Microstructural characterisation of Bi$_2$Se$_3$ thin films

N V Tarakina$^1$, S Schreyeck$^1$, T Borzenko$^1$, S Grauer$^1$, C Schumacher$^1$, G Karczewski$^{1,2}$, C Gould$^1$, K Brunner$^1$, H Buhmann$^1$ and L W Molenkamp$^1$

$^1$Experimentelle Physik III, Physikalisches Institut and Wilhelm Conrad Röntgen-Research Centre for Complex Material Systems, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
$^2$Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland

E-mail: nadezda.tarakina@physik.uni-wuerzburg.de

Abstract. The microstructure of Bi$_2$Se$_3$ thin films grown by molecular beam epitaxy on Si(111), InP(111)B and Fe-doped InP(111)B substrates has been studied in detail using scanning transmission electron microscopy. Films grown on Si(111) and InP(111)B substrates show the formation of twin domains: rotation twins (with the grain boundary perpendicular to the substrate) and lamellar twins (with the grain boundary parallel to the substrate). The presence of twins was confirmed by atomic-force microscopy (AFM) and X-ray diffraction (XRD). At the interface between Bi$_2$Se$_3$ film and Si(111) or InP(111)B substrates poorly crystallized layers of about 1 nm and 1.8 nm thickness, respectively, followed by well-crystallized Bi$_2$Se$_3$ layers, were found. The use of a Fe-doped InP (111) substrate with a rough surface enables the suppression of twin formation.

1. Introduction

Bismuth selenide, Bi$_2$Se$_3$, has been studied for many years as a promising material for thermoelectric [1-4], photoelectrochemical [5] and optical recording devices [6]. Together with Bi$_2$Te$_3$ and Sb$_2$Te$_3$, it was predicted to be a 3D topological insulator (TI) with semiconductor behaviour in bulk and protected topological states at the surface [7-8]. Topological surface states make Bi$_2$Se$_3$ thin films very attractive for applications in spintronics and quantum computing. Hence, the growth of high-quality thin films from this material is a first step towards exploiting its unique properties.

Molecular beam epitaxial growth of Bi$_2$Se$_3$ has been realized so far on different substrates: Si(111) [9-12], SrTiO$_3$(111) [13, 14], Al$_2$O$_3$(110) [15], GaAs(111)B [16], CdS(0001) [17], InP(111)B [18], double-layer graphene grown on SiC(0001) [19]. Many variable parameters, which have to be taken into account during the growth, together with crystallographic features of the thin film and the substrate can noticeably influence the quality of the film. Bi$_2$Se$_3$ crystallizes in a rhombohedral unit cell, space group $R-3m$, with unit cell parameters in hexagonal setting of $a = 4.143(5)$ Å and $c = 28.636(20)$ Å [20]. The crystal structure of Bi$_2$Se$_3$ can be described as a cubic close-packing of Se and Bi atoms. Three selenium and two bismuth layers alternate along the $c$-direction forming a so-called quintuple layer. One unit cell of Bi$_2$Se$_3$ consists of 3 quintuple layers connected to each other via van der Waals bonding. Bi$_2$Se$_3$ thin films connect to the substrate via van der Waals bonding as well, which enables growing Bi$_2$Se$_3$ on substrates with big lattice mismatches between substrate and film.

The main goal of this work is to study the microstructure of the Bi$_2$Se$_3$ thin films grown by
molecular beam epitaxy (MBE) on three different substrates, which should help to better understand the growth mechanism of Bi\textsubscript{2}Se\textsubscript{3}, and to further control the films’ quality.

2. Results and Discussion

The Bi\textsubscript{2}Se\textsubscript{3} thin films were grown on three different substrates (Si(111), InP(111)B, Fe-doped InP(111)B) by MBE in an ultra-high-vacuum MBE chamber with high purity Bi (99.99999%) and Se (99.9999%) source fluxes provided by standard effusion cells. Independent of the choice of substrate, all studied films were grown at 300 °C, which, as was found previously [18], is an optimal temperature to grow Bi\textsubscript{2}Se\textsubscript{3} by MBE. In the case of Si(111), prior to the growth, Bi was deposited on a Si(111)-(7x7) surface at 200 °C and then the substrate was heated up to 400 °C to obtain a Si(111)-(\sqrt{3}x\sqrt{3})-Bi surface. InP(111)B and Fe-doped InP(111)B wafers were etched with hydrofluoric (HF) acid before growth to remove oxide at the substrates surface. After growth, the samples were cooled down in a Se atmosphere to avoid the formation of Se vacancies. Details of the growth are given in Refs. [18, 21].

Selected-area electron diffraction (SAED) patterns of Bi\textsubscript{2}Se\textsubscript{3}/Si, Bi\textsubscript{2}Se\textsubscript{3}/InP and Bi\textsubscript{2}Se\textsubscript{3}/InP(Fe) samples taken along [100]\textsubscript{Bi\textsubscript{2}Se\textsubscript{3}} show a distribution of sharp spots, confirming the epitaxial growth of Bi\textsubscript{2}Se\textsubscript{3} on these substrates with the following crystallographic relations: normal to the growth plane [001]\textsubscript{Bi\textsubscript{2}Se\textsubscript{3}}∥[111]\textsubscript{substrate}, in-plane [100]\textsubscript{Bi\textsubscript{2}Se\textsubscript{3}}∥[1-10]\textsubscript{substrate} or [110]\textsubscript{Bi\textsubscript{2}Se\textsubscript{3}}∥[1-10]\textsubscript{substrate}. Bi\textsubscript{2}Se\textsubscript{3} reflections were indexed in a trigonal unit cell with parameters $a = 4.2$ Å and $c = 28.7$ Å. For the films grown on Si and InP substrates, SAED patterns display additional spots coming from twinned domains which can be attributed to the formation of both rotation twin domains (with twin boundary perpendicular to the substrate) and lamellar twins (with twin boundary parallel to the substrate). In the case of growth of Bi\textsubscript{2}Se\textsubscript{3} on Si(111), in some of the recorded SAED patterns the 00$l$ rows of spots are split into two components; the magnitude of the splitting increases with increasing distance from the direct beam. This splitting indicates a tilt (of about 1°) of the rotation twins with respect to each other in the $bc$ plane. Surface AFM measurements and X-ray diffraction in-plane rotational phi-scans obtained from these samples coincide with SAED data, confirming the presence of twins all over the film (Figure 1). No reflections from twin domains have been observed on the SAED patterns from the Bi\textsubscript{2}Se\textsubscript{3} film grown on a Fe-doped InP substrate.

![Figure 1](image.png)

**Figure 1.** Cross-sectional HAADF-STEM images of Bi\textsubscript{2}Se\textsubscript{3} on InP (top) and Si (bottom) with corresponding SAED patterns and X-ray diffraction in-plane rotation phi-scans.

The films grown on Si and InP substrates have a poorly crystallized layer at the interface about 1nm and 1.8nm thick, respectively, which is followed by well-crystallized Bi\textsubscript{2}Se\textsubscript{3} layers. By poorly crystallized layer we mean that the interface is not uniformly crystallized over the whole film; at some
regions we observe an amorphous layer and at some regions perfect quintuple layers directly at the interface. It is worth to mention that in the case of Bi\textsubscript{2}Se\textsubscript{3}/Si(111), in some regions the layers are not exactly parallel to the substrate (Figure 1), which coincides well with electron diffraction data (tilt of twin domains of about 1° relative to each other in the bc plane).

To study the formation of twins in detail we recorded high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of Bi\textsubscript{2}Se\textsubscript{3}/InP at different regions with twin domains (Figure 2). The rotation twin formation in Bi\textsubscript{2}Se\textsubscript{3} can be explained as follows: after the first atomic layer of Se is formed, a Bi layer can grow on top of it in two equally possible cubic close-packed atomic configurations. When two such equivalent but different regions meet a twin boundary is formed perpendicular to the growth plane. The observed rotation twins do not display sharp boundaries. Lamellar twins form a twinned domain boundary parallel to the growth plane. Three nonequivalent atomic positions in the Bi\textsubscript{2}Se\textsubscript{3} crystal structure allow three possibilities to form a lamellar twin: at the middle Se, edge Se and Bi positions within a quintuple layer. The experimentally observed lamellar twins show the formation of twins only at the edge Se layer in the quintuple layer, which connects to the following layer only by van der Waals interactions (Figure 2). The same type of planar twins has been observed experimentally and predicted by \textit{ab initio} calculations for bulk Bi\textsubscript{2}Te\textsubscript{3} [22]. We believe that the formation of such a twin is probably most plausible from an energetic point of view for the case of Bi\textsubscript{2}Se\textsubscript{3} as well.

Figure 2. HAADF-STEM cross-sectional image and corresponding crystal structure representation of (a), (b) rotational and (c), (d) lamellar twins in Bi\textsubscript{2}Se\textsubscript{3} grown on InP(111)B.

In the case of Bi\textsubscript{2}Se\textsubscript{3} grown on Si(111), twinned grains are slightly twisted in the ab plane, because the left and the right twins which appear in the same HAADF-STEM image cannot be equally resolved at the same time; a slight tilt of about 1° perpendicular to the grain boundary is required to bring the left twin perfectly oriented along the [100] direction.

Figure 3. HAADF-STEM images of the Bi\textsubscript{2}Se\textsubscript{3} thin film grown on a Fe-doped InP (111)B substrate. (a) Overview, (b) enlargement at the interface region.

In comparison with flat Si(111) and InP(111)B substrates, electron diffraction and X-ray diffraction patterns taken from the Bi\textsubscript{2}Se\textsubscript{3} thin film grown on a Fe-doped InP (111)B substrate with a rough surface show no presence of twin domains. Bi\textsubscript{2}Se\textsubscript{3} fills the cavities in the substrate, forming a perfect interface between the substrate and the first quintuple layer of the film (Figure 3). The absence of twins was also demonstrated by XRD and AFM experiments. It is worth to mention that this sample
also showed a 89% reduction of the carrier density compared to the carrier density obtained for Bi$_2$Se$_3$ flakes exfoliated from flat InP(111)B.

3. Conclusions
The microstructure of Bi$_2$Se$_3$ thin films grown by molecular beam epitaxy on Si(111), InP(111)B and rough Fe-doped InP(111)B substrates were studied in detail. We observed the formation of twin domains (rotational and lamellar) and a poorly crystallized layer at the interface in the case of both studied flat substrates. The use of a rough Fe-doped InP(111)B substrate allows to suppress twin formation and results in a clear interface between the substrate and the first quintuple layer in the film.

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