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Magnetic and Structural Study of (ZnTe)/Co Core-Shell Nanowires Grown by Molecular Beam Epitaxy

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Arrays of crystalline ZnTe nanowires grown by vapor–liquid–solid mechanism were covered with cobalt in a molecular beam epitaxy system. Magnetic and structural characterization of such core/shell nanowires was performed. Using scanning electron microscopy and transmission electron microscopy it was found that the mean shell thickness of cobalt was about 35% of the nominal deposition thickness. Deposited cobalt had a polycrystalline structure covering the ZnTe nanowires evenly along their length. With the increment of temperature during Co deposition the roughness of the nanowire sidewalls increases. Vibrating sample magnetometry measurements revealed that the magnetization easy-axis direction is perpendicular to the long axis of the nanowires, which is in agreement with theoretical predictions. Oxidation of Co shell does not change the anisotropy direction of such structures, however it increases their coercivity. Exchange bias effect at the interface of cobalt and cobalt oxides suggested by some authors is not responsible for such anisotropy orientation.

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1. Introduction

In the past decade self-assembled semiconductor free-standing nanowires (NWs) have been intensively studied. Flexibility in doping, diameters from several to tens of nanometers and lengths up to several μm make such structures a candidate for broad range of possible applications in logic gates and computing [1], self-assembling nanoscale devices [2], nanoscale electronic and opto-electronic devices [3]. Regarding magnetic nanowire structures applications such as recording media or biological sensors [4] or cell manipulation [5] are often considered. Hybrid ferromagnetic metal/semiconductor nanowire structures gives a new approach as it embraces two possible areas of applications, that of semiconductor NWs and that of ferromagnetic nanotubes.

In principle NWs grown by vapour–liquid–solid (VLS) method can be deposited using molecular beam epitaxy (MBE) even on lattice mismatched substrates without dislocations typical of 2D structures [6]. In this work the following method was used: deposition of a ferromagnetic material (cobalt) directly onto the surface of theretofore grown semiconductor NWs. Such ferromagnetic metal of a designed shape can form a nanomagnet on semiconductor nanowire producing a magnetic field changing many electronic properties of the semiconductor. The aim of this work was to obtain and characterize a model object for magnetic anisotropy study — (ZnTe)/Co core-shell nanowires.

2. Experimental details

ZnTe nanowires orientation to the substrate plane strongly depends on the crystallographic orientation, therefore the (111) GaAs substrate, where ZnTe nanowires grow perpendicularly to the substrate plane, was chosen. Growth process of long and straight ZnTe NWs was described in detail in Ref. [7]. The deposition of cobalt onto the side walls of NWs was performed in molecular beam epitaxy (MBE) system. Sample rotation and a small angle of Co deposition of 14° to the normal of the sample plane was used to obtain a complete coverage of ZnTe nanowires by cobalt film. The Co deposition rate was set to 0.03 nm/s. The samples with 10 nm nominal Co thicknesses were prepared at growth temperatures ranging from room temperature to 300 °C. For magnetic investigations the samples with 10 nm and 20 nm of Co nominal thickness were prepared without any protective layer as well as with 10 nm of Au. The Co nominal thickness corresponds to a deposition onto a flat substrate, therefore structural characterization of nanowires was necessary to reveal the real wall thickness of a cobalt shell covering ZnTe nanowire. Structural study was performed by means of field-emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray (EDX) analysis on Zeiss-Auriga CrossBeam SEM-FIB (focused ion beam), transmission electron microscopy (TEM) manufactured by FEI, type Titan CUBED 80-300. Analysis and interpretation of TEM images were carried out with DigitalMicrograph [8] software. Magnetic properties were studied using Oxford Instruments Vibrating Sample Magnetometer (VSM).

Samples were cleaved along one of the GaAs easy cleavage planes allowing to collect FE-SEM images in direction perpendicular to the sample surface. For EDX measurements the ZnTe nanowires covered with Co shell were separated from the GaAs substrate by sliding original sample over Si wafer.

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3. Results and discussion

Figure 1 presents FE-SEM images of ZnTe nanowires covered with 10 nm of Co at different temperatures during deposition, i.e. 20 °C, 100 °C, 200 °C and 300 °C. A spherical Au–Ga nanoparticle is clearly visible at the top of each nanowire. With the increasing deposition temperature the Co surface roughness of NWs side walls increases (see Fig. 1a–d), which is related to the increase of Co grains' sizes.

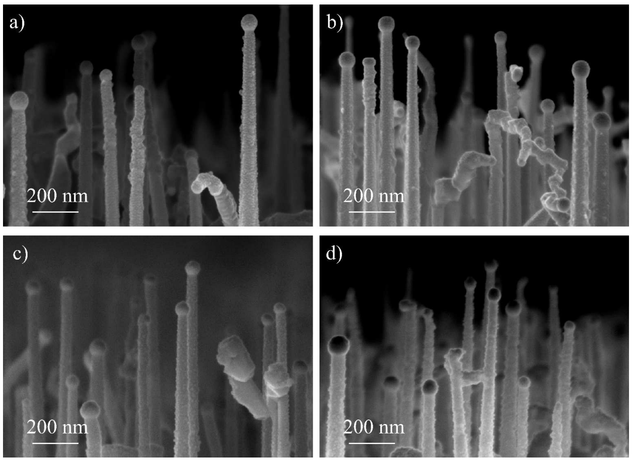

Fig. 1. SEM images of ZnTe nanowires with Co shell of 10 nm nominal thickness deposited at (a) 20 °C; (b) 100 °C; (c) 200 °C, (d) 300 °C.

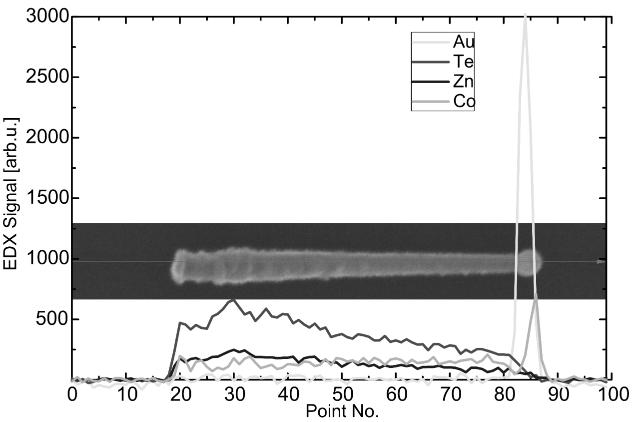

Fig. 2. EDX line profiles of cobalt coated ZnTe nanowire along the axis of the NW.

Sample rotation and small deposition angle of 14° to the sample normal during the growth allowed a uniform Co coverage of the whole nanowire along its length, which was confirmed by EDX study. Line profile of signal intensities of Co K_α, Zn K_α, Te L_α, and Au L_α lines along the NW are presented in Fig. 2. It is clearly visible that due to the slightly conical shape of the nanowire, Zn and Te line intensities are highest at the bottom of the NW, on the other hand, Co line intensity is constant along the length of the NW and Au is only visible at the spherical nanoparticle at the top of the NW. The increase of Co signal at the top of that nanoparticle is due to the fact that Co forms a cap during deposition process (perfectly visible in Fig. 3).

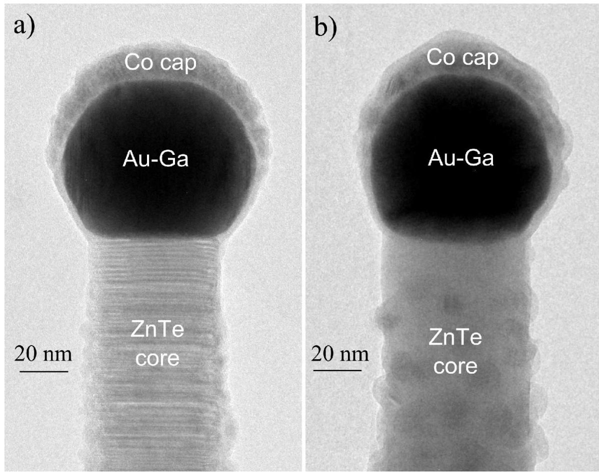

Fig. 3. TEM images of ZnTe nanowires with Co shell of 10 nm nominal thickness deposited at (a) 100 °C, (b) 300 °C.

Transmission electron microscopy allowed determination of the Co shell thickness covering ZnTe NWs. For the sample with 10 nm of Co nominal thickness deposited at 100 °C the measured Co shell thickness ranged between 3.0 to 4.1 nm with a mean value of 3.5 nm (see Fig. 4). As Co shell is polycrystalline, only a few Co grains with atomic planes parallel to electron beam direction are visible in Fig. 4.

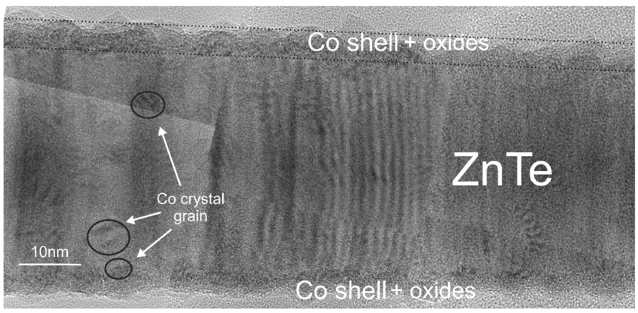

Fig. 4. The collage of six stitched TEM images of Co coated ZnTe NW with visible cobalt shell (dotted line is a guide for the eye) and cobalt crystal grains.

Two TEM images of ZnTe nanowires covered with 10 nm Co nominal thickness deposited at (a) 100 °C and (b) 300 °C are presented in Fig. 3. It can be noted that the Co shell is more deformed and larger crystallites are more visible in Fig. 3b than in Fig. 3a. This is a result of the Co crystal grains dimensions increasing with higher deposition temperature.

Both experimental results [9] and theoretical predictions [10] on Co hollow nanotubes have shown that the magnetization easy-axis direction is perpendicular to the long axis of the Co nanotube with wall thickness around several nm. The origin of such easy-axis magnetization direction is not clear yet. Some authors claim that it can be caused by magnetoelastic anisotropy induced by strain [10] or that it can be related to the exchange bias effect at the interface of Co and cobalt oxide formed on Co surface [10, 11]. Elimination of Co shell oxidation by deposition of a thin protective Au layer was then performed to check the validity of the second mechanism.

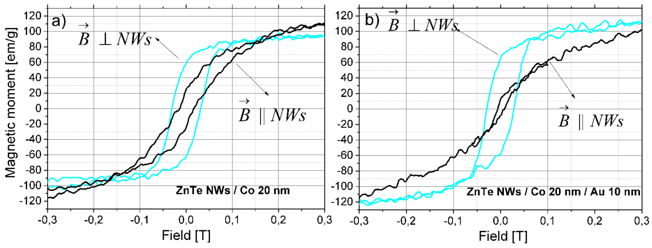

Fig. 5. Hysteresis loops of Co-coated NWs obtained by VSM at 300 K. (a) sample with 20 nm Co, (b) sample with 20 nm Co /10 nm Au.

Our experiments on (ZnTe)/Co core/shell NWs without Au cap layer have revealed similar anisotropy direction as for hollow Co nanotubes in Refs. [9, 10], i.e. the easy-axis magnetization direction is perpendicular to the NWs long axis (see Fig. 5a). In Fig. 5b the hysteresis loops for NWs with a protective layer of Au on Co shell are shown. It can be observed that the use of a Au protective layer does not change the easy-axis magnetization direction, which is still perpendicular to the NWs long axis. However, it causes a slight magnetic softening that is best seen for the easy-axis loops. Values of the coercive field for samples with and without the protective layer are presented in Table.

Values of coercive fields for samples measured in perpendicular direction of the applied magnetic field with respect to the NWs long-axis. TABLE

Sample	Coercive field [Oe] for $H \perp$NWs
10 nm Co	250
10 nm Co+Au	217
20 nm Co	313
20 nm Co+Au	288

It can be seen that without the protective Au layer on (ZnTe)/Co core/shell NWs the coercive field for the easy-axis loop increases by roughly 15% and 9%, for 10 nm and 20 nm of deposited Co, respectively. The observed behaviour can be related with higher surface anisotropy of Co shell and enhanced pinning of magnetic moments for magnetization reversal at the interface with Co oxides than with Au layer. However, Co oxides on (ZnTe)/Co core/shell NWs does not influence the easy-axis direction of magnetization and thus the exchange-bias mechanism proposed by some authors [10, 11] as the origin of such specific anisotropy direction is not confirmed for the studied core/shell system.

4. Conclusions

The aim of this study was to obtain and characterize (ZnTe)/Co core/shell nanowires that were produced in a two-step MBE growth process. Co deposition was realized at a small angle to the surface normal and with sample rotation to assure a uniform coverage of NWs and to obtain magnetic nanotubes having homogeneous wall thickness. Structural and morphological characterizations of these nanostructures were performed. The thickness of the Co shell surrounding the ZnTe nanowires was found to be 3.0 to 4.1 nm with a mean value of 3.5 nm for 10 nm of Co nominal deposition thickness at 100 °C. It was found that cobalt deposited on ZnTe nanowires has a nanocrystalline structure. VSM study of ZnTe nanowires with Co shell confirmed theoretical predictions that easy-axis of magnetization is perpendicular to the long axis of the nanotube. Furthermore, Co surface oxidation is a source of a small additional anisotropy, but it does not influence the easy-axis direction. Hence, the exchange bias effect at the cobalt–cobalt oxides interface, suggested by some authors, is not responsible for such anisotropy orientation.

Acknowledgments

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