Preparation of Thin Layers of Ferromagnetic Semiconductors

Koštejn, Martin
2013

Preparation of Thin Layers of Ferromagnetic Semiconductors

Martin Koštejn [1, 2]

[1] Department of Physical Electronics, Faculty of Nuclear Sciences and Physical Engineering. Czech Technical University in Prague

[2] Department of Aerosols and Laser Studies, Institute of Chemical Process Fundamentals of the ASCR, v. v. i.

Abstract

The paper reports on experiments of preparation Mn diluted in Si or Ge. These materials are potential ferromagnetic semiconductors. Thin layers have been prepared by reactive pulsed laser deposition of Mn target under small pressure of volatile precursor (silane or germane). We estimate initial temperature 1mm above surface as 1.9 eV. The prepared layers can contain 1-40% of Mn atoms in form of amorphous mixture of Mn and Si or nano-crystallized mixture of Mn and Ge. High temperature annealing or rapid laser annealing is needed for recrystallization of Mn:Si layers.

Key words: room temperature ferromagnetism; pulsed laser deposition; diluted magnetic semiconductors; silicides; germanides

Introduction

It is assumed that recent progress in electronics devices is nearly at its limit, and now it is important to find new principles which will lead to further miniaturization and further characteristic enhancements. One of the promising ideas is taking an advantage of a spin of an electron in addition to its charge. This field of research is called spin transport electronics or shortly spintronics.

Spintronics provides new opportunities how to improve electronic devices such as magnetic storage media, non-volatile memories, or sensors. Except high density magnetic storage media based on giant magnetoresistance, spintronics is still in its beginning mainly due to the absence of suitable materials for applied research.

Nowadays, the main research interest is focused on ferromagnetic semiconductors (FMS). These materials should combine the conducting properties of semiconductors with long-range ferromagnetic order. The major problem in this field is low Curie temperature (CT) of most such materials. CT is the temperature below which the ferromagnetic ordering arises, and it is possible to say that none of bulk FMS exhibits CT above room temperature. Therefore, it is very important to propose and fabricate a material with CT above room temperature in an applicable scale.

Since 1970's, many electronic devices have been based on III-V semiconductors, e.g. GaAs and InAs. In 1989, spontaneous ferromagnetic ordering was discovered in In1-xMnxAs and in 1996 in $Ga_{1-x}Mn_xAs$. In such materials, the CT can reach 160K with precise fabrication by molecular beam epitaxy technique (MBE).Using metal organic vapour phase epitaxy (MOVPE), the CT is reported to reach 333K in $In_{1-x}Mn_xAs$. The magnetic properties are highly dependent on concentration of the doping element. However, solubility of transition metals in III-V semiconductors is very low, so non-equilibrium fabrication methods are highly needed to prepare properly doped semiconductors. There was reported preparation of the material with (Ga,Mn)N composition, showing high CT above the room temperature.

But, at the same time, this material lost conducting properties, so the high CT is not present in the same phase as the semiconducting one [1].

Very promising seems to be IV semiconductors, e.g. silicon and germanium. Si is the most widely used semiconductor, so magnetic materials based on Si will be compatible with recent electronics. Ge possesses high intrinsic hole mobility in comparison with GaAs or Si. Preparation of highly doped semiconductors of group IV is, therefore, a good idea, but there is also a problem with solubility of transition metals. The most promising seems doping with Mn.

In the last decade, several experiments were carried out with DMS based on Si or Ge doped with Mn. The maximum solubility of manganese at thermal equilibrium in Si is equal to concentration 10^{-4}%. So the non-equilibrium method must be used to achieve higher concentration of Mn in matrix of the order of percent [2]. For preparation of thin layers of such materials the following techniques were successfully used: MBE, ion implantation, sputtering and thermal evaporation etc.

Qiao used magnetron sputtering to prepare Ge:Mn layers in a wide range of concentration from 5% to 29% in a form of small clusters [3]. The prepared layers show very weak ferromagnetic behavior up to room temperature. It was assumed that many phases of Ge:Mn were prepared on top of a substrate, and only some of them are magnetically active.

Using an ion implantation technique seems very interesting due to its ability to incorporate a large amount of Mn atoms into the host matrix. This method was used by Ko [4] to dope silicon. Concentration of Mn atoms was measured by SIMS, and although it was only 1.8% in the most doped sample, the results of measurement of magnetization temperature dependence show two drops in the magnetization at 640K and 820K. This indicates two different CTs and thus two different Si:Mn phases prepared by this technique. However, there is no direct evidence of the higher CT origin, and it could be explained by iron impurities detected by SIMS. The origin of CT at level 640K was assigned to Mn4Si7 precipitates.

With ion implantation there were prepared also Ge wafers doped with Mn by Ottaviano [5]. He reports Ge:Mn phase with CT almost 300K. There are also some reports with SiGe matrix e.g. Yu et al. [6]. In this case a combined matrix allows changing properties. The high CT about room temperature was reported for the different fractions of matrix.

Another method for preparation thin layers is pulsed laser deposition (PLD). With PLD there were prepared layers of Si or Ge doped with 15% of Mn atoms by Demidov [7,8]. For deposition Nd-YAG laser was used which sputter semiconductor or manganese target. The prepared layers show ferromagnetic properties up to 400K for both silicon and germanium.

The papers report successful growth of thin layer of silicon or germanium with magnetic properties induced by manganese atoms incorporated into the matrix; however, several different CTs were mentioned. The explanation of this contradiction lies in many possible outgoing compounds, because silicon and germanium likely forms many silicides and germanides. So, manganese atoms can be bound in three different positions. Due to their high diffusion in the silicon or germanium matrix, they can easily move together and separate themselves. The result is very inhomogeneous material with metallic precipitates. This material does not possess the desired properties, and it is desirable to avoid it. The next possible outcome is incorporation of manganese atoms into the unchanged matrix of semiconductor. This state is possible only for lower concentration of manganese, but still for a four order of magnitude higher than normal solubility. This outcome could be very homogeneous, and could possess magnetic properties, but the magnitude of these properties and CT are low. The last possibility is forming of stable phases of silicides or germanides. Present of these phases is usually report in form of small nanometer precipitates. The prepared material is less homogeneous due to the precipitates, but they are very small and may be well distributed among the layer, so it can still be considered homogeneous. Some precipitates could carry the spin ordering as dependent on the stoichiometric and crystallographic structure.
The main objectives of research of these materials are to reproducibly prepare layers with the magnetic properties up to room temperature, to analyse them, to determine phases, and to measure the conducting properties. It is welcome if the number of phases is small or even only one phase is present.

Experimental

For fabrication of thin layers we used laser based deposition which enables fast quenching of supersaturated solution of manganese and silicon or germanium. As a source of laser beam, we used ArF excimer laser with wavelength 193nm and energy in pulse 50mJ with repetition frequency 10Hz.
For preparation we used the reactive pulsed laser deposition when the laser is focused on the target made of polished manganese chip in a vacuum chamber. During laser ablation there is a small partial pressure of volatile precursor, in our case silane or germane. After laser pulse, the target receives high dose of energy and a small local hot spot is heated to a temperature of several tens of thousands kelvin. In this spot there are highly non-equilibrium conditions and some of the target material is ablated in the form of plasma plume. Highly ionized atoms in the plume interact with molecules of volatile precursor, destroy them and produce small particles. These particles are deposited onto a substrate.
For insight into the processes in the plume optical spectroscopy could be used. Highly ionized atoms emit spectra from their electron transition between two energy levels. From the spectra primary temperature can be determined.
The big advantage of PLD is versatility of the substrates determined to deposition. As substrate could be used everything what withstood vacuum. This variability is good for preparing examples for different analytical methods, e.g. Fourier transform infrared (spectroscopy) FTIR, UV-VIS and Raman spectroscopy, energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), electron paramagnetic resonance (EPR) and Superconducting quantum interference device (SQUID). FTIR, UV-VIS and Raman spectroscopies can identify some types of bonds and crystallization of the sample. EDX determines elementary composition on the surface of substrate. TEM provides us with information about the scratched off layer and besides an image it provides us with diffraction image of very small crystals. EPR is the method for measuring materials with one or more unpaired electrons which are essential to magnetic properties which can be measured by SQUID. The substrates can be thermally annealed to enhance crystallization.

Results and discussion

During laser ablation of Mn target under 20Pa of silane, UV-VIS spectra of plasma plume were measured. Sensor was set-up perpendicular to laser beam approximately 1mm above target in order to minimize the spectra from heated surface of the target. In range 190-900nm several emissions of Mn and Up to twice ionized Mn and Si atoms were identified in the plume. From peaks of twice ionized Mn (259.4, 293.9 and 344.2 nm) the temperature of the plume 1mm above the target was approximately determine equal to 1.9 eV. From ratio between twice ionized Mn peak at 259.4 nm and once ionized Mn peak at 279.4 nm an electron density 10e+19cm-3 was estimated. These parameters were estimated based on Saha-LTE model generated by NIST database which was compared with measured spectra in range 250-370nm (Fig.1).
Samples for FTIR and Raman spectroscopy were prepared under several different pressures. FTIR is able to detect even small amount of Si-H bond in the layer, however, no sign of Si-H bond was detected, so we presume that during deposition all Si-H bond is destroyed, and pure Mn:Si was prepared. Crystallization of silicon can be measured by Raman spectroscopy. A Raman spectrum for crystalized silicon should contain signal at 525cm^{-1} but no such signal was observed. So we presume that no crystallization is in the prepared layers.
EDX is detector in scanning electron microscope (SEM) and it can determine ratio between Si, Ge and Mn atoms. In prepared layers, the ratios of Mn atoms to Si or Ge atoms were determined. Dependence of Mn concentration on pressure of volatile precursor is on Fig. 2. Substrates were kept 5cm away from target. Volatile precursor pressure is variable and it is necessary to keep it constant during ablation, especially with germane as volatile precursor. Mn concentration quickly declines in dependence on pressure due to collisions of Mn atoms with molecules of volatile precursor. Ionized Mn atoms pass part of their energy on the others molecules and thus destroy them. Four hydrogen atoms were completely detached from silane and germane molecules.

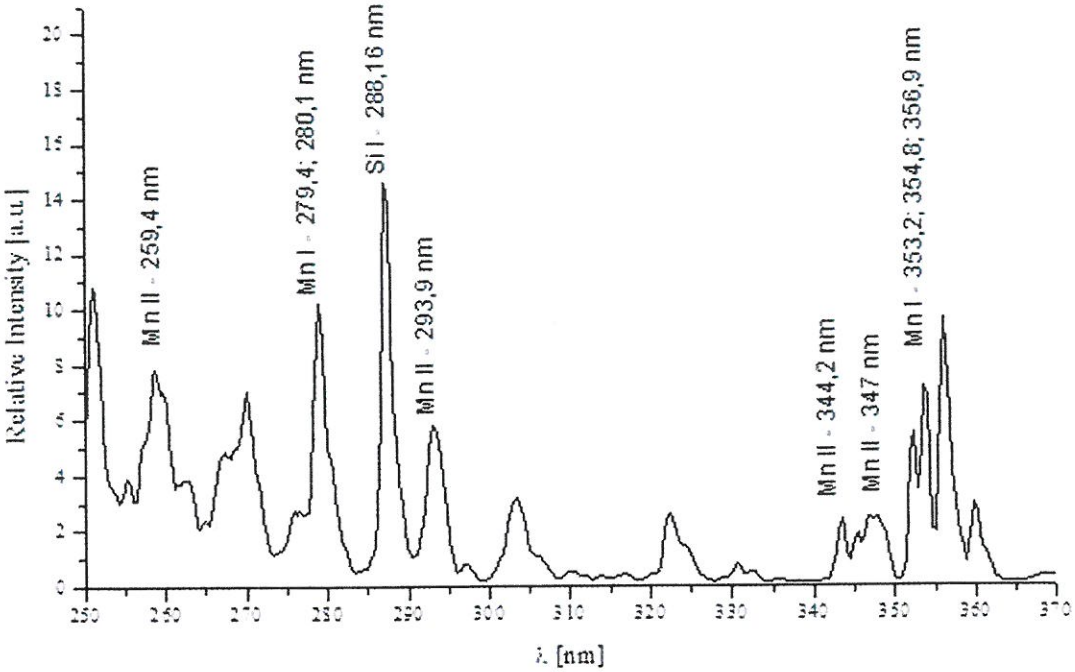

Fig.1: Optical spectra of the plasma plume 1 mm above Mn target in 20 Pa silane pressure.

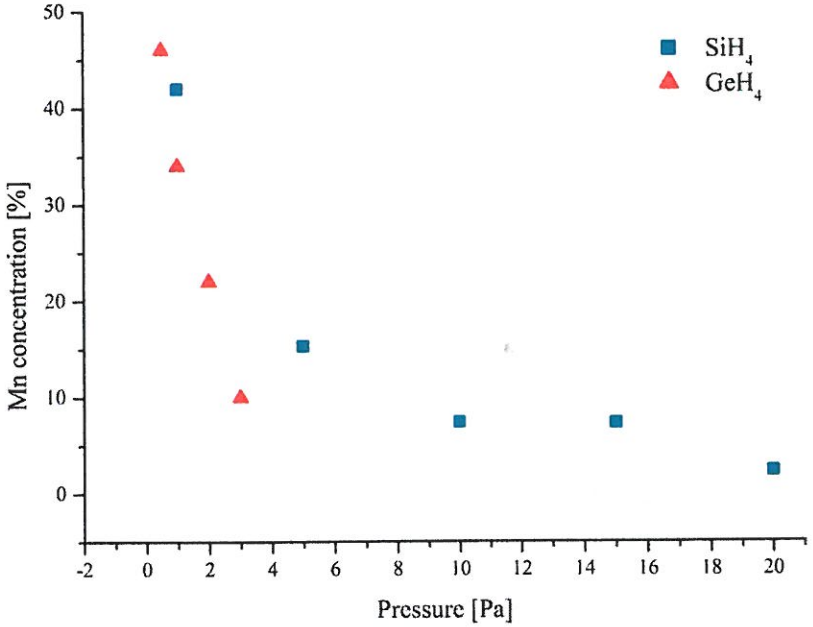

Fig. 2: Dependence of Mn concentration on volatile precursor pressure.

The layer had not high adhesion to the used substrates and it was easy to remove it and image it by SEM. On the Fig. 3 there is a layer after deposition under 20Pa of silane after 30min of deposition which was partially removed. Fig. 3 was measured under tilt 10°. The thickness was approximately 760nm and thus deposition rate was 0.4nm/s. Prepared layers had large surface roughness.

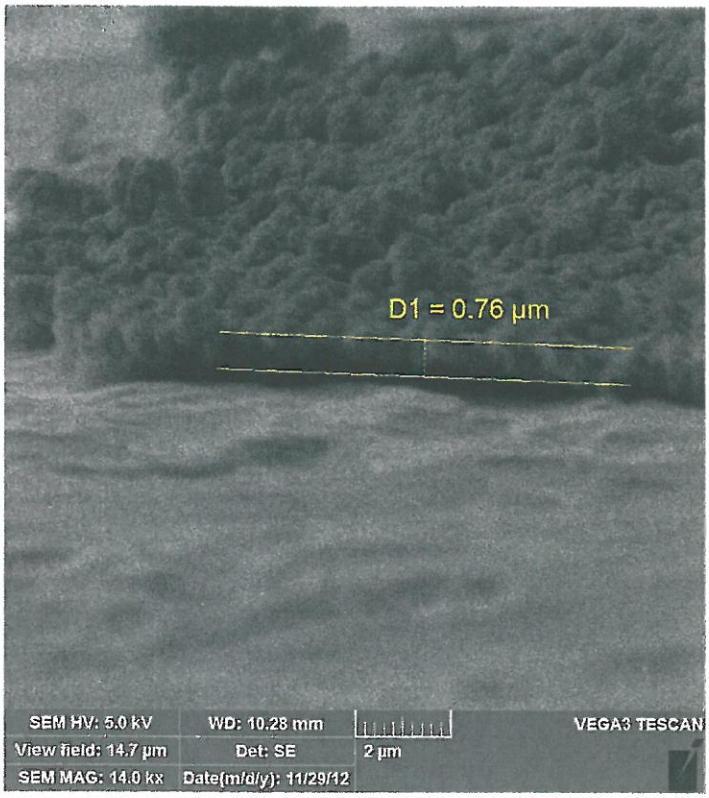

Fig. 3: SEM image of partially removed layer deposited under 5Pa of silane.

Diffraction of prepared layers was measured on TEM. Mn:Si layers without annealing were composite of small particles with diameter below 10nm. Diffraction image of these layers showed no clear point diffraction (Fig. 5). Two different annealing was tried to obtain crystallization in Mn:Si layers. By annealing to the high temperature 1100°C, higher adhesion and growing of the particles (to diameter 20-40nm) in the layer can be achieved (Fig. 4). The diffraction images were also changed, but expected separation of phases is not so clear (Fig. 6). There was diffraction pattern but mainly due to Si or Mn crystallization with only small possible amount of MnSi silicides.
The other type of annealing was rapid laser annealing. Few laser pulses from CO2 TEA laser was enough for recrystallization of deposit. The diffraction image (Fig. 7) shows clear diffraction pattern with good agreement with $Mn_{0.83}Si_{0.11}$ silicide reference.

EPR spectra of Mn:Si deposited onto alumina powder showed unpaired Mn electrons. Splitting factor g was determined as 2.05. Substrates with Mn:Si layers with two Mn concentration (10 and 23%) were measured by SQUID. Both layers were amorphous and only paramagnetic properties were measured. Substrate with 23% concentration of Mn showed magnetization up to 20K in contrast with the other concentration which shows magnetization only at temperature 2K. At this temperature, sample with 23% Mn had saturated magnetic moment 13 emu/g and sample with 10% Mn 11.7 emu/g.

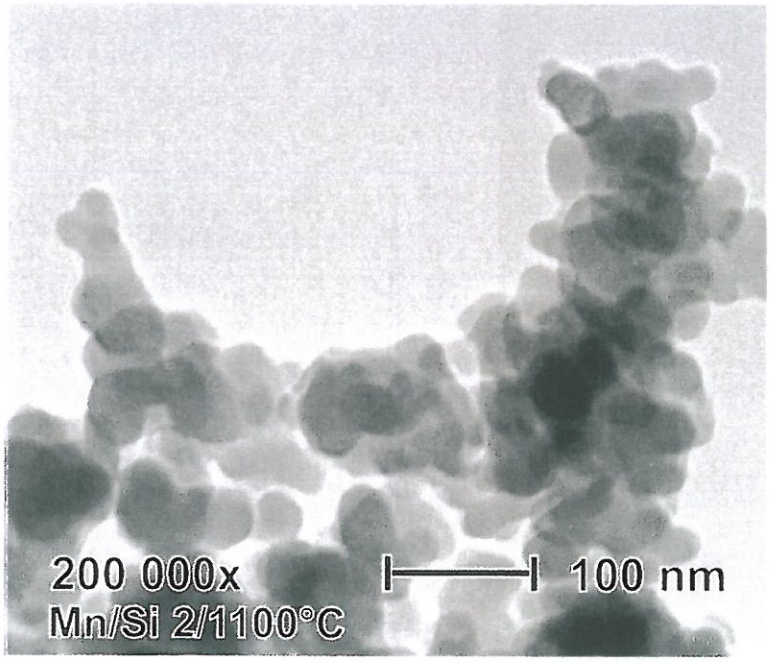

Fig. 4: TEM image of deposit annealed at 1100°C.

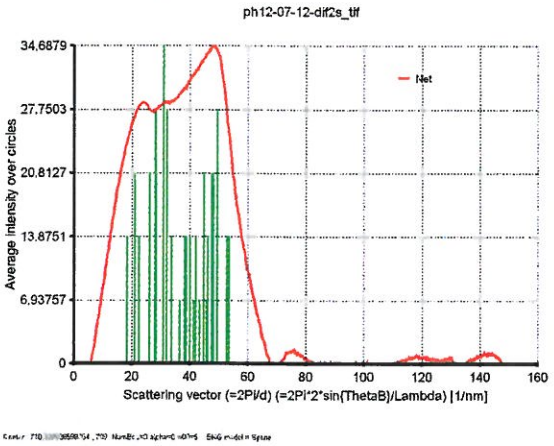

Fig. 5: Diffraction image of Mn:Si deposit as prepared with reference Mn_5Si_3.

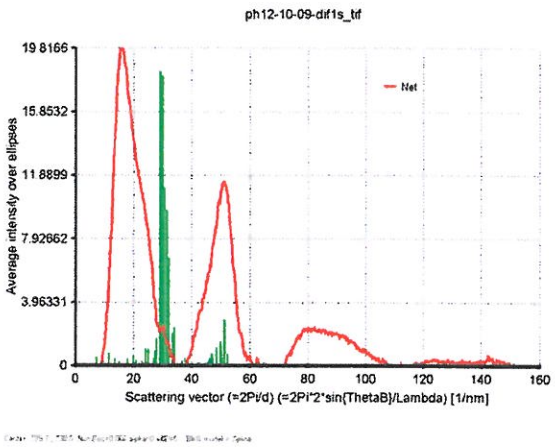

Fig. 6: Diffraction image of Mn:Si deposit after thermal anneling at 1100°C with Mn0.83Si0.11 reference.

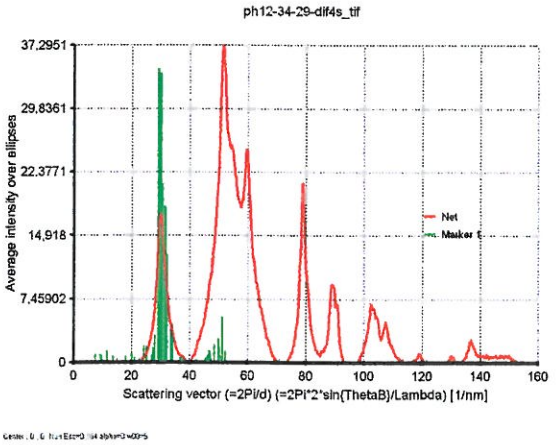

Fig. 7: Diffraction image of Mn:Si deposit after rapid laser annealing with $Mn_{0.83}Si_{0.11}$ reference.

Conclusions

The Mn:Si layers after deposition are amorphous or contain only very small crystallites below electron diffraction limit (1nm). The Mn:Ge layers after deposition exhibits signal from nano-crystallite Ge in Raman spectra. No Si-H bonds were detected in the layers, so we assume that hydrogen is not present in them.
Mn concentration can be tuned in broad range by varying the pressure of volatile precursor; however, it is needed to keep precise pressure of volatile precursor in order to obtain homogeneously doped layers. Molecule of germane has greater weight so the Mn concentration is decline more steeply as Mn ions lose their energy much faster.
Amorphous layers can be processed by thermal or laser annealing. Thermal annealing leads to germanium and manganese precipitation as well as emerging of silicides. Few pulses of laser annealing prepare silicide with clear diffraction pattern.
EPR measurement showed unpaired electron but only paramagnetic properties from Mn incorporated in Si matrix were observed in amorphous layers up to 20K.

Reference

[1] Tim, Carsten: Disorder Effect in Diluted Magnetic Semiconductors, J. Phys.: Condens. Matter 15, 2003, 1865-1896.

[2] Nakayama, Hiroshi; Ohta, Hitoshi; Kulatov, Erkin: Growth and properties of super-doped Si:Mn for spin-photonics, Physica B, 2001, 419-424.

[3] Qiao, S; Hou, D. et. al.: Structure, magnetic and transport properties of MnxGe1-x films, Physica B 403, 2008, 3916-3920.

[4] Ko, V.; Teo, K.L. et al.: Origins of ferromagnetism in transition-metal doped Si, J. of Applied Physics 104, 2008.

[5] Ottaviano, L.; Contineza, A. et al.: Room-temperature ferromagnetism in Mn-implanted amorphous Ge, Physical review B 83, 2011.

[6] Yu, S.S.; Cho, Y.M. et al.: Magnetic and electrical properties of MBE-grown (Ge1-xSix)1-yMny thin films, Current Applied Physics 6, 2006, 478-481.

[7] Demidov, E.S.; Danilov, Y.A. et al.: Ferromagnetism in Epitaxial Germanium and Silicon Layers Supersaturated with Manganese and Iron Impurities, JETP Letters 83, 2006, 568-571.

[8] Demidov, E.S.; Aronzon, B.A. et al: High-temperature ferromagnetism in laser-deposited layers of silicon and germanium doped with manganese or iron impurities, Journal of Magnetism and Magnetic Materials 321, 2009, 690-694.