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Mn_xGe_{1-x} thin layers studied by TEM, X-ray absorption spectroscopy and SQUID magnetometry

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Abstract

$Mn_{0.06}Ge_{0.94}$ samples have been grown by molecular-beam epitaxy on Ge(0 0 1)2 × 1. High-resolution transmission electron microscopy shows the coexistence of an ordered diluted $Mn_{0.06}Ge_{0.94}$ film and of nanoscopic crystallites, which were identified as Mn_5Ge_3 by electron diffraction. The magnetic properties of the $Mn_{0.06}Ge_{0.94}$ samples show a superposition of a paramagnetic behavior, due to the interaction of Mn atoms diluted in the Ge host, and a ferromagnetic behavior attributed to the Mn_5Ge_3 crystallites dispersed into the films. The Mn $L_{2,3}$ X-ray absorption spectra of the $Mn_{0.06}Ge_{0.94}$ films exhibit a lineshape typical of metallic Mn, with considerably reduced multiplet structure.

Keywords: Metal–semiconductor interfaces; Manganese; Germanium; Electron microscopy; Electron–solid diffraction; X-ray absorption spectroscopy; Soft X-ray photoelectron spectroscopy; Magnetic measurements

1. Introduction

The doping of semiconductors with 3d transition metals gives new kinds of materials, called diluted magnetic semiconductors (DMS), which are suitable for spintronic applications [1]. Mn-doped germanium is supposed to be a good DMS candidate because of its high Curie temperature [2]. Either ferromagnetic (FM) or paramagnetic (PM) properties have been observed in Mn–Ge DMS [3–6]. It is well known that the dilution of Mn atoms in a Ge matrix can lead to the formation of several kinds precipitates, such as $Mn_{11}Ge_8$, Mn_3Ge_2, and Mn_5Ge_3 [5,7–9], depending on different parameters such as substrate temperature, film thicknesses, and growth rate. These precipitates have FM behavior. Therefore they can lead to the observation of spurious magnetic properties not attributable to a true DMS, i.e., to Mn atoms in substitutional sites inside the Ge lattice. Up to now, the magnetic properties of Mn diluted in Ge are not completely understood due to the complexity of the films, mainly originating from the different sample preparation methods [3–6]. Another point under debate is the lineshape of the Mn $L_{2,3}$ X-ray absorption spectrum, which in spite of numerous works is not unanimously determined [10–14].

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In order to improve the knowledge of the mechanisms governing the magnetic properties of DMS, it is important to identify how the Mn atoms are included in the lattice of the semiconductor host and if Mn–Ge precipitates are formed. Recently, we prepared $Mn_{0.06}Ge_{0.94}$ films by molecular-beam epitaxy on a Ge(001)2×1 substrate [15].

In this work, the combination of high-resolution transmission electron microscopy (HRTEM), electron diffraction (ED), superconducting quantum interference device (SQUID) magnetometry and X-ray absorption spectroscopy (XAS) at the Mn $L_{2,3}$ edge has been used to scrutinize the properties of the $Mn_{0.06}Ge_{0.94}$ system.

2. Experimental

Samples with a $Mn_{0.06}Ge_{0.94}$ nominal composition were grown by molecular-beam epitaxy (MBE) on Ge(001)2×1 substrate kept at 520 K. Before the growth, the Ge(001) surface was cleaned by Ar ion sputtering and heating to 1100 K in a residual pressure below 2×10^{-10} mbar. A thin Ge capping layer was grown on some $Mn_{0.06}Ge_{0.94}$ samples to avoid surface oxidation. Mn_5Ge_3 films were grown by solid state epitaxy [14], i.e., by depositing Mn at room temperature onto a Ge(111)c(8×2) surface and subsequent annealing for several minutes at 720 K. The quality growth, which strongly depends on the annealing temperature, was monitored using reflection high-energy electron diffraction. HRTEM measurements were performed with a 200 keV beam along the [110] direction of the sample. Magnetization was recorded using a SQUID as a function of temperature (from 5 K to 300 K) and magnetic field (up to 20 kOe) applied parallel to the film surface. XAS and photoelectron spectroscopy (PES) measurements were performed on the D1011 beamline at MAX-lab (Lund, Sweden). XAS data were collected in total electron yield mode with a total energy resolution of 0.2 eV.

3. Results and discussion

3.1. HRTEM

Fig. 1a gives an HRTEM image of a 60 Å thick $Mn_{0.06}Ge_{0.94}$ film, grown on the Ge(001) surface. This cross-sectional picture indicates that the film is not fully homogeneous and presents two distinct regions along the [100] axis. The very high quality of epitaxy is demonstrated by the perfect alignment of the Ge(111) substrate planes with the (111) planes of the film and by the absence of impurities and of crystalline defects at the interface. In the epitaxial region (close to the interface), no contrast is induced by the dilution of Mn in the Ge matrix, which indicates that Mn atoms are mainly located in substitutional sites. In the top part of the deposited film, HRTEM images show a salt and pepper contrast typical of an out of phase object. This contrast is explained by the presence of randomly distributed nanocrystalline precipitates.

ED measurement reported in Fig. 1b provides further information on the film structure. The ED pattern is representative of the diamond structure along the [110] zone axis, but in additions there are well-defined sharp spots, not aligned with those of Ge substrate, that we unambiguously assigned to Mn_5Ge_3. No other precipitate phase has been identified in the samples. These observations were confirmed in thicker Mn–Ge layers, which present larger nanocrystallites in their top layer identified by ED as a Mn_5Ge_3 phase.

In a $Mn_{0.06}Ge_{0.94}$ film capped with 2 ML of Ge, denoted hereafter as Ge/$Mn_{0.06}Ge_{0.94}$ (see Sections 3.2 and 3.3), the

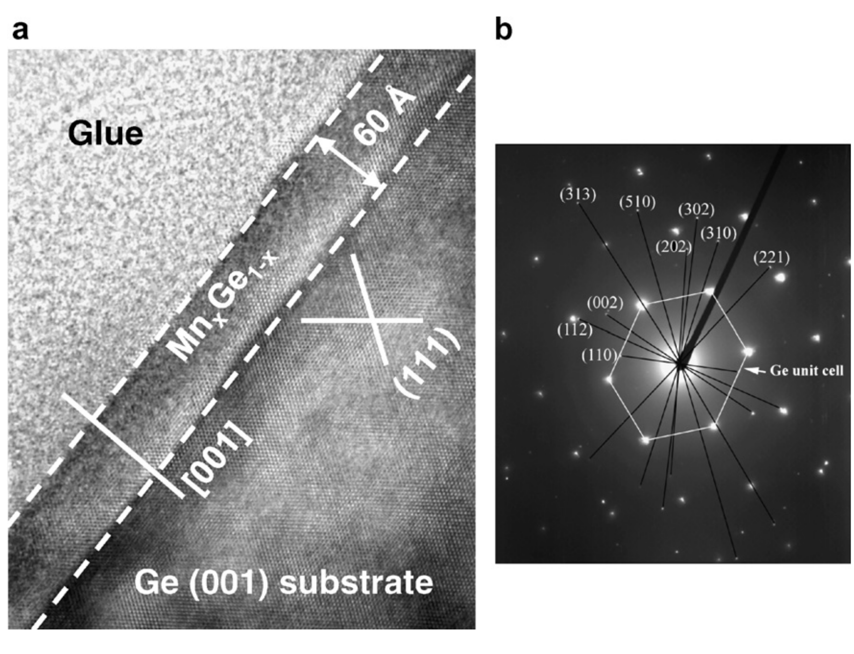

Fig. 1. Cross-sectional HRTEM image (a) and ED of capped $Ge_{0.94}M_{0.06}$ film (b).