High-resolution x-ray diffraction of epitaxial bismuth chalcogenide topological insulator layers

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Abstract

Stoichiometry and lattice structure of epitaxial layers of topological insulators Bi₂Te₃ and Bi₂Se₃ grown by molecular-beam epitaxy is studied by high-resolution x-ray diffraction. We show that the stoichiometry of Bi₂X₃₋δ (X = Te, Se) epitaxial layers depends on the additional flux of the chalcogens Te or Se during growth. If no excess flux is employed, the resulting structure is very close to Bi₁X₁ (δ = 1), whereas with a high excess flux the stoichiometric Bi₂X₃ phase is obtained. From the x-ray data we determined the lattice parameters of the layers and their dependence on composition δ, as well as the degree of crystal quality of the layers.

Keywords: topological insulators, epitaxy, high-resolution x-ray diffraction

Classification numbers: 1.00, 4.10, 4.11

1. Introduction

Topological insulators represent a new class of materials exhibiting unique electronic properties. Their bulk electronic structure corresponds to a conventional insulator with an open band gap, while at the surface a gapless two-dimensional (2D) topological surface state (TSS) is formed exhibiting a Dirac-like momentum-energy dispersion and spin-momentum locking [1–3]. In the prototypical bismuth chalcogenide topological insulators Bi₂X₃ (X = Te, Se), the surface states are topologically protected by time-reversal symmetry and are immune to surface impurities and backscattering. The bismuth chalcogenide topological insulators exist in a variety of rhombohedral/ hexagonal phases with different stoichiometric composition BiₚXₙ (denoted (mn) in this work) [4–6]. This creates a homologous series of structures that differ in the atomic layer stacking sequences. In this paper we use the hexagonal 4-index notation of crystallographic planes and vectors in reciprocal space, which follows from the hexagonal elementary unit cell; this representation is used instead of the rhombohedral description. The (mn) phases differ in the sequence of Bi and X basal (0 0 0 1) atomic planes along the c-axis of the lattices, however, only the (23) phase exhibits the topologically protected surface states.

Every ideal (mn) phase can be described as a sequence of X-Bi-X-Bi-X quintuple layers (QLs) and Bi–Bi double layers (DLs) [6]. In particular the most prominent (23) phase contains only QLs weakly bonded by van der Waals forces. Other phases like (43), (11), and (45) contain a certain number N of QLs between two subsequent DLs as exemplified by figure 1. Thus, N is related to (mn) by stoichiometry considerations by the simple relation:

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\( \frac{2}{3m/n - 2} = \frac{3}{\delta} - 1 \)  

Figure 1 show crystal structures of phases (23), (11), and (43), where the Bi–Bi DLs are highlighted as shaded areas, the elementary unit cells are denoted by black rectangles.

A number of works has been devoted to the investigation of bulk Bi\(_m\)X\(_n\) crystals, an extensive database of the results can be found in [9–13]. However, little is known about the real structure and crystal quality of Bi\(_m\)X\(_n\) thin films grown by molecular beam epitaxy (MBE). In our previous papers [14–16] we investigated the crystal structure of MBE grown epitaxial Bi\(_2\)Te\(_3\) and Mn-doped Bi\(_2\)Te\(_3\) layers using high-resolution x-ray diffraction (HRXRD) and x-ray absorption spectroscopy (EXAFS) and angle-resolved photoelectron spectroscopy (ARPES). We found that the chemical composition, crystal structure as well as the crystal quality substantially depend on the excess flux of Te during the MBE growth. In this paper we present a comparison of HRXRD results on Bi\(_m\)Te\(_n\) and Bi\(_m\)Se\(_n\) series (lower panel) measured in symmetric (23) and (11) phases, respectively (see below). Peaks denoted ‘S’ are the diffraction maxima of the BaF\(_2\) substrate. The shape of the diffraction curves considerably changes with the chalcogen to bismuth flux ratio. With increasing Se flux, some peaks strongly change their position; for instance the maximum at 000.17 in the (11) phase converts to 000.21 in the (23) phase in both investigated material systems. Some peaks remain almost unchanged—for instance, the 000.12 peak of the (11) phase, which is equivalent to 000.15 in the 23 phase; some pairs of peaks merge creating a strong peak in the (23) phase—for instance the 000.9 and 000.10 peaks of the (11) phase merge to 000.12 in the (23) phase. For Bi\(_m\)Te\(_n\), the peaks 000.9 and 000.10 for (11) also merge with increasing Se flux, but eventually completely disappear when reaching the (23) phase.

2. Experimental

The Bi\(_m\)X\(_n\) epitaxial layers were grown by MBE on BaF\(_2\) (111) substrates, using compound bismuth telluride, respectively, bismuth selenide effusion sources with nominal Bi\(_2\)Te\(_3\) composition. Additional pure Te (or Se) source was used to adjust the total chalcogen to bismuth flux ratio and thus, to tune the stoichiometry of the resulting films. For Bi\(_2\)Te\(_3\), the additional Te flux varied between 0 and 2.4 Å s\(^{-1}\), while for Bi\(_2\)Se\(_3\) layers we used Se fluxes up to 1.4 Å s\(^{-1}\), while the flux rate from the bismuth selenide and bismuth telluride sources was kept constant. The growth temperature was set constant to 350 °C for all samples, the layer thicknesses were between 350 and 500 nm. The details of the growth can be found in [15].

HRXRD measurements were carried out on a laboratory x-ray diffractometer equipped by a Cu sealed tube. A multilayer x-ray mirror and a channel-cut Ge monochromator were used to produce a parallel x-ray beam with CuK\(_\alpha\) wavelength. The scattered radiation was detected by a linear detector. Figure 2 shows the diffraction curves of the Bi\(_m\)Te\(_n\) (upper panel) and Bi\(_m\)Se\(_n\) series (lower panel) measured in symmetric reflection geometry, i.e. along the 000L crystal truncation rod. The blue (red) vertical dotted lines represent the theoretical positions of the 000L diffraction maxima in the (23) and (11) phases, respectively (see below). Peaks denoted ‘S’ are the diffraction maxima of the BaF\(_2\) substrate. The shape of the diffraction curves considerably changes with the chalcogen to bismuth flux ratio. With increasing chalcogen flux, some peaks strongly change their position; for instance the maximum at 000.17 in the (11) phase converts to 000.21 in the (23) phase in both investigated material systems. Some peaks remain almost unchanged—for instance, the 000.12 peak of the (11) phase, which is equivalent to 000.15 in the 23 phase; some pairs of peaks merge creating a strong peak in the (23) phase—for instance the 000.9 and 000.10 peaks of the (11) phase merge to 000.12 in the (23) phase. For Bi\(_m\)Te\(_n\), the peaks 000.9 and 000.10 for (11) also merge with increasing Se flux, but eventually completely disappear when reaching the (23) phase.
Figures 3 and 4 present reciprocal-space maps around asymmetric Bragg points measured in coplanar geometry for Bi$_m$Te$_n$ (figure 3) and Bi$_m$Se$_n$ (figure 4) films grown in each case with either a small or large chalcogen fluxes. In the maps we recognize the substrate 313 peak (denoted ‘S’) and the layer peaks (‘L’) 1–10.20 of Bi$_2$Te$_3$, 1–10.19 of Bi$_2$Se$_3$, and 1–10.16 of Bi$_1$Te$_1$ and Bi$_1$Se$_1$.

3. Analysis of the diffraction data

In the following, we present a simple structural model that enables to evaluate the HRXRD diffraction curves and determine the basic structure parameters. We start from a hypothetic hexagonal crystal structure built of identical virtual atoms. The structure consists of an ABCABC… stacking of two-dimensional hexagonal atomic planes with the inter-planar distance $d$. Such crystal produces a periodic sequence of the diffraction maxima along the symmetric rod 000$L$ at the reciprocal space coordinates $Q_p$

$$Q_p = \frac{2\pi}{d} p,$$

where $p$ is integer. Now we introduce a periodic chemical modulation replacing the virtual atoms by the Bi and X = Se,Te atoms. As we showed above, the structure period of a (nm) phase consists of $N$ QLs (determined using equation (1)) separated by a Bi–Bi DL. In the following we consider only the structures having a single Bi–Bi DL between two subsequent QL blocks; the $N$ values of these structures following from equation (1) must be integer. The distance $D$ between two subsequent DLs in these lattices is

$$D = (5N + 2)d,$$

if we assume that the inter-planar distances $d$ are not much affected by the chemical modulation. The vertical hexagonal lattice parameter $c$ of the unit cell must be obviously an integer multiple of $D$. Since the structures exhibit ABCABC… stacking of the basal planes, the total number of the basal planes in the elementary unit cell must be an integer multiple of 3:

$$c = 3d = sD = s(5N + 2)d,$$

where $s$ and $t$ are integers. In the (11) phase for instance, $N = 2$, $D = c = 12d$ (see, e.g. middle panel of figure 1). In the phase (43) with $N = 1$, accordingly $D = 7d$ and $c = 3D = 21d$ (see figure 1, right). The (23) phase with the topological surface states contains no Bi-Bi DLs, i.e. $D = 5d$ and $c = 3D = 15d$.

Such a perfectly periodic chemical modulation in the $c$ direction gives rise to a periodic sequence of diffraction peaks along the 000$L$ crystal truncation rod, which can be viewed as...
modulation superlattice satellites to the main peaks in equation (2). These satellite peak positions on the rod are

$$Q_i = \frac{2\pi}{D} l,$$

where $l$ is integer, while the reciprocal-lattice points on the 000L have the positions

$$Q_L = \frac{2\pi}{c} L,$$

with $L$ is integer. For instance, the ideal (23) phase exhibits the maxima at $Q_{(23)}^{(23)} = 2\pi l/(5d)$ and the reciprocal lattice points are at $Q_{L}^{(23)} = 2\pi L/(15d)$. Therefore, every third reciprocal lattice point corresponds to an allowed diffraction maximum, i.e. 3L = l. This is a result of the structure factor of the (23) unit cell. In the (11) phase all diffraction maxima are allowed, since $Q_{(11)}^{(11)} \equiv Q_{L}^{(11)} = 2\pi l/(12d)$.

In this model we did not yet consider differences in the lattice plane distances between the individual atomic (Bi, X) lattice planes in the crystal structure. The variation of the actual inter-planar distances along the c-axis direction affect the structure factor of the unit cell and consequently, the intensities of the diffraction maxima, but they do not influence the positions of the diffraction peaks, if $d$ in the above relations represents the mean inter-planar distance $\bar{d}$.

For the determination of the mean inter-planar distance $\bar{d}$ it is suitable to use the diffraction peaks of the homogeneous virtual crystal lattice in equation (2). The positions of these peaks depend only on $\bar{d}$ and they are not influenced by the chemical modulation. From the above analysis it follows that these peaks are equivalent to the peaks 000.15(23), 000.30(23)… and 000.12(11), 000.24(11)… of the (23) and (11) phases and consequently, $\bar{d}$ can be directly determined from their positions.

The lateral hexagonal lattice parameters $a$ (but also $\bar{d}$) can be determined from the positions of the layer peaks in the asymmetric reciprocal-space maps, the examples of which are depicted in figures 3 and 4. The modulation period $D$ and consequently the mean number $N$ of QLs between two following DLs and the, consequently, the stoichiometry parameter $\delta$ that is related to $N$ by equation (1) can be determined from the distance of nearest diffraction maxima along 000L according to

$$D = \frac{2\pi}{\bar{d} - \bar{d}_{-1}}.$$

For this purpose, we used the diffraction peak pairs highlighted by red rectangles in figure 2 and from the figure it follows that in both Bi$_m$Te$_n$ and Bi$_m$Se$_n$ systems, the values of $N$ increase with increasing chalcogenide flux so that $\delta$ decreases and the structures converge to the ideal (23) phase.

In figure 5 we present the resulting values derived for our sample series. Panels ((a) and (d)) display the $\delta$-dependences of the lateral lattice parameter $a$ and panels ((b) and (d)) that of the mean vertical lattice plane spacing $\bar{d}$. In both material systems, with decreasing $\delta$ (i.e. approaching the (23) phase), $a$ decreases, but the change of $a$ is much larger in tellurides than in selenides. Concerning the mean inter-planar distances $\bar{d}$ the tellurides and selenides behave in the opposite way. Approaching the ideal (23) phase, i.e. for $\delta \to 0$, $\bar{d}$ clearly increases in tellurides, while it slightly decreases in selenides (it is noted however, that for the latter system the changes are almost comparable to the error bars).

The comparison of the values $a$ and $\bar{d}$ obtained from our HRXRD measurement with data reported in literature is
not straightforward, since the available databases ([10] for instance) contain data for bulk crystals and our values correspond to epitaxial layers that are strained to some extent. In order to correct our data for the epitaxial strain we use the following formula based on linear elasticity and the fact that the (0001) sample surface is stress-free:

$$\mathcal{d}_{\text{relaxed}} = \mathcal{d}_{\text{strained}} \left( 1 + \frac{2C_{1333}}{C_{33}} \frac{a_{\text{strained}} - a_{\text{relaxed}}}{a_{\text{relaxed}}} \right)$$  \hspace{1cm} (8)

where $C_{1333}$ are the elastic constant, for simplicity assumed independent on the chemical composition. In the telluride systems we used the values of $a_{\text{relaxed}}$ for various ideal (mn) phases from [12] and determined the $a_{\text{relaxed}}$ of our samples from known stoichiometry parameters $\delta$ by quadratic interpolation. Then using formula (8) we calculated the corresponding relaxed values of $d$ and compared with data of ideal periodic phases in [9]. Indeed, our values of $d_{\text{relaxed}}$ correspond well to the values of the reported bulk (mn) phases. Therefore the structure of the epitaxial telluride layers is similar to the bulk structure. A corresponding analysis for our bismuth selenide layers was not possible, since the reported parameters $a_{\text{relaxed}}$ of various bulk (mn) materials tabulated in [7, 10, 12, 17–20] do not exhibit a clear monotonous dependence on $\delta$.

Finally, we address the structure quality of the layers. In case of a perfectly periodic sequence of QLs and DLs corresponding to a given (mn) phase, the 000L-diffraction curve would exhibit a periodic sequence of diffraction maxima in positions according to equation (5). A simple inspection of the measured data reveals that this is not the case except for the samples with zero additional chalcogen flux (corresponding to the (11)) phase and the sample for the (23) phase obtained at the highest flux values that does not exhibit any inserted Bi-DLs. In the intermediate cases, only some diffraction maxima survive. In order to describe this effect we developed a statistical model of a Bi$_m$X$_n$ lattice assuming that the number of QLs between two following Bi–Bi DLs is random with the mean value $N$. In reference [15] we presented the details of the model and a formula for the diffracted intensity averaged over all random sequences of QLs and DLs. The mean result of the model connects the full-widths at half maxima (FWHMs) $\delta Q$ of the modulation satellites with the root-mean square (rms) deviation $\sigma_N$ of the number of QLs between two DLs according to

![Figure 5](image-url)

Figure 5. Structure parameters of epitaxial Bi$_2$X$_{1-\delta}$ (X = Te, Se) layers determined from the HRXRD diffraction data as function of the stoichiometry $\delta$. Panels (a)–(c) and (d)–(f) display the results of Bi$_m$Te$_n$ and Bi$_m$Se$_n$, respectively. In (a) and (b) the dependences of the lateral parameter $a$ on $\delta$ are plotted, (c) and (d) show the $\delta$-dependences of the mean inter-planar distance $\mathcal{d}$, and (e) and (f) the $\delta$-dependences of the relative rms deviation of the number $N$ of quintuple layers between two following Bi–Bi double layers; this parameter is a measure of the crystal perfection. The color of the data points denoted (mn) represent tabulated bulk values taken from literature (see the main text for details). The open circles in (a) and (b) are the relaxed values of $a$ and $\mathcal{d}$, respectively, corrected to biaxial epitaxial strain. Only the relaxed values can be compared with the bulk data.
\[ \sigma_N \approx \frac{\delta Q(D^2)}{10\pi d}. \]  

This approximate relation was derived assuming that the broadening of the diffraction maxima due to the finite film thickness is negligible with respect to the broadening caused by disorder. Figures 5(c) and (e) show the resulting dependencies of the relative root mean square deviations \( \sigma_d/N \) on \( \delta \) as obtained for our Bi\(_{2n}\)Te\(_n\) and Bi\(_{2n}\)Se\(_n\) epilayers. From the figures it follows that both tellurides and selenides exhibit a similar behavior. The (11) phase (\( \delta = 1 \)) grown under zero additional chalcogen flux is well ordered; in this phase with \( N = 2 \sigma_d/N \) is very small. Increasing the flux, the mean number \( N \) of the QLs between the Bi DL increases. This results in a strong increase of \( \sigma_d/N \), meaning that the insertion of the Bi–Bi DL in the lattice structure is not very well correlated. For the samples grown with high chalcogen flux, \( N \to \infty \) and \( \sigma_N \to 0 \) from definition. In these curves, the FWHMs of the diffraction peaks indeed correspond to the full layer thickness.

4. Summary

High-resolution x-ray diffraction was performed for investigation of the lattice structure of bismuth chalogenide topological insulator epiayers of rhombohedral lattices Bi\(_{2n}\)X\(_n\) \( \equiv \) Bi\(_2\)X\(_{3-\delta}\) (X = Te, Se) grown by molecular beam epitaxy using different fluxes of the chalcogen atoms. It was demonstrated that for both tellurides and selenides with increasing chalcogen flux the structure evolves from Bi\(_1\)X\(_1\) (zero additional flux) towards Bi\(_2\)X\(_3\) (large additional flux), where the stoichiometry parameter \( \delta \) of the investigated structures was determined from the distance of the modulation satellites of the diffraction curves. This transition is connected with a change of the lattice parameters, i.e. with increasing flux the lateral lattice parameter \( a \) decreases both in selenides and tellurides, whereas the mean hexagonal (0001) lattice plane distances increases with increasing flux in the tellurides, but slightly decreases in selenides. For the evaluation of the structure quality we used our previously developed stochastic structure model to determine the mean-square deviation of the number of X-Bi-X-Bi-X quintuple layers present between consecutive Bi–Bi double layers. From our analysis we show that the Bi\(_1\)X\(_1\) Bi\(_2\)X\(_3\) phases are well ordered in both material systems, whereas for the intermediate compositions a high degree of disorder in the sequence of QL and DL layers exists that should significantly affect the topological and electronic properties of these materials.

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