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About Ge(Mn) diluted magnetic semiconductor

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ABSTRACT

Deposition of 0.5 monolayer of Mn by molecular beam epitaxy on the surface of a Ge(0 0 1) substrate, and annealing, allowed the fabrication of a cluster-free Ge(Mn) diluted solution. Electronic spin resonance (ESR) was used to study the magnetic properties of this solution. These measurements, combined with secondary ion mass spectrometry, atomic force microscopy, and Auger electron spectroscopy, show that the detected ferromagnetic signal is due to surface islands, while Mn atoms on Ge substitutional sites gives no detectable ESR signal.

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1. Introduction

The possibility to produce room-temperature magnetic semiconductors [1,2] could open an innovative route for fabrication of new devices [3–5], exhibiting extra logic states that could be exploited in new type of logical circuits. Several works [6–8] reported interesting results concerning magnetic properties of Mn-doped Ge structures, in particular, the possibility to produce Mn-doped Ge diluted magnetic semiconductor (DMS) [7,9,10]. Studies concluded that Ge(Mn) DMS could be fabricated with a Mn concentration up to 6% [7,9,10], and the Curie temperature variation of Ge(Mn) DMS versus Mn concentration was given for concentrations up to $\sim 3.4\%$ [11]. However, it was suggested that the Ge(Mn) DMS layers fabricated so far were not free of Mn–Ge clusters, which could be actually the source of the ferromagnetic signal measured in these Ge layers [9,12,13]. Indeed, aiming to increase Mn incorporation in Ge, synthesis of Ge(Mn) DMS has been mainly carried out using out-of-equilibrium processes [7,13,14], which can lead to cluster formation. A recent work [15] confirmed that diluted Mn atoms occupy lattice substitutional sites in Ge, and shown that the Mn solubility in Ge does not exceed 0.9 at% for $450 \leq T \leq 600\ ^\circ C$.

In this work, a diluted Ge(Mn) solution was produced using a well-known technique based on Mn bulk diffusion from the Ge surface [15], insuring the fabrication of a Ge(Mn) solution at thermodynamic equilibrium, free of clusters, which corresponds to the ideal case of a Mn-doped Ge DMS. Contrasting with most of the studies of ferromagnetism in semiconductors, which were unable to separate ferromagnetism contributions (intrinsic or extrinsic)

due to the use of magnetometry, electron spin resonance (ESR) was used to determine the origin of the ferromagnetism signal observed in the Ge(Mn) solution.

2. Experiments

The sample was prepared in a molecular beam epitaxy (MBE) chamber exhibiting a residual pressure (P) of $\sim 1 \times 10^{-10}$ Torr. A Sb-doped Ge(0 0 1) substrate with a resistivity of 0.34 Ω cm was dipped in a diluted HF before being loaded in the MBE chamber, where it was outgassed at $T = 450\ ^\circ C$ for several hours, before heating to 750 $^\circ C$ for few seconds to remove residual surface oxide. Once back to room temperature, 0.5 atomic monolayer of Mn was deposited on the surface of the Ge substrate. Once removed from the MBE set-up, the sample was annealed at 500 $^\circ C$ in a furnace under vacuum ($P < 7.5 \times 10^{-8}$ Torr) for 50 h. Secondary ion mass spectrometry (SIMS) was performed using an ADEPT 1010 Dynamic system operated at 2 kV with an O_2^+ primary ion beam having an impact angle of 40° compared to the normal of the sample surface. ESR measurements were performed using a conventional Bruker EMX spectrometer operating at 9.5 GHz. The samples were cooled down to 5 K and oriented using a high accuracy goniometer.

3. Results and discussion

The solid square profile presented in Fig. 1 corresponds to the corrected [16] Mn diffusion profile measured by SIMS in the sample. All the atoms that diffused in the Ge substrate were fully mobile, which exclude the formation of clusters [17]. In this sample, the maximum Mn concentration is $\sim 3.5 \times 10^{20}$ cm^{-3},

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corresponding to ~0.8 at%, which is significantly higher than the Sb background doping ($\sim 5 \times 10^{15}$ cm^{-3}) of the Ge substrate. Fig. 2(a) shows a typical ESR spectrum of the Ge(Mn) sample. A broad signal appears at zero magnetic field that is typical to a ferromagnetic spectrum at microwave frequency lower than the anisotropic gap (Fig. 2(a) black line).

In order to understand the origin of the ferromagnetic signal, the surface of the sample was studied using atomic force microscopy (AFM) in air. Fig. 2(b) presents an image of the sample surface topology after annealing. Mn–Ge islands are clearly observed. These islands can thus be at the origin of the ferromagnetic signal measured by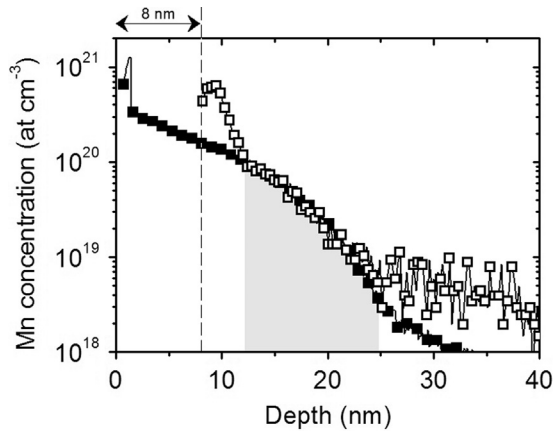 ESR. Aiming to separate the contribution of the isolated Mn atoms from the contribution of the surface Mn–Ge islands in the ESR signal, the sample was loaded in an ultra-high vacuum chamber equipped with Auger electron spectroscopy (AES), as well as with an Ar$^+$ ion gun. The sample surface was bombarded by Ar$^+$ ions with an energy of 2 kV, allowing to remove a thickness of ~8 nm of the sample. Fig. 3(a) presents the AES spectrum obtained in situ on the sample surface after ion bombardment. The low energy (peaks at 52 and 89 eV) and high energy (single peaks at 963 eV, double peaks at 1044 and 1056 eV, and triple peaks at 1130, 1147 and 1178 eV) Auger transitions corresponding to Ge atoms are clearly observed (red part of the spectrum in Fig. 3(a)). However, the detection of Mn is more difficult: a low energy transition at 40 eV (arrow in Fig. 3(a)) can correspond to Mn, but the usual triple peaks at 542, 589 and 636 eV cannot be resolved from the background noise. Fig. 3(b) presents ex situ AFM measurements performed in air after ion bombardment. The previous Mn–Ge islands have been removed, the observed surface roughness being the results of ion bombardment [18,19]. The open square profile presented in Fig. 1 corresponds to the Mn distribution in the sample measured by SIMS after ion bombardment. The front of this profile can result from both the pushing deeper in the Ge bulk of Mn atoms located at the surface of the sample during Ar$^+$ ion bombardment, as well as from the roughness effect on SIMS profiles (widening of the surface signal). However, one can note that the end of the profile can be well superimposed to the SIMS profile measured before Ar$^+$ ion bombardment, showing that part of the substitutional Mn atoms are still present in the sample after the surface treatment. Fig. 4 presents the ESR spectrum acquired on the sample after ion bombardment: no FMR is detected anymore (Fig. 2(a) red line).

Fig. 1. Mn SIMS profiles measured in the same Ge(Mn) sample before (solid squares) and after (open squares) Ar$^+$ ion bombardment of the surface.
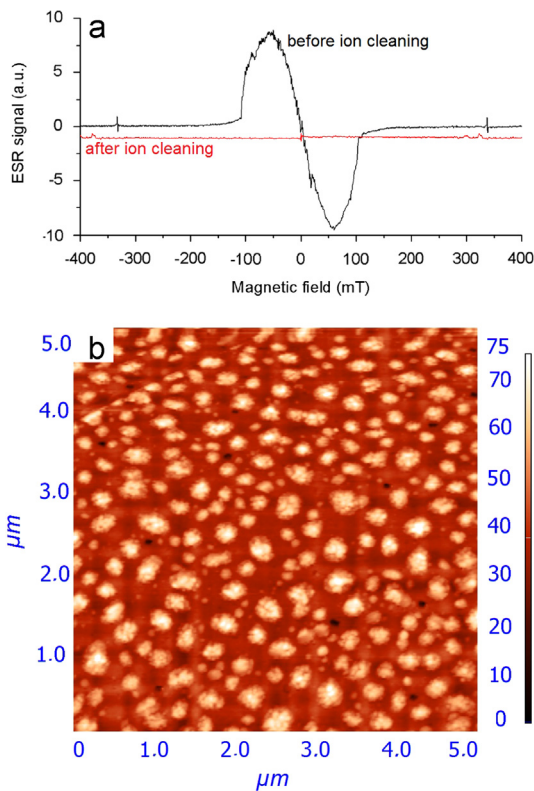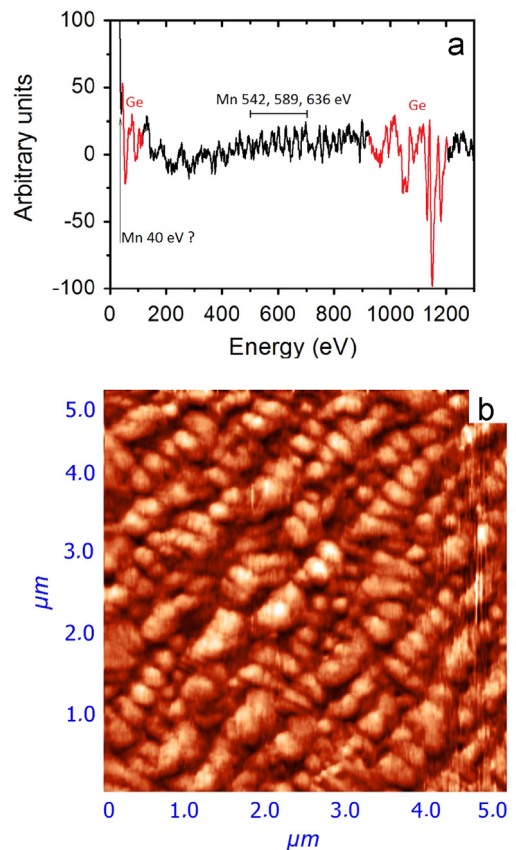

Fig. 2. (a) ESR signal versus magnetic field intensity measured in the same Ge(Mn) sample before (black solid line) and after (red solid line) Ar$^+$ ion bombardment of the surface. (b) AFM in air measurements performed on the sample surface before Ar$^+$ ion bombardment. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Characterizations of the Ge(Mn) sample surface after Ar$^+$ ion bombardment: (a) AES spectrum measured in situ; (b) ex situ AFM image (5×5 μm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
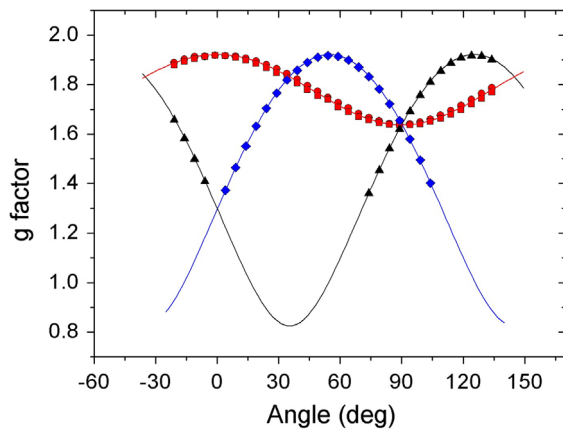
Fig. 4. Angular distribution of g-factors calculated using the resonance field measured on the Ge(Mn) sample after Ar^+ ion bombardment.

Consequently, the FMR signal measured before the surface treatment can be attributed to the Mn–Ge surface islands. Indeed, this signal is consistent with the signal of intermetallic Mn_5Ge_3 islands that are ferromagnetic and exhibit an anisotropy gap higher than 9.5 GHz, and lower than 30 GHz [20].

In order to detect the substitutional Mn atoms in Ge bulk, high sensitivity measurements have been performed on the clean sample and for many orientations of the magnetic field. Many sharp and anisotropic resonance lines have been seen. The g-factor of all lines have been calculated using the resonance field value: $g = h \times f/(\mu_b \times H)$ with h the Plank constant, f the microwave frequency, μ_b the Bohr magneton and H the value of the resonance field. The angular distribution of g factors is reported in Fig. 4. The experimental values (solid symbols) agree very well with the theoretical distribution of g factors in the case of Sb in Ge (solid lines). Despite that the Mn ion quantity in the sample is high enough to be detected, no other signal than the Sb one was detected. Ludwig and Woodbury [21] reported that only the Mn^{1-} electronic configuration can give an ESR signal in Ge. Thus, the absence of signal related to diluted Mn atoms can be interpreted as due to Mn ion electronic configuration different from Mn^{1-}.

4. Conclusion

A Ge(Mn) solid solution corresponding to the ideal case of Mn-doped Ge DMS was prepared. Highly sensitive ESR measurements combined with SIMS profiling, surface ion bombardment, and surface characterizations such as AFM and AES, demonstrated that even in Ge(Mn) samples free of Mn–Ge clusters in bulk, a ferromagnetic signal can be measured due to the formation of Mn–Ge islands on the surface of the sample. Once these islands were removed from the surface, the ferromagnetic signal disappeared, and only the paramagnetic signal of substitutional Sb atoms corresponding to the Ge substrate doping background could be detected. Mn atoms located on the Ge crystal substitutional sites are not ferromagnetic.

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