The effects of Mn concentration on structural and magnetic properties of Ge$_{1-x}$Mn$_x$ diluted magnetic semiconductors

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Abstract. Reflexion high-energy electron diffraction (RHEED), transmission electron microscopy (TEM) along with physical property measurement system (PPMS) were used to investigate the growth kinetics of Ge$_{1-x}$Mn$_x$ diluted magnetic semiconductors (DMS) grown on Ge(001) by means of molecular beam epitaxy (MBE). At a given intermediate growth temperature of 130 °C, we have identified the formation of successive heterogeneous phases when increasing the Mn concentration from 1 to 14 %: DMS phase containing nanosized Mn-rich clusters for $x$ below 2%, DMS phase containing high Curie temperature ($T_C$) nanocolumns for $x$ ranging from 5 to 6 %, DMS phase in which GeMn nanocolumns and Mn$_5$Ge$_3$ clusters coexist and then finally DMS containing mainly Mn$_5$Ge$_3$ clusters at Mn concentration higher than 12%. Our results confirm that the low solubility of Mn in Ge is the main origin of the formation of heterogeneous phases and provide evidence that it is extremely difficult to form a homogenous GeMn DMS even for Mn concentrations being below 2%. We also demonstrate that high-$T_C$ nanocolumns and Mn$_5$Ge$_3$ clusters are competing processes and the process window corresponding to the stabilisation of high-$T_C$ nanocolumns remains extremely tight.

1. Introduction

In recent years, diluted magnetic semiconductors (DMS), obtained by doping transition metals (TM) such as Mn, Ni, Fe, or Co into a host semiconducting matrix, have attracted great attention for their potential in combining ferromagnetic and semiconducting properties in a single material [1-3]. Among various materials, Ge:Mn-based DMS appears to be a promising candidate due to its compatibility with mainstream silicon technology, allowing a direct integration of future spintronic devices into the actual CMOS technology. For device applications, it is imperative to get DMS with Curie temperature being at least equal or above room temperature. This explains why up to now a great deal of interest has been focused on the investigation of the dependence of the Curie temperature of GeMn DMS on the growth parameters [4-10]. Among numerous growth parameters which can affect the GeMn growth behaviour, the growth temperature and the Mn concentration appear to be the most important parameters. Regarding the effect of the growth temperature, in order to overcome the low thermodynamic solubility of Mn in Ge, it appears natural to carry out growth at temperatures low enough to bring the system far from equilibrium. According to previous works, three main regions of temperatures have been identified: for temperatures above 180 °C, intermetallic Mn$_5$Ge$_3$ precipitates...
or clusters are often observed [11-17] and in some cases their magnetic properties entirely dominate the magnetic signature of the whole film; For temperatures below 80 °C, Mn-rich elongated structures and even amorphous Mn-rich precipitates are shown to be formed [18-20]. Of particular interest, in the intermediate temperature range between 110 to 150 °C, it has been shown that GeMn nanocolumns with Curie temperature higher than 400K can be stabilized [21, 22]. However, little is known about the effect of the Mn concentration on sequential Ge:Mn phase formation [23].

In this work, we report on the kinetics of phase formation of Ge$_{1-x}$Mn$_x$ films on Ge(001) as a function of the Mn concentration, ranging from 1 to 14 %. We have chosen an intermediate substrate temperature of 130 °C to avoid a direct formation of intermetallic Mn$_5$Ge$_3$ precipitates produced at high temperatures [17] or amorphous Mn-rich clusters at temperatures below 80 °C [20]. We have identified sequential phase transitions when increasing Mn content and such a phase evolution can be attributed to two effects: a low Mn solubility and a Mn segregation toward the film surface. In particular, we show that the formation of high-T$_C$ nanocolumn phase and intermetallic Mn$_5$Ge$_3$ clusters are two processes which are in competition and the process window for stabilisation of the nanocolumn phase is extremely tight.

2. Experimental

Ge$_{1-x}$Mn$_x$ films were grown by molecular beam epitaxy (MBE) on epi-ready n-type Ge(001) wafers with a nominal resistivity of 10 $\Omega$.cm. The base pressure in the MBE system is better than 5x10$^{-10}$ Torr. The growth chamber is equipped with a reflexion high-energy electron diffraction (RHEED) technique to control the cleanness of the substrate surface prior to growth and to monitor the epitaxial growth process. Ge$_{1-x}$Mn$_x$ films were obtained by co-deposition of Ge and Mn from standard Knudsen effusion cells, the Ge deposition rate was determined from RHEED intensity oscillations whereas the Mn deposition rate was deduced from Rutherford backscattering spectrometry (RBS) measurements. For Mn concentrations below 2%, the measurement uncertainty can reach a value of 10%. The standard growth rate used in this work is of 1 – 2 nm/min.

Structural analyses of the grown films were performed through extensive high resolution transmission electron microscopy (TEM) by using a JEOL 3010 microscope operating at 300 kV with a spatial resolution of 1.7 Å. The magnetic properties were investigated by using Quantum Design physical property measurement system (PPMS) in the temperature range from 5 to 350 K and with a magnetic field of 0.1T applied in the plane of samples. The diamagnetic contributions of Ge substrates were subtracted from the measurements, leaving the magnetic contributions of Ge$_{1-x}$Mn$_x$ films. The cleaning of Ge surfaces was carried out in two steps: a chemical cleaning to remove hydrocarbon related contaminants followed by an in-situ thermal cleaning at ~750°C to remove the Ge surface oxide layers. After this step, the Ge(001) surface generally exhibits a (2x1) reconstruction. To insure a good starting Ge surface prior to Ge$_{1-x}$Mn$_x$ growth, a ~30 nm thick Ge buffer layer was systematically grown at a substrate temperature of 600°C.

3. Results and discussion

Figures 1(a) and (b) respectively display RHEED patterns taken along the [1-10] azimuth of the clean Ge surface prior to growth and during Ge$_{1-x}$Mn$_x$ growth with Mn concentration being in the range from 1 to 2%. Prior to growth, the Ge surface is characterized by a well-developed 2x1 streaky pattern, indicating that the surface is clean and smooth. This is also confirmed by the observation of high-intensity Kikuchi lines, which overlap 1x1 and specular streaks, giving rise to localized reinforcements of intensity, as can be seen in the RHEED pattern. Compared to Ge surface, Ge$_{1-x}$Mn$_x$ surface exhibits a faint pattern with ½ streaks of weak intensity. Furthermore, three-dimensional spots due to transmission diffraction become visible. This indicates that even for Mn concentration as low as 1-2%, Ge$_{1-x}$Mn$_x$ films are somewhat disordered and the surface becomes rough. To understand such behaviour, we present in figure 1(c) a typical cross-sectional TEM image of the corresponding sample.
Dark contrast observed between Ge substrate and buffer layers is due to carbon contamination of the initial substrate surface occurred when the cleaning was not successful, this confirms the necessity of growing Ge buffer layers prior to Ge$_{1-x}$Mn$_x$ deposition. The white dotted line was added to indicate the interface between Ge buffer layers and Ge$_{1-x}$Mn$_x$ film. The image clearly reveals that the Ge$_{1-x}$Mn$_x$ film is not homogenous at all but contains Mn-rich clusters. The clusters have an average size of 1-2 nm and are randomly distributed in the film. It is worth noting that even for a Mn concentration reduced down to 1%, it was not possible to get homogenous Ge$_{1-x}$Mn$_x$ films.

![Figure 1](image.png)

Figure 1. (a, b): RHEED patterns taken along [1-10] azimuth of the Ge(001) surface prior to Ge$_{1-x}$Mn$_x$ growth (a) and during Ge$_{1-x}$Mn$_x$ growth with x being in the range of 1-2% (b). The specular streak (sp) together with 1x1 bulk-like and half-ordered (1/2) streaks are indicated. Three-dimensional spots arising from a rough surface are indicated by small arrows in (b). Typical cross-sectional TEM image observed for a Ge$_{1-x}$Mn$_x$ film with x ~ 2% (c).

![Figure 2](image.png)

Figure 2. Typical evolution with temperature of magnetization of Ge$_{1-x}$Mn$_x$ with Mn concentration of ~2%. A Curie temperature of around 150K is deduced and can be attributed to the DMS matrix. The superimposition of ZFC and FC curves suggests that nanosized Mn-rich clusters do not contribute to the magnetic properties of the grown film.

We show in figure 2 the temperature dependence of net magnetization (Ms) of a Ge$_{1-x}$Mn$_x$ film with x ~2%. The magnetization exhibits a monotonous and smooth decrease with increasing the temperature, suggesting that it arises from an unique phase. By making derivation of Ms versus temperature, a $T_C$ of ~150 K is deduced, a value expected for a Ge$_{1-x}$Mn$_x$ alloy with 2% of Mn. This suggests that the nanosized Mn-rich clusters do not contribute to the film magnetization, which is mainly dominated by the diluted matrix. We also note that for a Mn concentration of ~1%, a Curie temperature of only 80 K was observed.

When the Mn concentration increases to 5 - 6%, the Mn segregation has organized in a specific manner that conducts to the formation of nanocolumns. Figure 3 shows the surface morphology observed by RHEED and an overview of the nanocolumn formation by cross-sectional TEM. The
sample surface has become rougher, probably due to the presence of nanocolumns. TEM image shown in figure 3(b) reveals that most of nanocolumns are oriented perpendicular to the film, along the growth direction. The average size of nanocolumn is about 3-5 nm and no presence of Mn$_5$Ge$_3$ clusters are detectable. These results are very similar to those previously reported, in which Ge$_{1-x}$Mn$_x$ nanocolumns exhibit a Curie temperature well above 400 K [21, 22]. Our magnetic characterizations also confirm a Curie temperature higher than 350 K, the upper limit of temperature measurements in our PPMS. The authors of refs [21, 22] have attributed the composition of nanocolumns close to Ge$_2$Mn, an unknown Ge-rich phase in the Ge-Mn phase diagram. Recently, we use Laser Assisted Atom Probe Tomography (LA-APT) technique to investigate the Mn concentration inside nanocolumns and also in the matrix in-between nanocolumns. The obtained results, which will be published in a separate paper, clearly demonstrate that the Mn concentration in nanocolumns is neither constant nor close to Ge$_2$Mn.

Figure 3. (a): RHEED pattern taken along [1-10] azimuth during Ge$_{1-x}$Mn$_x$ growth with $x$ in the range of 5-6%. The specular streak (sp) together with 1x1 bulk-like and half-ordered (1/2) streaks are indicated. 

(b): Typical cross-sectional TEM image observed for Ge$_{1-x}$Mn$_x$ film with $x$ in the range of 5 – 6 %. The image reveals the formation of GeMn nanocolumns, which are separated by a DMS matrix less rich in Mn. Note that most of nanocolumns are oriented along the growth direction and perpendicular to the film layer.

With further increase of Mn up to ~14%, our results reveal a particular mechanism along which the formation of nanocolumns and Mn$_5$Ge$_3$ clusters is in competition. These results are depicted in figure 4: figures 4(a) and 4(b) report on the main features observed when the Mn concentration is in the range of 8 – 10 % whereas figure 4(c) and 4(d) correspond to Mn of 12 – 14 %. First of all, looking at the evolution of RHEED patterns, it can be clearly seen that the film surface roughness greatly increases at this Mn concentration range. For Mn concentration of 8 – 10 %, streaky features arising from reflexion diffraction have completely disappeared, only three-dimensional transmission diffraction is observed. When the Mn concentration reaches 12 – 14 %, diffraction patterns become so faint that polycrystalline features starts to appear.
Figure 4. RHEED patterns (a, c) and cross-sectional TEM images (b and d) of Ge$_{1-x}$Mn$_x$ film with high Mn concentrations.

- (a, b) for Mn concentration ranging from 8 to 10%.
- (c, d) for Mn concentration ranging from 12 to 14%.

Figures 4(b) and 4(d) provide an interesting view of the competition between Ge$_{1-x}$Mn$_x$ nanocolumns and Mn$_5$Ge$_3$ clusters. In figure 4(b), we still observe the presence of nanocolumns in the region near the interface (for thickness up to 30 nm starting from the interface). Going up to the film surface, one can recognize the presence of some Mn$_5$Ge$_3$ clusters and at the same time nanocolumns become disrupted and somewhat disordered. To understand such an evolution, it is important to recall that in Ge$_{1-x}$Mn$_x$ films, Mn$_5$Ge$_3$ clusters are a stable phase, they are formed each time the Mn concentration and/or the growth temperature become high enough whereas Ge$_{1-x}$Mn$_x$ nanocolumns are metastable, they transform into Mn$_5$Ge$_3$ clusters for thermal annealing at around 400 °C. The above phase transition can be explained as followed: at this growth condition of the substrate temperature of 130 °C and Mn concentration of 8 – 10%, the formation of Ge$_{1-x}$Mn$_x$ nanocolumns is still favorable. However, the Mn concentration inside nanocolumns should be high and in addition it increases along nanocolumns toward the film surface due to Mn segregation when the film thickness increases. When the Mn concentration reaches a maximal value of about 62 – 63 %, which is equal to Mn concentration in Mn$_5$Ge$_3$ compound, nanocolumns become metastable, resulting to the formation of Mn$_5$Ge$_3$ clusters in the region close to the film surface. Such an explanation also provides a good interpretation of the phase formation when the Mn concentration increases to 12 - 14%. At this Mn concentration range, a direct formation of Mn$_5$Ge$_3$ clusters becomes thermodynamically more favorable than nanocolumns. As can be seen in figure 4(d), no presence of Ge$_{1-x}$Mn$_x$ nanocolumns is visible even in the interface region. Mn$_5$Ge$_3$ clusters of very small size are formed at the interface just after the deposition of the first layers. The size of Mn$_5$Ge$_3$ clusters then increase with increasing the film thickness, due to Mn segregation toward the film surface. We also note that magnetization measurements (not shown here) confirm the coexistence of two Curie temperatures: one at ~304 K, which can be attributed to Mn$_5$Ge$_3$
clusters [24] and the other observed at around 107 K, arising from the diluted matrix. This value of 107 K is smaller than $T_C$ observed for a Ge$_{1-x}$Mn$_x$ alloy with 2% of Mn because the formation of Mn$_5$Ge$_3$ clusters are thermodynamically more favorable and it occurs by consuming Mn beforehand incorporated in substitutional sites of the diluted matrix.

4. Conclusion

In conclusion, we have chosen an intermediate and appropriate substrate temperature of 130 °C to investigate the sequential phase formation in Ge$_{1-x}$Mn$_x$ DMS as a function of the Mn concentration. We show that the low solubility of Mn is the main obstacle to form homogenous diluted magnetic semiconductors. Even for Mn concentration as low as 1%, we show that it is unable to form homogenous diluted materials. It should be possible to get homogenous materials for a lower Mn concentration but the Curie temperature will be very low. We have identified transition of successive Ge$_{1-x}$Mn$_x$ DMS phases when increasing the Mn concentration: DMS phase containing nanosized Mn-rich clusters for $x$ below 2%, DMS phase containing high-$T_C$ nanocolumns for $x$ ranging from 5 to 6 %, DMS phase in which GeMn nanocolumns and Mn$_5$Ge$_3$ clusters coexist and finally DMS containing mainly Mn$_5$Ge$_3$ clusters for Mn concentrations higher than 12 %. Obviously, the separation boundaries of these phases are not sharp, they depend on the Mn concentration and interestingly, also on the film thickness. We have provided evidence that the formation of high-$T_C$ nanocolumns and Mn$_5$Ge$_3$ clusters are competing processes and the process window for stabilizing the high-$T_C$ nanocolumn phase is very small. It is important to precisely control not only the Mn concentration but also the corresponding film thickness before nanocolumns can be transformed to Mn$_5$Ge$_3$ clusters due to Mn segregation toward the film surface.

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