Two-dimensional X-ray diffraction characterization of (Zn,Cd,Mg)Se wurtzite layers grown on Bi₂Se₃

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Abstract

The wurtzite structure of ZnSe, Zn_{0.49}Cd_{0.51}Se and Zn_{0.23}Cd_{0.25}Mg_{0.52}Se layers grown on Bi₂Se₃/sapphire (0001) by Molecular Beam Epitaxy (MBE) is reported. Structure characterization is studied by two-dimensional X-ray diffraction. Pole figures are calculated for cubic and hexagonal planes of the (Zn,Cd,Mg)Se family and compared to their expected values. The targeted wurtzite plane was (11-22), while the cubic ones were the (220) and (311). The results show that, under our MBE growth conditions, ZnSe, Zn_{0.49}Cd_{0.51}Se and Zn_{0.23}Cd_{0.25}Mg_{0.52}Se layers prefer to form the hexagonal (wurtzite) phase rather than the cubic one when grown on Bi₂Se₃/sapphire in (0001) direction. These results have implications for the next generation devices combining semiconductors and topological insulator materials.

Keywords – Topological Insulator, Semiconducting II-VI materials, two dimensional XRD, Molecular beam epitaxy;

I. Introduction

Topological insulators are of interest for the next generation solid state devices¹. Among topological insulators, bismuth selenide (Bi_2Se_3) is receiving attention for its unique topological features and promise in novel applications². Exotic behaviors arising from topological orders are predicted to be enhanced in structures comprising alternating layers of Bi_2Se_3 and band insulators. Thus, combining Bi_2Se_3 with conventional semiconductors in heterostructures will provide an exciting new dimension in materials design³. Recently new (Zn,Cd,Mg)Se-based II-VI semiconductor/ Bi_2Se_3 heterostructures grown by molecular beam epitaxy (MBE) have been reported in our group⁴. The (Zn,Cd,Mg)Se family of II-VI materials was chosen to combine with Bi_2Se_3 with the expectation that chemical compatibility of selenides will facilitate growth. In addition, they have comparable optimal MBE growth conditions, a small lattice mismatch and tunable bandgaps, making them ideal candidates for heterostructures grown by this technique. Despite the outstanding results reported, further analysis of the epitaxial relationships between the II-VI semiconductors and Bi_2Se_3 is needed to obtain a better understanding and optimization of their physical properties.

In conventional epitaxial growth processes, the growing layer typically exhibits the same crystal structure and the same orientation as the layer that lays beneath⁵. However, the van der Waals bonding nature of the Bi_2Se_3 material is expected to exert less influence on the overlayer structure since the van der Waals materials do not form interlayer covalent bonds⁶. The Bi_2Se_3 structure is described in terms of a layered hexagonal primitive cell with three, five-atom thick layers, often referred to as a quintuple layer⁷. On the other hand, a zinc blend three-dimensional structure is typically preferred by the (Zn,Cd,Mg)Se family rather than the hexagonal wurtzite structure. It has been suggested that under some MBE growth conditions, the hexagonal phase may be favored^{8,9,10} over the zinc blend, even when the latter may be thermodynamically favored. In this paper the preferred crystal structure (zinc blend or wurtzite) of II-VI semiconductors grown by MBE on Bi_2Se_3 is studied through the plotting of pole figures using a two-dimensional X-ray detector.

The data for pole figure calculations is often collected through a number of rotation scans (ϕ) at different tilted angles (ψ), and at 2θ fixed to the Bragg angle of the desired crystallographic plane using a point detector, a lengthy and time consuming process. Two-dimensional X-ray diffraction (XRD^2) provides advantages when plotting pole figures over X-ray diffraction. The XRD^2 refers to X-ray diffraction application using a two-dimensional (2D) detector. Two-dimensional detector collects diffracted X-rays in a large angular range in both 2θ and Ψ directions. The number of sample tilts required for complete pole

figure calculation is much less than with point detector. Moreover, diffraction from a number of crystallographic planes is collected simultaneously for a fixed 2D detector position due to a wide 2θ range of the detector. Therefore, XRD² measurements reduce the number of scan steps used to achieve a full pole figure, saving a considerable data collection time. In addition to the 2D detector technology, the plotting of pole figures involves processing of images and interpretation. The basics and advantages of X-ray diffraction measurements using a 2D area detector have been reported elsewhere¹¹.

In this paper, pole figures are calculated by XRD² techniques for different cubic and hexagonal planes for ZnSe, Zn_{0.49}Cd_{0.51}Se and Zn_{0.23}Cd_{0.25}Mg_{0.52}Se layers grown on Bi₂Se₃ layers grown on (0001) sapphire substrates. The selected hexagonal plane is (11-22), while the cubic ones are the (220) and (311). In addition, the same set of planes was examined on a sample of Bi₂Se₃ grown on sapphire and one of the pure bulk (0001) sapphire (the substrate). These additional measurements allow us to identify the pole figure signals originating from those other two materials. We find that under our growth conditions, the II-VI semiconductor layers exhibit a predominantly wurtzite structure, which may be a desirable feature for some applications.

II. Experimental details

Three samples (T37, T39 and T40) were investigated by the plotting of pole figures. In each case, single crystalline layers of ZnSe (T37), Zn_{0.49}Cd_{0.51}Se (T39) or Zn_{0.23}Cd_{0.25}Mg_{0.52}Se (T40) semiconductors were grown on a 6 nm layer of Bi₂Se₃ previously deposited on (0001) sapphire substrates by MBE. In addition a 6nm single layer of Bi₂Se₃ was grown on a sapphire substrate (T21), with no II-VI overlayers. The experimental details of the MBE growth have been reported elsewhere⁴. The compositions of T39 and T40 were chosen to minimize the in-plane lattice mismatch between the II-VI overlayer and the Bi₂Se₃. The XRD² data were collected on a Bruker Discover 8 X ray diffraction system with VANTEC-500 area detector. The system utilizes a parallel incident X-ray beam collimated by Gobbel mirror and 0.5 mm pinhole collimator. The detector was kept 200 mm away from the sample. Data collection simultaneously takes place in a wide 2θ range of about 30°.

In a pole figure measurement, the diffraction angle (2θ) is fixed for a targeted plane ($h_2k_2l_2$). Then, the sample is tilted at an angle ψ from the sample surface normal direction ($h_1k_1l_1$). For cubic and hexagonal systems, ψ may be found from the following equations 1 and 2, respectively¹²:

$$\cos \psi = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)}} \quad (1)$$

$$\cos \psi = \frac{h_1 h_2 + k_1 k_2 + \frac{1}{2}(h_1 k_2 + h_2 k_1) + \frac{3a^2}{4c^2} l_1 l_2}{\sqrt{(h_1^2 + k_1^2 + h_1 k_1 + \frac{3a^2}{4c^2} l_1^2)(h_2^2 + k_2^2 + h_2 k_2 + \frac{3a^2}{4c^2} l_2^2)}} \quad (2)$$

where a and c are the lattice constant and the height, respectively, for the corresponding hexagonal structure. Once 2θ and ψ are fixed, the sample is exposed to the X-ray beam while it rotates an ϕ angle around to the surface normal. Measurement results are saved as an image (frame).

To cover all plane reflections, the sample is rotated from 0° to 360° with a scan step of 10° . This implies that 36 frames will be collected during the full ψ rotation. The 36 frames provide a large amount of information for calculating the pole figures. In order to analyze the data, MULTEX by Bruker software allows loading a set of frames for the calculation of pole figures for any selected 2θ angle¹³. Furthermore, PILOT by Bruker software can integrate frame intensities into a one dimensional profile which provides a plot similar to conventional “Intensity vs. 2θ ” diffraction pattern. To identify the peaks, Powder Diffraction File (PDF) card information was used for ZnSe and Zn_{0.5}Cd_{0.5}Se. The quaternary material, Zn_{0.23}Cd_{0.25}Mg_{0.52}Se studied here has a similar lattice constant to Zn_{0.5}Cd_{0.5}Se, so the PDF card values for Zn_{0.5}Cd_{0.5}Se were used also for Zn_{0.23}Cd_{0.25}Mg_{0.52}Se.

An example of the pole figure calculation procedure described above is illustrated in Fig. 1 for a bulk (0001) sapphire substrate. Fig 1(a) displays a typical frame with the raw data for the XRD² measurement. The bright spot within the highlighted sector is a diffraction point from planes of sapphire single crystal. A bright spot is representative of single crystal diffraction in XRD² measurement. To convert the 2D data into a XRD pattern, the sector is integrated and transformed into a (θ - 2θ) pattern, as shown Fig 1(b). The graph displays a sharp peak at 53.8° which belongs to sapphire (20-24) plane¹⁴. Once the peak is selected, the program runs the same 2θ range over all 36 frames. The calculated pole figure is shown in Fig 1 (c), displaying three poles at about $\psi = 60^\circ$. These three poles are explained by the three-fold rotational symmetry of sapphire (R-

$\bar{3}C$ space group), while the ψ position corresponds to an angle of 57.6° formed between the (20-24) plane and the (0001) surface normal plane (see Eq.2). Thus, three important parameters are needed to identify a targeted plane: the 2θ diffraction peak, the ψ position, and the number of reflections or “poles”.

Fig.1. Measurement scheme for pole figures using the XRD² technique for a bulk a (0001) sapphire substrate. (a) XRD² data for one frame. The 2θ sector is highlighted. (b) The diffraction pattern as a result of integration in the highlighted sector. (c) Pole figure for (20-24) sapphire calculated over the 36 frames.

III. Results and discussion

Pole figures were computed for the three samples T37, T39 and T40. Fig.2 (a) displays the frame (inset) and its integrated diffraction pattern of the (11-22) plane in ZnSe measured for T37. The integrated diffraction pattern of ZnSe displays a clear peak at 53.8° , which is assumed to belong to the ZnSe (11-22) plane¹⁵. The calculated pole figure over the same 2θ range in Fig. 2b shows six clear poles at about $\psi = 58.6^\circ$ which matches with the calculated value for the (11-22) plane in ZnSe structure. This plane clearly shows its hexagonal features: $2\theta = 53.7^\circ$, $\psi = 58.6^\circ$ and 6 reflections, supporting the identification of the wurtzite phase. Two poles with weak intensity (dashed circles) can be also seen in Fig. 2b at about $\psi = 70^\circ$, $\phi = 50^\circ$ and $\psi = 60^\circ$, $\phi = 290^\circ$, which are assigned to traces of diffraction from the Al_2O_3 (20-24) and Bi_2Se_3 (20-25) planes^{14,16}, respectively. This assignment is based on the pole figure measurement results obtained for Bi_2Se_3 on sapphire (sample T21) which is shown in Fig. 2c. In Fig. 2c, the outer poles presumably belong to Bi_2Se_3 (20-25) at $\psi = 72.7^\circ$, while the inner poles correspond to Al_2O_3 (20-24) (as shown in Fig. 1c for pure sapphire).

Fig 2 The diffraction peak profile after frame integration (a) and pole figure (b) of the (11-22) plane in ZnSe (T37). (c) Pole figures for Bi₂Se₃/Al₂O₃ (T21) using the same experimental conditions as for the (11-22) ZnSe plane.

Similar results are presented for Zn_{0.49}Cd_{0.51}Se (T39) and Zn_{0.23}Cd_{0.25}Mg_{0.52}Se (T40) when the (11-22) plane was examined and they are shown in Fig. 3a and 3b, respectively. Both materials display a clear diffraction peak at about $2\theta = 51.8^\circ$ for (11-22) plane¹⁷. The insets show the frame raw data for each sample. The calculated pole figures over the 2θ range show six clear poles at about $\psi = 58.6^\circ$ for (11-22), also demonstrating the hexagonal phase of these layers. The 2θ value, ψ position, and 6 reflections in both samples allow to identify the targeted (11-22) plane in the (Zn,Cd,Mg)Se family, supporting the conclusion that the wurtzite phase is present. In addition, the pole figure of Fig. 3a for the T39 sample displays an extra pole at about $\psi = 60^\circ$, $\phi = 220^\circ$ assigned to the sapphire (20-24) plane. In T40 (Fig. 3b), the Bi₂Se₃ (20-25) and Al₂O₃ (20-24) poles are more clearly seen at $\psi = 72.7^\circ$ and $\psi = 60^\circ$, respectively.

Fig.3. The frame inset in its corresponding integrated diffraction pattern, and pole figures from (11-22) plane for (a) $\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se}$ (T39), and (b) $\text{Zn}_{0.23}\text{Cd}_{0.25}\text{Mg}_{0.52}\text{Se}$ (T40).

Fig.4 shows the diffraction peak profile (after frame integration) and the pole figures corresponding to the cubic (220) plane^{18,19} for ZnSe (a), $\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se}$ (b), and $\text{Zn}_{0.23}\text{Cd}_{0.25}\text{Mg}_{0.52}\text{Se}$ (c). From the integrated diffraction pattern of ZnSe (T37) two peaks at about 40.1° and 42.9° are seen, which are identified as the Bi_2Se_3 (10-1 10), and (10-1 11) planes. Also, one broad peak is observed between 45° and 50° . Over this wide range an ambiguity arises between (220) and (10-13) of ZnSe due to their proximal 2θ values of 45.2° and 49.5° , respectively. The pole figure made over this 2θ range shows six poles with about equal intensity, which suggests we are in the presence of a hexagonal system rather than a cubic system. Thus we conclude that we are seeing the pole figure for the hexagonal (10-13) plane of ZnSe. If a twinned cubic phase were present we would expect to see two sets of three alternating poles of different intensities.

Fig.4. Integrated diffraction pattern with its frame (inset) and pole figures from (220) cubic plane for (a) ZnSe (T37), (b) $\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se}$ (T39), and (c) $\text{Zn}_{0.23}\text{Cd}_{0.25}\text{Mg}_{0.52}\text{Se}$ (T40).

The integrated diffraction pattern from $\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se}$ (T39) and $\text{Zn}_{0.23}\text{Cd}_{0.25}\text{Mg}_{0.52}\text{Se}$ (T40), shown in 4b and 4c, respectively, display a sharp peak at 47.7° which originates from the (10-13) plane. Furthermore, a low intensity broad peak is shown, assigned to the previously observed plane of Bi_2Se_3 (10-1 10). There are no peaks for the (220) plane in either of the integrated patterns, expected at $2\theta = 43.5^\circ$, suggesting again the absence of the cubic phase. The pole figure from T39 shows six broad poles due to the overlapping of $\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se}$ (10-13) and Bi_2Se_3 (10-1 10) at $\psi = 32.2^\circ$ and 38.7° , respectively. This overlapping is more clearly evident in T40 where the six poles of the (10-13) plane are surrounded by three low intensity poles at slightly higher position, which belong to Bi_2Se_3 (10-1 10) at $\psi = 38.7^\circ$. The results show no evidence of the (220) plane: neither the 2θ peak nor the poles are seen. Thus, no evidence for the (Zn,Cd,Mg)Se cubic features were obtained, while the presence of the wurtzite structure is reinforced.

Finally, the (311) plane is examined in each sample and their integrated patterns and pole figures are displayed in Fig. 5 for (a) T37, (b) T39 and (c) T40. No peaks are displayed for the (311) plane in any of the 2θ diffraction patterns. In Fig 5c, for sample T40, a sharp peak at $2\theta = 47.7^\circ$ is seen which is consistent with the (10-13) wurtzite plane of $\text{Zn}_{0.23}\text{Cd}_{0.25}\text{Mg}_{0.52}\text{Se}$. The pole figures for all three samples display six poles with the same intensity just above $\psi = 30^\circ$ that we index for (10-13), according to previous results. Since neither the 2θ peak nor the poles are observed from the (311) plane, we conclude that there is no evidence for cubic features.

Fig.5. Frame (inset), integrated diffraction pattern and pole figures from the (311) cubic plane for (a) ZnSe (T37), (b) $\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se}$ (T39), and (c) $\text{Zn}_{0.23}\text{Cd}_{0.25}\text{Mg}_{0.52}\text{Se}$ (T40).

The results described above support the formation of a predominant metastable wurtzite phase in the three II-VI crystalline semiconductor layers grown on Bi_2Se_3 by MBE. These results suggest that the hexagonal symmetry of the Bi_2Se_3 surface allows the 3D II-VI crystal over layer to develop the wurtzite structure even when it is not the thermodynamically most stable surface. Wurtzite structures possess desirable properties that are different from their zinc-blend counterparts such as fewer glide planes and a polar band structure that may prove advantageous for some device applications. The possibility of intentionally stabilizing and optimizing the wurtzite phase of the II-VI overlayers by the appropriate choice of growth conditions¹⁰ is under investigation in our laboratory.

IV. Conclusions

The preferred crystal structure of ZnSe, $\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se}$, and $\text{Zn}_{0.23}\text{Cd}_{0.25}\text{Mg}_{0.52}\text{Se}$ layers grown by MBE on Bi_2Se_3 layers grown on sapphire were studied by two-dimensional XRD. To achieve this goal, pole figures were obtained for several cubic and hexagonal planes of the (Zn,Cd,Mg)Se family. The results displayed the presence of a predominant wurtzite phase through the observation of the (11-22) and (10-13) planes, showing their 2θ value and six poles at the corresponding ψ positions. On the other hand, there was no evidence of the cubic (220) and (311) planes: neither a peak at the appropriate 2θ values, nor the corresponding poles at ψ positions were observed for those two planes. We conclude that under the MBE growth conditions employed, the II-VI layers grown on Bi_2Se_3 -on-sapphire substrates exhibit a predominant wurtzite structure. The potential of stabilizing the wurtzite crystal structure in the (Zn,Cd,Mg)Se material system opens new fields for fundamental physics and devices design.

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