Journal of Magnetism and Magnetic Materials 374 (2015) 354–358

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Dependence of magnetic properties on the growth temperature of $Mn_{0.04}Ge_{0.96}$ grown on Si (001)

B. Toydemir, A.C. Onel, M. Ertas, L. Colakerol Arslan *

Department of Physics, Gebze Institute of Technology, 41400 Kocaeli, Turkey

ARTICLE INFO

Article history:
Received 23 May 2014
Received in revised form
15 July 2014
Available online 27 August 2014

Keywords:
Diluted magnetic semiconductor
MnGe
Ferromagnetic resonance phase
Curie temperature

ABSTRACT

The structural and magnetic properties of $Mn_{0.04}Ge_{0.96}$ thin films grown on Si (001) substrates at different growth temperatures were investigated. The films were grown by sequential deposition of MnGe and Ge multilayers using molecular beam epitaxy. It was found that the magnetic ordering and Curie temperature could be controlled by adjusting the distance between the Mn ions in the Ge spacer layer depending on growth temperature. We found that the samples grown below 130 °C contained highly disordered ferromagnetic Mn rich domains. Both structural and magnetic characterizations revealed that Mn_5Ge_3 precipitates were formed in Mn clusters free Ge matrix when the samples were grown at 150 °C. Both the Mn rich domains and Mn_5Ge_3 precipitates showed out of the plane magnetic anisotropy and similar ESR line shapes.

1. Introduction

Study on ferromagnetic semiconductors has attracted considerable research interest because of their potential applications in future generations of spin-based electronic devices [1,2]. In particular, Mn doped Ge based diluted magnetic semiconductors (DMSs) exhibit specific magnetic and transport properties which allow them to be used for high-frequency applications. Recent studies on these materials have shown that the growth condition and magnetic impurity concentration play a significant role in determining the spatial distribution of magnetic dopants and their magnetic coupling [3,4]. The key challenges for the growth of Mn doped Ge are the ability to increase the concentration and substitutional occupation of magnetic dopant in order to realize room-temperature ferromagnetism [5–8]. However, this is hindered by low solubility of Mn in Ge with a strong tendency to form ferromagnetic intermetallic phases or heterogeneous regions within the Ge matrix. In order to enhance the incorporation of Mn dopant into Ge, several non-equilibrium growth approaches have been made to synthesize Mn doped Ge such as ion implantation [9–12], molecular beam epitaxy (MBE) [13–16] and subsurfactant epitaxy [17].

In this present work, we have grown $Mn_{0.04}Ge_{0.96}$ thin films by alternating deposition of atomic-scale layers of Mn and MnGe to carefully control the distribution of Mn atoms in Ge. In this growth method, Mn atoms which are located at the interstitial sites diffuse upward and occupy substitutional sites of the next Ge layers because the Mn atoms tend to diffuse upward to the subsurface layer during the growth [18]. The diffusion range of Mn atoms in Ge spacer layers can be adjusted by varying the substrate temperature. A number of studies have shown that inhomogeneous distribution of Mn rich nanocolums and MnGe precipitates appears under low temperature deposition conditions for co-deposited MnGe thin films due to self-organization of dopant atoms [4,13,19,20]. However, we have found that depending on the growth temperature, an optimized multilayer approach can stabilize a single phase and structural transition in the layers can induce changes in magnetic phases.

To understand the magnetic phases in the samples at a microscopic level, electron spin resonance (ESR) measurements were carried out. ESR spectroscopy is a very useful method for evaluating magnetic ordering in DMSs. A few ESR studies have already been carried out on Mn implanted Ge thin films, and the inhomogenous nature of the films was investigated [10,21]. However a complete understanding of the influence of growth condition on the ESR spectra of Mn doped Ge thin films has not been achieved. The purpose of the experimental design is to investigate the effect of the growth temperature on the ESR spectra and identify contributions of different magnetic centers to the magnetic properties of the $Mn_{0.04}Ge_{0.96}$ thin films. In addition, the role of substrate temperature on Mn distribution has been studied based on the analysis of x-ray diffraction (XRD) and vibrating sample magnetometry (VSM).

2. Experimental

$Mn_{0.04}Ge_{0.96}$ films were grown by MBE on Si (001) wafers. Initially, Si substrates were rinsed in a 1:10 solution of

* Corresponding author.
E-mail address: lcolakerol@gyte.edu.tr (L.C. Arslan).

http://dx.doi.org/10.1016/j.jmmm.2014.08.049
0304-8853/

concentrated HCl and deionized water and annealed in ultrahigh vacuum (UHV) at 650 °C for several hours in order to remove the natural oxide layer. Surface order and cleanness were checked with low energy electron diffraction (LEED) and x-ray photoelectron spectroscopy (XPS). Prior to $Mn_{0.04}Ge_{0.96}$ deposition, a 35 nm thick Ge buffer layer was grown on atomically clean surface at 450 °C. Ge and Mn were consecutively evaporated from two different Knudsen cells. The nominal Ge and Mn deposition rates were monitored by a quartz-crystal microbalance and independently verified via ex-situ x-ray reflectivity measurement. The $Mn_{0.04}Ge_{0.96}$ films were grown by alternatively growing very thin Mn and MnGe layers for 40 periods, approximately 0.1 nm and 2.4 nm respectively, to overcome the low Mn solubility in Ge. Since the growth was performed at low growth temperatures, the Ge deposition rate was kept at 0.08 Å/s to obtain good epitaxial quality. The film quality was monitored insitu with LEED and XPS and exsitu by an x-ray diffractometer (Rigaku, SmartLab) with monochromatic Cu-Kα radiation. Magnetic properties at different temperatures were examined by means of a Quantum Design Physical Properties Measurement System with the field along the sample normal. An ESR experiments were carried out using a Joel x-band spectrometer equipped by an electromagnet which provides a DC magnetic field up to 2 T in the horizontal plane. Temperature was varied in the range 110–350 K using a variable temperature accessory JOEL ES-DVT4. A manganese (Mn) marker was used to calibrate g factors.

3. Results

Fig. 1 shows the XRD spectra of the $Mn_{0.04}Ge_{0.96}$ films grown at 100 °C, 130 °C and 150 °C. No traces of Mn metal and Mn-related secondary phases were detected for S100 and S130 films. However, when the growth temperature was increased to 150 °C, besides the diffraction peaks of Ge (400) and Si (400), a small peak appeared around 35.56°. This peak is the (002) diffraction of Mn_5Ge_3, which appears due to phase separation into Mn rich crystalline clusters embedded in the Ge matrix, indicating that Mn_5Ge_3 precipitates are highly oriented with their c-axis parallel to the Ge (001) direction. Therefore, the growth temperature is a critical parameter affecting the growth kinetics of Mn doped Ge films.

The magnetic hysteresis loops measured at 10 K for the $Mn_{0.04}Ge_{0.96}$ samples grown at different temperatures are shown in Fig. 2(a). The paramagnetic contribution from impurities in the substrate and diamagnetic contribution from the sample have been subtracted from the curves. A general finding is that lower growth temperature yields lower saturation magnetization (M_s) and coercivity (H_c) because of the limited interaction of Mn atoms sparsely distributed in and around the Mn rich layers. The magnetization loops taken at 10 K revealed that with the increase of the growth temperature, the coercive field of the thin films increases from 70 Oe to 1250 Oe at 10 K. The enhancement of coercivity is related to the anisotropic occupation of Mn ions in Ge. This very large coercivity is in good agreement with the behavior of larger-domain ferromagnets. Above 60 K the magnetization loops of S100 and S130 no longer exhibit hysteresis or remanence (not shown here). However, the coercive field of S150 was rapidly suppressed with the increase of growth temperature and reached 100 Oe at 300 K (see Fig. 2(b)). From the hysteresis loop, we can observe that the M_S, is clearly higher for S150 than those for S100 and S130, where the values of M_s are almost at the same level. Having an equal Mn concentration of 4%, magnetic moment of about 0.79 μ_B, 0.98 μ_B and 2.48 μ_B per Mn atoms was estimated assuming equal contributions from all the Mn atoms for S100, S130 and S150, respectively. The saturation magnetization values of the samples grown at lower temperatures are much lower than the magnetic moment of diluted Mn^{2+} ions, consistent with earlier observations [5]. This indicates that a large fraction of Mn atoms are located at the interstitial sites or form atomic clusters. As the growth temperature increases, Mn atoms are aligned in a certain crystallographic orientation. The saturation magnetization of S150 is comparable with the value of 2.6 μ_B/Mn obtained from Mn_5Ge_3 at 4.2 K [22]. We therefore assume that for the growth temperature of 150 °C a certain amount of Mn forms Mn_5Ge_3 clusters, consistent with the previous results [13,23,24].

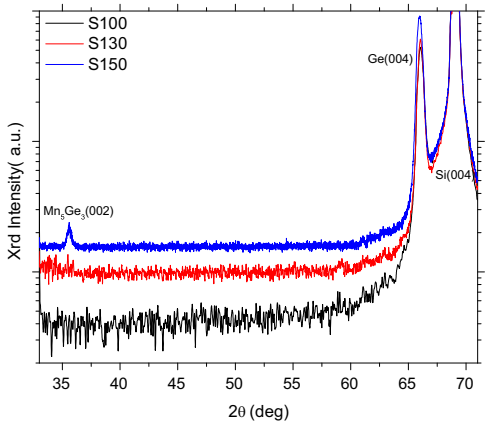

Fig. 1. XRD spectra measured for $Mn_{0.04}Ge_{0.96}$ thin films grown at 100 °C, 130 °C and 150 °C.

Fig. 3 shows the temperature dependence of the magnetization of the samples measured in a magnetic field H, of 1000 Oe from 10 to 350 K. Similar to the previous studies, two transition temperatures were observed [4,25]. The increasing signal below 25 K corresponds to the transition temperature of diluted Mn atoms, while the higher temperature transition at 105 K and 135 K, respectively, obtained from S100 and S130 is attributed to Mn rich regions in the Ge matrix. It is apparent that the increase in growth temperature resulted in the increase in diffusion of the Mn dopants. As a result, Mn atoms segregated and formed metallic regions in the Ge matrix. Upon increasing the number of magnetically active atoms and aligning them with an applied external field, mediated ferromagnetic ordering among local Mn spins was enhanced; hence magnetization and Curie temperature were increased. On the other hand, for the S150, a clear magnetization onset near room temperature was visible which is interpreted as the paramagnetic to superferromagnetic transition of Mn_5Ge_3 clusters.

ESR studies are probably the most sensitive method for detecting ferromagnetic order as well as the possible existence of other magnetic species [26]. In order to investigate in detail the magnetic states of the samples the magnetism has been measured by ESR with the external field parallel to the ab-plane of the samples in the temperature range from 110 to 320 K, and the results are shown in Fig. 4. The ESR spectra of S100 and S130 exhibit a single broad resonance line in the low temperature region. Since the undoped Ge does not produce any ESR signal, the ESR signal with g being near 2.002 is a new signal and associated with the introduction of Mn dopants which lead to the localization of electrons in $Mn_{0.04}Ge_{0.96}$. It is known that the Mn^{2+} ion has $3d^5$ and the ESR spectrum is expected to show six hyperfine transitions. However, the ESR spectra of Mn doped Ge samples investigated here show only a broad signal without splitting into additional peaks. The broad signal is attributed to ferromagnetic resonance, which arises from exchange interaction between Mn^{2+} ions. The integrated ESR intensity calculated through double integration of the absorption-derivative spectrum is shown in the inset in Fig. 4. In both S100 and S130, the ESR intensity follows a similar temperature dependence: as the temperature decreases