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Synthesis and Magnetic Characterization of Co-axial $Ge_{1-x}Mn_x$/a-Si Heterostructures

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ABSTRACT

A method for synthesizing $Ge_{1-x}Mn_x$/a-Si core-shell nanowires (x = 0.3-1 %) using a supercritical fluid deposition technique, with a homogeneous distribution of manganese along the entire lengths of the crystalline Ge cores, but not in the a-Si shells, is reported. Investigations into the magnetic properties of the heterostructured nanowires revealed a significant influence of the amorphous Si shell covering the surface of the core $Ge_{0.997}Mn_{0.003}$ nanowires, compared to pristine $Ge_{0.997}Mn_{0.003}$ nanowires with no a-Si coating. The magnetic data revealed diminished values of both the remanence and the saturation magnetization for pristine Mn-doped Ge nanowires at higher temperatures when compared to the $Ge_{1-x}Mn_x$/a-Si core-shell nanowires, whereas both these parameters increased as the temperature dropped down to 5 K. Differences in the temperature-dependent evolution of the coercivity were observed in the magnetically harder core-shell nanowires compared to the pristine $Ge_{0.997}Mn_{0.003}$ nanowires, showing a drop of 26 % at (5 K *vs.* RT) compared to a drop of 66 % for the pristine nanowires. The low dopant concentration (0.3(1) %) of Mn in the core-shell nanowires combined with the observed ferromagnetic properties, suggests a combination of the hole-mediated exchange and confinement processes as a reason for the observed properties. Our observations show the importance of a protective layer in covering the oxidation-sensitive dilute magnetic semiconductor nanowires.

KEYWORDS: Germanium, Nanowire, Heterostructure, Core-shell, Magnetic Properties, Structural Characterization.

INTRODUCTION

The design and controlled growth of one-dimensional (1D) nanostructures play a central role in nanowire research due to the tunable physical and chemical properties of these building blocks as a function of their morphology, size, phase and crystallographic orientation.[1, 2] Several mechanisms and strategies have been widely used to enable the growth of 1D nanostructures by vapor and liquid phase techniques.[1] Recently, the growth of axial heterostructured semiconductor nanowires was demonstrated to be controllable with sharp interfaces between segments [3], intentional twinning [4, 5] and kinking.[6] Alternatively, the physical properties of a nanowire can be altered by the deposition of a surrounding shell, where the shell can have a crystalline relationship with the nanowire core [7] or be of an amorphous architecture.[8]

Doping of group 14 semiconductors with traditional elements such as boron [9] and phosphorous [10] to alter their electrical properties has previously been described in the literature. In addition, impurity doping through the incorporation of transition metals in germanium has been achieved by supercritical fluid [11] and chemical vapor deposition techniques.[12] The resulting materials are members of the well-known dilute magnetic semiconductor (DMS) family, with potential applications in spin-based electronic devices.[13] Combining the two approaches of doping the Ge nanowire and the creation of a core-shell geometry should lead to altered physical performances, due to the saturation of dangling bonds at the core-shell interface and resulting oxidation protection of an active core material. In addition, Ge/Si core-shell structures have shown significantly enhanced electrical properties in field effect transistors devices compared to pristine Si or Ge nanowire materials, including higher charge carrier mobilities, ambipolar behavior and 1D hole gas characteristics.[14, 15] Here we describe the growth and characterization of single crystalline manganese-doped germanium/amorphous silicon ($Ge_{1-x}Mn_x$/a-Si) core-shell nanowires. The co-axial structures were formed by a two-step supercritical fluid deposition process. Structural (SEM and TEM) as well as compositional (EELS and XRF) characterization of the core-shell and pristine $Ge_{1-x}Mn_x$ nanowires are presented. The impact of the

shell on the magnetic properties of the $Ge_{1-x}Mn_x$ was investigated for low manganese concentrations (0.3(1) %), using a superconducting quantum interference device (SQUID).

EXPERIMENTAL DETAILS

Materials

Mn-doped Ge nanowires were grown in 5 ml stainless steel cells (High Pressure Equipment Company) at an optimized temperature of 698 K. The handling of the dry toluene and the reactant solutions in toluene (diphenylgermane (ABCR); monophenylsilane (Sigma-Aldrich) and manganese decacarbonyl (Sigma-Aldrich)), as well as the filling of the reaction cell and injection cell, was carried out in a glove box, using stringent conditions to minimize water exposure. The precursors to form the wires, diphenylgermane and manganese decacarbonyl, were injected into the growth chamber as a toluene mixture in the appropriate ratio required (Mn content 0.3 % $\leq$ x $\leq$ 1%). This low manganese concentration was deliberately chosen to prevent the formation of secondary manganese-rich phases, such as the ferromagnetic $Mn_{11}Ge_8$ and Mn_5Ge_3.

In a typical experiment a gold-coated silicon substrate was loaded into a stainless steel cell. The thickness of the sputtered gold layer used in this study was ~ 5 nm. The reaction cell and injection equipment were dried under vacuum at 363 K for 72 h and transferred into a glove box. 4 ml toluene was filled in the 5 ml reaction cell and the assembly heated to 698 K in a tube furnace, which pre-pressurized the reaction cell. After setting the pressure to 20.7 MPa, the injection cell, filled with 20 ml of toluene/diphenylgermane/manganese decacarbonyl solution (c_{Ge}=10.8 µmol ml^{-1}, c_{Mn}0.11-0.035 µmol ml^{-1}), was set to the identical pressure by an ISCO HPLC pump. The precursor solution was injected into the reaction cell at a rate of 1.5-2 ml h^{-1} over a time period of 60-240 min, under constant pressure conditions in a flow through configuration. After the first step of $Ge_{1-x}Mn_x$ nanowire growth the temperature was held at 698 K for 1 h and subsequently raised to 723 K for the growth of the Si shell. The pressure in the reaction cell was regulated to 27 MPa again and 0.5-1.5 ml toluene/monophenylsilane (c_{Si}= 4.0 µmol ml^{-1}) was injected into the reaction cell over a time period of

5-20 min. The temperature was held for 6 h to ensure decomposition of the precursor species. Finally the reaction cell was cooled to room temperature, depressurized and disassembled to access the reaction products.

Materials Characterization

The deposits of 1D Ge nanostructures were analyzed using a FEI Inspect F50 scanning electron microscope (SEM). The Ge nanowires were deposited on lacey carbon copper grids for TEM characterization. HRTEM images were acquired on a Jeol 2100 and STEM-EELS measurements were carried out using a JEOL 2010F field emission gun (S)TEM, working at 200 kV with a point-to-point resolution of 0.19 nm, coupled with a GIF spectrometer. X-ray fluorescence (XRF) data were acquired on a Bruker S2 PICOFOX total reflection X-ray fluorescence analyzer. Materials denoted in the manuscript containing 0.3(1) % manganese will have an uncertainty which is probably in the range of one tens of the doping level, but the value is with high certainty in the range of 0.2-0.4%; however we have to stress that the Mn level determined via XRF was always close to the concentration in the precursor cocktail. Literature data also suggest that modern XRF is capable to determine doping elements in high accuracy (difference between ICP-MS and XRF <10 % of the doping level) with moderate experimental efforts.[16]

Magnetization measurements were performed on $Ge_{0.997}Mn_{0.003}$/α-Si core-shell and $Ge_{0.997}Mn_{0.003}$ nanowires (predefined by the Mn concentration in the injection reaction and confirmed by XRF) as well as on undoped Ge nanowires (reference sample) using a superconducting quantum interference device (SQUID) magnetometer (MPMX XL, Quantum Design) in the temperature range T = 5 - 300 K and in fields up to 50 kOe. All samples were measured as a "bulk" of as-grown nanowires on their original Si/SiO_2 substrates. In the case of field-dependent magnetization measurements the total magnetic moment was corrected for the diamagnetic contribution originating from the substrate. In all of the experiments the magnetic field was applied at an arbitrary angle to the nanowire axis. As the

experimental error in determining the nanowire volume or mass was too high, only the total magnetic moment of the sample was considered in the paper. Standard precautions for working with low moment samples were undertaken. In particular, only ceramic tools were used for sample handling.

RESULTS AND DISCUSSION

Single crystalline manganese-doped germanium nanowires were grown by a SFLS growth mechanism [17] on gold-coated silicon substrates and coated in a second step with an amorphous silicon (a-Si) shell. A SEM image of the $Ge_{0.99}Mn_{0.01}$ nanowires is shown in figure 1(a). The absence of particle deposits as by-products on the nanowire surfaces and within the sample verifies the controlled growth of the nanowires without a macroscopic separation between the manganese and the germanium components. The presence of gold as a growth promoter is mandatory for Mn-doping of the germanium nanowires. In the absence of a gold seed Lensch-Falk *et al.* described a phase separation leading to the formation of syntaxially growing manganese-germanide/germanium axial nanowire heterostructures.[18] The liquefied Ge/Au droplet also incorporates manganese and as a result of the turbulent nature of the liquid the manganese is transported to the interface between the growing nanowire and the droplet, where it becomes incorporated into the germanium host matrix. The temperature at which the $Ge_{1-x}Mn_x$ nanowires were grown, *i.e.* 698 K, was intentionally higher than the growth temperature we typically employ in the gold-seeded growth of Ge nanowires, *e.g.* 653-683 K, due to the impact of the manganese dopant in the gold seed particles and the high melting points of gold manganese alloys.[19] High resolution transmission electron microscopy (HRTEM) images reveal the single crystalline nature of the manganese-doped Ge nanowires (figure 1(b)). A fast Fourier transformation (FFT) pattern of the HRTEM images, as shown in figure 1(b) (inset), supports the highly crystalline nature of the nanowires synthesized and allows determination of the nanowire growth direction. The large diameter (mean value of 40-80 nm in typical growth experiment) of the nanowires produced resulted in a prominent <111> growth direction, as expected in 1D germanium crystals with radial diameters exceeding 20 nm.[20]

Given the structural integrity of the $Ge_{1-x}Mn_x$ nanowires during a temperature rise to 723 K, we deposited a thin amorphous Si shell onto the surface of the nanowires by a second injection cycle. The thermal decomposition of monophenylsilane resulted in an amorphous silicon layer (a-Si) forming around the $Ge_{1-x}Mn_x$ nanowires as shown in figure 2(a). In addition to the shell formation, all of the initial manganese-doped germanium nanowires were extended along their axis by a silicon segment due to the presence of the gold growth seed (figure S1). The length of this Si segment depended on the amount of monophenylsilane injected into the reaction cell, but generally in our investigations was shorter than 1 μm for shell thicknesses of 25 nm. Temperatures used to decompose the precursor were high enough to grow silicon nanowires via the SFLS mechanism as described in the literature under similar conditions.[21] The segments can be identified by different Z-contrast in the SEM images as shown in figure S1. Figure 2(a) shows a HRTEM image of a synthesized $Ge_{0.99}Mn_{0.01}$/a-Si core-shell nanowire. The core is highly crystalline, as already observed in the pure $Ge_{0.99}Mn_{0.01}$ nanowires, while the shell thickness (between 5±2 - 25±4 nm) was controlled by the amount of monophenylsilane injected into the reaction cell. Given the slower decomposition rate of silane compared to diphenylgermane, the time for decomposition was extended to several hours at 723 K for deposition of the a-Si shell. The injection of the monophenylsilane was also carefully monitored and slowly executed to prevent local temperature gradients and the formation of new nucleation centers leading to particle growth and contamination of the wire deposit. The amorphous Si shell had a low level of carbon contamination due to the ability of monophenylsilane to crosslink with SiH_4 which is formed by a scrambling reaction of individual monophenylsilane molecules.[22] At higher temperatures used for Si nanowire growth by SFLS (50 K above the growth temperature employed here) amorphous shells were observed, which contained carbon impurities close to the detection limit, whereas no carbon containing shell was observed at the temperatures used in our studies.[23] However, potential carbon contamination should not be neglected when considering the shell crystallization to create a crystalline interface between the core and the shell for electrical transport studies.

The Mn dopant concentration and distribution in the nanowires was examined by total reflection X-ray fluorescence spectroscopy for the as-grown nanowire sample on the silicon substrate and electron energy loss spectroscopy (EELS) for individual nanowires. The bulk deposits of nanowires on silicon substrates showed Mn concentrations in the range between 0.3(1)-1.0(2) %, reflecting the concentrations of the Mn precursor used to grow the initial $Ge_{1-x}Mn_x$ nanowires. EELS line scans were performed to determine the local distribution of manganese in the core-shell structures as shown in figure 2(c). The XRF is analyzing a large area, which makes this technique insensitive to the actual whereabouts of the Mn. Therefore, EELS is used to investigate the local distribution of Mn in the wires. However, the EELS suffer from absorption effects and therefore quantification of Mn in Ge is difficult by this technique which is reflected by the quantification of the dopant (4-5 %) in figure 2(c). Accurate estimation of the doping level is impossible without the use of appropriate reference samples to calibrate the system and still this technique could lead to inaccurate results due to the measurement error of EELS in the 2-3 % range and therefore the more reliable XRF data are used. The HAADF image shown in figure 2(b) illustrates the direction of an EELS line scan taken across the diameter of a core-shell nanowire, as marked with an arrow. In the EELS analyses performed, Mn was found to be located exclusively in the Ge core of the nanowires and not in the Si shell, illustrating that Mn does not diffuse into the Si shell during prolonged annealing at 723 K. The concentration of Mn also did not vary across the core diameter, which reflects the homogeneous incorporation of Mn in the Ge host matrix and the absence of phase separation at the core-shell interface or cluster formation within the $Ge_{1-x}Mn_x$ core. The shell consists of amorphous Si, without prominent oxide formation as determined by EELS analysis, however a thin native oxide will built up on the surface of the amorphous silicon after prolonged time in an oxidizing environment. However, in our experiments the crystalline $Ge_{1-x}Mn_x$ core was protected against oxidation by the Si shell. In order to exclude local inhomogeneities due to the formation of Mn-rich inclusions or surface accumulation of the dopants, which would not be detectable by the techniques used, we limited the Mn content for the magnetic measurements to 0.3(1) %.

The magnetic properties of the synthesized core-shell nanowires were determined using a SQUID and compared with pristine manganese-doped germanium nanowires of the same manganese concentration. An obvious difference between the pristine $Ge_{0.997}Mn_{0.003}$ nanowires and the core-shell structures was in the temperature-dependent saturation moment (M_S). The $Ge_{0.997}Mn_{0.003}$/a-Si core-shell nanowires showed very weak changes with increasing temperature, whereas the $Ge_{0.997}Mn_{0.003}$ nanowires exhibited a drop in M_s with increasing temperatures. This drop in M_S is most likely attributed to surface oxidation of the pristine $Ge_{0.997}Mn_{0.003}$ nanowires after removal of the nanowires from the reactor and exposure to atmospheric moisture. This modification of the nanowire surface affects the material properties and the presence of dangling bonds on the surface. Moreover, the saturation magnetization was almost constant for the core-shell nanowires (2 % variation), whilst M_s of the pristine $Ge_{0.997}Mn_{0.003}$ nanowires changed by up to 19 % over the temperature range between 5-293 K (figure 3(a) and (b)). The Si shell will also be oxidized in the ambient conditions but the protective effect of the SiO_2 layer wrapping around the $Ge_{0.997}Mn_{0.003}$ core results in the unchanged saturation magnetization. On the other hand, in $Ge_{0.997}Mn_{0.003}$ nanowires a certain fraction of the Mn atoms will be trapped in an amorphous Ge oxide layer near the surface due to the homogeneous distribution of the dopant in the initially crystalline Ge nanowires. Most likely the significant drop in M_S for the pristine $Ge_{0.997}Mn_{0.003}$ nanowires originates from these Mn atoms in the oxidized layer being generally excluded from the long-ranged magnetic ordering. While at low temperatures some (partial) magnetic alignment in such a layer still can be achieved, at high temperatures thermal excitations will lead to an effective loss of the spin alignment. Theoretical investigations on crystalline manganese-doped Ge with high levels of O impurities leading to antiferromagnetic coupling are described in the literature; however these predictions cannot be applied to our system due to the crystalline Ge matrix and nearest neighbors of Mn atoms assumed in this theoretical model.[24]

For both the $Ge_{0.997}Mn_{0.003}$/a-Si core-shell and $Ge_{0.997}Mn_{0.003}$ nanowires the field dependences of the magnetic moment, *m(H)*, were characterized by open hysteresis and moment saturation at $H \approx 3$ kOe over the temperature range investigated, *i.e.* T = 5–293 K, (figure 3(a) and (b)). The results clearly

signify a long-range ordering of magnetic spins. The magnetic hysteresis is much more evident in the case of the core-shell nanowires. The effect is particularly notable at room temperature and can be characterized by a coercive field of H_c = 148 Oe and normalized remanence of m_R/m_S = 0.25, which is a significant improvement, *i.e.* about 2-fold increase of both parameters in comparison with $Ge_{0.997}Mn_{0.003}$ nanowires, where the corresponding values are H_c = 68 Oe and m_R/m_S = 0.12. It should be noted that the measured coercive field is significantly higher than previously measured in $Ge_{1-x}Mn_x$ nanowires [25, 26, 12] and nanodots [27] even though a higher Mn concentrations (up to 5 %) were described in these literature studies. The inset in figure 3(a) shows the original hysteresis curve at T = 293 K, which was not corrected for the diamagnetic contribution, and where both the saturation and coercivity can clearly be seen. The sizeable difference in the total magnetic moment measured in $Ge_{0.997}Mn_{0.003}$/a-Si and $Ge_{0.997}Mn_{0.003}$ samples originates from different volumes of the magnetic material. As the temperature decreases to T = 5 K, the overall shape of the hysteresis curve remains unaltered, although both materials become magnetically harder and their coercivity and remanence increase (figure 3(c)). At the same time, the difference between the Si-coated and pristine $Ge_{0.997}Mn_{0.003}$ nanowires diminishes at low temperature, which is particularly evident at T = 5 K where H_c = 200 and 196 Oe were obtained for core-shell and pure $Ge_{0.997}Mn_{0.003}$ nanostructures, respectively. In comparison, a hysteretic behavior has never been observed in undoped single crystalline Ge nanowires, where the *m(H)* dependence remained linear.

Dependence of the magnetic properties of the nanowires on their thermal history was studied by measuring temperature dependencies of the magnetic moment after applying different cooling procedures, *i. e.* (i) maximum field cooling (MFC) when the sample was cooled in a maximum magnetic field of $H_{cooling}$ = 50 kOe, (ii) zero magnetic field (ZFC) cooling, $H_{cooling}$ = 0, and (iii) field cooling (FC) when cooling and measurements were performed in the same field, $H_{cooling}$ = 100 Oe. In all cases the moment was measured in the warming cycle at H_{meas} = 100 Oe.

Figure 4 shows temperature dependencies of the magnetic moment, *m(T),* as measured after applying different cooling procedures to the $Ge_{0.997}Mn_{0.003}$/a-Si nanowires. When the sample was cooled in the

magnetic field (FC and MFC regimes), the magnetic moment gradually decreased with temperature. However, ZFC measurements showed the opposite tendency where a very broad temperature maximum was observed (figure 4(a)). The difference between FC and ZFC curves is plotted in figure 4(b). Bifurcation of curves starts above 300 K and becomes more pronounced at low temperatures. The resulting curve is smooth demonstrating the absence of any characteristic temperatures, which were observed previously in GeMn nanowires [28]. The difference between ZFC and FC curves signifies the irreversibility of the field-induced changes and indicates the presence of a magnetically ordered phase above room temperature, as also confirmed by a clear hysteresis loop (figure 3(a)). We do not observe any characteristic temperature transitions in our studies which could be attributed to either Curie or blocking temperatures of the most common binary ferromagnetic alloys, Mn_5Ge_3 (T_c = 296 K) and $Mn_{11}Ge_8$ (T_c = 274 K), in agreement with our structural results. Thus, the long-range ordering in $Ge_{0.997}Mn_{0.003}$/a-Si nanowires cannot be attributed to these common metallic alloys. Importantly, the MFC curve is significantly shifted above the FC one (figure 4(a)), indicating the field-induced nature of the observed long-ranged ordering. Additionally, we studied FC and ZFC dependencies in the higher applied field, H_{meas}= 1 kOe, (figure 4(c)). The results indicate that increasing the measurement field results in the bifurcation point shifting towards lower temperatures, which again points at field-induced effects. Typically the wide separation of the FC and ZFC m(T) curves in the whole temperature range signifies the presence of ferromagnetic precipitates or clusters. However, in the present work this explanation can be generally ruled out on the base of structural data. In addition, the morphology of the presented material has to be considered. It was pointed out that the carrier confinement strengthens the hole localization and, therefore increases the stability of magnetic polarons. In general, the hole concentration plays a very important role in conducting ferromagnetic ordering in DMSs [29] and large concentrations of holes are extremely favorable for a carrier-mediated ferromagnetism. Direct determination of the hole concentration requires transport measurements, which are not, unfortunately, possible with the present geometry of the sample. Finally, the valence-band offset is expected and has been previously observed in the Si/Ge heterostructures.[15, 30] The holes may get trapped in this two-

dimensional quantum well which leads to locally enhanced hole concentration. However, in the system studied here, *i.e.* a system with an amorphous Si shell, merely a small effect of the valence-band offset is expected in comparison to core-shell nanowires with a crystalline structure generally reported in literature.

By carefully considering all experimental data and compare our results with previously published data, we conclude that ferromagnetism observed in $Ge_{0.997}Mn_{0.003}$ and $Ge_{0.997}Mn_{0.003}$/a-Si nanowires is a results of the hole mediation process. Open hysteresis loops up to room temperature, very small temperature dependence of magnetization saturation and relatively small coercive field are typical for this type of the magnetic ordering and were, for example, observed in Ref.[27] in a similar system of GeMn/Si quantum dots. Following the methodology developed in this work, the experimental data from figure 3(a) were represented as Arrott plots (M^2 vs H/M) to extract the invert susceptibility $1/\chi$ which vanishes at the Curie temperature (see Figure S2).[31] The graph shows that χ is finite at 293 K and therefore T_c has not been reached. Mn ions in Ge produce two shallow acceptor levels, which generate holes itinerant between Mn ions and aligning their magnetic moments.[32] In conclusion, the observed ferromagnetic properties of Si/GeMn NCs can be explained by a combination of the hole-mediated exchange and confinement processes.

CONCLUSION

A two-step method has been developed to produce $Ge_{1-x}Mn_x$/a-Si core-shell nanowires (x = 0.3(1)-1(0.2) %) with a homogenous distribution of the manganese dopant concentration in the highly crystalline Ge core. The amorphous Si shell prevents the core from forming a native oxide surrounding the pristine $Ge_{1-x}Mn_x$ nanowires. The effect of the protecting shell can be observed in the magnetic properties, which showed significant differences between the coated and uncoated $Ge_{0.997}Mn_{0.003}$ nanowires. The presence of a magnetically ordered phase above room temperature was confirmed by a clear hysteresis loop. The ferromagnetic properties of $Ge_{0.997}Mn_{0.003}$/a-Si nanowires can be explained by a combination of the hole-mediated exchange and confinement processes. However, the understanding

of the observed phenomena is still far from complete. For example, combination of magnetization measurements with transport and magnetotransport studies will elucidate the nature of ferromagnetic ordering. In addition, element-specific magnetic measurements, *i. e.* XMCD, XPEEM, *etc*., would be essential for understanding the electronic structure and magnetic interactions in the here described DMS nanowires. In addition, studies are underway to develop a strategy to crystallize the Si shell for the evaluation of the electrical properties of such a DMS core/Si shell configuration.

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Supporting Information:

SEM images of the synthesized $Ge_{1-x}Mn_x$ / a-Si core-shell nanowires and Arrot plots. This information is available free of charge via the Internet at http://pubs.acs.org/.