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X-ray characterization of catalytically grown ZnTe and ZnMgTe nanowires

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Abstract

This paper reports on the results of detailed X-ray diffraction studies of ZnTe and ZnMgTe nanowires grown by molecular beam epitaxy. As the aim of proper interpretation of the X-ray measurements of samples consisting of large number of nanowires we defined a virtual unit cell as an averaged one from all really existing cells in the large number of nanowires. The studies revealed that average structure of nanowires is characterized by a minor rhombohedral distortion. The occurrence of this distortion is attributed to the specific defect structure in the majority of nanowires.

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1. Introduction

One-dimensional semiconductor nanostructures in the form of free-standing nanowires (NWs) have become the focus of many research laboratories over the last years. The NWs are very interesting not only from the point of view of basic physical properties, but also due to their potential applications in electronic and photonic devices. Using modern epitaxial growth techniques and the substrates activated by catalyst drops, NWs with section of the order of tens of nanometers and lengths up to tens of micrometers can be obtained. Developing reliable methods of growing nanowires made of II-VI semiconductors, particularly ZnTe, is quite important for several reasons. ZnTe is a direct band gap ($E_g = 2.4$ eV) semiconductor and it possesses properties that are attractive for both basic research and potential applications. In particular, ZnTe can be very heavily p-type doped with nitrogen (N), which allows obtaining the highest free hole concentration among all II-VI materials. In addition, II-VI tellurides are the best known diluted magnetic semiconductors (DMSs). Therefore they can provide an appealing bridge between 'spintronics' and the 'bottom up' approach for nanostructure formation. Finally, NWs made of tellurides are expected to become a basis for obtaining magnetic and p-type doped oxide NWs via the oxidation route (e.g. p-ZnMnO from ZnMnTe:N) (Janik et al., 2006, 2007). Ternary crystals of ZnTe with manganese ($\text{Zn}_{1-y}\text{Mn}_y\text{Te}$, a well-known member of the diluted magnetic semiconductor family), as well as ZnTe with magnesium (nonmagnetic $\text{Zn}_{1-x}\text{Mg}_x\text{Te}$) - both wide bandgap materials - merit special attention. One of the most efficient and universal methods for producing nanostructures from these materials is the molecular beam epitaxy (MBE) (Zaleszczyk et al., 2008, Janik et al., 2008).

The methods commonly used for structure characterization of NWs are field emission scanning electron microscopy (FE-SEM) and high resolution transmission electron microscopy (HRTEM). The first method gives a general view of an assembly of NWs, especially their spatial configuration with respect to each other and to the substrate. The HRTEM methods give the possibility of very precise visualisation of a single NW and of its arbitrarily chosen fragments. Then, using these

methods we are able to study local crystal structure, defect structure and also a chemical composition of the selected part of NW.

In the literature, the X-ray diffraction (XRD) methods are relatively seldom used for NWs studies. For example on the base of θ - 2θ scans Li et al., (2005) confirmed preferential (110) orientation of ZnTe NWs synthesized by pulsed electrochemical deposition from aqueous solutions into porous anodic alumina membranes. Neretina et al., (2007) has presented θ - 2θ measurement of vertically aligned CdTe NWs obtained by catalytically driven growth mode in pulsed laser deposition technique. This measurement shows one peak from CdTe originating from both the (111) zinc-blende and (0002) wurtzite orientations. Further measurements have been done using two-dimensional X-ray diffraction technique: detailed analysis of pole figures shows that observed peak must come almost entirely from the wurtzite phase. For non ordered growth of ZnS NWs obtained through thermal evaporation of zinc and sulfur powders on Si substrate (Zhang et al., 2007) and ZnMnS NWs obtained by the same method (Yuan et al., 2004) the X-ray polycrystalline patterns were shown. Two-axis XRD maps measured around the 111 reflection from InP nanowires were used for showing that the interplanar spacing in the NWs in the $\langle 111 \rangle$ direction is larger than that of bulk zinc-blende InP (Matilla et al., 2006). In this work we performed a more detailed studies of selected sets of NWs by X-ray diffraction methods. The aim was to answer the question what new can we say about NWs with help of X-rays and how we should understand the obtained results.

2. Experimental

The growth of ZnTe nanowires was grown in an EPI 620 MBE system, using a GaAs substrate with a gold layer deposited in a separate MBE chamber. Prior to the growth of NWs the nanocatalysts (Au-based nanoparticles) were formed by *in situ* annealing of the substrate. Three types of substrates used for the current studies, (100), (110) and (111)B oriented GaAs/Au, were mounted *on the same* molybdenum block. This assures the same growth conditions and allows for

direct comparison of NWs grown on substrates with different orientation. For the characterization of these NWs, field emission scanning electron microscopy, high resolution transmission electron microscopy, and energy-dispersive X-ray spectroscopy have been previously used. Here we report the X-ray diffraction (XRD) measurements performed using monochromatic synchrotron radiation ($\lambda = 1.54056 \text{ \AA}$) at the W1.1 beamline at DESY-HASYLAB. Two modes of measurement were applied: symmetrical ω - 2θ scan and coplanar 2θ scan in the glancing incidence geometry. In the first mode of measurement, the detector position (2θ angle) was coupled with the maximum intensity of the proper rocking curve (ω angle) resulting from the crystallographic orientation of the GaAs substrate. Such measurement permits to detect the lattice planes of NWs parallel to the crystallographic orientation of the substrate. In the second mode of measurement, the rotational axis of the sample (ω axis) was aligned exactly with the sample surface and then the sample was rotated about this axis by a small angle α (here equal to 1°). During measurement, the angular position of the sample with respect to the incident X-ray beam (α) remained fixed while the detector was rotated in the wide range of 2θ angles in the plane perpendicular to the sample surface. Such technique is suitable for studies of very thin polycrystalline layers.

3. Results

Three samples of ZnTe NWs on (100)-, (110)- and (111)-oriented GaAs substrates, as well as, two samples of ZnMgTe NWs on (100)-, and (110)-oriented GaAs substrates were a subject of X-ray measurements. The HRTEM studies of these samples revealed that growth axis of NWs is always $\langle 111 \rangle$, independently of substrate orientation. The SEM results also strongly suggest that the preferred growth axis must be $\langle 111 \rangle$. Figure 1 shows the side views FE-SEM images of the ZnTe NWs grown on differently oriented Au/GaAs substrate. For NWs grown on (100)-oriented substrate - Fig.1 (a) - four preferred orientations of NWs are observed, since there are four $\langle 111 \rangle$ type directions available. The inclination of NWs to the substrate surface is clearly visible in this

picture – they form an angle of $\sim 35^\circ$ with the substrate surface angle (between $\langle 111 \rangle$ directions and (100) lattice planes in cubic system is 35.3°). In Fig.1 (b) it is seen that the nanowires form also a very specific angle with the substrate surface - close to the 55° . In this case we observe the preferential growth of NWs only in two directions: $[1\ 1\ \bar{1}]_B$ and along $[1\ 1\ 1]_A$ since in cubic system there are two angles between $\langle 111 \rangle$ directions and (110) lattice planes: 54.7° and 0° . The majority of NWs grown on (111)B oriented substrate are vertical and some limited number form an angle 19.5° with the substrate – Fig. 1 (c). The inclined NWs form a 120° angle among each other according to angle relation between $\langle 111 \rangle$ directions and (111) planes in cubic crystal.

The FE-SEM studies indicate that all these nanowires have $\langle 111 \rangle$ growth axis oriented along $\langle 111 \rangle$ directions of GaAs substrate, regardless of the substrate orientation. The epitaxial character of NWs growth was also proved by X-ray diffraction measurements for these ZnTe NWs as well as for two samples of ZnMgTe NWs grown on (100) and (110) oriented substrates. The examples of the diffraction patterns obtained for ZnTe NWs on GaAs(100)-oriented substrate are shown in Fig. 2.

Analysis of the ω - 2θ pattern shows that the crystallographic orientation of the substrate imposes the orientation of the NWs: the strongest among observed reflections of ZnTe are indexed as 002, 004 and 006, respectively, which correspond to analogous reflections of the GaAs substrate. This means that the (001) lattice planes of the NWs are parallel to the (001) lattice planes of the substrate. The measurements performed for the NWs grown on (110) and (111)-oriented GaAs substrates lead to similar conclusions confirming the epitaxial relation between the substrate and the growing NWs.

Additional small peaks visible in Fig. 1a (e.g. those indexed as 111, 220, 311...), as confirmed by 2θ scan performed in the glancing incidence geometry (Fig. 1b), originate in the thin polycrystalline layer of ZnTe that forms directly on the GaAs substrate between the NWs. Practically all reflections registered in Fig. 1b are indexed as belonging to the polycrystalline phase

of ZB ZnTe. The lattice parameter calculated from this set of reflections is $a = 0.6100 \pm 0.0005$ nm what is very close to that of bulk ZnTe - $a = 0.6103$ nm (JCPDS 15-0746).

However, the lattice parameter of ZnTe NWs calculated from symmetrical 006, 440, and 333 reflections measured in ω - 2θ mode is larger than that for bulk ZnTe and equals to $a = 0.6112$ nm for (001)-oriented substrate, $a = 0.6109$ nm for (110)-oriented substrate, and $a = 0.6110$ nm for (111)-oriented substrate (all values are obtained with the accuracy of ± 0.0001 nm). These values, being larger than that of bulk crystal, suggest that the ZB unit cell of the NWs is distorted. Our model assumes that the distortion takes place along the $\langle 111 \rangle$ direction. The source of such deformation is the specific defect structure inside NWs visible in the HRTEM images. The majority of NWs contain a high number of stacking faults (disturbed layer arrangements) created along the growth direction of NWs; NWs without such defects are also present (Fig. 3). As it is known, the atoms on (111) planes of the face centered cubic structure (FCC) are arranged in a hexagonal pattern just like the atoms on the (0001) planes of the hexagonal closed-packed structure (HCP). The only difference between these two structures is the way in which these layers of atoms are arranged above one another. In HCP structure the layer stacking sequence can be written by ABABAB..., while the FCC structure has the sequence ABCABC... In II-VI material one layer is composed of a pair of atoms (one from group II and second from group VI), defining a single bilayer. Then in description of layers sequence in ZB and wurtzite (WZ) structures each letter represents a bilayer. The arrangement ABCABC... is proper for the ZB structure in $[111]$ direction, but it happens that it is disturbed and the sequence ABABAB... appears locally. Such sequence in ZnTe is characteristic for WZ structure. If the number of such stacking faults is high (our case) we have ZB and WZ structures of ZnTe, successively, like in a “non- periodic” superlattice.

The mean thickness of these different arrangements is ~ 1 - 2 nm what means that in the X-ray diffraction we will observe diffraction peaks originating from averaged values of interplanar spacing proper for (111) in ZB and (0001) in wurtzite ZnTe. This averaged spacing should be

different than that for (111) ZB lattice planes. Moreover, the strain effects between these two arrangements should be considered, similarly as in a superlattice, what induces an extra change in the interplanar distances along the NW axis. If so, a rhombohedral unit cell can be used for describing the averaged structure of a set of NWs. We named the unit cell defined above “virtual unit cell”.

The rhombohedral unit cell is characterized by two lattice parameters a and α , where $a = b = c$, $\alpha = \beta = \gamma \neq 60^\circ$. The relation between d value and lattice parameters for this system is given by:

$$\frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2 + l^2)\sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3\cos^2 \alpha + 2\cos^3 \alpha)} \quad (1)$$

So, the knowledge of at least two different interplanar spacing is necessary for description of such crystal structure. Unfortunately, for technical reasons (specimen holder which we used has limited rotation around the axis parallel to the sample normal) we could not measure asymmetric reflections for the studied samples, therefore, we used the interplanar spacing calculated from X-ray ω - 2θ scans obtained for 3 samples of ZnTe NWs with different orientations. Taking into account that all these samples were grown simultaneously in the same growth conditions as well as the results of HRTEM studies, we assume that the defect structure has the same character in all these NWs, so the unit cell distortion should also be the same. Then, we have used d_{600} , d_{440} values changing properly their hkl indices as follows: from 600 in cubic cell to 330 in rhombohedral one and from 440 to 422, respectively (the 333 index is the same in these two cells).

$$\frac{1}{d_{330}^2} = \frac{18(1 - \cos \alpha)}{a^2(1 - 3\cos^2 \alpha + 2\cos^3 \alpha)} \quad (2)$$

$$\frac{1}{d_{422}^2} = \frac{8(3 + 2\cos^2 \alpha - 5\cos \alpha)}{a^2(1 - 3\cos^2 \alpha + 2\cos^3 \alpha)}$$

(3)

Solving the set of equations (2) and (3) for the set of ZnTe NWs we obtained the lattice parameters $a = 0.43196 \pm 0.00005$ nm and $\alpha = 60.06 \pm 0.01^\circ$ for our virtual unit cell. Similar calculations performed for $\text{Zn}_{1-x}\text{Mg}_x\text{Te}$ NWs ($x \approx 0.17$) grown on the (001)- and (110)-oriented GaAs substrates gave the rhombohedral unit cell with parameters: $a = 0.43528 \pm 0.00005$ nm and $\alpha = 60.04 \pm 0.01^\circ$.

In order to check the correctness of these results we calculated the d_{333} value for the first rhombohedral unit cell and compared it with the experimental d_{333} value obtained for (111)-oriented ZnTe NWs – these values differ from each other by 0.00006 nm. We also tested the precision of such calculations - we took the d_{600} , d_{440} values of not deformed ZB unit cell of ZnTe and next we have calculated parameters of the rhombohedral unit cell from equations (2). As the result we obtained rhombohedral values: $a = 0.43156$ nm and $\alpha = 59.992^\circ$ which differ by $\Delta a = 0.00001$ nm and $\Delta \alpha = 0.008^\circ$ from the proper (60°) ones. This gives us the confidence that the results of our calculations are reliable within the limits given by above testing procedure.

4. Discussion

According to the results of HRTEM studies of all investigated in this work ZnTe based NWs, the specific defect structure inside a single NW, for majority of them, was detected. Especially important is the presence of high number of stacking faults created along the growth direction of the NW. The X-ray diffraction measurements give the averaged results from relatively large volume of studied sample. It is obvious that for NWs samples the X-ray diffraction gives the results from large number of single NWs. From this point of view, the crystal structure determined on the base of X-ray studies should be treated as an averaged one. It is particularly important in the case of our

samples where the averaging process takes place in two steps: within each NW and on the set of these NWs. It is noteworthy that NWs without defects or with a low number of them also exist. Therefore we proposed the term “virtual unit cell” for description of real crystal structure of a set of NWs. In such categories our results should be understood.

According to our studies the crystal structure of ZnTe based NWs differs from that in the bulk material: due to the defect structure created during growth of NWs the zinc-blende unit cell is distorted to the rhombohedral one. The shape of such virtual unit cell is the same for ZnTe and ZnMgTe NWs (the angle α is practically the same in both cases), while the a parameter of ZnMgTe NWs is larger due to bigger size of Mg atoms partially occupying Zn sites.

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Figure captions

Fig. 1. FE-SEM side-view images of ZnTe NWs grown on (100) – (a), (110)- (b) and (111)B (c) oriented GaAs substrates. The wires are inclined to the substrate at angles 35.3° (a), 54.7° (b), 90° and 19.5° (c) depending on the crystallographic orientation of the substrate. The growth axis of each wire is parallel to the $\langle 111 \rangle$ GaAs direction. The lattice parameter of NWs calculated from reflections 600, 440 and 333 (it means in the direction perpendicular to the substrate) is larger than that for bulk ZnTe (see text below).

Fig 2. The X-ray diffraction patterns obtained for ZnTe NWs grown on (001)-oriented GaAs substrate (a) – symmetrical ω - 2θ scan and (b) – coplanar 2θ scan in the glancing incidence geometry.

Fig. 3. Two types of NW structure near the top: (a) – high density of stacking faults with thin twin segments, (b) – top part of a NW being free of defects; (c) and (d) magnified views of part (a) and (b), respectively. Upper dark shape visible in (a) and (b) is the Au-based eutectic particles (Janik et al., 2007).

Fig. 1.

Fig 2.

Fig. 3.