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Application of Synchrotron Radiation to Study the Surface Atomic Structure of 2d Materials

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Abstract. In this paper, the current state of X-ray photoelectron diffraction and holography methods are considered. A brief overview of surface research methods is given. The photoelectron diffraction method is attractive for use because of its sensitivity to the chemical environment, as well as its large depth of analysis (units of nanometers). The paper presents the application of methods for studying the atomic structure of bismuth chalcogenides Bi_2X_3 (X: Se,Te). The results of the holography were verified by theoretical modeling of diffraction patterns using the EDAC algorithm.

INTRODUCTION

The study of the surface is a topical issue. In various fields of science, the concept of surface can be interpreted in different ways. So, what a surface is? In surface science the surface is an interface between two phases (vacuum and solid) where physical and chemical processes are studied. The characteristic surface size is several atomic layers. Understanding surface phenomena requires knowledge of the types of atoms, their positions, binding mechanisms, and so on. The objects of research here are films, ultrathin films, multilayer systems, and various coatings. In this article, we will consider the study of the atomic structure of topological insulators Bi_2Se_3 and Bi_2Te_3 by X-ray photoelectron diffraction (PD) and holography (PH). The article is structured as follows: section 1 will briefly describe the main methods of surface investigation. In section 2, some mathematical calculations of the method of photoelectron holography will be given. Section 3 contains information about the systems under study. Finally, section 4 shows the results of reconstruction of the atomic location.

1. SURFACE RESEARCH METHODS

Currently, there are many modern well-developed methods of surface analysis. In this section, we will describe the most used methods of surface investigation. Note that among the methods described below, synchrotron radiation is required for Photoelectron Diffraction (PD), EXAFS, and ARPES. Low Energy Electron Diffraction (LEED) is widely used for surface analysis. A significant drawback of LEED is the lack of information about atomic identity.

X-ray absorption spectroscopy methods are now also widely used for surface properties research. Here we can highlight the SEXAFS method, which is a surface analog of the EXAFS method. Synchrotron radiation also allows to use another advantage – spin polarization.

In 1986, Binning and Rohrer won the Nobel prize for their invention of a new class of electron microscopes, the scanning tunneling microscope. [1] Since then, this has continued to evolve, forming new subtypes of microscopes, such as the atomic force microscope. The main disadvantage is the lack of information about the underlying layers.

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The Auger Electron Diffraction (AED) and X-ray Photoelectron Diffraction (PD) methods are close relative. There are two operating modes in PD: scanned-angle PD and scanned-energy PD. The first of them works at constant energy with changes in the polar and azimuthal angles. The second mode, is a changing of the energy of photons, respectively. It follows that PD can be performed without radiation under laboratory conditions in the scanned-angle mode.

TABLE 1. Comparison of widely used methods for studying the surface [2]

	Scanned-angle PED	Scanned-energy PED	AED	LEED	EXAFS	STM/ AFM
Type of atoms	+	+	+	-	+	-
Chemical state specific	+	+	+	-	+	-
Bond direction	+	+	+	-	+	+
Bond distances	+	+	+	-	-	+
Adsorption site symmetries	+	+	+	-	-	+
Coordination number	+	+	+	-	-	+
Position accuracies, A	0.05	0.05	< 0.05	0.05	*	0.3
Short-range order (10-20 A)	+	+	+	-	+	+
Long-range order (> 100 A)	-	-	-	+	-	+
Synchrotron radiation	-	+	-	-	+	-

Based on the comparison table, it is clearly visible that XPD and AED diffraction methods are perfectly suitable for surface research. Radiation for the above methods is only required for scanned-energy PD, but the most effective surface study can be obtained using scanned-angle PD with energy changes, i.e., the combined use of two PD modes. This type of scanning, both in angle and energy, has certain advantages. For example, in the high-energy region, the direct focus effect prevails, and when the energy decreases, the backscattering effects increase. Joint research allows us to study the surface more comprehensively.

X-ray photoelectron diffraction can be applied to the determination of atomic arrangements also for impurity atoms occupying specific sites in the crystal lattice, and adsorbed atoms on metal surfaces and semiconductor surfaces, as well as adsorbed molecules, overlayers, epitaxial films, surfactants, and interfaces on the crystal surfaces. Exfoliated graphene flakes, quasi-crystal surfaces have also been examined [3].

2. X-RAY PHOTOELECTRON HOLOGRAPHY

John J. Barton proposed an approach in which photoelectron diffraction can be interpreted as a holography, and the result of diffraction (a diffraction pattern) can be considered as a hologram. Thus, a 3D reconstruction of the solid surface is possible from a two-dimensional diffraction pattern [4]. To date, photoelectron holography has significantly advanced and has its own set of methods. One of the most advanced is the method proposed by the Matsushita group, SPEA-MEM. The method is formed by two components: the Scattering Pattern Extraction Algorithm, in which the key feature is the use of the scattering pattern function (SPF), and the iterative maximum entropy method, which minimizes the error of calculations [5-7].

A photoelectron hologram can be recorded as follows:

$$\chi(\vec{k}) = I(\vec{k}) - I_0(\vec{k}) = \sum_L \left| \varphi_L(\vec{k}) + \sum_h \psi_L(\vec{k}, \overrightarrow{a_h}) \right|^2 - \sum_L \varphi_L(\vec{k}),$$

$I(\vec{k})$ and $I_0(\vec{k})$ the intensity of the scattered and non-scattered photoelectron, respectively, and functions $\varphi_L(\vec{k}), \psi_L(\vec{k}, \overrightarrow{a_h})$ are wave functions of the emitter wave and the scattered wave, respectively.

2.1 Scattering Pattern Extraction Algorithm part of algorithm

Matsushita group introduces the atom distribution function $g(\vec{a})$ and the scattering pattern function (SPF) $t(\vec{k}, \vec{a})$, which describes the hologram pattern caused by the scattering atom. The image of an atom is given by $|\vec{a}|g(\vec{a})$.

$$\chi(\vec{k}) = \int t(\vec{k},\vec{a})g(\vec{a})d\vec{a}$$
$$\chi = T \cdot G$$
$$t(\vec{k},\vec{a}) \equiv |\vec{a}| \sum_{L} 2\Re[\varphi_L(\vec{k})\,\psi_L(\vec{k},\overrightarrow{a_h})] + |\psi_L(\vec{k},\overrightarrow{a_h})|^2$$

In this model, the forward focusing peak direction and the center of the interference rings indicate the direction of the scattering atoms, and the frequency of the interference rings indicates the atomic distance between the emitter and the scattering atom. In the backscattering region, SPF is easily affected by thermal fluctuations and fluctuations in the position of the atom.

2.2 Maximum entropy method part

The atomic image can be obtained by solving the equation above. The entropy maximum method was proposed as a solution. Error of the hologram ($\chi_e(\vec{k})$)) calculated as the difference between the experimental ($\chi_m(\vec{k})$) and calculated by holograms. Adjusted entropy with the use of the hologram errors is defined as

$$S = -\sum_{j}^{M} g^{(n)}(a_j) \ln \frac{g^{(n)}(a_j)}{g^{(n-1)}(a_j)} - \lambda C$$
$$C = \frac{1}{N}\sum_{i}^{N} \frac{\left|\chi_e(\vec{k})\right|^2}{\sigma^2} - 1 = \frac{1}{N}\sum_{i}^{N} \frac{\left|\chi_m(\vec{k}) - \chi(\vec{k})\right|^2}{\sigma^2} - 1$$

where n is the number of iterations, σ is the standard deviation of the noise of the experimental hologram, and N and M are the number of sampling points of the hologram and the number of voxels of the atom distribution function, respectively. The calculation procedure looks like this:

1) $g(\overrightarrow{a_j})$ is initially set to 1.
2) the gradient function of the root-mean-square error C is calculated using the error hologram.
3) $g(\overrightarrow{a_j})$ is corrected using the maximum entropy method using a gradient function.
4) steps (2) and (3) are repeated until the atomic distribution function $g(\overrightarrow{a_j})$ converges.

Photoelectron holography is more effective with multiple diffraction patterns. Therefore, the use of radiation is necessary, and in multi-energy mode it is obtained better.

3. RESEARCH SYSTEM AND EXPERIMENTAL DETAILS

This paper contains a reconstruction of the local arrangement of atoms of topological insulators, namely, the layered compounds of bismuth chalcogenides Bi2Se3 and Bi2Te3. Quintuple layer (QL) slabs (X-Bi-X-Bi-X), which followed by a van der Waals (vdW) gap, of these compounds is shown in figure 1. It was shown in [8] these materials have a Dirac cone in the band gap at the point Γ. For Bi2Se3 semiconductor energy gap is about 300 meV and Bi2Te3 energy gap in range 100-150 meV. Bi_2Se_3 and Bi_2Te_3 n-type single crystals were grown using the Bridgman method. Single crystals and epitaxial films of Bi_2X_3 chalcogenides (X: Te,Se) were provided for research by Prof. L. Yashina. Measurements were carried out at the U49-2 PGM1 at Helmholtz-Zentrum Berlin. The p-polarized synchrotron radiations to incident on the sample surface at an angle of 40 ° were used. The energy resolution of the monochromator separating the hv line from the continuous spectrum of synchrotron radiation is about 200 meV. To carry out measurements by photoelectron holography and diffraction on the U49-2 PGM1 line, an original electronic spectrometer with a toroidal analyzer was installed for ARPES studies with high resolution [9]. A feature of the toroidal analyzer is the simultaneous registration of photoelectrons in a fixed range of kinetic energies at polar angles of ± 90 ° relative to the normal to the sample surface with a resolution of 0.5 °. Changing the azimuthal angle is achieved by rotating the sample around the normal to its surface with a step of 1 ° in the range of at least 180 °. The area of kinetic energies is limited to 50 channels, i.e. at a scanning step of 0.1 eV, it is 5 eV. This approach allows one to drastically reduce the measurement time and obtain complete 2π-pictures with a high angular resolution.

The surface of Bi_2X_3 layered crystals is prepared by cleaving in vacuum along an inter-QL plane, forming chemically pure and structurally perfect surfaces Bi_2Se_3 and Bi_2Te_3 [10].

Topological insulators differ from classical insulators in that the latter are completely insulators, while topological insulators exhibit dielectric properties in volume, and the surface is conductive. Topological states of materials are a relatively new field of spintronics which is currently being actively developed. Among the main applications are quantum computers, spin field-effect transistors, and devices based on spin memory.

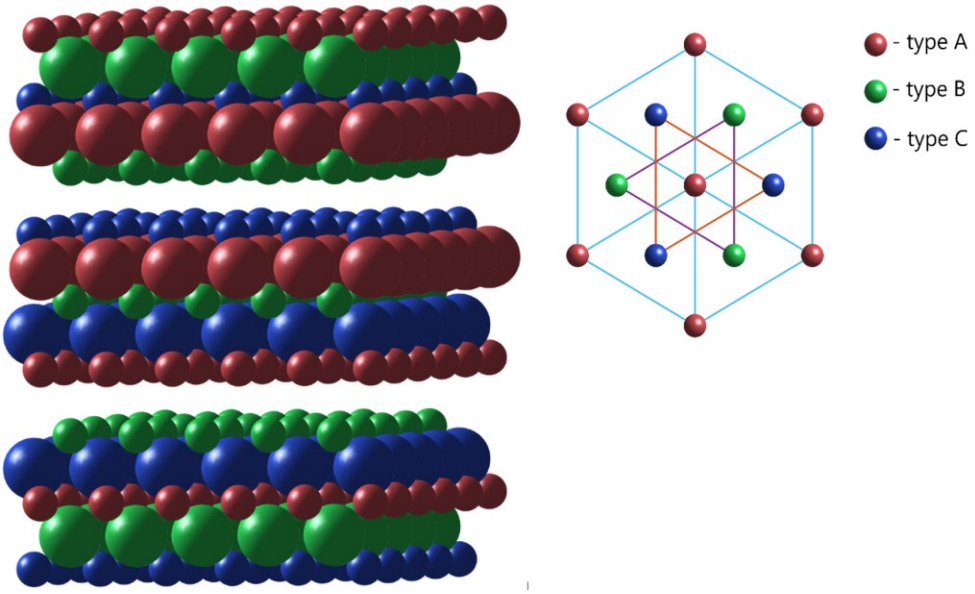

FIGURE 1. The unit cell of the Bi2Te3 crystal comprised of four QLs and belonging to the space group R$\bar{3}$m.

4. RESULTS AND DISCUSSION

In this section, we will briefly discuss the results of reconstruction of the atomic environment. Figure 2 shows a hologram, which made in multi-energy mode. One of the features of a multi-energy hologram is a more distinct image and the absence of artifacts.

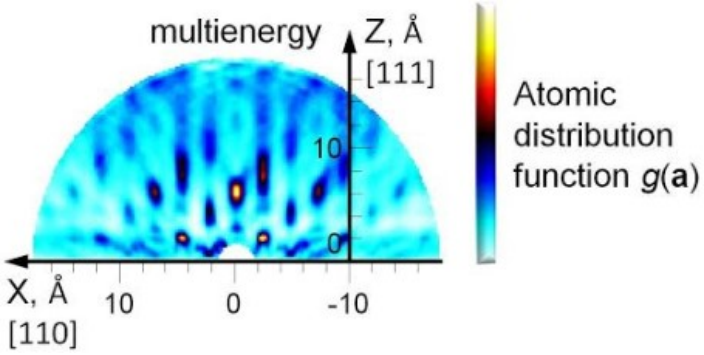

FIGURE 2. The multi-energy format of hologram. The multi-energy format of the photoelectron holography method allows to analyze the structure of the immediate environment both above and below the emitter atom

Figure 3 shows experimental diffraction patterns performed at different energies (165, 305, 646 and 846 eV). According to Barton, these diffraction patterns, presented in stereographic form, are taken to be experimental holograms. When analyzing diffraction patterns, it can be seen that artifacts appear in the upper part of the image in the region of high kinetic energies. This indicates that it is possible to restore the position of atoms at a large distance from the emitter, compared with low kinetic energies.

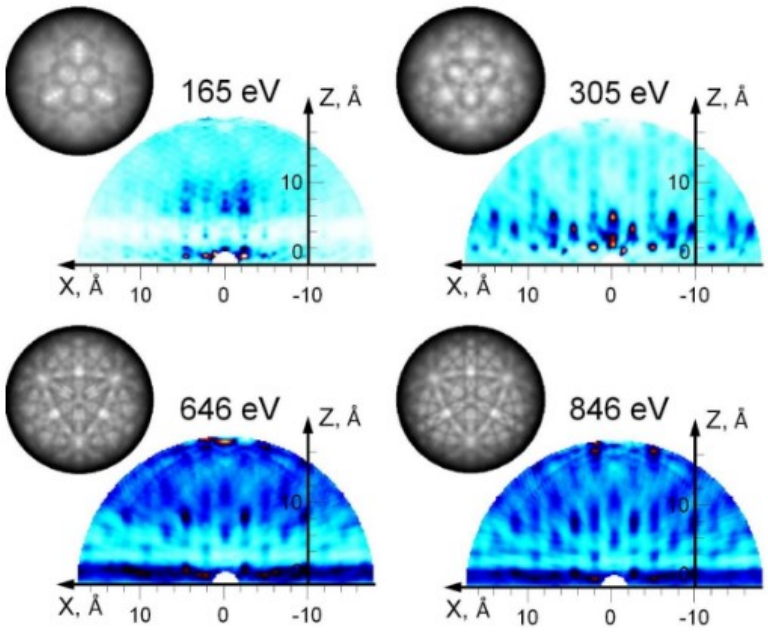

FIGURE 3. Experimental hologram Se 3d performed at energies 165, 305, 646 and 846 eV

Figure 4 shows the result of reconstruction of the Bi2Se3 surface from a two-dimensional image (diffraction pattern) to real space. The green color corresponds to the Se atoms and the red color corresponds to the Bi. The location of the atoms was obtained using the SPEA-MEM algorithm.

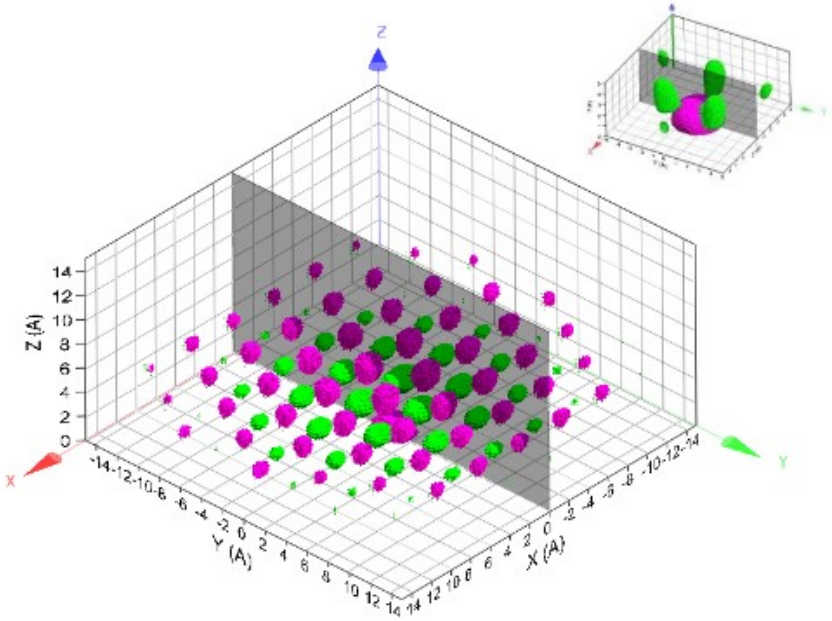

FIGURE 4. Result of reconstruction of Bi2Te3 chalcogenide using the SPEA-MEM algorithm. The upper-right corner shows the atomic image of Se as the emitter atom.

To verify the results of the reconstruction was performed the simulation algorithm EDAC (Electron diffraction in atomic cluster) developed by F. Javier Garcia de Abajo, M.A. Van Hove and C.S. Fadley [11]. This approach involves building an atomic cluster with the necessary parameters set of atomic cluster and radiation.

CONCLUSION

In this paper, it was shown that the study of the atomic environment of the surface can be effectively achieved by photoelectron diffraction. To do this, the experimentally obtained diffraction pattern can be considered as a hologram, opening the possibility to study the surface using holographic methods. The paper considers the approach proposed by the Matsushita group (SPEA-MEM) to topological insulators Bi_2X_3 (X: Se, Te). Thus, the inverse problem of reconstruction of the atomic environment was solved.

Currently, the authors see the development of the method of spin-polarized photoelectron holography (SPPH). This will allow us to study near-surface magnetism in various types of nanostructures, for which the magnetic order may differ significantly from the order of the corresponding bulk materials.

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