Direct observation of band bending in topological insulator Bi$_2$Se$_3$

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The surface band bending tunes considerably the surface band structures and transport properties in topological insulators. We present a direct measurement of the band bending on the Bi$_2$Se$_3$ by using the bulk sensitive angular-resolved hard x-ray photo spectroscopy (HAXPES). We tracked the depth dependence of the energy shift of Bi and Se core states. We estimate that the band bending extends up to about 20 nm into the bulk with an amplitude of 0.23–0.26 eV, consistent with profiles previously deduced from the binding energies of surface states in this material.

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Topological insulators (TIs), a new quantum state, are characterized by robust metallic surface states inside the bulk energy gap, which are due to the topology of bulk band structures. A large amount of efforts were devoted to observe the topological surface states of many TI materials (and references therein) by surface-sensitive experiments. Specially, Bi$_2$Se$_3$ is one of the most extensively studied TI materials because of its simple Dirac-type surface states and large bulk gap.

Surface band bending (SBB) effects of Bi$_2$Se$_3$ has been commonly observed in angle-resolved photoemission spectra (ARPES) and transport measurements. The SBB is usually caused by surface degrading in ambient environment and surface doping, with a downshift of the surface Dirac point, indicating an electron-doped surface. SBB induces a quantum confinement and modifies the surface and bulk bands dramatically. A clear feature of SBB in Bi$_2$Se$_3$ is a pair of Rashba-splitting bands above the Dirac cone. In transport experiments, SBB is also supposed to affect the measurement in a considerable way by directly tuning the bulk and surface charge carrier densities. So far, this surface band bending has only been deduced from Rashba-splitting of the conduction bands measured by ARPES, that is mainly sensitive to several surface atomic layers, although SBB is predicted to extends in an order of 10 nm distance from the surface into the bulk. A direct measurement of SBB from the surface into the bulk region is yet to be performed.

In this Letter, we reported the direct observation of SBB on the Bi$_2$Se$_3$ surface by HAXPES, a bulk sensitive method. The hard x-ray excitation ($\sim$8keV) produces photoelectrons with high kinetic energy and consequently high inelastic mean free path ($\lambda$) resulting in an enhanced probing depth. HAXPES has been successfully utilized in the study of Heusler TIs. The SBB can be directly measured in photoelectron spectroscopy by controlling the escape depth in the photoemission process to track the depth dependence of core level energies. Such controlling can be achieved by changing the photon energy and consequently the inelastic mean free path, as demonstrated by Himpsel et al. for low photon energy regime. The precision of this approach however depends on the energy distribution and the determination of the Fermi edges for different photon energies. Here, we propose the angular resolved HAXPES as an alternative to control the photoelectron escape depth, keeping constant all the experimental parameters: photon energy, incidence angle and probed region. This is possible thanks to the high energy wide-acceptance objective lens setup specially developed for this purpose. The objective lens enlarges the effective acceptance allowing the measurement of the photoelectron angular distribution with a fixed incident angle. In this work, we measured the angular distribution of the photoemission of Bi$_2$Se$_3$ core levels, from where we observed the electric potential variations from bulk to surface.

Figure 1: (a) Schematic of the experimental geometry. The angular distribution of photoemission is simultaneously measured in the range from 0 (normal) to 60°, being related with the electron escape depth $\lambda^0$, where $\theta$ represents the emission angle. (b)Model for SBB in Bi$_2$Se$_3$, where $\Delta V$ represents the bending amplitude. (c) Representation of normal photoemission of Se 2p$_{3/2}$. The vertical bars indicates the depth-dependent contribution of Se 2p$_{3/2}$ to the normal photoemission.
Bi$_2$Se$_3$ single crystals were synthesized from stoichiometry mixture of high purity (> 99.99%) of bismuth (Bi) and selenium (Se). The elements were sealed in a dry quartz ampoule under a pressure of 10$^{-6}$ Torr. The sealed ampoule was loaded into a vertical furnace and heated to 800°C at a rate of 60°C/hour followed by 12 hours soaking. For a single crystal growth, the temperature was slowly reduced from 800°C to 500°C and thereafter by 100°C/hour to room temperature. This procedure resulted in silver-colored single crystals size of 10 mm.

For HAXPES measurements, the crystal sample was exfoliated and kept in the air for few seconds in order to ensure the saturation of adsorption process at surface, in such a way to eliminate any time-dependent effect. The experiment was performed at BL47XU at Spring-8 (Japan) using 7.94 keV photon energy and π-linearly polarized light. The energy and angular distribution of the photoexcited electrons was analyzed using a high energy VG Scienta R4000-HV hemispherical analyzer. The objective lens, set in front of the analyzer, enlarge the effective acceptance angle to about 60° with an angular resolution of 1°. The homogeneity and precision of the system was checked by mapping the angular distribution of Au 4f peaks. The overall energy resolution was about 230 meV. The angle between the electron spectrometer and the photon propagation was fixed at 90°. Incoming photons was set to impinge on the sample at 60° from its surface normal, in such a way that the angular distribution of incoming electrons is measured from -2 to 62° with respect to the sample normal. Sample temperature was kept at 40 K. Figure 1 illustrates how the depth profile of core shift can be extracted from the angular distribution of the photoemission by considering an effective escape depth $\lambda^0 = \lambda \cos(\theta)$, being $\theta$ the emission angle. Figure 1a and 1c show the relationship between SBB and the depth dependence of a core level energy shift. The vertical bars in Figure 1c indicate the energy position of the Se 2p$_{3/2}$ peak for different depths. $\Delta V$ represents the bending amplitude in both figures. The depth dependence of the energy shift of core levels mimics the band bending profile.

Symbols in Figure 2 represent the experimental energy distribution curves (EDC) for Se 2p$_{3/2}$ and Bi 3d$_{5/2}$ core state photoemission. The spectra are summed up over slices of ±2° about the photoemission direction indicated by the label on the right of each curve. The curves were normalized by the peak intensity. Direct inspection of the EDC indicates an energy shift in the core level peaks, as represented by the solid curved line. A total shift of -75(1) meV from $\theta = 0°$ to $\theta = 60°$ for both Se 2p$_{3/2}$ and Bi 3d$_{5/2}$ peaks was determined by Voigt function fitting. $\lambda$ is calculated by TPP-2M formula to be $\lambda_{Bi} = \lambda(5.3keV) = 8.7nm$ and $\lambda_{Se} = \lambda(6.5keV) = 9.4nm$ for Bi3d$_{5/2}$ and Se2p$_{3/2}$ respectively. Providing the large electron escape depth and kinetic energies, the measured EDC can only be originated by a bent potential which extends from surface up to a distance of the same order of magnitude than $\lambda$. Therefore, the observed shifts indicate that bulk-core levels ($z > z_i$) have smaller binding energy than core-levels near to the surface ($z \sim 0$). This remarkable result consists in the direct observation of the band bending in Bi$_2$Se$_3$, indicating a downward bending from bulk to surface.

For a quantitative analysis, we model the angular distribution $I(\theta, E_k)$ by the following equation:

$$I(\theta, E_k) = \int_0^\infty dz \ e^{-z/\lambda \cos(\theta)} \left[ L(\Gamma, b, E_0(z)) + I_0 \right]$$  

where $I_0$ represents the constant background, and $L$ is a Lorentzian function. The Lorentzian shape is given by $\Gamma$ and $b$, representing the background asymmetry and spectral linewidth respectively. The peak is centered in different energies $E_0$ according to the depth position $z$. $E_0(z)$ mimics the band bending (see Figure 1).
The band bending depth profile depends on detailed characteristics of the charge distribution near the surface. As simplest approach we modeled the band bending profile as a quadratic function, extending for a distance \( z = z_l \) from the surface \( (z = 0) \). This approach allows the evaluation of the extension \( z_l \) and strength \( \Delta V \) of the band bending in Bi\(_2\)Se\(_3\) by refining \( E_0(z) \):

\[
E_0(z) = \begin{cases} 
\Delta V (z - z_l)^2 + E_0^{bulk} & z < z_l \\
E_0^{bulk} & z \geq z_l
\end{cases}
\] (2)

For comparison with the experimental data, the calculated spectra \( I(\theta, E_k) \) were convoluted with a Gaussian representing the total energy resolution (FWHM=230 meV). The curves were refined by the minimization of the mean square error (MSE). The optimized parameters for Se 2p\(_{3/2}\) and Bi 3d\(_{5/2}\) peaks are shown in Figure 3. The energy shift profile mimics the band bending in the Bi\(_2\)Se\(_3\).

### Table I: Optimized parameters for Bi 3d\(_{5/2}\) and Se 2p\(_{3/2}\) peaks. The variation of \( E_0(z) \) from bulk value is shown in Figure 3.

| Parameters | Bi 3d\(_{5/2}\) | Se 2p\(_{3/2}\) |
|------------|----------------|----------------|
| \( E_0^{bulk} \) | 5359.52 eV | 6507.40 eV |
| \( \Gamma \) | 2.47 eV | 1.20 eV |
| \( b \) | \(-0.40 \times 10^{-2}\) | \(-3.20 \times 10^{-2}\) |

Figure 3: (Color online): Energy shift depth profile for Se 2p\(_{3/2}\) and Bi 3d\(_{5/2}\). The energy shift profile mimics the band bending in the Bi\(_2\)Se\(_3\).
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