Multilayers of GaAs/Mn deposited on a substrate of GaAs (001)

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Abstract. In this work GaAs/Mn multilayers were deposited on GaAs (001) substrates by R.F magnetron sputtering technique, varying the deposition time \( t_g \). Scanning electron and atomic force Microscopy studies were realized on the surface of the samples in order to determine the morphology and average roughness. X-ray diffraction spectra show that our samples tend to do amorphous. Raman spectroscopy at room temperature was employed to analyze the structural properties of the samples. We found that for a GaAs film taken as reference, the Raman spectra is dominated by the transverse (TO) and longitudinal (LO) modes located at 266 cm\(^{-1}\) and 291 cm\(^{-1}\), respectively. However, for the GaAs/Mn multilayers the TO and LO modes decrease dramatically, and the Mn Raman modes in the range of 100 cm\(^{-1}\) and 250 cm\(^{-1}\) are evidenced. Additional new peaks located around 650 and 690 cm\(^{-1}\) are only observed for the samples with high Mn content. By using the mass reduced model we estimate that the Mn related peaks are located at 650.2 cm\(^{-1}\) and 695.2 cm\(^{-1}\), in good agreement with the experimental data, these peaks are correlated with excitations due to \((\text{Mn})_m\text{As}_n\) localized structures.

1. Introduction
The relatively recent discovery of ferromagnetic III-V semiconductor-based materials with Curie temperatures \( T_c \) as high as 185 K has now raised interesting fundamental issues regarding the origin of ferromagnetism in materials such as \( Ga_{1-x}Mn_x\text{As} \) [1-3]. The introduction of relatively small concentration of magnetic elements into nonmagnetic host semiconductor leads to dramatic change of the magneto-optic properties upon application of magnetic fields. In these III-V semiconductors, \( Mn^{2+} \) acts as an acceptor, generating free holes in the valence band. The ferromagnetism in these materials arises from the exchange interaction between these holes and the \( Mn^{2+} \) ions, and it is generally believed that there is a direct correlation between the Curie temperature \( T_c \) and the holes density [4]. However, a high Mn concentrations MnAs clusters can be formed. Depending on the growth conditions phase separation occurs, and either nanosize MnAs clusters are formed into the GaAs matrix or \( Ga_{1-x}Mn_x\text{As} \) regions with a low Mn concentration are generated [5]. In general, \( Ga_{1-x}Mn_x\text{As} \) thin films have been grown employing molecular beam epitaxy. However, there are few reports on deposition of \( Ga_{1-x}Mn_x\text{As} \)
films by radio frequency (RF) magnetron sputtering. Sputtering deposition is one alternative that offers the possibility of deposition of $Ga_{1-x}Mn_xAs$ thin films at low cost and simple processing procedures. In this work, we report the study of structural and optical properties of GaAs/Mn multilayers grown by using RF magnetron sputtering technique. The samples were characterized by different techniques in order to determine their structural characteristics, chemical composition, surface morphology, crystal structure and optical properties.

2. Experimental Details

$Ga_{1-x}Mn_xAs$ films were grown by RF planar magnetron sputtering with two cooled targets of 1 inch diameter each one, and controlled by independent RF sources. The targets used were a (100) oriented GaAs wafer and Mn block. The growth temperature ($T_g$) was monitored using a thermocouple embedded in the substrate holder. No substrate bias was used, and the base pressure was of $1.2\times10^{-6}$ Torr. The flow rate gas was controlled by using a needle valve. The films were deposited on (100) GaAs substrates located at 5 cm from targets. The substrates were cleaned by using standard methods. Before deposition the working pressure was held constant at $1.2\times10^{-3}$ Torr, and the plasma between target and main shutter was initiated using Argon gas 99.9% purity. Then, the main shutter was opened to start the deposition alternating GaAs and Mn layers. The samples consist of three GaAs/Mn cycles, two types of samples were prepared with different GaAs and Mn deposition times: A) GaAs(15 min)/Mn(15 min) and B) GaAs(60 min)/Mn(60 min). A 30 sec. interruption time was introduced between the deposition of the GaAs and Mn layers, while the plasma is stabilized. The growth temperature was fixed at 500°C and the working pressure was held at $1.2\times10^{-3}$ Torr. The films surface morphology was analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) in non-contact mode. X-ray diffraction (XRD) using a CuK$_\alpha$ radiation source was used to evaluate the films crystalline structure. The structural properties were also studied by micro Raman scattering (RS) using the 632.8nm line of a He-Ne laser with a power of 20m.

3. Results and Discussion

Figure 1 (a) and (b) show plan view SEM images (with a magnification of x 10,000) for the samples type A and B, respectively. From these images we observe that the surface of sample A is flat and smooth. However, the surface of sample B is composed of larger grains. In Fig. 1 (c) and (d), we show the AFM images on a 1x1 $\mu$m$^2$ scale for samples A and B, respectively. By comparing these images, we can observe that there exists a strong difference in the morphology of these samples, probably due to the thickness of the samples. For the sample A the surface is smooth with a 3 nm RMS roughness and small (9.8 nm mean height) grain size. However, for the sample B the surface is porous formed of spherically shaped grains (20.6 nm of mean height) with a value of 8.4 nm in RMS roughness [6].

To evaluate the crystalline quality of the GaAs/Mn multilayers, X-ray diffraction was performed in a $\theta$-2$\theta$ configuration. Fig. 2(a) and (b) shows the x-ray curves of Mn bulk and GaAs film taken as references. The peaks located at $2\theta = 34.8$, 42.9, 47.7, 52.2, 60.4, 73.4, and 78.7 degrees in the Fig. 2(a) correspond to the crystallographic planes of $\beta$-Mn polycrystalline phase. In the Fig. 2(b) we only observed the (200)GaAs and (400)GaAs main peaks, located at $2\theta = 31.7$ and 66.2 degrees. For the GaAs/Mn multilayer type A (Fig.1(c)), additional to the GaAs main peaks we note peaks not well defined labeled by (*), corresponding to the $Mn_4As_3$ phase. However, for the GaAs/Mn sample type B (Fig.1(d)), peaks corresponding to the $Ga_5Mn_3$ phase appeared[7]. We observed that increasing the growth time of the individual layers of GaAs/Mn, the X-ray peaks are more defined, which may be due to an improvement of the crystalline quality of the samples caused possibly by the interdiffusion of Mn atoms into GaAs layer, or the re-evaporation of Ga and As atoms that are bonded to Mn to form GaAsMn.
Figure 1. Plan view SEM images (left side) taken in a 1 µm scale and x10000 amplification and AFM images (right side) taken in a 1x1 µm² area of GaAs/Mn multilayers grown at a deposition time of: a) $t_g = 15$ min., b) $t_g = 60$ min. and 500 °C substrate temperature.

Figure 2. XRD curves of: a) Mn, b) GaAs layers taken as reference, c) and d) are the spectra of GaAs/Mn Multilayers grown by varying the deposition time per each layer: c) $t_g = 15$ min. and c) $t_g = 60$ min, and $T_g = 500$ °C substrate. The peaks labeled as (+) and (*) in this Figure denote the GaMn phase, and MnAs phase, respectively.

In Fig. 3(a) we show the Raman spectra of the GaAs film reference grown at $T_g = 500$ °C and $t_g = 60$ min. In this spectrum the first order Raman scattering LO and TO modes from GaAs are observed at 266 and 291 cm$^{-1}$, respectively. These modes present a redshift of 2 cm$^{-1}$ probably due to stress effects [9]. Raman spectra obtained for GaAs/Mn multilayers type A and B are shown in the Fig. 3 (b) and (c), respectively. In the Raman spectra of Fig. 3
(b), is evident that the intensity of the TO and LO modes tend to disappear completely, and a broader band from 150 to 270 cm$^{-1}$ appeared, which indicates that the zincblende structure was strongly deformed by the inclusion of the Mn atoms. This suggests that the Mn atoms affected the GaAs lattice as a whole, due to a structural disorder caused by vacancies, MnGa complex or Mn-Mn clusters formation [10,11]. In order to analyze the superimposed phonon modes, the Raman spectrum was fitted by using four Lorentzian functions. We found that the peaks located at 195, 212.7, 229.9 and 247 cm$^{-1}$ are related to vibrational modes of Mn and As, as a consequence of the structural disorder and other built-in defects for samples with high Mn concentrations [12].

On the other hand, the Raman spectrum of the Fig. 3(c) shows a broader band from 238 to 265 cm$^{-1}$. A more detailed analysis of this band by using four Lorentzian functions, allowed us identify the TO and LO modes related to GaAs and two additional Raman modes located at 309.8 cm$^{-1}$ and 332 cm$^{-1}$ associated with GaAsMn alloys. This result is in agreement with the X-ray results shown in Fig. 1(d), where a phase separation (labeled by (+)) is observed for this sample. The high Mn concentration introduced during growth at high substrate temperature allows the zincblende matrix to form MnAs clusters, and a phase separation occurs. Note that a coupled LO-phonon plasmon mode has been reported to appear in epitaxial GaMnAs layers [13], this mode could be present in sample B (Fig. 3(c)). On the other hand, new phonon modes located around 654 cm$^{-1}$ and 694 cm$^{-1}$ near to the 2LO GaAs second order mode are observed in our samples (b) and (c). These modes have been assigned to disorder activated Raman modes at the Brillouin zone boundary corresponding to the acoustic and optical phonon branches due to the incorporation of Mn-As pairs or Mn$_m$As$_n$ cluster formation on GaAs matrix [14,15].

In order to theoretical estimate the frequency of these Raman modes, we used the mass reduced model given by the following equation [16]:

$$\omega_{Mn_mAs_n} \approx \omega_{2LOGaAs} \sqrt{\frac{\mu_{GaAs}}{\mu_{Mn_mAs_n}}}$$  \hspace{0.5cm} (1)

where $\omega_{2LOGaAs}$ is the frequency of 2LO (580 cm$^{-1}$) phonon mode and $\mu_{GaAs}$, $\mu_{MnAs}$ are the reduced masses of the Ga-As and Mn$_m$As$_n$ pairs, respectively. The value of the Raman frequency calculated for us using the Eq.(1) is 650.2 cm$^{-1}$ (Mn$_2$As$_3$) and 695.2 cm$^{-1}$ (Mn$_{12}$As$_3$). This value is in good agreement with the experimental value centered at 654 cm$^{-1}$ and 696 cm$^{-1}$ for
sample A and sample B, respectively. The formation of \((\text{GaAs})_n\text{Mn}_m\) complex has been predicted theoretically by G.L. Gutsev, et al [17]. Clusters are likely formed by MnAs units because the pure Mn
clusters possess the antiferromagnetic coupling of local excess spin densities beginning with \(m = 5\), that drastically reduces the cluster magnetic moments. The reason for the MnAs clusters formation in the sample with high Mn content could be the existence of very small aggregates of Mn atoms in the GaAs layers, which would act as nucleation center for the clusters nucleation. The study of cluster formations is interesting, because the clustering of Mn atoms inside the GaAs host is a possible path toward increasing the Curie temperature important to technological applications in spintronics. Besides, MnAs which is a ferromagnetic metal at room temperature is on the focus of attention because it can be successfully integrated with semiconductors such as GaAs [18].

4. Conclusions
We have studied the properties of GaAs/Mn multilayers grown by R.F magnetron sputtering. X-ray diffractions show that the samples have a poor crystalline quality. In Raman scattering studies we found that in addition to some conventional modes that were also observed in GaAs, a broader band from 150 to 260 cm\(^{-1}\) appeared due to a structural disorder caused by vacancies, MnGa complex or Mn-Mn clusters formation. For the sample with high Mn content, new bands around of 650 cm\(^{-1}\) and 695 cm\(^{-1}\) are evident, probably due to a \((\text{Mn})_m\text{As}_n\) cluster formation. The theoretical calculations of these modes by using the mass reduced model are in good agreement with experimental data.

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