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Disorder effects produced by the Mn and H incorporations on the optical absorption edge of $Ga_{1-x}Mn_xAs$:H nanocrystalline films

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ABSTRACT

The optical absorption edges of nanocrystalline $Ga_{1-x}Mn_xAs$:H films ($0.000 \leqslant x \leqslant 0.081$) prepared by sputtering were analyzed. The influence of Mn and hydrogen incorporations were both investigated. The energy dispersive X-ray spectroscopy and X-ray diffraction measurements show that the films are nanocrystalline and do not display any evidence of Mn segregation, or of any other secondary phase formation. The transmittance measurements in the ultraviolet–visible–near infrared range allow us to calculate the absorption coefficient, the optical gap, and the Urbach energy. The hydrogenated $Ga_{1-x}Mn_xAs$ films presented wider gaps and smaller Urbach energies than its non-hydrogenated counterparts. In the hydrogenated films a linear correlation was observed between the decrease of the optical gap and the increase of the Urbach energy, which we have attributed to potential fluctuations and disorder induced by the Mn incorporation.

1. Introduction

At present there is a great interest in the introduction of Mn in GaAs to produce a diluted magnetic semiconductor (DMS), being the resulting compound a potential candidate to development of semiconductor devices with the control of the electronic spin (spintronics) [1–4].

The ferromagnetism in $Ga_{1-x}Mn_xAs$ compounds is observed when the Mn concentration is well above ($x \sim 0.03$–0.05) [2] the Mn solubility limit in GaAs ($\sim 1.0 \times 10^{18}$ cm^{-3}, ~ 0.002 at.%). Thus, the Mn incorporation in adequate concentrations is not an easy task and requires the utilization of special preparation techniques, in which the films are grown far from the thermodynamic equilibrium conditions [1–3]. The disorder caused in the crystalline GaAs by the Mn incorporation in random substitutional Ga sites open an interesting perspective to investigate the presence of these impurities in films with disordered structure.

The growth of $Ga_{1-x}Mn_xAs$ compounds by Molecular Beam Epitaxy (MBE) require relatively low substrates temperatures (LT-MBE; $\sim$250 °C) and high growth rates. This results in higher disorder degree and higher defects density [1–3] in the $Ga_{1-x}Mn_xAs$ films when compared with the best crystalline GaAs films growth by MBE. The search for solutions for this problem and the use of simple preparation techniques stimulate the search of new preparation techniques of $Ga_{1-x}Mn_xAs$ films.

The RF magnetron sputtering technique is a versatile technique for growing homogeneous semiconductor films with good mechanical and optical properties [5–8] using relatively low substrate temperatures. The films produced by sputtering generally present much poorer electronic quality as compared to the ones prepared by MBE [3,5–10], nevertheless when considering the preparation of amorphous or polycrystalline materials at low substrate temperatures, the sputtering is a simple and much less expensive alternative technique.

It is known that the presence of hydrogen (H_2) during the deposition process significantly decrease the defect density inside the gap and the electronic disorder in films prepared by sputtering [10,11] and in some cases also in films produced by MBE

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[12–14]. In the GaAs films prepared by sputtering, it was observed that the hydrogenation decreases the residual tensions of the lattice. This occurs because the hydrogen decrease the bond angles fluctuations between the Ga and As and passivate distorted and wrong-bond sites, decreasing the tails and gap state density [15]. However, in spite of the improvement caused in the electronic structure, recent reports have shown that the hydrogen is responsible to the Mn sites passivation in ferromagnetic $Ga_{1-x}Mn_xAs$, decreasing the free holes and the ferromagnetic characteristics like the Currie temperature and the spontaneous magnetization [16–18].

In this work, disorder effects caused by the Mn incorporation on the optical absorption edge of $Ga_{1-x}Mn_xAs$ and $Ga_{1-x}Mn_xAs$:H nanocrystalline films prepared by sputtering are analyzed. We have focused in the effects caused in the optical absorption edge based on ultraviolet–visible–near infrared (UV–Vis–NIR) transmittance measurements. Optical gap and Urbach energy were calculated using these measurements. X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX) experiments were used in the structural characterization of the films.

2. Experimental details

We have used a specially built RF magnetron sputtering system to produce the films. A 100 mm diameter, 6 mm thick electronic grade undoped GaAs wafer (Ramet Technology) was used as the target in a planar diode configuration. The target to substrate distance was 50 mm in all depositions. The system configuration was described in more detail elsewhere [19,20].

Ar and H_2 (6 N purity) were used as sputtering gases. Different quantities of millimeter sized Mn slabs were displaced along a target ring sputtered track of internal (external) diameter of 25 mm (35 mm) associated to the higher magnetic field of the magnetron. This disposition was used to assure high efficiency in the co-sputtering of the Mn pieces. The residual pressure in all depositions were smaller than 1×10^{-7} Torr, and consisted mainly of water vapor, as analyzed prior to the depositions by a residual gas analyzer (KJL Accu-Quad). The substrates used simultaneously in each deposition were, ESR grade fused silica (a-SiO_2), Si (100), GaAs (100), and stainless steel, to use in the X-ray diffraction, optical and infrared absorptions, and electron microscopy experiments.

The total gas pressure, RF power, and H_2 gas flux used in the depositions were established in a sequence of depositions of GaAs:H films used for the optimization of the optical and structural properties of the starting material [21]. The parameters that produced the smaller E_0 values and higher optical gaps of the hydrogenated GaAs films were kept constant during all depositions of this investigation, as shown in Table 1. Both hydrogenated and non-hydrogenated $Ga_{1-x}Mn_xAs$ samples were prepared using a sequence of different Mn concentrations. The x range was chosen in correspondence with the crystalline $Ga_{1-x}Mn_xAs$ that exhibit ferromagnetic properties.

Energy dispersive X-ray spectroscopy (EDX) analysis of the films deposited onto stainless steel substrates were performed in order to determine the film composition and specially to measure the Mn concentration effectively incorporated by the films. These measurements were made in a Zeiss DSM 960 scanning electron microscope. The presence of As–H and Ga–H and bonds in the samples was confirmed by the existence of absorption bands in ~2050 and ~1600 cm^{-1}, respectively, in the infrared transmittance spectra measured with the help of a Nicolet Magna 760 FTIR spectrophotometer.

X-ray diffraction measurements were performed in a θ–2θ detection geometry with fixed incidence angle of 3°. A rotating anode Rigaku Ultima 2000+ diffraction setup was used in the experiments. The scanning parameters and geometry were fixed in all experiments allowing direct comparison between samples.

The transmittance measurements in the absorption edge (0.5–2.5 eV) were performed on films deposited onto a-SiO_2 substrates. In these measurements we have used a Lambda 9 Perkin–Elmer spectrophotometer with integrating sphere apparatus. In order to check for light scattering effects the measurements were performed both in the regular sample compartment and in the entrance door of the integrating sphere. As the differences between the measurements were insignificant any effects of light scattering were disregarded in the range of wavelengths used in the experiments.

The transmittance measurements were used in order to determine the absorption coefficients of the films. The Cisneros' method for transmittance [22] was used to determine the refractive index, absorption coefficient and thickness in the less absorbing (low Mn content) samples, with the help of a computational routine. The optically determined thicknesses were compared with independent measurements performed with a perfilometer (Dektak ST Profiler). The absorption coefficient of the highly absorbing, high Mn content samples were determined using the mechanically measured film thickness, the refractive index estimated from reflectance measurements [23] and the high absorption routine applied to the transmittance spectra [22].

The absorption coefficient in the absorption edge was used to determine the optical gaps [24,25] and the Urbach energy parameters (E_0) [26,27]. We have used both the E_{04} [25], the energy in which the absorption coefficient is 1×10^4 cm^{-1}, and E_{Tauc} [24],

Table 1
Deposition parameters of $Ga_{1-x}Mn_xAs$ hydrogenated and non-hydrogenated films prepared by RF magnetron sputtering

Sample name	Sample composition	H_2 flux (sccm)	Relative Mn area in the target (%)*	x (±0.005)	Deposition rate (Å/s)	Film thickness (nm)
SP49	GaAs	0.0	0.0	0.000	1.05	1130
SP50	GaAs:H	3.0	0.0	0.000	1.08	1060
SP51	GaMnAs:H	3.0	1.4	0.005	1.35	1440
SP52	GaMnAs:H	3.0	1.4	0.004	1.22	1310
SP57	GaMnAs:H	3.0	3.1	0.001	0.79	860
SP54	GaMnAs:H	3.0	6.7	0.005	1.32	1430
SP55	GaMnAs	0.0	6.7	0.004	0.73	790
SP56	GaMnAs:H	3.0	12.5	0.011	1.31	1420
SP63	GaMnAs:H	3.0	19.9	0.057	1.02	1160
SP61	GaMnAs	0.0	28.4	0.068	0.65	700
SP58	GaMnAs:H	3.0	33.4	0.081	0.78	850

* The area covered by the Mn pieces relative to the magnetron disk surface (internal radius of 2.5 cm and external radius of 3.5 cm, concentric with the target) was displayed in the forth column, while the measured values of the Mn content x were displayed in the fifth table column. The constant parameters used during depositions were: RF Power: 30 W, Ar flux: 20.0 sccm, pressure: 1.5×10^{-2} Torr, substrate temperature: ~60 °C, deposition time: 180 min.