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Ultra-fast annealing manipulated spinodal nano-decomposition in Mn-implanted Ge

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Abstract

In the present work, millisecond-range flash lamp annealing is used to recrystallize Mn-implanted Ge. Through systematic investigations of structural and magnetic properties, we find that the flash lamp annealing produces a phase mixture consisting of spinodally decomposed Mn-rich ferromagnetic clusters within a paramagnetic-like matrix with randomly distributed Mn atoms. Increasing the annealing energy density from 46, via 50, to 56 J/cm² causes the segregation of Mn atoms into clusters, as proven by transmission electron microscopy analysis and quantitatively confirmed by magnetization measurements. According to X-ray absorption spectroscopy, the dilute Mn ions within Ge are in d⁵ electronic configuration. This Mn-doped Ge shows paramagnetism, as evidenced by the unsaturated magnetic-field-dependent X-ray magnetic circular dichroism signal. Our study reveals how spinodal decomposition occurs and influences the formation of ferromagnetic Mn-rich Ge-Mn nanoclusters.

Keywords: Ion implantation, flash lamp annealing, spinodal decomposition, Ge-Mn nanoclusters

1. Introduction

Transition-metal (TM)-doped nanostructures embedded in semiconductors, self-assembled by spinodal decomposition, have generated considerable interest during the past decade due to their prospect for realization of high-

Curie temperature (T_C) spintronic devices [1-4]. Particularly, Ge-based ferromagnetic semiconductors [4-16] involving nano-sized Mn-rich precipitates, e.g. Ge_{1-x}Mn_x nano-columns [10-12] or Mn₅Ge₃ nanoclusters/nanoparticles/nanospheres [13-16], always exhibit a Curie temperature above room temperature. Thus, it has been of great interest for intentionally achieving such nanoclusters with high T_C

Figure 1. Scheme of the preparation of ferromagnetic Mn-rich clusters in the Ge substrate by ion implantation and FLA. Firstly, Mn ions are implanted into (001) Ge wafers and the surface region becomes amorphous. To recrystallize the implanted region, a pulsed flash lamp is used. The energy density of the flash lamps is gradually changed to manipulate the Mn spinodal decomposition [26, 27].

through controlling self-organized aggregation, e.g. by molecular beam epitaxy [10, 17], atomic layer deposition [4, 7, 8] as well as ion implantation followed by furnace annealing [14]. However, TM nanoclusters mostly appear under equilibrium conditions. Thus, their size and composition strongly depend on the competition between temperature and growth rate. Generally, the phase segregation occurs at high processing temperature (above 300°C) and slow crystallization [18-21]. On the contrary, low-temperature molecular beam epitaxy (below 200°C) and ultra-fast recrystallization induced by nano-second pulsed laser annealing enable TM atoms to be uniformly distributed in semiconductor matrices [22-25]. Therefore, it is of great interest to manipulate the spinodal decomposition of TM in semiconductors that can be manipulated by balancing the processing temperature and crystallization rate.

Flash lamp annealing (FLA), in the range of 400 μ s to 20 ms [26, 27], has been confirmed as a useful technology to recrystallize ion-implanted semiconductors, e.g. GaAs_{1-x}N_x [28, 29], Ga_{1-x}Mn_xAs [30, 31], hyper-doped Si [32, 33], etc. Interestingly, according to a study by Potzger *et al.*, α -Fe nanoparticles formed during FLA of Fe-implanted ZnO, opening a new avenue to induce TM-rich nanocluster formation in semiconductor matrices [34-37] also by FLA. Moreover, the possibility to tune FLA annealing energy and pulse duration provides prerequisites to flexibly manipulate ferromagnetic TM-rich nanocluster phase formation.

In the present work, FLA was employed to recrystallize Mn-implanted Ge wafers and to drive the spinodal decomposition. The flash lamp treatment leads to ferromagnetic Mn-rich nano-clusters within a paramagnetic matrix in which Mn atoms are uniformly distributed. Through tuning the annealing energy density while keeping a constant flash pulsed duration (3 ms), the recrystallization of the Ge matrix and the phase separation can be well manipulated: the increased annealing energy density gradually results in the spinodal decomposition of the dilute Mn in matrix into Mn-rich nanoclusters.

2. Experimental

Preparation of the ferromagnetic Mn-rich clusters within Ge is schematically displayed in Figure 1 [26, 27]. To this end, intrinsic n-type (001) Ge wafers were implanted with Mn ions at liquid nitrogen temperature to avoid surface roughening and secondary phase formation during the implantation process. Double-step implantation was employed in order to obtain a box-like Mn distribution. The implantation energies and fluences were set to be 100 keV and $5 \times 10^{16} \text{ cm}^{-2}$ for the 1st implantation and 30 keV and $1 \times 10^{16} \text{ cm}^{-2}$ for the 2nd implantation. Stopping and Range of Ions in Matter (SRIM) calculation indicates that the Mn concentration reached the 10 % atomic density over a depth of 100 nm. To recrystallize the implantation-induced amorphous surface layer, all samples were annealed using a pulsed flash lamp system which is based on low-pressure Xenon-filled flash lamps coupled to a capacitor bank. The annealing energy densities of 46, 50, and 56 J/cm² were selected with a pulsed duration of 3 milliseconds. The annealing process was performed in N₂ gas flow. Detailed parameters of the samples preparation are listed in Table 1. Raman spectroscopy and cross-sectional transmission electron microscopy (TEM) were conducted to analyze the structural properties of the implanted and annealed samples. To study the Mn distribution in the surface layer, spectrum imaging analysis based on energy-dispersive X-ray spectroscopy (EDXS) was used in scanning TEM (STEM) mode. X-ray absorption spectroscopy (XAS) / X-ray magnetic circular dichroism (XMCD) measurements were performed at the beamline UE46/PGM-1 at BESSY II (Helmholtz-Zentrum Berlin). Temperature- and magnetic-field-dependent magnetic properties were measured by a super-conducting quantum interference device (SQUID, Quantum Design MPMS) magnetometer in the temperature range of 5~350 K.

Table 1. Implantation energies, fluences, and the annealing energies of samples GeMnasimp, GeMn46J, GeMn50J and GeMn56J.

Sample	Imp. Energy (keV)	Fluences ($10^{16}/\text{cm}^2$)	Annealing Energy (J/cm^2)
GeMnasimp	100 / 30	5 / 1	-
GeMn46J	100 / 30	5 / 1	46
GeMn50J	100 / 30	5 / 1	50
GeMn56J	100 / 30	5 / 1	56

3. Results and Discussion

The Raman spectra of a pristine Ge wafer, the as-implanted sample, and the three flash-lamp-treated samples are shown in Figure 2. It is worth noting that the penetration depth of a 532 nm laser in Ge is about 40 nm, therefore, the influence from the Ge substrate beneath the Mn-doped layer can be excluded. For the reference Ge wafer, the Ge-Ge Raman active phonon mode is located at 300.5 cm^{-1} with a full width at half maximum (FWHM) of 2.7 cm^{-1} . After implantation, the peak shifts to 296.4 cm^{-1} with a remarkable broadening (FWHM = 5.6 cm^{-1}), indicating the amorphization of the implanted region. The FLA leads to a recrystallization of the implanted region, which is confirmed by the sharper Ge-Ge phonon mode at around 298.4 cm^{-1} . Moreover, the peak intensity is increased gradually with the FLA energy, indicating the enhancement of the crystalline quality of flash-lamp-treated Ge. The shift of the TO phonon mode towards lower wavenumber compared to an undoped

Figure 2. Raman spectra of samples GeMnasimp (circles), GeMn46J (up-triangles), GeMn50J (diamonds), and GeMn56J (left-triangles). A Ge wafer (squares) is placed as the reference.

Ge wafer can be accounted to tensile strain and the coupling of phonons with carriers or Mn doping. The implanted and flashed samples show a carrier concentration in the range of 10^{18} cm^{-3} (extracted from Hall Effect data) which is slightly above the Mott limit and definitively not enough to cause the shift of the TO phonon mode by 2 cm^{-1} . Therefore, the blue shift of the TO phonon mode is caused by Mn-Ge alloy formation and the polycrystalline nature of the flashed surface layer.

The microstructure evolution of FLA-treated GeMn samples upon raising annealing temperature / energy density

Figure 3. (a-d) Cross-sectional bright-field TEM images and (e-h) corresponding Mn element distributions obtained by EDXS for the same field of view for Mn-doped Ge: (a) and (e) show sample GeMnasimp, (b) and (f) sample GeMn46J, (c) and (g) sample GeMn50J, and (d) and (h) sample GeMn56J. While the inset in (a) displays the amorphous nature of the Mn-rich precipitates in the as-implanted sample, the inset in (b) shows their crystalline nature after FLA.

Figure 4. (a) magnetic-field-dependent magnetic hysteresis loops at 20 K and (b) temperature-dependent magnetization of zero-field and field cooling under a field of 100 Oe of samples GeMnasimp (squares), GeMn46J (circles), GeMn50J (up triangles) and GeMn56J (down triangles).

is studied by cross-sectional TEM, as presented in Figure 3. As indicated by the light-gray color of the top layer, having a thickness of approximately 150 nm, Mn implantation leads to a complete amorphization of germanium. The nano-sized dark-gray spots within this amorphized surface region, suggest that the segregation of Mn has already occurred during the implantation process. According to high-resolution TEM [inset of Fig. 3(a)], the Mn-rich particles are amorphous. Thus, we can conclude that the low-temperature Mn implantation does not prevent the Mn segregation, but prohibits the crystallization. However, flash lamp treatment with the lowest energy density of 46 J/cm² causes the crystallization of the Mn-rich clusters, as confirmed by the lattice-fringes in the HRTEM image in the inset of Fig. 3(b). Simultaneously, the surrounding Ge gets polycrystalline during FLA, as indicated by the varying diffraction contrast in the top layer of Fig. 3(b). Moreover, the interface between the implanted layer and the single-crystalline Ge substrate starts to become rough. Comparing Figs. 3(a) and (b), one even recognizes a shift of this interface into the direction of the sample surface, indicating at least partial single-crystalline regrowth at the interface to the Ge substrate. The gradually increased annealing energy density via 50 J/cm² up

to 56 J/cm² leads to the formation of larger Ge grains accompanied by a rougher interface to the single-crystalline Ge substrate, which is shifted further to the sample surface (Figures 3(c) and (d)). After FLA at 56 J/cm² for 3 ms (sample GeMn56J), the Ge grains reach a size of up to 50 nm. The full recrystallization of the implanted layer is in good agreement with the micro-Raman investigations, where the sample annealed at the highest energy density exhibits the strongest peak.

To obtain chemical information and, in particular, the evolution of the Mn distribution in the as-implanted and annealed samples, spectrum imaging analysis based on EDXS is performed in STEM mode. Figures 3(e-h) present the Mn element maps for the same field of view as shown in the corresponding bright-field micrographs in Figures 3(a-d). The as-implanted sample reveals the formation of nano-sized Mn-rich clusters which agree with the dark-gray spots in Figure 3(a). Moreover, the fact that Mn atoms did not diffuse towards the surface suggests, that Mn out-diffusion is prevented during the low-temperature implantation process. During FLA for 3 ms, however, Mn starts to diffuse both, towards the surface and towards the Ge substrate. In addition, the size of the Mn-rich clusters increases. After annealing with an energy density of 56 J/cm² the nanocluster size reaches up to 40 nm and Mn is substantially accumulated at the surface, where it gets oxidized. The Mn appearance at the sample surface is a direct evidence of strong Mn out-diffusion, during such short non-equilibrium thermal annealing.

Figure 4(a) displays the magnetization versus magnetic field (M - H) curves of as-implanted and FLA samples recorded at a temperature of 20 K. The diamagnetic background of the Ge substrate was subtracted by the M - H curve at 400 K which is above the Curie temperature. At 400 K, the temperature-independent diamagnetic signal mainly contributes. For the as-implanted sample, the nearly zero coercivity implies a (super)paramagnetic-like feature. This is in contrast with the previous study of ferromagnetic Mn-implanted ZnO without any annealing [37]. Such difference can be due to the fact that the low-temperature implantation prevents the crystallization of Mn-rich clusters. However, when compared with the as-implanted sample, GeMn46J presents an open hysteresis loop, implying that ferromagnetic coupling starts to appear after the flash lamp treatment. This is consistent with the results of Raman spectroscopy (Figure 2) and TEM (Figure 3) that the formation of Mn-rich clusters starts after annealing at an energy density of 46 J/cm². Increasing the annealing energy density to 50 J/cm², the saturation magnetization of the sample GeMn50J doubles, suggesting that more Mn atoms are incorporated into the ferromagnetic phases. Moreover, the “wasp-waist” shape of the hysteresis implies a signature of phase mixture consisting of hard and soft magnetic components. Details will be

discussed further in next section. For sample GeMn56J, the magnetization decreases substantially due to out-diffusion of Mn towards the surface, where it gets oxidized, as confirmed by STEM-EDXS analysis.

Figure 4(b) shows the temperature-dependent zero-field cooling (ZFC) and field cooling (FC) magnetization measurements at a 100 Oe field. In agreement with the M-H curves, sample GeMnasimp shows overlapped ZFC/FC curves due to its paramagnetic nature. After annealing, all samples show openings between the ZFC and FC curves. For the annealed sample, the ZFC magnetization essentially increases with increasing temperature with a broad plateau and then decreases above 280 K. This is a specific feature of superparamagnetic nanoclusters with a broad size distribution. After cooling down to 5 K under zero-field condition, magnetic moments of Mn atoms are frozen at a random state, since the 100 Oe field is not enough to overcome the blocking energy barrier. However, during the warming procedure, such blocking barrier is reduced by thermo-agitation, thus more moments are polarized by the magnetic field and an increased magnetization is observed. In the ZFC curve of sample GeMn50J, two down-turns appear at around 245 K and 275 K, respectively. Such two down-turns hint at two different phases with different blocking energy barriers. According to the results in reference [38], similar magnetic transitions were observed in Mn_xGe_{1-x} single crystals and attributed to $Mn_{11}Ge_8$ and Mn_5Ge_3 , respectively. Bulk Mn_5Ge_3 is ferromagnetic with a transition temperature of around 300 K, and for $Mn_{11}Ge_8$ two

transition temperatures at around 150 K and 280 K have been identified [38]. Considering the nanocrystalline nature of our samples, it is reasonable to attribute the two phases with transition temperatures at around 245 K and 275 K to $Mn_{11}Ge_8$ and Mn_5Ge_3 , respectively. Another transition is also noted that in the FC curve of sample GeMn50J, around 50 K, which can be related with the second transition of $Mn_{11}Ge_8$ at lower temperature [38]. However, no diffraction peaks of $Mn_{11}Ge_8$ or Mn_5Ge_3 are observed in the X-ray diffraction pattern, probably due to the small number of Mn-rich clusters in the Ge matrix.

To quantitatively study the magnetic properties of the flash-lamp-treated GeMn samples, the Langevin function for two components (a hard component with a larger coercivity and a soft component) is employed to fit the magnetic hysteresis loops at 20 K by the expression [21, 39]:

$$M = M_1 L[C_1(H \pm H_c)] + M_2 L[C_2 H] \quad \text{Eq. (1)}$$

where M_1 and M_2 present the magnetization of hard ferromagnetic and soft paramagnetic-like components, respectively; H_c is the coercivity of the hard-magnetic component; C_1 and C_2 are constants proportional to the initial magnetic susceptibility, and L is the Langevin function:

$$L[x] = \coth(x) - \frac{1}{x} \quad \text{Eq. (2)}$$

In Figure 5(a), a vanishing coercivity implies a pure soft paramagnetic-like phase in GeMnasimp. For the annealed samples, the fits by Eq. 1 quantitatively tell the fraction of the hard ferromagnetic and soft paramagnetic-like phases. Upon increasing the annealing energy from 46, via 50, to 56 J/cm², the percentage of hard magnetic component increases

Figure 5. Normalized magnetic field dependent magnetization (squares) of the samples (a) GeMnasimp, (b) GeMn46J, (c) GeMn50J, and (d) GeMn56J at 20 K. Experimental results (squares) of the magnetic hysteresis loops for FLA samples at 20 K are fitted by two Langevin functions (Eq. 1): a hard component (triangles) and a soft one (circles).

Figure 6. (a) X-ray absorption spectra (XAS) for parallel (μ^+) and antiparallel (μ^-) helicity and magnetization and (b) X-ray magnetic circular dichroism (XMCD) spectra, for samples GeMnasimp and GeMn56J measured at 4.2 K under an external field of 6 T applied perpendicular to the surface-plane. The XMCD spectra of the samples (c) GeMnasimp and (d) GeMn56J under different magnetic field from 0 to 6 T at 4.2 K. The insets show the magnetic field (H) dependent L_3 XMCD peaks of samples GeMnasimp and GeMn56J.

from 30%, via 55%, to 70%. Such phenomenon is consistent with the EDXS results that the magnetization percentage of the ferromagnetic Mn-rich cluster increases in the Mn-doped matrix with raising annealing energy density at the cost of the dilute paramagnetic-like Mn atoms.

X-ray absorption spectroscopy (XAS) / X-ray magnetic circular dichroism (XMCD) are used to study the element-

resolved magnetic properties as the characteristic absorption edges of electrons lying at different orbits of particular element. Herein, Figure 6(a) shows the Mn $2p$ - $3d$ XAS recorded for parallel (μ^+) and antiparallel (μ^-) alignments of the photon helicity. The measurement was performed in the total electron yield mode under a magnetic field of 6 T at 4.2 K. Before the measurement, samples were etched in dilute HCl in order to remove the surface Mn oxide layer. Total electron yield is only sensitive to the very surface region of the probed specimen, therefore has less possibility to probe the Mn in the clusters (see Fig. 3). As shown in Figure 6(a), the most pronounced peaks at around 640 eV and 652 eV correspond to the Mn L_3 ($2p_{3/2}$ to $3d$) and L_2 ($2p_{1/2}$ to $3d$) levels, respectively. For the as-implanted sample, two broad peaks appear at the L_3 and L_2 edges, which give a similar characteristic as in Mn-doped amorphous Si [40]. However, in the sample annealed at the energy density of 56 J/cm², the multiple-peak structure at L_3 edge of XAS spectra indicates Mn ion at d^5 state which is observed in Mn_{1-x}Ge_x dilute magnetic semiconductors (DMSs) [41]. By performing ($\mu^+ - \mu^-$), the XMCD spectra are obtained as shown in Figures 6(b-d), and the XMCD peaks at L_3 and L_2 states reconfirm the spin-splitting state of Mn in the layer. For the as-implanted sample at 4.2 K (Figure 6c), with increasing magnetic field from 0 to 6 T, the magnetic spin-splitting at the L_3 edge does not present any saturation behavior, which is in agreement with the result shown in Figure 5(a) that the as-implanted sample is paramagnetic. For the annealed sample GeMn56J, the intensive XMCD signals at both L_3 and L_2 edges exclude the possibility that antiferromagnetic MnO contributes to the Mn d^5 state. Additionally, similar to GeMnasimp, at 4.2 K an unsaturated spin-splitting at the L_3 edge also indicates a paramagnetic feature, but with much larger spin-polarization (Figure 6d). Observed paramagnetism is due to the Mn atoms diluted in the Ge matrix. The similar paramagnetism was observed in (Ga,Mn)As DMS doped with low Mn concentration of $\sim 0.3\%$ [42]. Where under a field of 6 T at 4.2 K, the spin polarization at L_3 is 4% and 30% for samples GeMnasimp and GeMn56J, respectively, indicating that the flash lamp treatment activates implanted Mn ions.

Figure 7 displays the electronic transport properties of all annealed samples. For Ge_{1-x}Mn_x DMS, Mn doping in Ge matrix introduces not only local moments but also holes, thus enabling a p -type conducting character [9]. As shown in Figure 7(a), the sheet resistance of all three annealed samples decreases with increasing temperature, which presents a canonical insulating feature. Similarly, in GaMnAs with low Mn concentration ($\sim 0.3\%$), the paramagnetic sample also presents insulating behavior, due to the absence of itinerant holes [42]. Moreover, higher resistance is detected in the samples annealed at higher energy densities. This is interpreted by the reduced carrier concentration since the dilute Mn concentration is further decreased by spinodal

Figure 7. (a) Temperature-dependent sheet resistance of samples GeMn46J (triangles), GeMn50J (circles) and GeMn56J (squares). (b) Magnetic field dependent Hall resistance of these three samples at 5 K.

decomposition. This is confirmed by the increase of the Hall resistance (Figure 7b). The positive slope of all samples indicates that the transport carriers are holes. Importantly, the slope of the Hall resistance (Hall coefficient) increases with increasing FLA energy density, manifesting the reduction of the hole concentration. The hole concentration extracted from the resistance curves decreases from $3.3 \times 10^{18} \text{ cm}^{-3}$, via $3.1 \times 10^{18} \text{ cm}^{-3}$, to $2.7 \times 10^{18} \text{ cm}^{-3}$ as the annealing energy increases, which is consistent with the decrease of the Mn concentration diluted in the Ge layer. However, it is worth noting that at 5 K no anomalous Hall effect is observed, due to the non-percolation of the Mn-rich nanoclusters, meanwhile the paramagnetic anomalous Hall signal from dilute Mn is probably too weak to be distinguished from the ordinary Hall signal.

4. Conclusions

In conclusion, the spinodal nanodecomposition in Mn-implanted Ge matrix is manipulated by pulsed flash lamp treatment. All annealed samples present a mixture of a paramagnetic-like phase and Mn-rich ferromagnetic

nanoclusters. According to the TEM/EDXS results and the fitted magnetic hysteresis loops by Langevin function, we found that upon increasing annealing energy, the magnetization percentage of Mn-rich ferromagnetic nanoclusters increases in the Mn-doped matrix. The results reveal the possibility of manipulating Mn spinodal decomposition in the Ge matrix by tuning the annealing energy of flash lamp treatment.

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