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Growth of skyrmionic MnSi nanowires on Si: critical importance of the SiO2 layer

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The thickness of the SiO2 layer on the Si substrate plays the key role in obtaining high yield growth of cubic B20 MnSi skyrmion nanowires. A growth phase diagram was constructed based on systematic studies of various growth conditions.
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ABSTRACT

MnSi in B20 structure is a prototypical helimagnet that forms a skyrmion lattice, a vortex-like spin texture under applied magnetic field. We have systematically explored the synthesis of single crystal MnSi nanowires via controlled oxide-assisted chemical vapor deposition and observed a characteristic signature of skyrmion magnetic ordering in the MnSi nanowires. The thickness of the SiO$_2$ layer on the Si substrate plays the key role for obtaining a high yield of B20 MnSi skyrmion nanowires. A growth mechanism was proposed that is consistent with the existence of an optimum SiO$_2$ thickness. A growth phase diagram was constructed based on the extensive studies of various growth conditions for various MnSi nanostructures. The persistence of both the helicoidal and skyrmion magnetic ordering in the one-dimensional wires was directly revealed by ac and dc magnetic measurements.

Introduction

A magnetic skyrmion lattice, a vortex-like spin texture recently observed in chiral magnets, is of great interest to future spintronic data storage and other information technology applications[1–14]. The origin of the magnetic skyrmion phase can be traced to the anti-symmetric Dzyaloshinski-Moriya (DM) interaction that is allowed in space groups lacking inversion symmetry [15–17]. The combined effect of a large ferromagnetic exchange and a weak DM interaction is to twist the magnetization into a long-period spiral that can be tens to hundreds of nanometers in length. As these spirals are only weakly bound to the underlying lattice in cubic systems, they can be readily manipulated with modest applied fields. Prototypical materials with skyrmion ordering are those compounds with cubic B20 structure, like MnSi and FeGe. The skyrmion lattice in MnSi appears in a small region (known as the A phase) of the H-T phase diagram in bulk samples, but in 2D samples like thin films the

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skyrmion phase is much more robust\cite{4,11,14,18}. It is of great interest to determine the properties of the skyrmion phase in quasi-1D nanowires to see the effect of an extra dimensionality limitation. The persistence of the skyrmion ordering in one-dimensional MnSi nanowires may be very promising for spintronics applications as the magnetic domains and individual skyrmions could be manipulated with small currents\cite{8,10,19}. Recently, several reports have appeared about the successful synthesis of high-quality MnSi nanowires via chemical vapor deposition, using MnCl\(_2\) or Mn vapor as a precursor gas \cite{20–23}. Real-space observations have confirmed the existence of skyrmions in quasi-1D MnSi nanowires by using Lorentz TEM \cite{24}. In this paper, we have systematically explored the synthesis of free-standing single crystal MnSi nanowires via controlled oxide-assisted chemical vapor deposition. We have also observed the characteristic signature of skyrmion magnetic ordering in MnSi nanowires with magnetization measurements. In contrast to the other MnSi wire growth techniques and the conventional oxide-assisted growth method employed in the growth of Si nanowires \cite{25–29}, in this work the SiO\(_2\) layer on a Si substrate was used to assist and precisely control the growth process. The thickness of the SiO\(_2\) layer plays a critical role in order to obtain a high yield of stoichiometric, well-crystallized B20 MnSi nanowires; a growth phase diagram was constructed based on the investigated growth parameters. The ac and dc magnetic properties of MnSi nanowires reveal the persistence of both the helicoidal and skyrmion magnetic ordering in the one-dimensional wires.

1 Experimental

1.1 Sample Preparation.

All the samples were synthesized in a custom-designed chemical vapor deposition (CVD) system. The system has precise control of growth temperature, gas flow rate, gas pressure, and distance from substrate to precursor, as schematically shown in Fig. 1(a). In order to get reproducible growth, it was necessary to first pump the system down to a fixed pressure \((3 \times 10^{-2} \text{ Torr}) \) for all the samples) before filling with argon gas. Mn powder was spread flat on the bottom of a porcelain crucible, and then a Si(001) wafer with different SiO\(_2\) thickness \((0, 1, 50, 100, 200, 300, 500 \text{ and } 1000 \text{ nm}) \) was placed above (avoid direct contact) the Mn powder, with the surface of the wafer face down. The distance between the Mn powder and Si wafer was adjusted using layers of supporting wafers of Si to avoid contamination from other elements. The Mn powder was evaporated and deposited onto the Si wafer under an Ar gas environment. The Ar gas is used to adjust the environmental pressure in order to control the Mn vapor; the flow rate was varied from 140 to 300 sccm \(\text{(standard cubic centimeters per minute)} \) and the pressure was maintained between 50 and 625 Torr. The syntheses were carried out at temperatures between 750°C and 950°C, lasting from 40 minutes to 160 minutes. Hydrogen terminated Si wafers were produced by HF acid etching which removes the native oxide \cite{30}; they are contamination-free and chemically stable for subsequent processing as the surface silicon atoms are covalently bonded to hydrogen. An oxidation free Si(001) surface can be achieved after annealing the hydrogen terminated Si wafer to 600°C in an Ar gas environment. Controllable SiO\(_2\) layers were thermally grown on Si substrates at 1200°C. There are 6 parameters involved in the MnSi nanowire growth \(\text{(growth temperature, duration of growth, Ar gas flow rate, Ar pressure, distance between the wafer and the precursor, and SiO\(_2\) layer thickness)} \). After extensive initial screening tests, the optimized growth conditions for stoichiometric and crystalline MnSi wires was determined to be 850°C, 80 minutes, 140 sccm, 625 Torr, 500 \(\mu\) m from sample to precursor, and 100 nm of SiO\(_2\) on the substrate.

1.2 Analytical Techniques.

A Zeiss Merlin Scanning electron microscope (SEM) equipped with a Bruker SDD energy dispersive X-ray spectrometer (EDX) were used to characterize the microstructure and composition of the nanowires in this study. Transmission electron microscopy (TEM) was also carried out on selected specimens, using a Hitachi HF-3300 TEM/STEM at 300 kV. The EDX analysis was carried out in both the SEM and TEM. For the SEM analysis, the nanowires were analyzed either on the original substrates or after dry transfer to SEM carbon tapes. For the TEM study, the nanowires were first removed from the substrate and transferred onto a holey carbon film supported by a...
200-mesh copper grid. The results were consistent. The data shown in this manuscript are from SEM/EDX. The optimized growth was repeated many times. For each growth, SEM/EDX mapping was performed on at least 4 nanowires. All the nanowires were confirmed to be single crystal although some of the wires were covered by amorphous silicon dioxide layer. X-ray diffraction was used to confirm the primary phase of the samples (peaks of MnSi, MnSi$_3$ and MnSi$_7$). As the signal from the wires was very small compared to the substrate, the omega offset was set to 2-3° to minimize the substrate signal. For magnetization measurements, dc and ac magnetic properties of the synthesized material were characterized with a Quantum Design magnetic property measurement system (MPMS)\cite{31,32} with and without substrates. No qualitative differences were observed. The data shown in this paper were obtained without substrates. The nanowires were transferred by gently applying Kapton tape to the substrate to pick up many nanowires and then firmly affixing the tape to a clean silicon substrate. The tape and clean silicon substrate were checked and confirmed to be diamagnetic. The presence of the wires on the tape was verified using SEM and EDX.

2. Results and discussion

The growth of MnSi nanowires was first tried on both a Si wafer with a natural oxidation layer of a few nanometers and hydrogen terminated Si wafers without oxidation layer. Following the procedure described in Refs. [20,21] and fine-tuned in our study (experiment section), MnSi nanowires were only occasionally found to grow around the edges of wafers. We found that the number of nanowires that will grow on an oxidation-free Si wafer is very small. Furthermore, while somewhat more wires were observed to grow on wafer with a native oxide layer, the yield was still small. Interestingly, we noticed that if the growth was conducted under a poor vacuum (the base pressure of the growth system worse than 3×10$^{-2}$ Torr), the number of wires on the silicon wafer increased dramatically. This observation clearly indicates that the growth is not a simple physical vapor deposition of Mn on Si, but a chemical reaction with O$_2$ is involved.

To verify and quantitatively control the effect of oxygen on the growth of MnSi wires, the thickness of the SiO$_2$ layer on the Si substrates was varied in series of comparison experiments. For precise comparison, the growth was repeatedly carried out with all the other experimental conditions remaining exactly the same while changing the SiO$_2$ thickness from 0 nm up to 1000 nm. The number of wires on the substrate increased dramatically when the SiO$_2$ layer was introduced. Fig. 1 and Fig. 2 show the morphological, crystalline and compositional results from wafers with different SiO$_2$ layer thicknesses. The diameter of the nanowires is in the range of 100 to 600 nm, and the length is of the order of tens of micrometers. Fig. 1(b) to (e) are the SEM images of the wires from Si wafers with 100 nm, 300 nm, 500 nm and 1000 nm SiO$_2$ layer thicknesses, respectively. Wires from the 100 nm SiO$_2$ wafer have the best morphology in terms of quantity, size uniformity and even distribution on the surface. The crystalline structures of the wires on various SiO$_2$ thicknesses are very different, too (Fig. S1).
The Mn/Si composition ratio of the wires can be found using EDX analysis. Shown in Fig 2 (a) is an SEM image of nanowires grown on 100 nm SiO$_2$ at 850°C, for 80 minutes. The TEM image and electron diffraction pattern confirm the single crystal nature of the wires. Fig. 2 (b) shows the comparison of the EDX spectrum (normalized to the Si peak) from individual wires of samples with different oxide layer thicknesses. The atomic ratio of Mn/Si from EDX depends on the SiO$_2$ layer thickness. The Mn/Si ratio varies from 0.6 (low oxide thickness) to around 5.3 (thickness of 200 nm and above) (Fig. S2).

These observations point to an optimum SiO$_2$ layer thickness for the growth of MnSi nanowires with high yield and correct stoichiometry and reveal the significant role of the SiO$_2$ layer in the growth, which can be understood as an oxide-assisted growth. The elemental Si required for the MnSi wires is unlikely to come from the surface of SiO$_2$ layer for two reasons: the growth behavior is strongly dependent on the thickness of SiO$_2$ layer, and the reaction temperature (850°C) is much lower than the dissociation temperature of SiO$_2$ (1400°C). The contribution of Si from the silicon spacers cannot be ruled out, but the fact that the stoichiometric and B20 MnSi wires grow well only on 100 nm SiO$_2$ layer wafer proves the key role of the thickness of the SiO$_2$ layer, because the contribution of the Si spacers is the same for all the samples. These results also suggest the role of SiO$_2$ in assisting the growth, as the direct supply of Si from the spacers is constant and unlimited for all samples. The similar sensitivity to SiO$_2$ thickness was also observed in the growth of other B20 silicide nanowires although the SiO$_2$ thickness was much thinner (1-2nm), and the authors pointed out that “a new NW growth mechanism might be at play” [33–35].

There is an optimum SiO$_2$ thickness for the growth (100 nm in our specific setup), in which the supplies of SiO, Si and Mn reach an equilibrium condition. This fact eliminates the most straightforward growth mechanism in which Mn directly chemically reacts with SiO, because it does not utilize the “thickness” of the SiO$_2$ layers. At elevated temperature, the intermediate product SiO can be formed by chemical reaction of SiO$_2$ + Si $\rightarrow$ 2SiO at the interface of the Si wafer and the adjacent SiO$_2$ layer [36,37]. The initial formation of the SiO at the interface should have happened during the growth of the SiO$_2$ layer (1200°C). The two key roles that SiO plays during the growth are: first, after diffusing from the interface to the surface of wafer, SiO acts as a nucleation site which adsorbs surrounding Si and Mn atoms for the one-dimensional wire growth. It was observed previously in Si nanowire growth by laser ablation that much higher nanowire yield could be achieved by introducing SiO$_2$ powder into the Si target to form SiO [38]. Secondly, during the diffusion process from the Si/SiO2 interface to the surface, the reverse reaction also takes place, creating Si interstitials, and the reaction repeats at the newly created interfaces. This diffusion process not only diffuses SiO from the interface to surface, but also largely enhances the self-diffusivity of Si atoms through the SiO$_2$ layer to the surface [39] to achieve correct Mn and Si stoichiometry. The significant diffusion of SiO and reverse reactions could happen around 900°C or even lower [39–41]. The mechanism by which the decomposition of SiO$_2$ to SiO occurs in the temperature range of 900-1050°C is not very clear, although it was proposed based on TEM and SEM observations that after the formation and lateral development of holes in the oxide, elemental Si...
inside the holes supplies Si for reaction with SiO$_2$ at the periphery, so the volatile product of SiO can be formed [39][40]. At the surface of the SiO$_2$, chemical reactions such as $2\text{SiO} + 2\text{Mn} \rightarrow 2\text{MnSi} + O_2$, $2\text{SiO} + \text{Mn} \rightarrow \text{MnSi} + \text{SiO}_2$, or $\text{Si} + \text{Mn} \rightarrow \text{MnSi}$ are needed to form the MnSi nanowires. It is worth emphasizing that this growth process involves an oxidation-reduction reaction, or an oxide assisted synthesis method, to differentiate it from other growth mechanisms [42][43]. The MnSi nanowires with correct stoichiometry and B20 structure can be grown only under narrow growth conditions; small changes of any parameter lead to a dramatic change of the product structure and composition because of the complexity of the growth process. As there are multiple parameters involved in the growth, we designed a final batch of samples as follows to construct a growth phase diagram: 5 samples were grown under optimum conditions by changing only growth temperature, 4 samples by only changing growth time while keeping all other optimum conditions, and 4 more samples by only changing distance between the wafer and the precursor while other parameters remained constant using the optimum values. Additionally, 8 more samples (0, 1, 50, 100, 200, 300, 500 and 1000 nm of SiO$_2$ layer) were grown under optimum conditions to finalize the best SiO$_2$ thickness. The growth phase diagrams summarizing results on those samples are plotted in Fig. 2 (c) and (d), in which only the final batch of samples are marked using diamonds. Other than the oxidation layer thickness which was discussed above, the growth temperature, reaction time, and the distance between substrate and precursor, the argon pressure and gas flow rate were also systematically investigated. From the phase diagram, we can see that the B20 MnSi nanowires can only be grown in the red area. The width of the wires can be tuned from 100 nm to 600 nm by changing the growth temperature within this area. The high yield one-dimensional growth can be qualitatively explained by the theory of supersaturation, with the SiO$_2$ layers as acting to control the supersaturation ratio. In order to enhance one-dimensional growth, the two-dimensional growth probability $P_N$ should be suppressed. This probability is given by: $P_N = B \exp \left( -\frac{\pi \sigma^2}{kT \ln \alpha} \right)$, where $\alpha$ is the supersaturation ratio which is equal to $p/p_o$, where $p$ is actual vapor pressure and $p_o$ is equilibrium vapor pressure at growth temperature $T$, $\sigma$ is surface energy of a solid whisker, $B$ is a constant and $k$ is the Boltzmann constant [44]. Reducing temperature and supersaturation ratio can be tuned by the thickness of the SiO$_2$ layer. In this case the thicker the SiO$_2$ layer becomes the lower the Si or SiO concentration becomes as these species need to diffuse from the bottom to the surface of SiO$_2$ layer. This analysis suggests that the diameter of the nanowires can be further reduced by further increasing the SiO$_2$ layer thickness and growth time, and meanwhile decreasing the growth temperature. The magnetic measurements of the samples support the structural and compositional results. The nanowires were transferred by gently applying a Kapton tape to the growth substrate and then firmly affixing the tape to a clean silicon substrate. Shown in Fig. 3 (a) are the magnetization curves near the 29 K helimagnetic transition plotted on an expanded scale. The transition is clearly apparent for the MnSi wires grown on 100 nm SiO$_2$ layer measured at 10 Oe. The cusp close to Tc is a clear signature of the formation of the helical state, which only exists at small field (the cusp disappears when the field exceeds 1000 Oe) [3,45]. The magnetic measurements were done with magnetic field parallel and perpendicular to the surface of the wafer (in-plane and out-of-plane). Although there are a few nanowires pointing away from the growth substrate, the majority of wires are aligned on the substrate, while the orientation in plane of the substrate is random. In this configuration, the out-of-plane magnetic data shows the sum of the magnetization perpendicular to the wires’ long axis; while the in-plane data shows the azimuthal average of all the wires on the surface plane. From both temperature dependent and field dependent data in Fig. 3 (a), the magnetic behavior in-plane looks a little bit stronger than out-of-plane. The growth direction of the wires is [110] [20,21], and the helical domains point out of
the (111) face, which is 35° from (110). So the projection of the helical contribution out-of-plane is around 71% of the in-plane contribution. This is likely the reason for the small difference in the two directions although as addressed above the magnetic data is the average of the wires. Further studies using local techniques such as micro SQUID are necessary to fully quantify the magnetic anisotropy.

The isothermal ac susceptibility and DC magnetization as a function of magnetic field confirm the existence of the skyrmion phase (A phase) in the nanowires. Fig. 3 (b) shows the comparison of the ac susceptibility with the susceptibility $\mu_0 dM/dB$ calculated from the dc magnetization $M$ at 28 K, just below the transition temperature. The isothermal ac susceptibility as a function of field was measured under an excitation amplitude of 1 Oe and 8 Hz ac magnetic field applied in-plane. Measurements performed as the magnetic field is increasing and decreasing show characteristic features which have been shown to be signatures of the A-phase [6,46–49]. Other than the reduced value of ac susceptibility, we also observed the extra peaks in the $\mu_0 dM/dB$ which is a characteristic feature of A-phase formation as explained in detail in Ref [46]. The $\mu_0 dM/dB$ curve shows two lower kink regions (700-1150 Oe and 1150-2300 Oe) and three transition maxima (700, 1150, 2300 Oe). By increasing the field, the magnetic structure goes from helical to conical ordering (from $B_{c1}$ to $B_{c1}^*$), then from conical to A-phase (in between $B_{c1}$ and $B_{c2}$). At 26.5 K, the first maximum in $\mu_0 dM/dB$ (which represents the helical-to-conical transition) is still visible, but the two peaks related to the A-phase transition almost disappear. Please note that as the mass of the nanowires is much smaller (0.06 mg for the sample shown) than the bulk single crystals, the signal-to-noise ratio of the data is not as good as that of the literature[46]. Other than the extra noise, our data are consistent with the above-mentioned reference.

The field dependence of the ac susceptibility $\text{Re}(\chi_{ac})$ and dc magnetization changes strongly in the narrow temperature window from 26 K to 28.5 K and for $B \leq 4000$ Oe. Fig 3(c) shows the evolution of the $\text{Re}(\chi_{ac})$ approaching from low $T$ to $T_c$. The blue and red dashed lines are guides to the eye for $B_{c1}$, $B_{c2}$ and $B_{c1}^*$, $B_{c2}^*$. At 26 K, there is a shallow dip in the middle; a well-pronounced local minimum has developed near 27.8 K. The characteristic feature is present up to 28.5 K and by 29 K is completely smeread. The quasi-1D effect, in the range we studied (100 nm to 600 nm), is very weak.

![Figure 3](image)

**Figure 3** dc and ac magnetization obtained on MnSi nanowires. (a) In and out of plane anisotropic magnetization (see text for definition) under dc field of 10 Oe. The kink around 29 K is the signature of helical magnetic order. The inset shows the field dependence of the magnetization at 10 K. (b) The comparison of the ac susceptibility $\text{Re}(\chi_{ac})$ (blue), $\text{Im}(\chi_{ac})$ (red) with the susceptibility $\mu_0 dM/dB$ (black) calculated from the field dependence of the dc magnetization $M$ (purple, right Y axis) at 28 K. The isothermal ac susceptibility as a function of field measured under excitation field of 1 Oe and 8 Hz ac magnetic field applied in-plane at 28 K. (c) The evolution of the $\text{Re}(\chi_{ac})$ approaching from 26 K to $T_c$ 29 K. The blue and red dash-lines are guides to the eye for $B_{c1}$, $B_{c2}$ and $B_{c1}^*$, $B_{c2}^*$.

3. Conclusions

The growth conditions of MnSi nanowires have been studied. Different Mn-Si compositions can be selected by tuning growth parameters. The key parameter for high yield, stoichiometric, and well-crystallized growth of cubic B20 MnSi wires is the thickness of the SiO$_2$ layer. A growth phase diagram was constructed that provides a systematic guide for selective growth of nanowires with different compositions. The ac and dc magnetic properties of MnSi nanowires reveal the presence of helimagnetic and skyrmion magnetic phases in the one-dimensional wires. Theoretical modeling will be required to fully understand growth phase diagram and validate the conjectured growth mechanism.

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Electronic Supplementary Material: Supplementary material (further details of the XRD, EDX and magnetization on different structures) is available in the online version of this article at http://dx.doi.org/10.1007/s12274-***.**** (automatically inserted by the publisher).

References


Electronic Supplementary Material

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**Fig. S1** XRD spectroscopy of nanowires samples prepared on Si substrate with different SiO$_2$ thickness, 1 nm, 100 nm and 1000 nm. Different crystalline structures were obtained for different samples. On the sample with only native oxide layer (1 nm), peaks of Mn$_4$Si$_7$ are dominant (black). However, on sample with 100 nm SiO$_2$ layer, the dominant structure is the MnSi with exact ratio of 1:1 composition (red). While for samples with 1000 nm oxide layer, as showing blue, the main structure become Mn$_5$Si$_3$. 

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Fig. S2 Mn/Si atomic ratio obtained using EDX spectroscopy from nanowires samples prepared on Si substrate with different SiO$_2$ thickness. SiO$_2$ layer thickness dependence of the quantified atomic ratio of Mn/Si from EDX. The Mn/Si ratio increases when the oxide layer thickness increases. At low oxide thickness, the Mn/Si ratio is as low as 0.6; when the oxide layer thickness becomes 200 nm and above, the composition start to approaching 5:3. The Mn/Si atomic ratio plot is consistent with the crystalline structure development in the XRD (from Mn$_4$Si$_7$ to MnSi and Mn$_5$Si$_3$).

Fig. S3 Temperature dependences of the dc magnetizations from different samples measured at 1000 oe. The magnetic measurements of the samples support the structural and compositional results. The comparison of the temperature dependent magnetization measured using SQUID magnetometer, which shows three different magnetic transitions between 2 K up to 300 K (Fig. S3). The 29 K transition is from skyrmion helimagnetic ordering in MnSi, and the transition around 65 K corresponds to a antiferromagnetic transition between a non-collinear AF1 and a collinear AF2 magnetic structure of Mn$_5$Si$_3$ (100 K). The ferromagnetic transition near 220 K is quite intriguing as it has received only a little attention in the literature. The origin of this transition is likely to be the formation of a dilute magnetic semiconductor with composition Si$_{1-x}$Mn$_x$ ($x<<1$) in which a very small percentage of Mn atoms are incorporated into Si during the sample processing. Mn$_{3x}$ is a very weak ferromagnetic phase with Tc of 40 K and a saturation moment of 0.012 $\mu_B$/Mn, so the contribution to the phase to the magnetization curve is very small.

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