Raman spectroscopy of MBE-grown ZnTe and Zn_{1-x}Mn_{x}Te nanowires

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Abstract. We report on the first studies of the optical properties of MBE-grown ZnTe-based nanowires (NWs). The growth of ZnTe and Zn_{1-x}Mn_{x}Te nanowires was based on the Au-catalyzed vapour-liquid-solid mechanism and was performed on GaAs substrates having various orientations. The investigated NWs have a zinc-blende structure, an average diameter of about 30 nm, a typical length between 1 and 2 μm, and are aligned along the <111> directions of the substrate. The structure characterization of the NWs was carried out by means of X-ray diffraction and scanning electron microscopy. Raman spectra of either as-grown NWs on GaAs substrate or of NWs removed from the substrate and deposited onto Si were collected at low or ambient temperatures. Under resonant condition, a set of LO-phonon replica was observed.

1. Introduction and motivation

One-dimensional semiconductor nanostructures such as nanowires (NWs) are very promising candidates for applications in nanoscale electronic and optoelectronic devices. Among them, the II-VI NWs such as ZnO, ZnS, ZnSe, or ZnTe have attracted considerable attention during the last few years because of their possible magnetic properties when doped with transition metals. In particular, NWs based on ZnTe and containing manganese could 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. However, papers devoted to zinc chalcogenides are not very numerous and successful growth by various methods of NWs containing tellurides as well as their properties have only been described in a few references [1-6]. MBE growth of ZnTe NWs offers some advantages in comparison to alternative growth methods as it allows the possibility to build more complicated structures like NWs made of multinary compounds or heterostructures. Raman scattering is a powerful tool for the study of structural and crystalline properties of nanostructures but, as far as we know, no Raman data for a single ZnTe NW have been yet reported. Most of results published until now is limited to micro-Raman spectra taken at RT for as-grown NWs.
samples only. However, because there is always a thin layer made of the grown material at the base of the wires it is crucial to make sure that the measured Raman signal is caused by the wires themselves by performing Raman scattering on NWs removed from their substrate and deposited on another suitable material, like e.g. silicon. The aim of the present work was to investigate the Raman scattering in ZnTe and Zn$_{1-x}$Mn$_x$Te NWs, both as-grown and separated from the substrate.

2. Experimental
ZnTe and Zn$_{1-x}$Mn$_x$Te NWs were grown in an EPI 620 MBE system equipped with a low temperature effusion cells and reflection high-energy electron diffraction (RHEED). The growth process based on the Au-catalyzed vapour-liquid-solid mechanism was performed from elemental Zn, Te, and Mn sources on (001), (011), and (111)-oriented, semi-insulating GaAs substrates. NWs with an average diameter of about 30 nm and a typical length from 1 to 2 µm were grown by this method. More details about this technology can be found in Ref. [5]. After the growth, pictures of the wires were taken using a scanning electron microscope (FE-SEM Leo 540). The NWs structure and chemical composition were determined from X-ray diffraction. Raman scattering measurements were performed using 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 15 K. At ambient temperature, spectra of a single NW could be acquired using the x100 objective of a microscope coupled to the spectrometer which ensured a diffraction limited spot diameter of the order of 1 µm. During the low-temperature measurements, samples were placed on the cold finger of a continuous-flow helium cryostat.

3. Results and discussion
Analysis of the X-ray diffraction patterns shows that the crystallographic orientation of the substrate imposes the orientation of the NW so that NWs growth axes were oriented along <111>-type directions of the substrate. In the case of mixed crystal, due to the large difference of the lattice parameter of ZnTe and zincblende MnTe the composition could be determined by the X-ray diffraction with relatively high accuracy. The NWs with a mixed crystal composition as high as x = 0.40 were obtained and analyzed. The preferred orientation of NWs is well seen on photographs taken with the use of FE-SEM. Figure 1 and figure 2 show SEM images of side view and of 45° angle view of Zn$_{1-x}$Mn$_x$Te NWs sample containing about 35% of Mn. One can see a small decrease of the

**Figure 1.** Side view FE-SEM image of Zn$_{0.65}$Mn$_{0.35}$Te/GaAs(110) NWs.

**Figure 2.** 45° angle view FE-SEM image of Zn$_{0.65}$Mn$_{0.35}$Te/GaAs(110) NWs.
NWs diameter as a function of NW length. Small crystallized droplets of metal catalyst on the top of each NW confirm the catalytic growth mechanism.

In the upper part of figure 3, the Raman spectrum of as-grown NWs on (001) GaAs substrate taken at temperature of 15 K using the 514.5 nm Ar$^+$ laser line is plotted. A line near 209 cm$^{-1}$ at the frequency of ZnTe LO-phonon as well as several LO-phonon replicas at multiple of this frequency is observed. The observation of such replicas in good quality crystals is classical when the excitation is resonant with the exciton and has been frequently reported for direct band gap semiconductors [7, 8].

The phonon frequencies of the LO and of the replicas are the same as those observed for bulk material. It rules out a possible phonon confinement effects in the analyzed NWs. The observation of a well defined, narrow LO-phonon structure and its replicas is on the other hand a direct proof of the good crystalline quality of the grown NWs. The 514.5 nm line used for measurements was selected from all the lines of the Ar$^+$ and Kr$^+$ lasers in this energy region because it gives the largest signal. Its energy is the closest to the exciton energy of bulk ZnTe at 15 K [9] so if an electron confinement effect is present in the NWs under consideration it should be very weak. On this figure as well as on the next figures, the group of lines observed between 90 cm$^{-1}$ and 150 cm$^{-1}$ (labelled Te) is due to Raman scattering on trigonal tellurium clusters. Precipitates of this material are usually present in MBE grown tellurium compounds and are easily observed by Raman spectroscopy because of the high cross section of this crystal.

A similar spectrum is observed for NWs which have been removed from the substrate and deposited on a (100) silicon wafer (figure 3 bottom), demonstrating that the origin of the scattering is indeed the NWs. The intensity of the signal is smaller because of the reduced density of the deposited wires as compared to that of as-grown NWs.

The top panel of figure 4 shows the Raman spectrum (T = 15 K, $\lambda = 514.5$ nm) of Zn$_{0.7}$Mn$_{0.3}$Te NWs deposited on Si. Both the 1 LO and the 2 LO phonons structures are observed. The bottom panel of figure 4 compares the 1 LO phonon in NWs of the mixed and pure materials. It shows a frequency shift towards higher frequency of the LO phonon of the alloy. The mixed crystal composition estimated from the Raman scattering by the modified Genzel model described in [10] corresponds to that resulting from X-ray diffraction measurements.

**Figure 3.** Raman spectra of as-grown ZnTe NWs on GaAs substrate (top) and of NWs deposited on Si (bottom).

**Figure 4.** Raman spectra of Zn$_{0.7}$Mn$_{0.3}$Te NWs on Si substrate (top), and comparison of the ZnMnTe and ZnTe LO phonon lines (bottom).
The presence of LO-phonon replicas has also been demonstrated for a single ZnTe NW as shown in figure 5. The spectrum was acquired under microscope at ambient temperature. The 530.9 nm line of the Kr⁺ laser was preferred to the 514.5 nm, as it is resonant with the exciton of bulk ZnTe at room temperature.

4. Conclusions
The successful growth of pure binary ZnTe as well as mixed Zn₁₋ₓMnₓTe NWs allowed to observe the Raman scattering on optical phonons (including several LO-phonon replicas) which demonstrates the good structural and electronic properties of the NWs. Up to now, no phonon or electron confinement effects could be observed. The possibility of growing alloys in nanowires geometry opens the possibility of band structure engineering of the NWs based on II-VI compounds.

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References
[1] Li Y, Ding Y and Wang Z 1999 Adv. Mater. 11 847-50
[2] Li L, Yang Y, Huang X, Li G and Zhang L 2005 J. Phys. Chem. B 109 12394-8
[3] Huo H B, Dai L, Xia D Y, Ran G Z, You L P, Zhang B R and Qui G G 2006 J. Nanosci. Nanotechnol. 6 1182-4
[4] Huo H B, Dai L, Liu C, You L P, Yang W Q, Ma R M, Ran G Z and Qui G G 2006 Nanotechnology 17 5912-5
[5] Janik E et al. 2006 Appl. Phys. Lett. 89 133114
[6] Dong A, Wang F, T L Daulton T L and Buhro W E 2007 Nanoletters 7 1308
[7] Klochkikhin A A, Morozenko Ya V and Permegorov S A 1978 Fiz. Tverd. Tela 20, 3557
[8] English translation, Sov. Phys. Solid State 20 2057-62
[9] Feng Z C, Perkowitz S and Becla P 1991 Solid State Commun. 78 1011-4
[10] Pässler R, Griebel E, Riepl H, Lautner G, Bauer S, Preis H, Gebhardt W, Buda B, As D J, Schikora D, Lischka K, Papagelis K and Ves S 1999 J. Appl. Phys. 86 4403-11
[11] Peterson D L, Petrou A, Giriati W, Ramdas A K and Rodriguez S 1986 Phys. Rev. B 33 1160-5