Materials Sciences and Applications, 2015, 6, 533-538
Published Online June 2015 in SciRes. http://www.scirp.org/journal/msa
http://dx.doi.org/10.4236/msa.2015.66057

Direct Structural Evidences of Epitaxial Growth $Ge_{1-x}Mn_x$ Nanocolumn Bi-Layers on Ge(001)

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Received 25 January 2015; accepted 12 June 2015; published 15 June 2015

Abstract

Molecular Beam Epitaxy (MBE) system equipped with *in-situ* Reflection High-Energy Electron Diffraction (RHEED) has been used for (Ge, Mn) thin film growth and monitoring the surface morphology and crystal structure of thin films. Based on the observation of changes in RHEED patterns during nanocolumn growth, we used a *real-time* control approach to realize multilayer structures that consist of two nanocolumn layers separated by a Ge barrier layer. Transmission Electron Microscopy (TEM) has been used to investigate the structural properties of the GeMn nanocolumns and GeMn/Ge nanocolumns bi-layers samples.

Keywords

GeMn Diluted Magnetic Semiconductors, Muti-Layers, GeMn Nanocolumns, Thin Film, Epitaxial Growth

1. Introduction

The trigger in spintronics can be attributed to the discovery of giant magneto-resistance (GMR) in metallic multilayers by A. Fert and P. Grunberg in 1988 [1] [2]. Today, it has led to unbelievable storage capacity of hard disks and the development of a new generation of memories, called magnetic random access memories (MRAM). The concept of spin transistors, proposed by Datta and Das in 1990s, has motivated important research and tremendous improvements have been achieved during the last decades. The development of active spin devices, such as spin transistors or diodes, calls for new materials, which are enable to efficiently inject spin-polarized currents into standard semiconductors.

Recently, special attention both in experiment and theory has been given to group-IV $Ge_{1-x}Mn_x$ diluted mag-

How to cite this paper: Le, T.G. (2015) Direct Structural Evidences of Epitaxial Growth $Ge_{1-x}Mn_x$ Nanocolumn Bi-Layers on Ge(001). *Materials Sciences and Applications*, **6**, 533-538. http://dx.doi.org/10.4236/msa.2015.66057

netic semiconductors (DMS) due to its potentiality in spin injection into semiconductors and compatibility with mainstream Si-based electronics [3]-[10]. Among numerous phases of $Ge_{1-x}Mn_x$ DMS, GeMn nanocolumns appears to be the most interesting because it is a unique phase exhibiting Curie temperature higher than 400 K [3]-[7]. Thus, the synthesizing multilayers of $Ge_{1-x}Mn_x$ nanocolumns represent great interests for spintronic applications, such as spin valves or giant magneto-resistance (GMR) multilayers. However, controlling Ge overgrowth on the $Ge_{1-x}Mn_x$ nanocolumn layer or realizing multilayers of $Ge_{1-x}Mn_x$ nanocolumns poses many problems due to the inhomogenous surface of $Ge_{1-x}Mn_x$ nanocolumn layer. The origination of those problems is the appearance of Mn_5Ge_3 clusters during the $Ge_{1-x}Mn_x$ nanocolumn growing process. Hence, to exploit the exciting magnetic and semiconducting properties of nanocolumns for device applications, a natural question arising is how to isolate nanocolumns from metallic Mn_5Ge_3 clusters.

This paper is devoted to presenting the growth bi-layers of $Ge_{1-x}Mn_x$ nanocolumns on Ge(001) based on the real-time control approach. We provide the evidence that with the help of *in-situ* characterization of RHEED, we are able to precisely control the growth of nanocolumn/Ge stacked layers without any metallic Mn_5Ge_3 cluster for the realization of giant magneto-resistance (GMR) multilayers.

2. Experimental

The cleaning of Ge surfaces was carried out in two steps: a chemical cleaning to remove hydrocarbon related contaminants followed by an *in-situ* thermal cleaning at ~750˚C to remove the Ge surface oxide layers. After this step, the Ge(001) surface generally exhibits a (2 × 1) reconstruction. To insure a good starting Ge surface prior to $Ge_{1-x}Mn_x$ growth, a ~30 nm thick Ge buffer layer was systematically grown at a substrate temperature of 600˚C.

$Ge_{1-x}Mn_x$ films were grown by molecular beam epitaxy (MBE) on epi-ready *n*-type Ge(001) wafers with a nominal resistivity of 10 Ω·cm. The base pressure in the MBE system is better than 5×10^{-10} Torr. The growth chamber is equipped with a reflexion high-energy electron diffraction (RHEED) technique to control the cleanness of the substrate surface prior to growth and to monitor the epitaxial growth process. $Ge_{1-x}Mn_x$ films were obtained by co-deposition of Ge and Mn from standard Knudsen effusion cells, the Ge deposition rate was determined from RHEED intensity oscillations whereas the Mn deposition rate was deduced from Rutherford backscattering spectrometry (RBS) measurements. The standard growth rate of $Ge_{1-x}Mn_x$ alloys used in this work is of 1 - 2 nm/min. Structural analyses of the grown films were performed through extensive high resolution transmission electron microscopy (TEM) by using a JEOL 3010 microscope operating at 300 kV with a spatial resolution of 1.7 Å.

3. Results and Discussion

As shown in our previous studies, under certain condition (C_{Mn} ~ 6%; T_{Growth} ~ 130˚C), the epitaxial growth of a GeMn layer on Ge(001) substrate at low temperature resulted in the formation of the nanocolumns, which are alongated along the [001] direction, consistent with surrounding Ge matrix, and exhibit T_C higher than 400 K [3]-[6]. We also show that the formation of high-T_C nanocolumns and Mn_5Ge_3 clusters is competing process and the process window for stabilizing only high-T_C nanocolumn phase is relatively limited. The formation of nanocolumns is found to depend not only on the Mn concentration but also on film thickness. During the growth, Mn continuously segregates toward the film surface and high-T_C nanocolumns are found to transform to metallic Mn_5Ge_3 precipitates when the Mn concentration inside nanocolumns exceeds a highest value about 40 at% [3]. At a given Mn content, by means of TEM analyses one can determine the film thickness at which Mn_5Ge_3 clusters are formed. However, such a kind of analyses requires a great number of TEM investigations, which should be carried out at numerous Mn contents. We propose a real-time control approach to realize multilayer structures consisting of nanocolumns separated by a Ge barrier layer.

In **Figure 1**, we present a real-time evolution of RHEED patterns versus the film thickness, observed during $Ge_{1-x}Mn_x$ growth with a Mn content of 6%. Starting from a well-developed two-dimensional RHEED pattern of the Ge surface prior to growth (**Figure 1(a)**), nanocolumns grow up to a film thickness of ~80 nm and the corresponding RHEED pattern is still characterized by a pr two-dimensional (2D) behavior, except some reinforcement of intensity around bulk-like three-dimensional (3D) spots (indicated by white arrows in **Figure 1(b)**). Note that a streaky pattern and half-ordered streaks are still observable at this growth stage, and the RHEED pattern consist of three-dimensional spots on the 1 × 1 streaks and the reappearance of 2 × 1 streaky pattern has been attributed to the signal of nanocolumn phase (discussed in [3] [4] [7]). When Mn_5Ge_3 clusters are formed for film thicknesses above 80 nm, the film surface becomes so rough that the pattern is predominantly constituted of 3D spots (**Figure 1(c)**). With a further increase of the film thickness, the density and also the size of Mn_5Ge_3 clusters increase, the growing surface becomes highly disordered and the pattern exhibits very faint 3D spotty patterns (**Figure 1(d)**).

In short, for a given Mn content, using RHEED analyses we are able to set up the thickness range in which only nanocolumns are formed (up to 80 nm) and can detect in *real-time* the beginning of Mn_5Ge_3 formation. Thus, if we interrupt the film growth at the moment of 3D spot appearance, then grow on top a Ge barrier layer, it becomes possible to produce nanocolumn/Ge stacked layers without any metallic Mn_5Ge_3 cluster.

Working on this direction, we display in **Figure 2** the successful growth 80 nm thick of $Ge_{0.96}Mn_{0.06}$ nanocolumns free of Mn_5Ge_3 clusters. Dark contrast corresponds to Mn-rich regions while regions with a brighter contrast arise from the diluted matrix. According to an overall view of the layer structure, shown in low-scaled images in (**Figure 2(a)**) we can see that the GeMn nanocolumns observed here are very similar to those reported in Ref. 7. A slight difference is that the average diameter of these nanocolumns, which is ~5 - 8 nm, is higher than those previously reported. As can be seen in a high-resolution TEM image taken around a column inside the layer (**Figure 2(b)**), nanocolumns are epitaxial and perfectly coherent with the surrounding diluted lattice. No defects nor presence of Mn_5Ge_3 clusters are visible.

These results indicate that, we have already synthesized successfully $Ge_{1-x}Mn_x$ nanocolumns which are coherently match the lattice of the surrounding matrix, and GeMn film exhibits the same diamond structure as Ge pure, which shows a perfect single crystal in epitaxial relationship with Ge buffer layer. Furthermore, as have

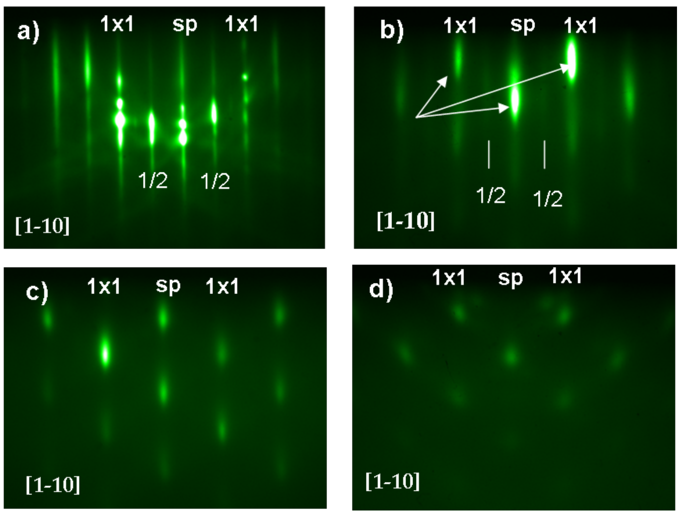

Figure 1. RHEED patterns taken along [1]-[10] azimuth during the growth of a ~130 nm thick $Ge_{1-x}Mn_x$ film with x ~0.06; The specular streaks (sp) together with (1 × 1) bulk-like streaks and half-ordered (1/2) streaks arising from the surface reconstruction are indicated. (a) Pattern from a Ge surface prior to growth; (b) pattern observed during growth for film thickness below 80 nm; (c) for film thickness in the range between 80 and 100 nm; (d) for film thickness of around 130 nm.

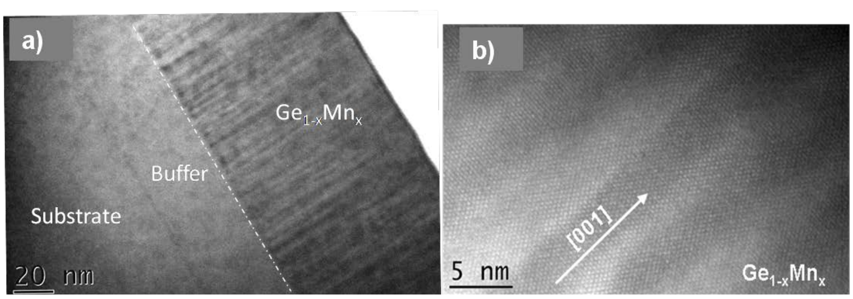

Figure 2. Typical cross-sectional (a) and High-resolution TEM images taken inside the film (a) of an 80 nm thick $Ge_{1-x}Mn_x$ film grown at 130˚C and with x ~0.06.

been discussed, with the help of *in-situ* characterization of RHEED, we are able to precisely control the growth of nanocolumn/Ge stacked layers without any metallic Mn_5Ge_3 clusters. Next step, we will carry out the synthesis of two layers of $Ge_{1-x}Mn_x$ nanocolumns separated by Ge barrier, and characterize the structural properties and the formation of these two layers.

As has been presented, although have three-dimensional spots on the 1 × 1 streaks due to the presence of nanocolumns, the growth a layer of $Ge_{1-x}Mn_x$ nanocolumns is almost layer-by-layer with the dominion of 2D diffraction pattern which has 2 × 1 reconstructions persistent during the growth [3] [4]. This condition allows to epitaxial grow on top the layer of Ge and then, $Ge_{1-x}Mn_x$ nanocolumns layer. The growth procedure is simple: we alternate opening and closing the shuttle of the Mn cell while keeping the Ge cell open to grow successively a $Ge_{1-x}Mn_x$ nanocolumn layers and a separating layer of Ge. The temperature is kept constant at 130˚C during deposition. The layer thickness depends mainly on the deposition time of Ge element which is about 6 nm/min. In this growth condition and Mn concentration of 6%, 80 nm thick of the sample is well accorded to have an epitaxial layer of nanocolumns without Mn_5Ge_3 dominate whole over the sample, (illustrated in **Figure 2**). Therefore, in this section we decided to grow two layers of $Ge_{0.94}Mn_{0.06}$ with the thickness of 80 nm for each one.

We display in **Figure 3** an example in which *in-situ* RHEED is used to monitor three successive growth stages: the first nanocolumn layer, the Ge spacer layer and then the second nanocolumn layer. We note that upon growth of the Ge spacer layer, it is possible to completely smooth out the surface of the first nanocolumn layer and obtain a completely 2D RHEED pattern, similar to that of the clean Ge surface if the Ge spacer thickness is high enough (>5 nm). The patterns shown in **Figure 3(c)** and **Figure 3(d)** correspond to a Ge overlayer of only ~8 nm thick and one can notice that the intensity of 1/2 streaks in **Figure 3(c)** has become more visible compared to the **Figure 3(a)** pattern.

This behavior can be understood as follow, after depositing the first and the second $Ge_{0.94}Mn_{0.06}$ layers, the RHEED pattern exhibits the signal of the nanocolumns phase which shows the rougher of the surface due to the presence of Mn atoms; however, after depositing Ge barrier (without contribution of Mn atoms), the roughness

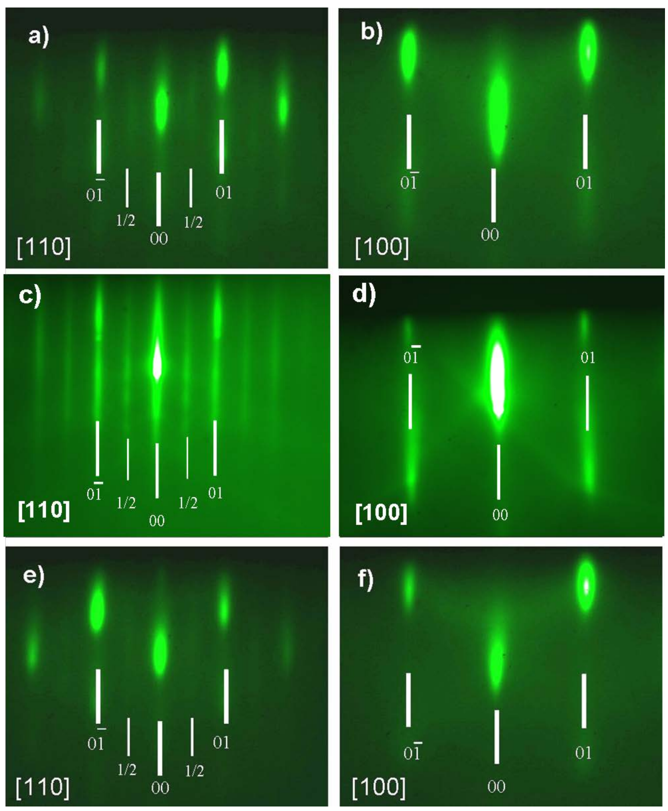

Figure 3. Evolution of RHEED patterns taken along [110] and [100] azimuths; ((a), (b)) after the formation of the first layer of $Ge_{0.94}Mn_{0.06}$ nanocolumns; ((c), (d)) After growth of the Ge spacer and ((e), (f)) after regrowth of the second layer of $Ge_{0.94}Mn_{0.06}$ nanocolumns.

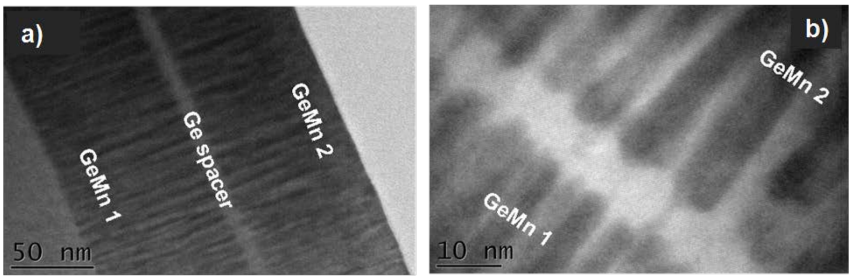

Figure 4. Typical cross-sectional (a) and high-resolution (b) TEM images of two $Ge_{0.94}Mn_{0.06}$ nanocolumn layers separated by a ~8 nm thick Ge spacer layer.

of the surface is decreased with the reappearance clearer of 2 × 1 streaky patterns. The RHEED pattern after depositing the second layer is almost the same with the first one indicates that the 2D growth is well controlled and the process of multilayer growth is completely reproducible.

Figure 4(a) represents a typical cross-sectional TEM image of the corresponding sample (C_{Mn} ~ 6%). Two nanocolumn layers, each of them has a thickness of ~80 nm, are clearly separated by a thin Ge barrier layer of 8 nm thick. It is important to notice that a structure consisting of two nanocolumn layers is completely free of Mn_5Ge_3 clusters. Another interesting feature, which can be observed in a high-resolution TEM image shown in **Figure 4(b)**, is that nanocolumns in the upper layer are found to grow on the top of nanocolumns in the lower layer, giving rise to a vertical correlation between nanocolumns along the growth direction.

The above vertical alignment of nanocolumns along the growth direction has been observed in other multilayer systems, in particular, in multilayers of InAs/GaAs [11]-[13] and Ge/Si quantum dots [14]-[16]. This indicates that the structure investigated here can be considered as a standard case of self-organization. Thus, based on previous results, we can get better understanding about the growth kinetics of GeMn nanocolumn multilayers.

4. Conclusion

By combining the observation of changing in RHEED patterns and TEM image of the samples, we have provided a clear evidence that we successfully control the growth of nanocolumn/Ge stacked layers without any metallic Mn_5Ge_3 clusters. Of particular interest, we have observed the vertical ordering of nanocolumns along the growth direction. It is probable that propagation of strain fields induced by buried nanocolumns is the driving force for this vertical self-organization. Investigating the formation of bilayers of nanocolumns separated by a thin spacer layers and studying magnetic coupling interactions of nanocolumns through a nanometer thick spacer layer are in progress.

Acknowledgements

This work was supported by the National Foundation for Science and Technology Development (NAFOSTED) under grant number of 103.02 - 2013.66. The author would like to thank Prof. Vinh LE THANH and Dr. Minh Tuan DAU—Centre Interdisciplinaire de Nanoscience de Marseille (CINaM-CNRS), France for their helps.

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