Molecular beam epitaxy of single phase GeMnTe with high ferromagnetic transition temperature

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ABSTRACT
Ferromagnetic Ge1−xMnxTe is a promising candidate for diluted magnetic semiconductors because solid solutions exist over a wide range of compositions up to xMn = 0.5, where a maximum in the total magnetization occurs. In this work, a systematic study of molecular beam epitaxy of GeMnTe on (1 1 1) BaF2 substrates is presented, in which the Mn concentration as well as growth conditions were varied over a wide range. The results demonstrate that single phase growth of GeMnTe can be achieved only in a narrow window of growth conditions, whereas at low as well as high temperatures secondary phases or even phase separation occurs. The formation of secondary phases strongly reduces the layer magnetization as well as the Curie temperatures. Under optimized conditions, single phase GeMnTe layers are obtained with Curie temperatures as high as 200 K for Mn concentrations close to the solubility limit of xMn = 50%.

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1. Introduction
Carrier induced ferromagnetism in diluted magnetic semiconductors has attracted tremendous interest for applications in spintronic materials and devices [1,2]. Among the less explored materials, Ge1−xMnxTe is a promising candidate, as already in bulk material ferromagnetism at temperatures up to 150 K was shown [3]. Moreover, recent work has found Curie temperatures as high as 190 K in the heteroepitaxial layers [4,5]. In contrast to Mn-based III–V compounds, Mn2+ ions are isoelectronic to the group IV intrinsic p-type carrier concentration due to native cation vacancies. For Mn concentrations between xMn = 20% and 60%, bulk GeMnTe adopts the cubic rock salt structure [3,6] with its lattice constant decreasing with an increase in Mn content. At higher Mn concentrations phase separation occurs [6].

Molecular beam epitaxy (MBE) has only been recently employed for the growth of GeMnTe layers [4,5,10–14]. However, the reported data on magnetic properties of the layers, in particular, Curie temperatures TC have varied over a wide range. While most studies have found highest TC values for Mn concentrations near 50% [5,11,12], Fukuma et al. [4] have recently reported the best results for Mn concentrations around 10% when MBE growth is performed at low growth temperatures. To resolve this issue, in the present work, a systematic growth study of GeMnTe was performed, in which the Mn concentration as well as growth conditions were varied over a wide range. The results demonstrate that for single phase GeMnTe growth only a narrow window of growth conditions exist. In particular, at low as well as high substrate temperatures, secondary phases or even phase separation occurs. Under optimized conditions, high quality GeMnTe layers are obtained with Curie temperatures as high as TC = 200 K for Mn concentrations of xMn = 46%.

2. Experimental
GeMnTe was grown onto BaF2 (1 1 1) substrates by molecular beam epitaxy using a stoichiometric GeTe effusion cell and elemental Mn and Te beam flux sources. For all samples, the...
GeMnTe growth rate was set to 0.5 monolayers (ML) per second (≈0.6 μm/h). The substrate temperature was carefully calibrated using an optical pyrometer with an accuracy better than ±5 °C and was varied in the range from 260 to 310 °C. All flux rates were measured precisely using a quartz crystal microbalance moved into the substrate position. The ratio of the Mn flux to the GeMnTe growth rate yields the ternary Ge$_{1-x}$Mn$_x$Te composition of the layers, which was varied between $x_{\text{Mn}}=20\%$ and 50\%. To retain the correct stoichiometry, excess Te flux (∆difference between Te and Mn flux) between 0.1 and 0.3 ML/s was used for growth. For the employed substrate temperatures, the entire excess Te flux re-evaporates from the layer surface due to the high Te vapor pressure. On the contrary, the GeTe and Mn re-evaporation rates are small for substrate temperatures below 330 °C. Therefore, a unity sticking coefficient of GeTe and Mn was assumed.

The growth and structural properties of the samples were studied using in situ reflection high-energy electron diffraction (RHEED) and high resolution X-ray diffraction. For the latter, a Seifert XRD3003 P3S diffractometer with a channel cut Ge monochromator and a collimating X-ray mirror in front of the detector was used. For selected samples, additional structural information was obtained by transmission electron microscopy (TEM) using a JEOL 2011 FaSTEM operated at 200 keV. The magnetic properties were determined using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS2), measuring the magnetization $M(T)$ as a function of temperature $T$, as well as $M(H)$ hysteresis loops at fixed $T$. The diamagnetic background of the substrate was carefully subtracted in these measurements.

### 3. Results

To determine the dependence of the magnetic properties on the MBE growth conditions, three series of samples were grown with three different Mn concentrations of $x_{\text{Mn}}=20\%$, 30\% and 46\%. In the first two series, the substrate temperature $T_s$ was varied from 260 to 300 °C and the excess Te flux $J_{\text{Te}}$ from 0.1 to 0.3 ML/s. For the $x_{\text{Mn}}=46\%$ series, $T_s$ was varied between 290 and 310 °C and the excess Te flux was set to 0.2 ML/s.

For all samples, GeMnTe growth on BaF$_2$ (1 1 1) starts in a 2D manner. This is exemplified by the RHEED patterns depicted in Fig. 1 for GeMnTe with $x_{\text{Mn}}=20\%$ grown at $T_s=260$ °C (left hand side) and 280 °C (right hand side). Immediately upon growth initiation, 2D streaks appear as demonstrated by Fig. 1(a) and (d) for 10 and 5 nm GeMnTe thickness, respectively. During further growth, the streaks become spotty due to a roughening of the growing surface, as illustrated by the RHEED patterns of Fig. 1(b) and (e) recorded after 50 nm GeMnTe deposition. For low growth temperature at 260 °C, the 2D streaks subsequently disappear and a completely spotty transmission diffraction pattern is formed (see Fig. 1(c)). Moreover, additional diffraction spots appear, indicating not only a strong surface roughening but also the formation of secondary phases. On the contrary, at higher growth temperatures a 2D streaked RHEED pattern is reformed during further deposition, such that at the end of the growth process at 500 nm GeMnTe the 2D surface is regained (see Fig. 1(f)). The same general trend is also observed for samples with higher Mn content, indicating that for low-temperature growth below 280 °C precipitation of secondary phases occurs.

Fig. 2(a) summarizes the structural properties of the $x_{\text{Mn}}=20\%$ samples, as revealed by X-ray diffraction scans along the $q_z$-direction normal to the surface, spanning the whole $q$-space from the (1 1 1) to (3 3 3) Bragg reflection. Evidently, the Ge$_{0.8}$Mn$_{0.2}$Te samples grown at 300 and 280 °C (upper traces in Fig. 2(a)) are single phase, exhibiting only the expected (1 1 1), (2 2 2) and (3 3 3) GeMnTe layer peaks located at the right hand side of the sharp BaF$_2$ substrate peaks, without any signatures of other secondary phases. The normal lattice constant of the Ge$_{0.8}$Mn$_{0.2}$Te layers is determined as 6.0 Å and the small right hand side shoulder of the layer peaks is due to the rhombohedral GeMnTe lattice distortion present when the Mn concentration is lower than 30%. From X-ray reciprocal space maps around the (2 2 2) and (1 5 3) reflections (not shown), the lattice distortion angle was deduced as 89.5° for $x_{\text{Mn}}=20\%$. The full width at half maximum of the peaks is smallest for the sample grown at 300 °C, indicating a better structural quality as the substrate temperature is increased.

When for the same excess Te flux of $J_{\text{Te}}=0.3$ ML/s the growth temperature is lowered, the GeMnTe layer peaks almost completely disappear and several other peaks emerge. This is shown by the second lowest XRD scan in Fig. 2(a). The peaks left to the substrate peaks indicated by arrows are identified to arise from zinc-blende (zb) MnTe, whereas the other peaks originate from other Ge-rich phases. The peak marked “*” roughly fits to the (1 1 1) peak of pure Ge, but the other two peaks marked “o” could not be fitted to any of the known Ge–Mn–Te phases [15–17], on which, however, only limited amount of literature exists. When the excess Te flux is reduced to 0.1 ML/s, the structural quality of the sample significantly improves and the ternary Ge$_{0.8}$Mn$_{0.2}$Te peaks are partially regained (see lowest trace in Fig. 2(a)). This indicates that the driving force for phase decomposition at low growth temperatures is reduced at small Te overpressures, i.e., a closely stoichiometric flux composition. In fact, when high excess Te fluxes exceeding ∼1 ML/s are used a similar phase decomposition is also found even at higher growth temperatures. Thus, only a narrow window of growth conditions for single phase GeMnTe growth exists.

The magnetic properties of the four Ge$_{0.8}$Mn$_{0.2}$Te samples are summarized in Fig. 2(b), which displays the remnant magnetization $M(T)$ measured as a function of temperature after 1 T field cooling from room temperature to 4 K. Evidently, the sample grown at the highest temperature of 300 °C (red line) shows the highest remanent magnetization and the highest ferromagnetic Curie temperature $T_C$ of around 60 K as indicated by the arrow. For the samples grown at a lower $T_s=280$ °C (purple line), the remanent...
similar sample series was grown with \( T_s \) largest opening and the highest saturation magnetization value. The insert of Fig. 2(b), where the sample grown at 300°C scans displayed in Fig. 3(a), the same basic trend as for the and the same excess Te flux conditions. As shown by the X-ray resolution X-ray diffraction scans along the \( [111] \) growth direction of the samples grown at 260°C, with excess Te flux of \( J_{Te}=0.3 \) ML/s and of \( T_s=260 \) °C with \( J_{Te}=0.1 \) ML/s (red, purple, blue and black lines, respectively). Panel (a) shows high resolution X-ray diffraction scans along the \( [111] \) growth direction from the \( (111) \) to the \( (333) \) Bragg reflection. Panel (b) shows the temperature dependent remanent magnetization \( M(T) \) of the samples measured at zero external field \( H_{ext} \) after 1 T field cooling to 4 K. The insert displays the corresponding hysteresis loops recorded at 4 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

For \( x_{Mn}=30\% \) samples is observed, namely, single phase growth for substrate temperatures of 280 and 300 °C, and multiphase growth at 260 °C. For the single phase samples (upper two curves of Fig. 3(a)), Ge\(_{0.7}Mn_{0.3}Te \) is practically cubic with a lattice constant of 5.94 Å, whereas for the 260 °C samples (lowest two traces of Fig. 3(a)), the same secondary peaks appear as already observed for the \( x_{Mn}=20\% \) samples (cf. Fig. 2(a)). In particular, at low temperature a zinc blende MnTe phase is formed as indicated by the arrows, as well as additional phases with the same peak positions at \( q_s=1.84, 1.98, 2.57 \) and \( 4.27 \) Å\(^{-1} \) as marked by “s” and “o” in Fig. 3(a). For the \( x_{Mn}=30\% \) samples grown at 260 °C, weak peaks from the ternary GeMnTe still remain and the reduction of the excess Te flux did not yield the same marked improvement of structural quality as for the \( x_{Mn}=20\% \) samples. The \( M(T) \) magnetization curves of the \( x_{Mn}=30\% \) samples depicted in Fig. 3(b) clearly show ferromagnetic behavior for the layers grown at \( T_s=280 \) and 300 °C, with critical temperature \( T_c \) of...
around 75 K as indicated by the arrows. Obviously, there also exists a weak ferromagnetic signature at temperatures up to 110 K. This deviation from the classical mean field behavior is attributed to local non-uniformities of the alloy composition [5]. The multiphase samples grown at $T_s = 260$ °C exhibit only a very small, i.e., a factor of five times smaller, remanent magnetization. Thus, the secondary structural phases are either non-magnetic or antiferromagnetic such as zb-MnTe and the residual ferromagnetic signal arises from the small fraction of GeMnTe regions in the samples. Indications for the presence of antiferromagnetic zb-MnTe in the samples are also found in the magnetization measurements at nonzero external fields (not shown), in which a small peak in the $M(T)$ curves appears at temperatures around 50 K, which is close to the antiferromagnetic Neél temperature $T_N$ of zb-MnTe [8].

Increasing the Curie temperature requires further increase in Mn content. To this end, we have grown a set of samples with $x_{\text{Mn}} = 46\%$ under optimized growth conditions at $T_s = 290, 300$ and $310$ °C with an excess Te flux of 0.2 ML/s. According to the X-ray diffraction scans depicted in Fig. 4(a), all three samples exhibit strong and quite sharp diffraction peaks from ternary Ge$_{0.54}$Mn$_{0.46}$Te (vertical dashed lines in Fig. 4(a)) with a cubic lattice constant of 5.90 Å. The $T_s = 300$ °C sample (middle trace) is single phase without any traces of secondary phases, whereas the 290 °C sample (upper trace of Fig. 4(a)) shows an additional small and broad hump at $q_z = 3.42$ Å$^{-1}$, corresponding to zb-MnTe with $a_0 = 6.36$ Å. This indicates that a small fraction of the material is incorporated as MnTe clusters in the layer. The sample grown at $T_s = 310$ °C (lowest curve of Fig. 4(a)), on the contrary, exhibits a small additional shoulder on the left hand side of the cubic GeMnTe peak. This peak arises from the presence of an additional hexagonal MnTe phase in the sample, with a corresponding lattice constant of $c = 6.71$ Å.

The tendency for formation of hexagonal MnTe in the layers strongly increases at temperatures above 310 °C. At $T_s = 330$ °C and above, the hexagonal MnTe peaks completely dominate the X-ray spectra (see Ref. [5]), meaning that at higher growth temperatures predominantly hexagonal MnTe is formed instead of a mixed ternary GeMnTe alloy. This decomposition is corroborated by the cross-sectional transmission electron microscope images of two GeMnTe samples with $x_{\text{Mn}} \sim 50\%$ grown at $T_s = 310$ and $330$ °C depicted in Fig. 5(a) and (b), respectively. The 310 °C grown sample exhibits only cubic GeMnTe with rock salt structure, distorted, however, by the presence of stacking faults (see high resolution TEM image in the lower panel of Fig. 5(a)), whereas the 330 °C grown sample displays large regions where hexagonal MnTe is present. As evidenced by the high resolution TEM image of Fig. 5(b), these regions can be clearly discerned from the cubic regions due to their different lattice periodicity in the [1 1 1] direction. Between the cubic and hexagonal regions apparently no lattice defects such as misfit dislocations are formed. This is due to the fact that the in-plane lattice constant of hexagonal MnTe of $a = 4.14$ Å is practically identical to the in-plane lattice constant of cubic GeMnTe of $a_0 = a_0/\sqrt{2} = 4.17$ Å, meaning that within the growth plane both compounds are practically lattice-matched.

The $M(T)$ magnetization curves of the $x_{\text{Mn}} = 46\%$ sample series are summarized in Fig. 4(b). Again the sample grown at 300 °C shows the highest remanent magnetization, which is directly correlated with the observed highest GeMnTe peak intensity in the X-ray spectra of this sample. In fact, for all three samples, the measured low temperature saturation magnetization scales linearly with the (2 2 2) GeMnTe peak intensity, in agreement with our recent findings reported in Ref. [5]. What is most notable, is that the ferromagnetic transition temperature $T_C$ is at around 200 K for all three samples, which is the highest value so far reported for the Ge$_{1-x}$Mn$_x$Te compounds. This indicates that under optimized growth conditions $T_s$ values as high as those of Mn-based III–V compounds can be obtained.

### 4. Conclusions

The systematic study of the dependence of structural and magnetic properties of ferromagnetic Ge$_{1-x}$Mn$_x$Te on the MBE growth conditions has shown that only within a narrow window of growth conditions single phase ternary GeMnTe layers can be obtained. At lower or higher growth temperatures, precipitation of secondary phases or even phase separation occurs, in which zinc blende MnTe is formed at low temperatures and hexagonal MnTe at high temperatures. The use of high excess Te flux also enhances the
tendency for zinc-blende MnTe precipitation. Under optimized conditions, high quality single phase GeMnTe epilayers with high Mn content and high Curie temperatures up to 200 K are obtained.

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References


Fig. 5. Cross sectional transmission electron microscopy images of Ge_{1-x}Mn_{x}Te layers on BaF_{2} (1 1 1) with (a) \( x_{Mn} = 52\% \) grown at \( T_{s} = 310 \, ^{\circ}C \) and (b) \( x_{Mn} = 48\% \) grown at \( T_{s} = 330 \, ^{\circ}C \). The excess Te flux was \( f_{Te} = 0.2 \) and 0.45 ML/s. The lower panel shows the sample regions indicated by the dashed boxes with higher magnification. Also indicated in (b) are the regions with GeMnTe rock salt structure (rs) and of hexagonal (hex) MnTe with NiAs structure.