Journal of Alloys and Compounds 630 (2015) 78–83

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Electrical transport mechanisms and structure of hydrogenated and non-hydrogenated nanocrystalline $Ga_{1-x}Mn_xAs$ films

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ARTICLE INFO

Article history:
Received 1 November 2014
Received in revised form 7 January 2015
Accepted 8 January 2015
Available online 17 January 2015

Keywords:
Electrical properties
Diluted magnetic semiconductor
Sputtering
Space charge effects

ABSTRACT

The mechanisms of electrical conductivity in hydrogenated and non-hydrogenated nanocrystalline $Ga_{1-x}Mn_xAs$ ($0.000 \leqslant x \leqslant 0.081$) films were analyzed, first from a macroscopic perspective, followed by microscopic analysis to investigate the energy levels for trapping electric charges. The analysis of the current–voltage and resistivity–temperature characteristics allowed the development of a model based on the morphology and structure of the films. This model takes into account the main aspects of the transport above 300 K. Space charge limited current (SCLC) mechanism was observed in Mn-free films and is associated with deep trap states located at 0.10 and 0.22 eV below the conduction band. In samples containing Mn, the dark conductivity is highly dependent on the presence of hydrogen. This effect was related to the grain boundaries and interstitial regions of the films, in which the density of gap states is expected to be reduced by the presence of hydrogen.

1. Introduction

The incorporation of a considerable amount of Mn (several percent) in substitution sites, replacing Ga atoms in the GaAs, can produce ferromagnetic characteristics in the material [1–9]. These properties make $Ga_{1-x}Mn_xAs$ an interesting diluted magnetic semiconductor (DMS) for the production of devices with effective spin control [10]. Nevertheless, the difficulty of incorporating large amounts of substitutional Mn in $Ga_{1-x}Mn_xAs$ crystals, due to the low solid solubility of Mn in GaAs, limits the increase of the critical temperature and, therefore, the realization of spintronic devices operating above room temperature [11]. An interesting aspect of these materials is that the spin coherence lengths are greater than the carrier mean free path, suggesting that spin polarized transport can occur even with a relatively high defect density and disorder in magnetic semiconductors. In this way, the potential for increasing the solid solubility in disordered structures raises interest in the very complex electric transport properties of disordered semiconductors with incorporated transition metals. Even though there is much interest, the electrical transport mechanisms in nanocrystalline $Ga_{1-x}Mn_xAs$ have not been reported in the literature.

$Ga_{1-x}Mn_xAs$ films produced by the RF magnetron sputtering technique are frequently polycrystalline and they allow the incorporation of Mn above the limits observed in monocrystalline $Ga_{1-x}Mn_xAs$ films, without the detection of either of Mn segregation or formation of Mn-rich phases. The small dimensions of crystallites, which have estimated mean sizes of a few nanometers [12], reduce the average electronic mobility in the material, due to the increase of density in potential barriers among the grains by unity of volume. This structural disorder implies highly complex systems and, therefore, the existence of several concurrent mechanisms in the transportation of electrical charge.

The models of Seto [13] and Bruneaux et al. [14], which were successfully applied to polycrystalline Si and SnO_2:F, respectively, simplify the analysis of the transport mechanism by considering the charge trapping inside the crystals and grain boundaries as the dominant effect of transport in disordered materials. Therefore, in principle, these models can be qualitatively tested in nanocrystalline $Ga_{1-x}Mn_xAs$, despite the highly complex charge transport in this material.

The aim of this research is to identify the dominant electrical transport mechanisms existing above room temperature in hydrogenated and non-hydrogenated nanocrystalline $Ga_{1-x}Mn_xAs$ films with different Mn cation concentrations. We analyzed the electrical conductivity, as a function of the temperature, and the current versus voltage characteristics, in continuous current, for samples

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http://dx.doi.org/10.1016/j.jallcom.2015.01.032
0925-8388/

deposited by RF magnetron sputtering. The structural characteristics were analyzed using Rietveld Method.

2. Material and methods

The analyzed films were produced by RF magnetron sputtering. Mn was incorporated in the films by the co-sputtering of small Mn blades arranged on an electronic grade GaAs single crystal target in an atmosphere of pure Ar (99.9999%) or a mixture of Ar and H_2 (99.9999%) for the hydrogenated films. The variation of Mn content incorporated in the films, as a function of its concentration on the target, was determined by the energy dispersive electron spectroscopy (EDX) technique using a Zeiss DSM 960 scanning electron microscope. Films were deposited simultaneously onto undoped Si (100) and GaAs (100), and fused silica (a-SiO_2); the latter were used for the conductivity and XRD analysis. Substrates were not intentionally heated, but the substrate surface temperature raised during depositions to 330 ± 10 K as measured by a thin thermocouple placed in a reference substrate. Pereira and da Silva provided a more detailed description of the deposition procedure [12]. A pure GaAs single crystal slab was used as a reference for the EDX composition calibrations. These results are shown in Table 1.

X-ray diffraction (XRD) experiments were carried out using a Rigaku Ultima 2000+ diffractometer, with Li filtered Cu Kα radiation. The measurements were performed in a θ–2θ geometry for a fixed time. Structural analysis by Rietveld refinement was performed using the General Structure Analysis System (GSAS) software [15] with the interface Experiment Graphical User Interface (EXPGUI) [16]. The refinements followed two paths; the first considered only the Crystallographic Information File (CIF) of GaAs phase (41674-ICSD), even for doped samples, and the second path considered the percentage of atomic manganese added to each sample, i.e., the amount of manganese atoms that had replaced the gallium atoms was taken into account when the crystallographic data was provided to the software. The two types of refinements were performed because it was not possible to find a CIF file for the phase of GaAs:Mn that had the same concentration of manganese as the samples under study.

Parallel Au electrical contacts, with 10 mm length and 1 mm separation, were deposited by thermal evaporation, in vacuum, along the free film surface. Finally, the samples were subjected to thermal annealing in vacuum at 550 K for 20 min, to promote the diffusion of the contacts. The XRD measurements and electrical transport were made on twin films, deposited onto fused silica substrates. The Rietveld analysis was performed on diffractograms measured in the as grown condition. In order to check for possible Mn segregation during the annealing used in the electrical transport measurements, cumulative sequential annealing at 393 K and 573 K were performed on twin samples, each lasting for 20 min. The XRD experiments indicate that the only significant changes due to annealing were observed on non-hydrogenated $Ga_{0.919}Mn_{0.081}As$ where the (220) and (311) peaks become defined only after treatment at 573 K. No diffraction peak related to Mn or MnAs were observed in the diffractograms. A shoulder in the (220) peak is the only indication that some initial stage of segregation is about to occur after the annealing at 573 K on the non-hydrogenated, $x = 0.081$ sample.

Measurements of the current as a function of the voltage at various temperatures ($I \times V \times T$) and the conductivity as a function of the temperature ($\sigma \times T$) were made in vacuum (of the order of 10^{-5} Torr) by using a cryostat. The electric signal was measured with a Keithley electrometer, model 6517A, connected to a microcomputer through a GPIB (National Instruments GPIB – IEEE 488.2) interface.

3. Results

3.1. Structure of the Films

The Rietveld analysis of the XRD data for hydrogenated films with Mn inserted showed that the unit cell volume decreased slightly, while the crystallite size underwent a slight increase, with increasing manganese concentration (Table 2). In contrast, non-hydrogenated materials displayed a negligible increase (comparable to the determination error) in the unit cell volume, while the crystallite sizes decreased significantly (Table 2). Variation in the lattice parameter with the presence of manganese is associated with the differences between the ionic radii of Ga and As (Vegard's law) [17]. Segregated, Mn rich, or other unexpected phases were not observed in the samples studied. The graphs shown in Fig. 1, correspond to the refinements where the CIF file was used with the substitution of Ga for Mn in the proportions shown in Table 1. Peaks associated with the planes (111), (220), (311) of GaAs with zinc-blend structure were observed [18].

In order to qualitatively estimate the crystalline/amorphous fraction of both hydrogenated and non-hydrogenated films of $Ga_{1-x}Mn_xAs$ as a function of Mn concentration, integrated intensities were calculated under the three diffraction peaks associated with the (111), (220) and (311) planes. Table 2 shows the relation between the sizes of the crystallites (determined by the Rietveld method) and integrated intensities with respect to the concentration of Mn. In hydrogenated films with increasing Mn concentration, it is observed that the crystallites had a slight increase in their size and a reduction in the crystalline fraction, suggesting a reduction in the number of crystallites with practically constant size. Moreover, in the non-hydrogenated films, the concentration of Mn reduced the size of the crystallites and increased the crystalline fraction. This suggests that in these films, a greater density of crystallites with smaller dimensions should exist as the concentration of Mn increases.

3.2. Electrical properties

Fig. 2 shows the results of measuring the conductivity in the dark as a function of the temperature of hydrogenated and non-hydrogenated samples with different Mn concentrations. It was observed that, for the same Mn concentration, the hydrogenated film (sample H) has lower conductivity compared to the non-hydrogenated (sample G). The incorporation of Mn in non-hydrogenated films increased the conductivity, at 300 K, from 1.5×10^{-1} S/m to 2.07×10^{1} S/m, while the concentration (fractional) increased from 0.004 (sample C) to 0.057 (sample G). In hydrogenated films, also at room temperature, the conductivity varied from 2.35×10^{-8} S/m to 6.02×10^{-2} S/m, for concentrations of Mn from 0.004 (sample B) to 0.057 (sample H).

Current–voltage measurements carried out at different temperatures (J–V–T) were used to investigate the regimes of electrical conductivity in the films. We chose to work with temperatures above 300 K to be able find energy levels of deep traps in the films. Fig. 3a and b shows the current density, at room temperature, for the sample A (without manganese) and sample D (with a concentration of 1.1% manganese), respectively. The J–V curves for sample A (Fig. 3a) show a linear slope only at low voltage values (<0.10 V). Lampert and Mark [19] classify this linear dependence as an "Ohmic regime" ($I \propto V$), a definition used in this work. For voltage

Table 1
Deposition parameters of hydrogenated and non-hydrogenated $Ga_{1-x}Mn_xAs$ films prepared by RF magnetron sputtering. The constant parameters used during deposition were RF power, 30 W; Ar flux, 20.0 sccm; pressure, 1.5×10^{-2} Torr; substrate temperature, ~330 K; deposition time, 180 min; and target substrate distance, 50 mm.

Sample label	Sample composition	H_2 flux (sccm) (±0.2)	Bias voltage (V)	X (±0.005)	Film thickness (nm)
A	$Ga_{1-x}Mn_xAs$:H	3.0	69.5	0.000	1060 (±40)
B	$Ga_{1-x}Mn_xAs$:H	3.0	70.0	0.004	1310 (±)
C	$Ga_{1-x}Mn_xAs$	0.0	61.3	0.004	790 (±60)
D	$Ga_{1-x}Mn_xAs$:H	3.0	68.0	0.011	1420 (±110)
E	$Ga_{1-x}Mn_xAs$:H	3.0	58.2	0.081	850 (±60)
F	$Ga_{1-x}Mn_xAs$	0.0	79.0	0.081	1000 (±80)
G	$Ga_{1-x}Mn_xAs$	0.0	80.0	0.057	1000 (±80)
H	$Ga_{1-x}Mn_xAs$:H	3.0	74.5	0.057	1160 (±70)