Příprava tenkých vrstev feromagnetických polovodičů

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2012

Dostupný z `http://www.nusl.cz/ntk/nusl-180537`

Preparation of Thin Layers of Ferromagnetic Semiconductors

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Abstract

The paper reports on the experiments of preparation Mn diluted in Silicon. Si:Mn can be a material with the potential of room temperature ferromagnetism. Si:Mn have been prepared by pulsed laser deposition of Mn target under 20 Pa of silane by ArF laser. We estimate initial temperature 1 mm above surface as 1.9 eV. The prepared supersaturated layers contain 11% of manganese atoms, and they are formed by small particles. Diffraction images show no crystallization of Mn or Si, but there are signs of formation of silicides. The prepared material is amorphous or it contains only nanosized crystals below our limit of detection. Electron paramagnetic spectra show unbounded electrons which are needed for ferromagnetic properties. By annealing to 1100℃ changes in the crystallization and start of silicon and manganese separation were observed.

Klíčová slova: room temperature ferromagnetism; pulsed laser deposition; diluted magnetic semiconductors; silicides

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.

The origin of FMS lies in 1960's in the discovery of ferromagnetic ordering in CrBr3 by Tsubokawa and in Eu chalkogenide which both are semiconductors. Magnetic properties of FMS emerged from partially filled shell of the metal ions. These materials have shown that a combination of ferromagnetism and semiconducting properties is possible. Their CT is very low, and their properties are still not compatible with those of the mainstream semiconductor device materials. In 1970 there were prepared materials based on II-IV and IV-VI semiconductors diluted with transition metal by Galazka. These materials are called diluted magnetic semiconductors (DMS). The magnetic properties arise from transition metal atoms incorporated in a host matrix which provides the semiconductor properties. The CT was still low, but, as revealed, the change of stoichiometric composition is a way to tune such properties as a bangap, luminescence etc. DMS based on IV-VI semiconductors is much easier to dope through the control of defects, and, as a consequence, CTs around 100K were obtained in these materials.

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 Ga1-xMnxAs. In such materials, the CT can reach 160K with precise fabrication by molecular beam epitaxy technique

(MBE).Using metal organic vapor phase epitaxy (MOVPE), the CT is reported to reach 333K in In1-xMnxAs. 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 seem 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 nanometric 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 analyze 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. As a source, we used ArF excimer laser with wavelength 193nm. 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 silane. After shot of the laser, the target receives high dose of energy and a local hot spot is made which can reach a temperature of several tens of thousands kelvin. Under these conditions some of the target material is ablated in the form of plasma plume. Highly ionized atoms in the plume interact with a silane molecule, destroy it and produce small particles of Si:Mn. 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 conditions 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), and electron paramagnetic resonance (EPR).

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. The substrates can be thermally annealed to enhance crystallization.

Results and discussion

The first series of experiments leads to base research of resulting properties of deposit under 20Pa of silane.

At first optical spectra were measured and ionized states were identified. Sensor was set-up perpendicular to laser beam approximately 1 mm above target in order to minimize the spectra from heated surface of the target. In range 190-900 nm several emissions of Mn and Si ions were identified. Twice ionized atoms of Mn and Si were present at 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).

Under the same condition, the layers on Cu, quartz and glass substrates were prepared in order to measure FTIR, UV-VIS and Raman spectroscopy. FTIR is able to detect even small amount of Si-H bond in the layer. No sign of Si-H bond was detected, so we presume that during deposition all Si-H bond is destroyed, and pure Si:Mn was prepare. By Raman spectroscopy some other bonds can be measured, for example between Si atoms, but mainly if they are in crystal form. No sign of Si crystal phase was detected, so we presume that layer of silicides was prepared.

EDX is detector in scanning electron microscope (SEM) and it can determine ratio between Si and Mn atoms. In prepared layer, the amount of Mn atoms was determined as nine times smaller than Si atoms. So we presume that we prepared Si layer with 11% of Mn atoms. In EDX spectrum was present significant amount of oxygen.

The layer had not high adhesion to the used substrates and it was easy to scratch it off and imaged it by TEM (Fig.2). The layers are composite of the small particles. But there are no clear point diffraction images of these particles. By annealing to the high temperature 1100℃, higher adhesion and growing of the particles in the layer can be achieved. The diffraction images are also changed, but expected separation of phases is not so clear.

For measuring EPR spectra Si:Mn were deposited under set conditions onto an alumina powder. An EPR spectrum (Fig.3) has characteristic shape and we assume that spectrum around 3465 G is corresponding to unpaired Mn electrons. We determined splitting factor g=2,05.

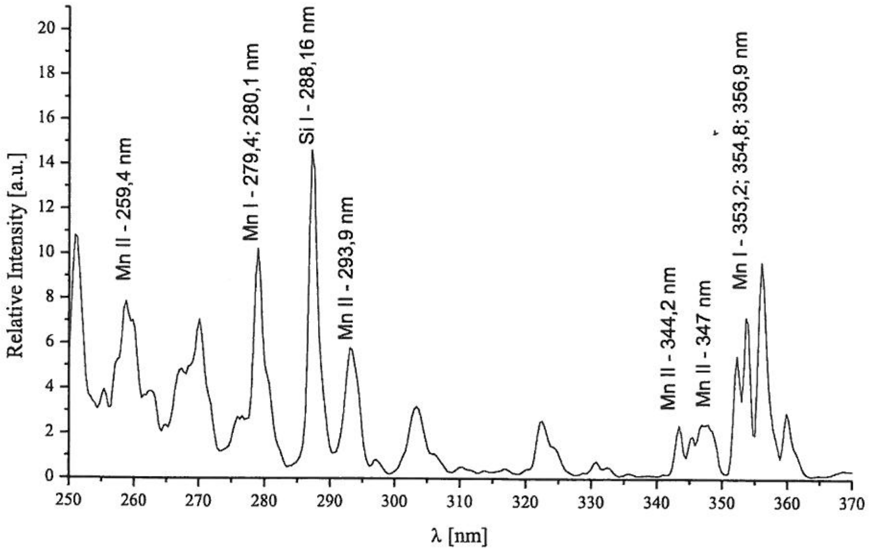

Fig.1: Part of optical spectra of the plasma plume 1 mm above Mn target in 20 Pa silane pressure.

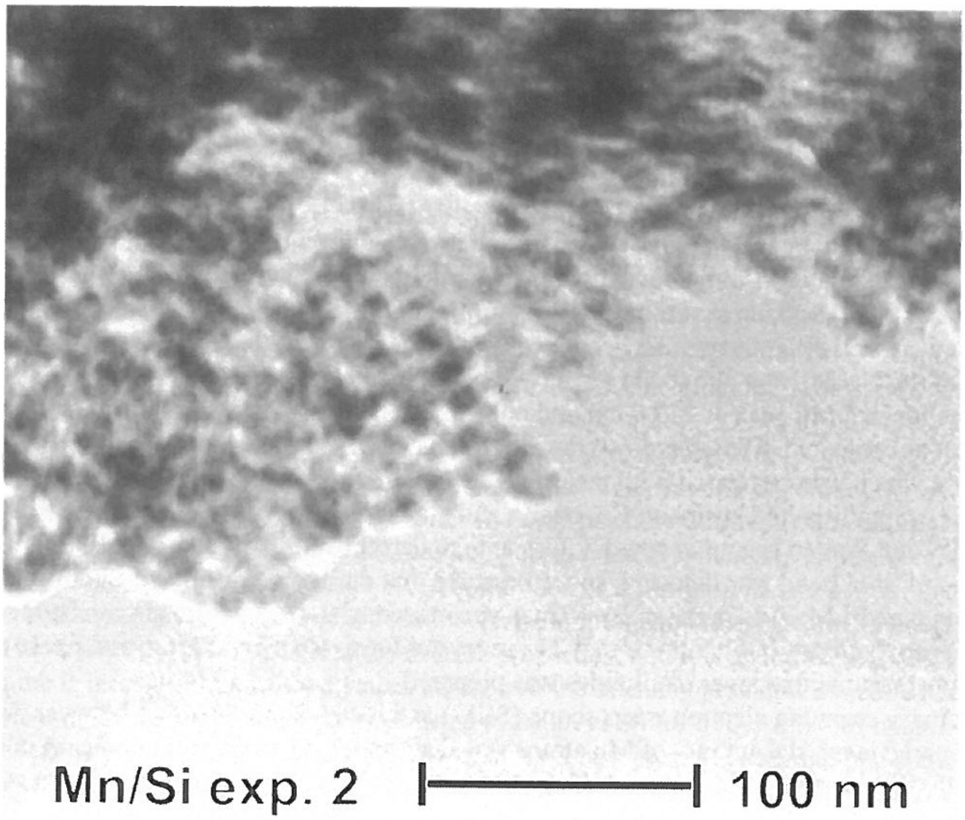

Fig.2: TEM image of prepared Si:Mn layer.

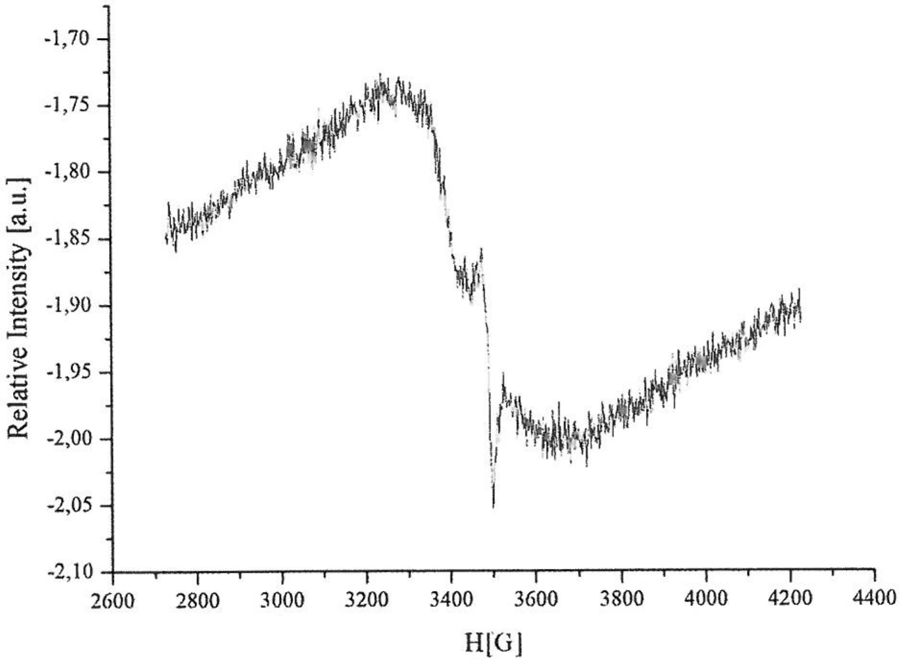

Fig.3: EPR spectrum of alumina powder after deposition of Si:Mn.

Conclusions

The prepared layers are amorphous or contain only very small crystallites below electron diffraction limit of detection (1nm). The layers are made of Si and Mn; no Si-H bonds were detected, so we assume that hydrogen is not present in the layers. Mn to Si ratio is up to 1:9 as revealed from the EDX analysis. The superficial layer of the deposit contains oxygen from surface oxidation which is evidenced by Si-O vibration observed in the FTIR spectrum. Following X-ray photoelectron spectroscopy (ESCA) study is necessary to confirm this result.

The layers made under these conditions have only weak adhesion to the glass substrate. Adhesion can be improved by annealing of the sample or by lower pressure of silane during ablation process. But both changes of parameters result in structure and elemental composition changes. The electron diffraction images are diffused which proves amorphous character of the sample. Annealing at 1100℃ leads to crystallization, as revealed by electron diffraction rings. EPR spectrum shows presence of unpaired electrons and thus possible magnetic properties of the sample. In addition presence of fine EPR band structure originating from manganese atoms present in the silicon matrix was observed.

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