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This work reports on the magnetic properties of Ge$_{100-x}$Mn$_x$ (x=0–24 at. %) films prepared by cosputtering a Ge+Mn target and submitted to cumulative thermal annealing treatments up to 500 °C. Both as-deposited and annealed films were investigated by means of compositional analysis, Raman scattering spectroscopy, magnetic force microscopy, superconducting quantum interference device magnetometry, and electrical resistivity measurements. All as-deposited films (either pure or containing Mn) exhibit an amorphous structure, which changes to crystalline as the annealing treatments are performed at increasing temperatures. In fact, the magnetic properties of the present Ge$_{100-x}$Mn$_x$ films are very sensitive to the Mn content and whether their atomic structure is amorphous or crystalline. More specifically: whereas the amorphous Ge$_{100-x}$Mn$_x$ films (with high x) present a characteristic spin glass behavior at low temperature; after crystallization, the films (with moderate Mn contents) are ferromagnetic at room temperature. Moreover, the magnetic behavior of the films scales with their Mn concentration and tends to be more pronounced after crystallization. Finally, the semiconducting behavior of the films, experienced by previous optical studies, was confirmed through electrical measurements, which also indicate the dependence of the resistivity with the atomic composition of the films. © 2010 American Institute of Physics.

I. INTRODUCTION

The study of ferromagnetic (FM) semiconductor materials corresponds to a very active field of research due to their great potential in spintronics. Allied to the interest in FM compounds such as Ga$_{100-x}$Mn$_x$As (Ref. 1) and Zn$_{100-x}$Co$_x$O$_2$ for example, the doping of either Si or Ge with magnetic species deserves special attention. Indeed, due to their compatibility with the actual (micro)electronics industry, the development of FM Si- or Ge-based materials is expected to be at the origin of a considerable commercial-technological breakthrough. In this respect, the pioneering studies on Ge$_{100-x}$Mn$_x$ films showed a Curie temperature $T_c$ that increases (from 25 to 116 K) with the Mn concentration, as well as FM behavior at two different ordering temperatures. More recent experimental work suggested the absence of magnetization down to 2 K, whereas the codingoping with Fe (Ref. 6) or Co (Ref. 7) could lead to ferromagnetism up to 209 K and 270 K, respectively. In most of these studies, however, the Mn concentration is relatively low and/or its distribution tends to be inhomogeneous. These features, in association with different methods of preparation-processing or characterization of the samples, avoid the accurate description of the material as well as its application in real devices. In fact, it is common sense that Ge-based FM compounds will be of importance only when presenting semiconducting functionalities and magnetic ordering at $T_c$’s closed to (or higher than) the room temperature. Consequently, Ge films containing uniformly distributed high Mn concentrations are required to achieve reasonable $T_c$ values. However, high Mn contents may cause a metallic behavior and/or a large number of neighboring Mn atoms with antiferromagnetic coupling, for example. Considering that the solid solubility of Mn in Ge is limited by thermodynamic criteria, it is important that film preparation should be carried out under nonequilibrium conditions. The cosputtering deposition method perfectly fulfills such condition, generally producing materials with an amorphous atomic structure. While the magnetic behavior exhibited by amorphous materials can be partially explained by the fact that the charge and spin states are most sensitive to the local environment, its precise origin is still under debate and, clearly, more research are needed to advance our scientific knowledge on the subject.

Driven by the above facts, this work contains a study of Ge thin films prepared by cosputtering and containing Mn up to 24 at. %. Even though the amorphous character of the as-deposited films, thermal annealing at increasing temperatures induces their crystallization. Following this procedure, the electrical and magnetic properties of the cosputtered Ge$_{100-x}$Mn$_x$ films have been systematically investigated as a function of their Mn concentration and atomic structure.

II. EXPERIMENTAL DETAILS

The samples considered in this work were prepared by radio frequency (13.56 MHz) sputtering a 5” crystalline Ge target in an atmosphere of pure argon. The insertion of Mn...
into the Ge network was achieved by placing suitable pieces of metallic Mn on top of the Ge target, in which case, the Mn concentration is proportional to the Mn-to-Ge relative target area. For comparison reasons, one Mn-free Ge film was also prepared following identical conditions. The films, typically 1700 nm thick, were deposited on crystalline (c-) quartz, c-Si, and glass substrates kept at 150 °C during deposition. The atomic composition of all as-deposited films was determined by energy dispersive x-ray spectrometry (EDS) obtained from a 20 keV electron beam impinging on a ∼100 × 100 μm² area. According to the EDS measurements, Mn was successfully incorporated into the Ge host under the following nominal concentrations: 0.0 (Mn-free), 0.1, 0.3, 1.2, 3.7, 15.4 and 24.0 at. %.

After deposition the films were submitted to cumulative isochronal (15 min each) thermal annealing treatments at 200, 300, 400, and 500 °C under a continuous flow of argon. Based on the EDS data, the Mn concentration remains essentially the same after thermal annealing the films as well as its distribution is rather homogeneous.

The atomic structure of the Ge₁₀₀−ₓMnₓ films was examined via Raman scattering spectroscopy by exciting the films with a HeNe laser (632.8 nm wavelength) in the backscattering geometry. Sample areas of typically 1 mm² were analyzed using an average power density of ∼200 μW mm⁻².

The magnetic properties of the films were investigated by superconducting quantum interference device (SQUID) magnetometry and magnetic force microscopy (MFM). The dark electrical resistivity of the films has been measured using the standard dc van der Pauw technique. Except when explicitly indicated, all measurements were conducted at room temperature.

III. RESULTS AND DISCUSSION

The Raman scattering spectra of some representative Ge₁₀₀−ₓMnₓ films are displayed in Fig. 1. According to the Raman results, all as-deposited films are essentially amorphous (regardless of their Mn content) as evidenced by a broad scattering signal at ∼270 cm⁻¹. Moreover, the development of Ge crystallites (scattering signal at ∼300 cm⁻¹) takes place by thermal annealing at 400 °C (x ≥ 15.4 at. %) and at 500 °C (x ≥ 1.2 at. %). Samples with x ≤ 0.3 at. % also crystallize, but only after treatment at >500 °C. Therefore, it is obvious that the annealing procedure induces the crystallization of the Ge₁₀₀−ₓMnₓ films and that the Mn concentration reduces the crystallization temperature.

FIG. 1. (Color online) Raman spectra of Ge₁₀₀−ₓMnₓ films deposited on crystalline quartz substrates: (a) Mn-free, (b) Ge₉₆.₃Mn₃.₇, and (c) Ge₇₆.₀Mn₂₄.₀. The spectra correspond to samples as-deposited and after thermal annealing at the temperatures indicated in each spectrum. The scattering signals at approximately 270 cm⁻¹ and 300 cm⁻¹ correspond to the presence of amorphous Ge and Ge crystallites, respectively. The spectra have been normalized and vertically shifted for comparison purposes.
more, at 5 K [inset Fig. 2(c)], the magnetization does not saturate, even at applied external fields as high as 50 kOe. These features are distinctive of either superparamagnetic or spin glass systems.\(^{20}\) Here is important to notice that no information about the film morphology at the nanometer scale (using for instance transmission electron microscopy) is provided. Consequently, the considered sample could be inhomogeneous and may contain dispersed magnetic nanostructures. Therefore, the observed magnetic behavior might be due to superparamagnetic nanostructures antiferromagnetically coupled by long range dipolar interactions, for instance. However, taking into account that Fig. 2(c) correspond to the data of an amorphous film with a large Mn content—which enhances the competition of different magnetic states\(^{13,20}\)—the phenomenon is typical of spin glass.

Figure 3 gives support to the previous statement by means of magnetization measurements (of the amorphous Ge\(_{76.0}\)Mn\(_{24.0}\) film) under the ZFC and FC regimes. According to the figure, it is possible to verify the “freezing” of spins at the blocking (or freezing) temperature \(T_f \sim 50\) K.\(^{20}\) Moreover, the inset Fig. 3 shows the magnetization signal as a function of the time. In such a case, the signal has been measured at 5 K (below the “freezing” temperature), with no external magnetic field or with 10 kOe. Despite the fact that the irreversibility of ZFC-FC curves is often associated to spin glass systems, the existence of a frozen state can be better elucidated by measuring the frequency dependence of the magnetic susceptibility.\(^{17}\) In fact, the time-dependent magnetic behavior (with response times as longer as \(~10^3\) s), shown in the inset Fig. 3, corroborates the spin glass phenomenon in the amorphous Ge\(_{76.0}\)Mn\(_{24.0}\) film.\(^{12,20}\) At this point, it is important to notice that the freezing temperature \((T_f \sim 50\) K\)) obtained in the present work is slightly

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**FIG. 2.** (Color online) Magnetization as a function of temperature of Ge\(_{96.3}\)Mn\(_{3.7}\) films [(a) as-deposited and (b) after thermal annealing up to 500 °C] and Ge\(_{76.0}\)Mn\(_{24.0}\) films [(c) as-deposited and (d) after thermal annealing up to 400 °C]. All measurements have been carried out under ZFC conditions and the signals were corrected by the contribution due to the crystalline quartz substrate. The insets show the magnetization signal, at 5 K, as a function of an applied external field. Based on the experimental data the following coercive fields apply: (a) 0.1 kOe, (b) 1.3 kOe, (c) 1.5 kOe, and (d) 0.6 kOe.

**FIG. 3.** (Color online) Magnetization as a function of temperature of the Ge\(_{76.0}\)Mn\(_{24.0}\) film, as-deposited. The measurements have been carried out under ZFC and FC conditions, with \(H = 1\) kOe. The difference between the ZFC and FC curves reveals a freezing temperature \((T_f \sim 50\) K\)) around 50 K. The inset shows the magnetization signal (at 5 K) as a function of time. The time-dependent measurements have been performed as follows: (circles) the sample was field cooled with a magnetic field of 10 kOe from 300 to 5 K. After temperature stabilization and a waiting time of \(~30\) s, the external field was switched off and the magnetization was recorded as a function of the elapsed time. The magnetization of the initial point is denoted as \(M(t)\) to which \(M(t)\) (the magnetization at time \(t\)) was normalized; (squares) the film was ZFC from 300 to 5 K. Similarly, after temperature stabilization and a time of \(~20\) s, an external field of 10 kOe was applied and the magnetization was recorded as a function of the time. Here the magnetization \(M(t)\) was normalized by the magnetization of the final point \(M(t)\). All signals were corrected by the contribution due to the crystalline quartz substrate.
higher than that reported (\(T_c \approx 20\) K) for Ge\(_{100-x}\)Mn\(_{x}\) films with similar Mn contents.\(^{12,13}\) Within the possible reasons for this discrepancy one can mention: (a) the preparation method (cosputtering versus thermal evaporation or molecular beam epitaxy) and conditions, which can give rise to materials with quite different structural characteristics,\(^{11}\) (b) the sample thickness,\(^{21}\) (c) the influence of the substrate onto the stress present in the films,\(^{22}\) (d) the unintentional presence of impurities, etc. In any case, it is clear that the spin glass phenomenon takes place when a large amount of Mn is inserted in an amorphous host.

After crystallization (and development of the Mn\(_2\)Ge\(_3\) phase), the data of Fig. 2(d) shows that the Ge\(_{76.0}\)Mn\(_{24.0}\) film is FM and with \(T_c \approx 300\) K. Consistent with the Mn concentration and with the crystalline nature of the film, at 5 K [see the insets Figs. 2(a), 2(b), and 2(d)], the magnetization saturates at higher values and remains at increasing temperatures (not shown).

The experimental data of Fig. 2 also indicates the following coercive fields: 0.1 kOe for the amorphous Ge\(_{96.3}\)Mn\(_{3.7}\) film; 1.3 kOe for the Ge\(_{96.3}\)Mn\(_{3.7}\) film after crystallization; 1.5 kOe for the amorphous Ge\(_{76.0}\)Mn\(_{24.0}\) film; and 0.6 kOe for the Ge\(_{76.0}\)Mn\(_{24.0}\) film after crystallization.

The Mn-free, Ge\(_{96.3}\)Mn\(_{3.7}\), and Ge\(_{76.0}\)Mn\(_{24.0}\) films were further investigated through MFM. The measurements were performed, under room conditions, in the lift mode by means of a Co/Cr coated tip magnetized just before scanning. With the purpose of evaluating the magnetic activity of these three films, the MFM tip scanned a \(\sim 20\) \(\mu\)m long line across a crystalline quartz substrate partially covered by the desired Ge film (see sketch in Fig. 4). By adopting this procedure, at the bare substrate-film edge, the MFM tip will experience a signal difference which is proportional to the magnetic response of the probed region. Considering that crystalline quartz gives no magnetic contrast in the MFM measurements, the observed MFM signal is exclusively due to the Ge\(_{100-x}\)Mn\(_{x}\) films. In fact, and in accord with the literature\(^{18}\) and our SQUID results, no MFM signal has been observed from both the amorphous and crystallized Mn-free Ge films. Also, and in order to confirm that the MFM signal is mainly of magnetic nature,\(^{23}\) the measurements were carried out at a fixed tip-to-sample (substrate+film) distance \(d\) in the 100–2500 nm range. The main results of these MFM measurements, in conjunction with the SQUID data, are shown in Fig. 4.

The experimental data of Fig. 4 indicates that: (1) the MFM signal decreases with the distance \(d\)—demonstrating the magnetic character behind the interaction between the MFM tip and the sample; (2) except for minor deviations in the MFM signals obtained with the lowest \(d\) values, which were clearly affected by the experimental conditions (temperature, film thickness, and instrumental resolution, for example), the MFM signal scales with the magnetization of saturation, as obtained from the SQUID measurements, (3) indeed, the MFM signal increases with [Mn] and after the crystallization of the Ge\(_{100-x}\)Mn\(_{x}\) films, and (4) as far as absolute magnetic data are available (such as those given by SQUID magnetometry, for example) the adopted experimental procedure can provide a convenient method to analyze the magnetic properties of microsized (or submicromsized) isolated systems.

As stated before, the present Ge\(_{100-x}\)Mn\(_{x}\) films have been investigated by means of resistivity measurements based on the van der Pauw technique.\(^{16}\) The room temperature resistivity values (\(\rho_{RT}\)) corresponding to films as-deposited and after annealing at 400 and 500 °C are shown in Fig. 5. Furthermore, the \(\rho_{RT}\) values are consistent with the results obtained by the optical\(^{15}\) and magnetic investigations in the sense that they are sensitive to the Mn concentration and to the structure of the films. More specifically, the set of experimental data indicates that: (a) \(\rho_{RT}\) can decrease by almost four orders of magnitude with the insertion of Mn; (b) \(\rho_{RT}\) tends to increase as the films are becoming more crystalline; and (c) depending on the Mn concentration and whether the films are amorphous or crystalline, \(\rho_{RT}\) presents values intermediary between those typically found in semiconducting Ge (\(\rho_{RT} \approx 10^{-3}\) \(\Omega\) cm) and the MnGe\(_x\) germanide phase (\(\rho_{RT} \approx 10^{-4}\) \(\Omega\) cm).\(^{12,24}\) The decrease in \(\rho_{RT}\) with [Mn] can be explained by the increase...
of electronic defect states as more Mn (a foreign species) is introduced into the Ge host. Thermal annealing the films at increasing temperatures, on the other hand, increases $\rho_{RT}$ due to the suppression of defect states and/or by favoring another mechanism of carrier transport. Curiously, for [Mn] $>1$ at. %, the $\rho_{RT}$ values of the films annealed at 500 °C are smaller than those presented by the films annealed at 400 °C. Considering the development (and/or increase in the size) of Mn$_2$Ge$_3$ crystallites at these annealing temperatures, the observed phenomenon can be due: to a decrease in the carrier mobility (mainly because of scattering processes), allied to the low resistivity of the germanide phase. In any case, the resistivity measurements displayed in Fig. 5 have a good correspondence with the information provided by other experimental techniques, and substantiate the semiconductor character of the present Ge$_{100-x}$Mn$_x$ films. Finer details concerning the transport mechanisms and electronic properties of these films require the realization of temperature-dependent resistivity measurements.

**IV. CONCLUDING REMARKS**

The information contained in this manuscript was based on a series of Ge$_{100-x}$Mn$_x$ (x=0–24 at. %) films prepared by the cosputtering technique. The films were studied according to their Mn concentration and atomic structure—as imposed by annealing the films at increasing temperatures. Both as-deposited (essentially amorphous) and thermally annealed films were investigated mostly by Raman scattering spectroscopy, SQUID, MFM, and electrical resistivity measurements. The main experimental findings can be summarized as follows: (1) all Ge$_{100-x}$Mn$_x$ films become crystalline at temperatures that depend on the Mn concentration; (2) there exists a close correspondence between the magnetic (and electric) properties of the films with [Mn] and with their atomic structure; (3) after crystallization, most of the Mn-containing films are FM up to the room temperature; (4) the amorphous films with the highest [Mn] exhibit a spin glass behavior at low temperature; and (5) a combination of the MFM and SQUID techniques is proposed in order to probe the magnetic properties of microsized isolated structures.

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