized with respect to the experimental electron counts \(I_i\) \((i = 1, \ldots, N)\), and their Poisson errors \(\sigma_i = \sqrt{I_i}\). The result is displayed on top of experimental data in figure 2, and with detailed individual components in figure 3. We find the two beat frequencies \(\omega_{5,6}/2\pi = 2.44 \pm 0.03\) THz and \(\omega_{4,5}/2\pi = 4.40 \pm 0.04\) THz, with the uncertainties estimated from the 1\(\sigma\) level of the \(\chi^2\) function. The energy intervals which correspond to the beat frequencies are \(\Delta E_{4,5} = 18.2 \pm 0.1\) meV and \(\Delta E_{5,6} = 10.1 \pm 0.1\) meV. Considering the small uncertainties of these values, measuring beat frequencies in the time domain provides improved energy resolution over the measurement of electron energy which cannot resolve the three states. The fit function also includes exponentially decaying contributions of the individual states. However, the fit yields large uncertainties for their decay constants, which is probably due the low amplitude of the \(n = 4\) and \(6\) contributions. Among the individual components the \(n = 5\) state dominates the signal, whereas the populations of the other states are smaller. This indicates that the \(n = 5\) state is in resonance with a sharp, occupied surface state of the Bi(111) surface, and the \(n = 4\) and \(n = 6\) states are populated from the same initial state, however, at a lower rate according to the spectral profile of the laser pulse.

The results shown so far give firm evidence that the observed peaks indeed originate from IPS. We have also verified further properties of image states not shown here: all three IPS exhibit a free electron-like dispersion in momentum space parallel to the surface, they are sensitive to the polarization of the probe photon, and they are quenched easily upon adsorption of a thin layer of a dielectric with a large band gap (\(n\)-nonane).

4. Discussion

Although the wave functions of the observed image states are mainly located in the vacuum, their energies and lifetimes are closely connected to the electronic structure of the material and its surface. First of all, the image potential is quantitatively related to the polarizability of the material. Secondly, bound states in front of the surface are terminated on the material side by a projected band gap which reflects electrons in a particular region of reciprocal space. And thirdly, the lifetimes of the image states are affected by scattering processes with electrons, phonons and defects.

With respect to Bi(111), polarizability is a particularly interesting aspect since the bulk material is semimetallic, whereas the surface (consisting mainly of the top bilayer) is metallic [1]. According to equation (3), the binding energies of the IPS depend on the dielectric constant of the surface. In order to derive the dielectric constant from 2PPE experiments, we fit the measured data in two ways: first, \(E_n\) of equation (3) is fit directly to the peak positions of table 1. The vacuum level \(E_{\text{vac}}\), the \(\beta\) factor (which represents the dielectric constant \(\epsilon\)), and the quantum defect \(a\) are fit parameters. The results and their \(\chi^2\) functions are shown in the left panel of figure 4. \(\chi^2\) is calculated analogous to equation (6) except that, here, the data points are energies. The error estimates \(\sigma_i\) are quoted in table 1. The best fit is obtained if \(\beta\) is fixed at 1 (\(\epsilon = \text{metallic}\)), and if the \(n = 2\) and \(3\) data points are included only. However, as can be seen in the figure, the \(\chi^2\) function is flat in the interval \(\epsilon > 100\), and thus, the metallic and semimetallic cases cannot be distinguished with proper statistical significance. As another shortcoming, this result does not fit the energy differences \(\Delta E_{4,5}\) and \(\Delta E_{5,6}\) obtained from quantum beat spectroscopy. To resolve this problem, in a second approach, we fit the energy differences \(\Delta E_n = E_{n+1} - E_n\) instead of absolute energies. This way we can include the measured quantum beat energies, and the fit now has just two parameters: \(\beta\) and \(a\). The
results are shown in the right panel of figure 4. The best fit is obtained for $\beta = 0.989 \pm 0.020$, and $a = 0.036 \pm 0.063$ if, again, the first data point is ignored. In terms of dielectric constant this result corresponds to $\epsilon = 187 \pm 361$. Thus, the mean value appears to be higher than the bulk value, indicating a slight enhancement of the surface polarizability as opposed to the bulk value. However, given the large uncertainty, such a conclusion is not statistically significant. In other words, the measured IPS energies do not unambiguously identify either the metallic or semimetallic case.

As mentioned before, including the $n = 1$ data point results in a significantly worse fit (broken lines in figure 4) with both fit models. This is because the fit model assumes that the quantum defect $a$ is constant over the whole range of the IPS series, whereas, in fact, it varies continuously from $1/2$ at the p-like bottom to 0 at the s-like top of the projected band gap [10]. Based on its binding energy, and $\beta$ and $E_{\text{vac}}$ derived from the best fit of $n \geq 2$, the quantum defect of the $n = 1$ state is $0.10 \pm 0.04$. For $n \geq 2$, it drops to $\approx 0.04$ as discussed above. Considering the variation of $a$ across the gap, the small measured values $a \lesssim 0.1$ on Bi(111) indicate that the image states are located in the upper half of the band gap. With the observed energy range of the IPS, a band gap which spans at least the range between 3.57 and 4.27 eV is expected. Most likely it is even larger, especially at the lower end. In figure 5, we compare our experimental findings with two common band structure calculations, one by Liu and Allen in the TB model [18], and the other one by Gonze et al in DFT [17]. Both calculations are shown along the $\Gamma T$-direction which corresponds to the (111)-axis, the axis of detection in
Figure 5. Comparison of 2PPE initial and intermediate state levels to ultraviolet photoemission spectroscopy (UPS) data \[2, 16\], density functional theory (DFT) band structure \[17\], and tight-binding (TB) calculation \[18\]. The band structures were calculated along $\Gamma T$. The shaded blocks outline the projection along $\Gamma T$ which corresponds to the (111)-axis.

Our 2PPE experiments. While the TB calculation predicts a band gap above 1.7 eV, the lower gap boundary of the DFT calculation (4.1 eV) seems too high when compared with the energy of the $n = 1$ IPS (3.57 eV). As to the upper boundary of the gap, the calculations do not include higher lying bands. Experimentally, Ast and Höchst have determined the onset of a final state band in UPS at 6.7 eV \[16\]. This bulk band may constitute the upper boundary of the band gap.

The lifetimes of the IPS are related to their energetic position in the gap because proximity to the gap boundaries leads to hybridization with bulk states and thus reduced lifetime. The other significant decay process is scattering with valence band electrons \[6\]. As discussed above, the IPS on Bi(111) lie well within the gap. If the DOS at the Fermi level was indeed as low as for bulk bismuth, one would expect long lifetimes. However, even on the metallic Cu(001) which has comparable gap size and IPS alignment, the lifetimes are longer: 40, 120 and 300 fs for $n = 1, 2$ and 3, respectively \[19\]. Hence, the shorter IPS lifetimes are likely another manifestation of the enhanced DOS, and thus the metallic character of the Bi(111) surface.

The Bi(111) surface is one of only few surfaces where quantum beats in the image state are observed. This has to do with several restrictive requirements on the electronic structure. First of all, IPS must be observable and have lifetimes which are longer than the oscillation periods of $\approx 200$ fs. Further, at the time of excitation the wavepacket must be spatially confined because the intensity oscillations arise due to the spatial oscillations of the wavepacket and the $z$ dependence of the photoemission matrix element \[11\]. Indeed, like on Cu(001), this initial spatial confinement is achieved on Bi(111) by excitation from an occupied surface state at $\Gamma$ which has been observed in ultraviolet photoemission at 0.2–0.3 eV below the Fermi level \[3, 20\], as indicated in figure 5.

Our findings may as well compare to the structurally and electronically similar antimony. Using inverse photoemission, Straub and Himpsel reported a binding energy of $0.76 \pm 0.1$ eV for the $n = 1$ IPS on Sb(111) \[21\]. This value is, considering the error limits, just slightly higher than our result on Bi(111).
5. Conclusions

Like many metallic surfaces, Bi(111) supports a series of IPS which show up as intense peaks in 2PPE spectra. They are supported by a gap that includes at least the energy range from 3.57 to 4.27 eV in the unoccupied projected band structure along Γ\textsubscript{T}. Although the binding energies of IPS can in principle be a measure for the polarizability, the effect on Bi(111) is too low to be distinguishable from the bulk value. However, the relatively short lifetimes compared with e.g. copper are indicative of an enhanced DOS near the Fermi level.

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