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Raman scattering studies of MBE-grown ZnTe nanowires

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We report on the first studies of the optical properties of MBE-grown ZnTe nanowires (NWs). The growth of ZnTe NWs was based on the Au-catalyzed vapour–liquid–solid mechanism and was performed on (001), (011), or (111)B-oriented GaAs substrates. Investigated NWs have a zinc-blende structure, the average diameter of about 30 nm, and typical length between 1 and 2 μm. Their growth axes are oriented along <111>-type directions of the substrate. The structural characterization of the NWs was performed by means of X-ray diffraction, using the synchrotron radiation corresponding to the wavelength of $\mathrm{CuK}_{\alpha 1}$ radiation W1 beamline at Hasylab DESY). The macro-Raman spectra of either as-grown NWs on GaAs substrate or of NWs removed from substrate and deposited onto Si were collected at temperatures from 15 K to 295 K using Ar^+ and Kr^+ laser lines. Strong enhancement of ZnTe-related LO-phonon structure was found for an excitation close to the exciton energy. Our studies revealed also the presence of small trigonal Te precipitates, typical of tellurium compounds.

Key words: *ZnTe nanowire; Raman scattering; MBE growth; lattice dynamics*

1. Introduction

The II–VI one-dimensional nanostructures such as ZnO, ZnS, ZnSe, or ZnTe nanowires (NWs) have attracted a lot of attention during the last few years due to their unique properties and potential applications in electronics and optoelectronics. Most available experimental data concern ZnO and papers devoted to metal chalcogenides are not very numerous. In particular, the crystal growth and properties of NWs made from telluride compounds seem to be restricted to some reports on ZnTe NWs obtained by various methods [1–8], on CdTe NWs [9–11], and on HgTe NWs [12].

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MBE growth of ZnTe NWs using the vapour–liquid–solid (VLS) method has been reported previously by some of the present authors [5]. The MBE technique offers some advantages in comparison to the alternative growth methods (e.g., chemical vapour deposition or precipitation from solutions). In particular, the future fabrication of more complex NWs structures made of heterojunctions or multinary compounds should be easier because of the versatility of the MBE technique.

Raman scattering is a powerful tool for characterizing the structural properties of semiconductors. However, among the above mentioned papers describing the growth and properties of ZnTe NWs only one is devoted in part to this experimental technique [3]. The Raman spectroscopy is not very often applied also for investigations of other NW systems because of possible large intensity of luminescence in the spectral range close to the frequencies of interest. In the case of II–VI based NWs, Raman spectra have been accumulated on CdTe [9,10], CdSe [13], CdS [14], ZnSe [15,16], ZnS [17–19], several papers concern also ZnO pure or transition metal doped.

It should be stressed that in a typical case Raman scattering study on NWs is limited to the Raman spectrum taken at room temperature (RT) on as-grown sample (usually, NWs are not separated form the substrate after the catalytic growth). Only one example of the Raman studies on II–VI based NWs removed form the substrate and another one reporting on low temperature studies can be found in the literature for semiconductor systems mentioned above ([14] and [10], respectively).

The goal of the present work was to study the structural properties of MBE-grown ZnTe NWs by means of Raman scattering investigating both as-grown NWs and NWs separated from the substrate.

2. Experimental

ZnTe NWs were grown in an EPI 620 MBE system equipped with the low temperature effusion cells and reflection high-energy electron diffraction (RHEED). The growth was performed from elemental Zn and Te sources on (001), (011), and (111)B-oriented, semi-insulating GaAs substrates. The growth process was based on the Au-catalyzed vapour–liquid–solid mechanism. The thin gold layer (from 3 Å to 20 Å thick) annealed in high vacuum prior to the NWs growth was applied as a source of catalytic nanoparticles. ZnTe NWs with an average diameter of about 30 nm and the typical length 1–2 μm were grown by this method. More details about the applied technology may be found in [5]. Several pictures have been taken after the growth with a scanning electron microscope (FE-SEM Leo 540).

The standard structural characterization of NWs was performed using synchrotron radiation at the W1.1 beamline at Hasylab (DESY) in Hamburg. The monochromatic X-ray beam of the wavelength $\lambda = 1.54056$ Å (corresponding to CuKα_1 radiation) was selected for such a purpose. Two modes of measurements were applied, namely symmetrical ω–2θ scan and coplanar 2θ scan in the glancing incidence geometry. These measurements allowed one to separate the contributions due to the polycrystalline layer on the top of the substrate from that due to NWs. The described measurements allowed us also to check the preferred orientation of NWs and to correlate it with the substrate orientation.

All Raman scattering measurements were performed in a quasi-backscattering geometry using a Jobin-Yvon U1000 spectrometer equipped with holographic gratings, a S20 photomultiplier, and a photon counting system. The macro-Raman spectra of either as-grown NWs on GaAs substrate or of NWs removed mechanically from substrate and deposited onto Si wafer were collected at temperatures from 15 K to 295 K. For the low-temperature measurements, samples were placed on a cold finger of a continuous flow helium cryostat. Several Ar^+ and Kr^+ laser lines served for the excitation but most results were accumulated with the use of 514.5 nm Ar^+ laser line. The typical spectra were collected within the frequency range from 0 to 650 cm^{-1} with a spectral resolution close to or below 2 cm^{-1} but in selected cases the Raman scattering studies were continued up to 1500 cm^{-1}. Typical laser line power was in the range 25–50 mW, the laser spot on the sample surface had a diameter of about 100 μm.

3. Results and discussion

For MBE-grown ZnTe NWs the growth axis is always oriented along <111> directions of the substrate. This means that for (001)-oriented GaAs one can expect four <111>-type orientations of NWs in space, for (011)-oriented substrate only two, and for (111)GaAs four orientations. The photographs taken with the use of FE SEM confirmed the presence of all the mentioned orientations of NWs (in the case of (111) -oriented GaAs only (111)B substrates have been applied).

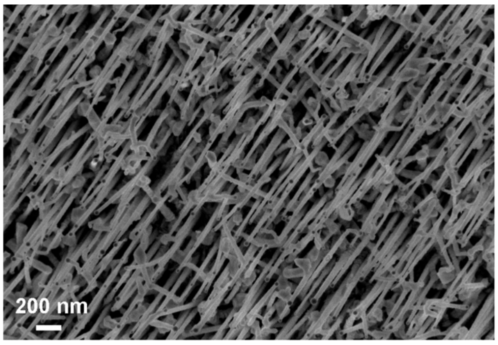

Fig. 1. FE SEM image of as-grown ZnTe nanowires on (011) oriented GaAs substrate (plane view)

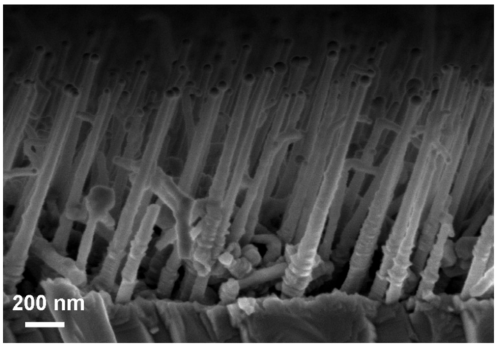

Fig. 2. The cross sectional view of the same sample as that from Fig. 1 taken by means of FE SEM (viewed along the $<\bar{1}\bar{1}0>$ axis)

Figure 1 shows a picture taken along the axis normal to the (011) oriented GaAs substrate (top view). As one can see, the NWs are randomly distributed on the GaAs surface but their projections onto this surface are preferentially aligned along one direction (parallel to <110>) and confirm the expectation. The second photograph taken from the side for the same sample (Fig. 2) clearly demonstrates that a majority of NWs is inclined and form the angle of 54.7° relative to the substrate plane. Similar properties of NWs have been analyzed in the previous paper concerning ZnTe NWs grown on (100)-oriented substrates [5] and will be also a topic of a separate report dedicated to structural properties of ZnTe NWs grown on (110)- and (111)B-oriented substrates. Previous studies of electron diffraction (described in [5]) and current X-ray diffraction results clearly demonstrated the zinc-blende structure of all investigated ZnTe NWs, they also suggest a single crystal character of these NWs, except the stacking faults in the lower part of NWs and in the catalyst semisphere on the top of each NW (seen in Fig. 2). These details will also be discussed elsewhere.

Figure 3 gives an example of the Raman spectrum taken for as-grown NWs. The feature near 208 cm^{-1} is the ZnTe LO-phonon line. Both the frequency of this mode and its full width at a half maximum (FWHM) correspond to the values typical of high-quality ZnTe single crystals and are an optical proof of a high structural quality of the NWs. The presence of the frequency shift due to the size effect that was reported and analyzed previously [20] was not observed in our data since the mean diameter of our NWs was 30 nm, larger than that causing this size effect. The feature corresponding to the optical phonon overtone (the ZnTe 2LO phonons) is also present, and will be discussed later.

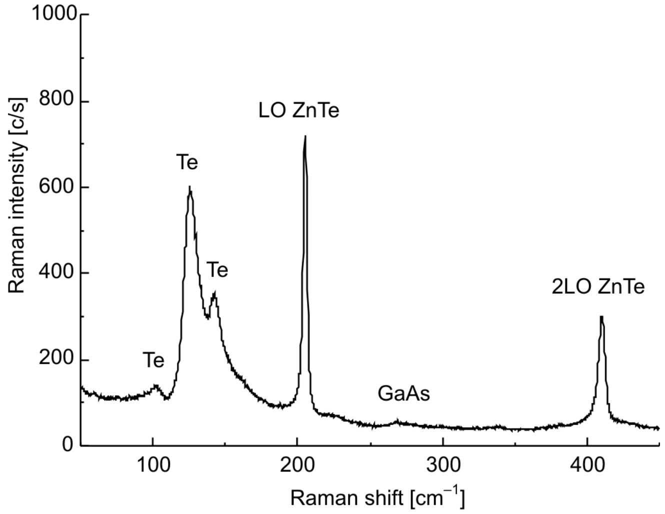

Fig. 3. Raman scattering spectrum of as-grown ZnTe/GaAs(011) NWs sample taken at room temperature. The wavelength λ of the Ar^{+} laser excitation line was 514.5 nm and the applied power 50 mW

The peaks in the spectral range between 100 cm^{-1} and 150 cm^{-1} are due to the Raman scattering on phonons in precipitates of small crystals of trigonal tellurium (see, e.g., [21]). Such peaks can be found in all spectra taken on various specimens.

A high-quality MBE-growth of ZnTe requires an excess of tellurium and therefore all ZnTe-based materials grown by this technique (thin layers or quantum structures) always contain such Te precipitates as well. Because of very small sizes and very low concentrations of these precipitates, their presence cannot usually be detected by standard characterization methods like, e.g., X-ray diffraction. However, due to the high scattering cross section of the trigonal Te, Raman spectroscopy is a very sensitive method that can be used to detect the presence of this secondary phase in an investigated crystal. For example, using this method the presence of Te precipitates (resulting from small non-stoichiometry) have been also found in bulk CdTe crystals grown by the Bridgman method. It should be also pointed out that the existence of these precipitates in our samples cannot even be revealed by X-ray diffractometry performed in glancing incidence, using as strong source as a synchrotron radiation.

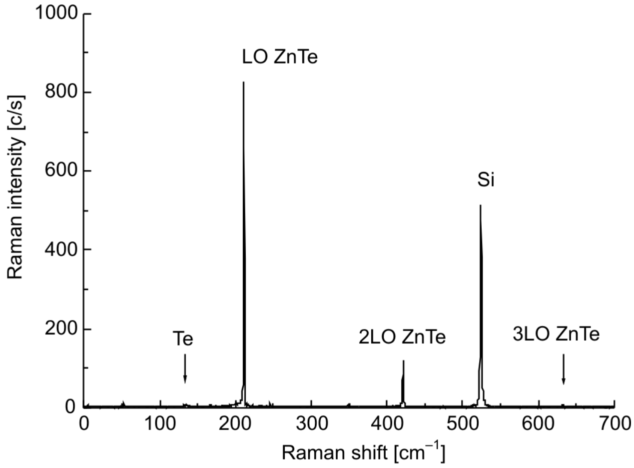

Fig. 4. Raman scattering spectrum taken at 15 K on ZnTe NWs removed from GaAs substrate and deposited on Si (NWs from the same sample as that analyzed in Fig. 3). The wavelength λ of the incident Ar$^+$ laser line was 530.9 nm and the applied power 25 mW

In order to separate a possible Raman scattering signal coming from the thin polycrystalline film on the substrate (as observed in Fig. 2) from that originated in the NWs, the same measurements were repeated for NWs removed from the GaAs substrate and deposited in a random manner on a Si substrate. Such samples placed on a cold finger of the cryostat have been cooled down to temperature of 15 K. Figure 4 shows the Raman spectrum taken at this low temperature on a typical sample prepared in the manner described above. The observed temperature shift of ZnTe LO-phonon frequency corresponds well to the behaviour of the bulk crystal. A structure at 520 cm^{-1} due to the optical Si phonon is of course also visible. The Te-related signal is no longer easily seen – its intensity is a few orders of magnitude smaller than that corresponding to the ZnTe LO phonon. This finding demonstrates that probably most of the trigonal Te precipitates were located inside the thin polycrystalline layer on the substrate.

The small remaining Te-related peaks can be caused either by the part of layer transferred together with NWs to the Si substrate or by the Te precipitates inside NWs itself.

ZnTe, like most of the II–VI semiconductors, is a direct gap material for which the resonance in Raman scattering has been intensively investigated [22–26]. In particular, it has been demonstrated that under a resonant excitation on the exciton several ZnTe LO-phonon mode replicas can be observed in good quality crystals [25, 26]. The resonant condition which can be achieved both for the incident photon energy and for the scattered photon energy depends also on temperature because of the temperature dependence of the exciton frequency [27]. Our preliminary Raman scattering measurements, performed for various frequencies of the exciting laser beam on ZnTe NWs confirmed this behaviour, observed previously in bulk ZnTe. In particular, in our experiment the 2LO-phonon replicas have been observed for selected excitation laser lines having energy close to that of exciton both at RT and at low temperature (Figs. 3 and Fig. 4, respectively). More precise studies of the Raman scattering, performed in function of the excitation frequency are, however, clearly required. This could reveal the expected modification of the resonance frequency value caused by the confinement effects in thin NWs. This type of measurements is in progress now.

4. Conclusions

We have reported the studies of MBE-grown ZnTe NWs by means of the Raman scattering. The macro-Raman spectra have been taken both on as-grown ZnTe/GaAs NWs and on ZnTe NWs removed from the substrate and placed on an Si wafer. Such measurements performed at room temperature and at 15 K demonstrated a high quality of the investigated NWs. The presence of residual, small crystalline Te precipitates, typical of tellurium compounds was also detected. Additionally, the ZnTe LO-phonon replicas were observed under the resonant scattering condition. The temperature dependence of the resonant enhancement of Raman scattering will be a topic of future studies.

The optical confirmation of the high quality of MBE-grown ZnTe NWs, reported in this paper, is important in view of their possible applications as very versatile building blocks for future nanoelectronics. A successful growth of such ZnTe-based NWs opens also an opportunity for future band structure engineering in the nanowire configuration, enabled by the possibility of mixing of ZnTe with other tellurides, e.g. CdTe and MgTe. NWs based on ZnTe can play a particularly important role in the bottom-up approach to spin-operating (spintronic) nanodevices due to the ease of both Mn incorporation and p-type nitrogen doping of this semiconductor.

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