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Engineering the magnetic properties of $Ge_{1-x}Mn_x$ nanowires

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Possible origins of room-temperature ferromagnetism in GeMn nanowires (NWs) are investigated. Arrays of $Ge_{1-x}Mn_x$ NWs and $Ge/Ge_{1-x}Mn_x$ nanocables (NCs) ($x=1\%-5\%$) have been synthesized within the pores of anodized alumina oxide (AAO) membranes. The influence of annealing on the magnetic properties of $Ge_{1-x}Mn_x$ NWs is studied. The room-temperature ferromagnetism is preserved after the postfabrication annealing in inert atmosphere ($T_{ann}=750\ ^\circ C$) demonstrating overall compatibility of $Ge_{1-x}Mn_x$ NWs with conventional complementary metal-oxide semiconductor technology. The role of oxygen in high-T_C ferromagnetic ordering is investigated in double-phased NCs with a Ge sheath. Despite a barrier to oxygen migration from the AAO membrane, samples still display room-temperature ferromagnetism, hence, ruling out any significant role of oxygen in the explanation of the high T_C in the system. The magnetic properties of the one-dimensional $Ge_{1-x}Mn_x$ nanostructures can be understood by considering interface related phenomena. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2694052]

I. INTRODUCTION

Diluted magnetic semiconductors (DMSs) with a Curie temperature T_C above room temperature are essential components of many proposed spintronic devices. In DMS nanowires (NWs) the magnetic properties are altered (often enhanced) due to strong confinement effect and shape anisotropy. Significant attention has been recently devoted to the experimental realization of group IV DMS for its full compatibility with conventional complementary metal-oxide semiconductor (CMOS) technology. An observation of room-temperature ferromagnetism in GeMn NWs[1,2] and nanocolumns[3] was reported recently. Ferromagnetism in the diluted GeMn system is generally considered to be an intrinsic phenomenon,[4,5] and fundamental questions concerning its microscopic origins have to be addressed. Both annealing[6] and influence of nonmagnetic codoping[7] are potential methods for modification of electronic and magnetic structures of the DMS material. Literature results on the annealing of DMS NWs are highly controversial: both significant enhancement of magnetic properties[8,9] and their independence of thermal annealing[10] have been reported depending on the initial material, fabrication methods, and conditions of the experiment.

In this report we study the influence of annealing on the magnetic properties of $Ge_{1-x}Mn_x$ NWs and investigate the role of oxygen in high-T_C ferromagnetic ordering.

II. SAMPLE PREPARATION

$Ge_{1-x}Mn_x$ NWs ($x=1\%-5\%$) with the diameter of 60 nm and the length of $\sim 60\ \mu m$ were synthesized within porous anodized aluminum oxide (AAO) templates at $T_{gr}=500\ ^\circ C$ under the pressure of 37.5 MPa using the supercritical fluid (SCF) technique.[1] Each sample was split into two halves. One part was further annealed for 4 h at $T_{ann}=750\ ^\circ C$ in N_2 atmosphere. In a separate experiment, we have fabricated arrays of double-phased $Ge/Ge_{1-x}Mn_x$ nanocables (NCs) ($x=1\%-5\%$) with the GeMn core diameter of ~ 60 nm, Ge sheath thickness of ~ 7.5 nm, and length of $60\ \mu m$. Consequently, the magnetic core of the $Ge/Ge_{1-x}Mn_x$ NCs is identical to the $Ge_{1-x}Mn_x$ NWs both in dimensions and chemical composition. Structural characterization of samples was carried out using scanning and transmission electron microscopes (SEM and TEM). X-ray diffraction (XRD) data were collected using Cu $K\alpha$ radiation (40 kV and 35 mA). Magnetization measurements were performed using a superconducting quantum interference device (SQUID) magnetometer at temperatures between 1.8 and 370 K and in fields up to 20 kOe. A magnetic field was applied along the NW long axis. Correction for a diamagnetic contribution was done on all of the data.

III. EXPERIMENTAL RESULTS

Details of the thorough structural and stoichiometric characterization of the basic $Ge_{1-x}Mn_x$ NWs have been published previously.[1] The analysis revealed that individual Mn ions are well separated from each other and surrounded by oxygen and germanium atoms rather than other neighboring Mn ions. Figure 1(a) demonstrates a typical SEM image of an array of $Ge/Ge_{0.97}Mn_{0.03}$ NCs partly liberated from the AAO matrix. An x-ray diffraction pattern of pristine $Ge_{0.97}Mn_{0.03}$ NWs and its annealed counterpart is shown in Fig. 1(b). No qualitative difference between two patterns can be seen, proving the absence of major structural changes caused by the annealing process. The analysis shows a polycrystalline nature of the NWs with all the peaks indexed to

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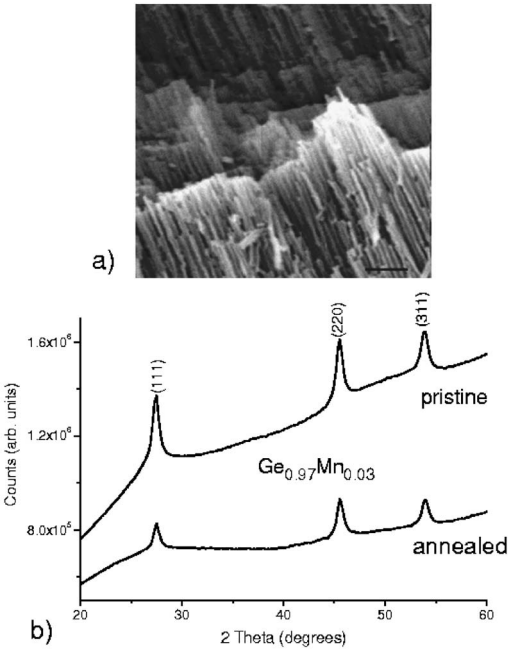

FIG. 1. (a) SEM image of $Ge/Ge_{0.97}Mn_{0.03}$ NCs partly liberated from the membrane. Scale bar is 2 μm. (b) X-ray diffraction pattern in arrays of pristine and annealed $Ge_{0.97}Mn_{0.03}$ NWs within the pores of the AAO membrane.

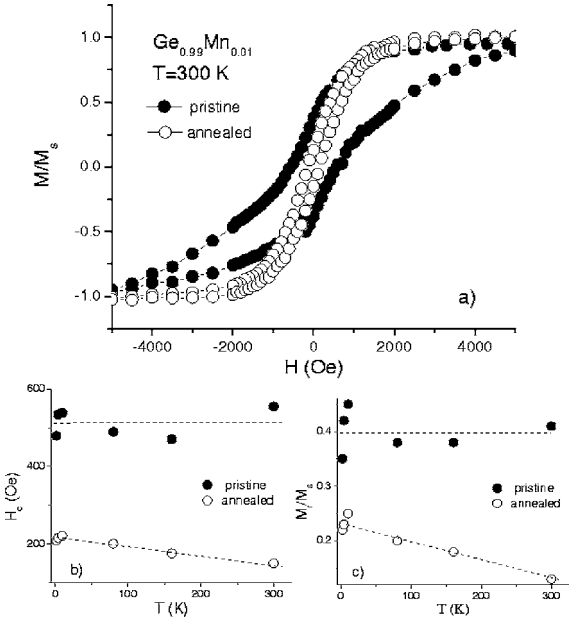

FIG. 2. (a) Magnetization curves for pristine and annealed $Ge_{0.99}Mn_{0.01}$ NWs as measured at 300 K. Temperature dependences of coercive field (b) and remanence (c) for the same sample.

the cubic germanium phase. X-ray diffraction patterns for the $Ge/Ge_{1-x}Mn_x$ NC samples are concentration independent and identical to those of the single-phased $Ge_{1-x}Mn_x$ NWs. While there is no obvious evidence of second phase formation (either oxides or alloys) in these systems, the limitations of the method do not allow one to rule out the formation of a small amount of the second phase conclusively.

Results of room-temperature magnetization measurements for arrays of pristine and annealed $Ge_{0.99}Mn_{0.01}$ NWs are shown in Fig. 2(a). The hysteresis curve for the pristine sample is typical for a ferromagnetically ordered medium, i.e., saturates at low fields, $H_s \cong 3$ kOe, and have a rectangular shape and large coercive field, $H_c \cong 600$ Oe. The magnetic properties of the samples are barely temperature sensitive in a wide temperature interval, $T=4-300$ K. After annealing, the $Ge_{1-x}Mn_x$ NWs retain their room-temperature ferromagnetic properties. The $m(H)$ curve has a more uniform rectangular shape. The annealed $Ge_{0.99}Mn_{0.01}$ NWs show a more distinctive temperature dependence of the coercive field and remanence [Figs. 2(b) and 2(c)]: $H_c = 150-230$ Oe and $M_r=(0.12-0.25)M_s$, respectively. The M_s value remains unaffected by annealing, being of the order of 3.7 ± 0.2 emu/cm^3 as measured at $T=300$ K. However, the annealed sample reveals about 30% higher M_s value at $T=1.8$ K, being $M_s=7.3$ and 9.3 emu/cm^3 in the pristine and annealed samples, respectively. Thus, the annealed $Ge_{0.99}Mn_{0.01}$ NWs demonstrate a stronger temperature dependence of magnetization. This implies a lower Curie temperature of the annealed sample which, however, still exceeds 370 K (the highest available in the measurement setup). Changes in the M_s value induced by annealing may reflect small structural transformations within the NWs which are beyond the sensitivity of the structural techniques used. Decrease of the coercive field after the heat treatment implies reduction of the sample anisotropy due to an improvement of the crystalline structure of $Ge_{0.99}Mn_{0.01}$ NWs. One of the possible routes of effective annealing is an enhanced ability of interstitial Mn defects to diffuse out laterally,[6] which should be especially prominent in a system with reduced dimensions.[8] Although the existence of a ferromagnetic GeMnAl alloy cannot be completely ruled out, its presence in the GeMn NWs is very unlikely as usually this compound forms at much higher concentrations of Mn ($x \geqslant 20\%$).[11] Yet, structural experiments with much finer spatial and compositional resolution, such as extended x-ray absorption fine edge structure (EXAFS), are needed and currently are being undertaken.

In our system, the AAO membrane serves as the main intrinsic source of oxygen in GeMn NWs,[1] and its influence on the magnetic properties cannot be excluded.[2,12,13] To limit the oxygen migration from the AAO membrane, double-phased NCs with the Ge sheath thickness of ~7.5 nm were fabricated. Further, we compare the magnetic properties of the single-phased GeMn NWs and the double-phased Ge/GeMn NCs with the same concentration of the magnetic impurity and lateral dimensions of the magnetic core. While NWs with the lowest Mn concentration ($x=1\%$) show well-established ferromagnetism at $T=300$ K [see Fig. 2(a)], the double-phased $Ge/Ge_{0.99}Mn_{0.01}$ NCs reveal weak magnetic ordering: $H_c=40-70$ Oe and $M_r=0.05M_s$ over the whole temperature range. Nevertheless, a pronounced S-shape and saturation of the $m(H)$ curve persist up to 370 K. The presence of a paramagnetic contribution to the net magnetic moment was observed at $T<20$ K. These results indicate an existence of very weak ferromagnetic ordering in $Ge/Ge_{0.99}Mn_{0.01}$ NCs. However, as the Mn concentration in NCs increases, $x \geqslant 3\%$, the hysteresis curves become similar to those observed in the single-phased NWs and signify a

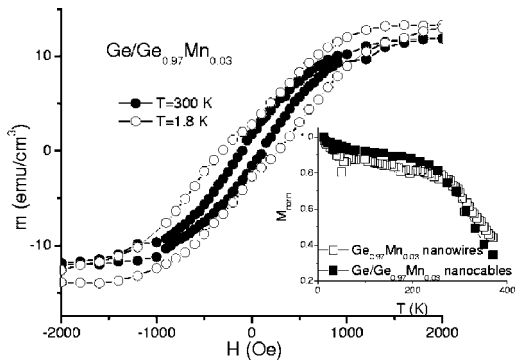

FIG. 3. Magnetization curves for $Ge/Ge_{0.97}Mn_{0.03}$ NCs. Inset shows temperature dependences of the normalized magnetization, $M_{norm}=M(T)/M(T=4\text{ K})$, for $Ge/Ge_{0.97}Mn_{0.03}$ NCs and $Ge_{0.97}Mn_{0.03}$ NWs as measured at $H=1$ kOe.

ferromagnetic type of ordering: $H_c=110-300$ Oe, $M_r=(0.15-0.21)M_s$, and $H_s=2$ kOe (Fig. 3). The temperature dependence of magnetization clearly shows that the transition temperature is significantly above 300 K (see inset in Fig. 3). The lower coercive and saturation fields in the NCs indicate a smaller intrinsic anisotropy in the double-phased system as compared with the single-phased NWs. Thus, our results demonstrate that the double-phased NC samples still display ferromagnetism above room temperature despite the fact that the sheath layer significantly reduces the oxygen migration. This study rules out any significant role oxygen may play in the room-temperature ferromagnetism of the system investigated here. A higher critical concentration of Mn required for the ferromagnetic ordering could be explained by considering the state of the interface in single- and double-layered nanostructures. Our earlier structural results [EXAFS and x-ray absorption near-edge structure (XANES) techniques] show the increased Mn concentration at the NW-AAO interface.[1] Thus, the NW core is Mn depleted, whereas the vicinity of the interface is rich on the magnetic impurity. Yet, it was not possible to determine the precise distribution of manganese atoms along the NW diameter. A higher concentration of Mn ions implies a significant distortion of the interface area due to both a larger atomic radius of Mn ($R_{Mn}=1.40$ Å as compared to $R_{Ge}=1.25$ Å) and a lattice mismatch at the interface with the amorphous AAO. Such distortion causes broadening of Mn wave functions and may augment exchange interactions due to the modified crystalline field. However, in the NCs only the first cause of distortion remains, which implies a significantly smaller modification of the exchange coupling if the Mn concentration is insufficient. Therefore, more Mn atoms are required to observe ferromagnetic properties in agreement with the experiment. Lower anisotropy of the NCs also implies a reduced influence of the interface in the system.

In addition to these effects which depend on the microscopic structure of the NW interface, a more general surface-related phenomenon may take place in one-dimensional (1D) GeMn structures. A considerable enhancement of the surface magnetic moment has been demonstrated in conventional metallic ferromagnets even at the macroscopic scale. The effect originates in a decreased coordination number and a correspondent reduction of the bandwidth for both the majority- and minority-spin states. The relative contribution of the surface increases with reduced dimensionality of the sample and plays the most prominent role in 1D and zero-dimensional (0D) systems. Whereas generally very little is known about DMS materials at the nanoscale, in our previous research we demonstrated that the magnetic moment per unit volume does increase with the inverse of the NW diameter.[2] Thus, surface effects of both fundamental nature and related to the interface microstructure (e.g., oxidation state and local environment of the Mn ions) are the likely sources of ferromagnetism in the one-dimensional $Ge_{1-x}Mn_x$ NWs.

In summary, we studied possible sources of room-temperature ferromagnetism in $Ge_{1-x}Mn_x$ NWs. The high-T_C ferromagnetism is preserved after the postfabrication annealing, demonstrating overall compatibility of $Ge_{1-x}Mn_x$ NWs with the conventional CMOS technology. The role of oxygen in the high-T_C ferromagnetic ordering has been investigated. The results rule out a significant role of oxygen in the magnetic properties of $Ge_{1-x}Mn_x$ NWs. This study provides insights into the microscopic origin of the high-T_C ferromagnetism in 1D GeMn nanostructures, drawing particular attention to the importance of the interface state and surface related phenomena.

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