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Evidence of magnetic vortices formation in Mn-based sub-micrometre structures embedded in Si–Mn films

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Abstract

Mn-containing amorphous (a-)Si films were prepared by sputtering a silicon + manganese target in an atmosphere of pure argon. After deposition the films were thermally annealed in the 300–900 °C temperature range and investigated by Raman scattering spectroscopy, atomic-force microscopy and magnetic-force microscopy (MFM) techniques. For comparison purposes, one Mn-free a-Si sample was also prepared and annealed under similar conditions. The experimental results indicate that (1) manganese was effective and homogeneously incorporated into the a-Si matrix, as revealed by compositional measurements, (2) the as-deposited films (either pure or containing Mn) are essentially amorphous and (3) thermal annealing at increasing temperatures induces the crystallization of the samples. In fact, the crystallization onset of the sample containing ~20 at% of Mn, for example, coincides with the appearance of structures (typically 750–1200 nm large and 300–400 nm high) surrounded by the MnSi1.7 silicide phase. These sub-micrometre structures correspond to Mn-containing Si crystallites that, because of their typical size and composition, exhibit magnetic activity as suggested by the presence of magnetic vortices in MFM measurements carried out at room temperature. The development of these structures as well as the probable origin of their magnetic behaviour is discussed in view of some characteristics of the samples.

(Some figures in this article are in colour only in the electronic version)
interesting feature since charge and spin states are sensitive mostly to the local environment so the magnetic activity existing in c-Si or c-Ge should also be observable in amorphous (a-)Si or a-Ge.

Based on these facts, and looking for further details concerning the properties of Mn-containing Si materials this letter reports on the synthesis and structural–magnetic characterization of amorphous Si–Mn films.

The Si–Mn films were deposited by radio frequency (13.56 MHz) sputtering a Si target (99.999% pure) partially covered with suitable pieces of Mn (99.999% pure) in an atmosphere of high purity argon. Following this approach, the Mn concentration in the samples was determined by adjusting the relative Mn-to-Si target area in a process that is known by cosputtering [5]. The films were deposited onto polished Si (100) substrates kept at 150 °C and were ~1700 nm thick as indicated by profilometry measurements. After deposition the samples were submitted to cumulative (15 min long) thermal annealing at 300, 450, 600, 750 and 900 °C under a continuous flow of argon. Si–Mn films with manganese estimated to be in the ~0.1–20 at% concentration range and one Mn-free Si sample were prepared under the same deposition conditions. The structure of the films was investigated by Raman scattering spectroscopy (488.0 nm excitation wavelength) in the backscattering geometry. Details concerning the surface topography and magnetic properties of the Si–Mn samples were achieved through atomic-force microscopy (AFM) and magnetic-force microscopy (MFM) analysis. The AFM measurements were performed in the tapping mode, whereas the MFM ones in the lift mode by means of a Co/Cr coated tip magnetized just before scanning. All experimental characterizations were carried out at room temperature.

The atomic composition of all films was determined independently by energy dispersive x-ray (EDS), Rutherford backscattering (RBS) and x-ray photoelectron (XPS) spectroscopic techniques. The experimental results provided by these methods are very similar (within ~15% deviation) and, consistently, proportional to the Mn-to-Si relative target area. In addition to the effective insertion of Mn species in the Si matrix, the compositional analysis also indicates that they are homogeneously distributed. Because of the deposition method and conditions all as-deposited films are amorphous as confirmed by the Raman measurements. As the thermal annealing advances, in contrast, the Si–Mn films show crystallization signals that are accompanied by the growth of thermal annealing advances, in contrast, the Si–Mn films show amorphous as confirmed by the Raman measurements. As the annealing temperature.

Figure 1 illustrates the Raman spectra of the SiMn20% film as-deposited and after thermal annealing at 600 °C. The Raman spectrum of the Mn-free film as-deposited is also shown for comparison. As can be seen from figure 1, both Mn-free and SiMn20% films exhibit a broad and featureless Raman signal at ~465 cm\(^{-1}\) in a clear indication of their disordered atomic structure [6]. The presence of 20 at% of Mn in the Si matrix, and consequent metallic-like character of the SiMn20% film, is also evident from its Raman spectrum [7]. After annealing at 600 °C all samples present Si crystallites (scattering signal at ~522 cm\(^{-1}\)) and, due to the presence of Mn, have their surface partially covered by small structures whose number is proportional to the annealing temperature. A thorough analysis of these structures by means of EDS, Raman spectroscopy and optical microscopy measurements, respectively, show that (1) their Mn content is 17 ± 1 at%, in contrast to the 20 ± 1 at% measured outside and in the as-deposited samples; (2) they correspond mainly to Si crystallites with a small amorphous component, that are surrounded by a smooth surface consisting of Si crystallites, amorphous Si and the MnSi\(_{1.7}\) silicide [8] phase (figure 1) and (3) their lateral dimensions stay in the ~800–1300 nm range.

Taking advantage of the presence of these structures with chemical–structural characteristics slightly different from their surroundings, the SiMn20% film was further investigated by Raman imaging. In this case, the image was achieved by defocusing the laser spot to illuminate a region approximately 15 µm in diameter. The resulting Raman signal passed through...
SiMn20% film after thermal annealing at 600°C with the formation of Mn-silicides resulting from Mn layers and lower solubility of Mn, most of the Si crystallites tend to disperse along the film but, because of the higher diffusivity as the annealing temperature increases, there are Si crystallites diffusion of Mn and the formation of some Mn-silicide phase. As the crystallization of a-Si begins, it is accompanied by the scattering signal at 275 cm\(^{-1}\) (figure 1) in agreement with the coexistence of the MnSi\(_1\)\(_x\)\(_{7}\) silicide phase and comparatively higher Mn concentration.

The development and main characteristics of the observed sub-micrometre structures are consistent with the diffusion coefficients and the solubility of Si and Mn, as well as with the kinetics of formation of the Mn–Si phases. While the solubility of any metal in Si is limited by its very low energy of vacancy formation, the solubility of Si in Mn stays around 14% [10]. This fact, associated with the six orders of magnitude difference between the diffusion coefficients of Si and Mn (\(D_{Si} \sim 10^{-7} D_{Mn}\)) [11], suggests that, as soon as the crystallization of a-Si begins, it is accompanied by the diffusion of Mn and the formation of some Mn-silicide phase. As the annealing temperature increases, there are Si crystallites dispersed along the film but, because of the higher diffusivity and lower solubility of Mn, most of the Si crystallites tend to accumulate on the surface of the sample. This picture agrees with the formation of Mn-silicides resulting from Mn layers deposited onto Si (1 0 0) [11, 12]: (a) the MnSi phase starts to grow at 400°C and is completed at 500°C, (b) further thermal annealing induces the appearance of MnSi\(_1\)\(_x\)\(_{7}\) that is completed at 600°C and is stable at higher temperatures and (c) during the formation of the Mn-silicide the growth is from the surface into the volume of the sample.

The morphology and magnetic characteristics of the SiMn20% sample were investigated by means of AFM and MFM measurements (figure 2). Based on the AFM results the observed structures are typically \(\sim 750-1200\) nm large and 300–400 nm high. At these dimensions, the contrast shown by the MFM images occurs because of force gradients between the FM tip and the magnetic activity present on the sample’s surface. In this study, the MFM images were achieved after topography measurements (tapping mode) followed by sample surface scanning at a constant 200 nm height (lift mode). According to this procedure, no van der Waals forces are expected to be detected, and any change in the vibration amplitude of the cantilever is proportional to the gradient of magnetic fields perpendicular to the sample surface [13]. Finally, it is worth noting that no MFM contrast was observed in the Mn-free film and SiMn20% sample as-deposited nor after scanning the samples under the tapping mode.

According to the literature [14], the MnSi\(_1\)\(_x\)\(_{7}\) silicide phase comprises several stoichiometries (Mn\(_{11}\)Si\(_7\), Mn\(_{19}\)Si\(_9\), Mn\(_{26}\)Si\(_{26}\), Mn\(_{35}\)Si\(_{45}\) and Mn\(_{57}\)Si\(_{47}\)) that, for [Mn] \(\lesssim 30\) at%, take place up to \(\sim 1150°C\). In terms of their magnetic properties, pure Si is diamagnetic and metallic Mn is antiferromagnetic with a Neél temperature of 100 K [15, 16]. Moreover, MnSi\(_1\)\(_x\)\(_{7}\) and MnSi are paramagnetic with Curie temperatures equal to 47 K and 30 K, respectively, and all the other Mn-silicide phases are known to be either nonmagnetic or antiferromagnetic. Nonetheless, the image contrast present in figure 2(b) is a clear indication of the magnetic activity present in sample SiMn20%.

Whereas the FM behaviour observed in Mn-doped GaAs can be satisfactorily explained by the model proposed by Dietl et al [17], through a RKKY-type indirect exchange mechanism, the origin of FM activity in Si–Mn and Ge–Mn systems is rather controversial. Apparently, FM in these systems is highly influenced by sample details such as the preparation method and/or atomic structure, Mn concentration, thermal treatments and carrier type [3, 15, 18, 19]. Also, the insertion of relatively high amounts of Mn in Si, such as the ones experienced in this contribution, promotes the formation of FM Mn aggregates and should be at the origin of the observed magnetic activity (figure 2(b)). In fact, such a statement is supported by the following observations: (1) the presence of Mn dimers, whose formation energy is predicted to be lower than that corresponding to the sum of their separate constituents, favours FM coupling [20], and (2) MnSi\(_1\)\(_x\)\(_{7}\) precipitates are believed to enhance the magnetization by mediating the exchange coupling between the FM Mn clusters [21]. In addition to the presence of magnetic activity in the sample under study, it also produces a remarkable contrast in the MFM images of figure 2(b). The FM materials are known to form domain structures to reduce their magnetostatic energy that, at very small dimensions such those experienced by a (sub-)micrometre dot, for example, adopts the configuration of a curling spin or magnetization vortex [22]. When the dot thickness becomes much smaller than the dot diameter, all spins tend to align in-plane. In the curling configuration, the spin directions change gradually in-plane in order to maintain the exchange energy and to cancel the total dipole energy. The development of these magnetic vortices is well documented in the literature and its comprehensive description can be found in many works [23, 24]. In this study, basically, the observed magnetic contrast occurs because of variations in the magnetization orientation along the sub-micrometre structures (figure 2(b)). In other words, the presence of these Mn-based structures (Mn dimers in combination with the MnSi\(_1\)\(_x\)\(_{7}\) phase) leads to the appearance of magnetic activity, whose main characteristics are highly influenced by the size
Figure 3. (a) Magnetic-force microscopy image of an isolated sub-micrometre structure present in the SiMn$_{20\%}$ film after thermal annealing at 600 $^\circ$C. Its height profile (as obtained by AFM) and corresponding MFM voltage along the horizontal, vertical and diagonal dashed lines drawn in (a) are represented, respectively, in (b), (c) and (d). Note the MFM voltage pattern due to the presence of magnetic vortices in the structure.

and shape of the structures. Figure 3 shows the surface topography in connection with the measured magnetic contrast of a single sub-micrometre structure. The figure also displays the height profile and MFM voltage achieved under horizontal (figure 3(b)), vertical (figure 3(c)) and diagonal (figure 3(d)) scans along the structure.

It is interesting to observe the quite different topographic (AFM profile) and magnetic (MFM voltage) patterns achieved from the very same structure exclusively due to the presence of magnetic activity. The effect of manganese on the formation of these magnetic vortices is also remarkable suggesting that, once the structure is formed, the Mn distribution is non-uniform (and/or highly influenced by the presence of MnSi$_{1.7}$) around it.

In summary, sputter-deposited Si films (Mn-free and containing $\sim 20$ at$\%$ of Mn) were thermally annealed and investigated according to its composition (EDS, RBS and XPS), structure (Raman scattering), morphology (AFM) and magnetic properties (MFM). The analysis of these experimental results allowed us to conclude that Mn species were effectively incorporated into the amorphous Si matrix and that thermal annealing at 600 $^\circ$C induces the development of sub-micrometre structures surrounded by Si crystallites, amorphous Si and the MnSi$_{1.7}$ silicide phase. These sub-micrometre structures, essentially Mn-containing Si crystallites that present magnetic activity as indicated by the MFM measurements, take place because of differences between the solubility and the diffusivity of Si and Mn. The origin of their magnetic activity is tentatively associated with the presence of small Mn clusters in association with the MnSi$_{1.7}$ silicide phase. Finally, because of their shape and small dimensions the observed structures exhibit magnetic activity in the form of vortices as clearly indicated by the MFM images.

Acknowledgments

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References

[1] See, for example, Zutic I, Fabian J and DasSarma S 2004 Rev. Mod. Phys. 76 323 and references therein


