Magnetism and electronic properties of Mn:Ge(111) interfaces probed by core level photoemission spectroscopy

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Abstract. The electronic and magnetic properties of Mn:Ge(111) interfaces have been investigated by photoelectron spectroscopy and SQUID magnetometry. An ordered, metallic and ferromagnetic, Mn:Ge(111) interface and a disordered, semiconducting and paramagnetic, MnₓGe₁₋ₓ surface alloy have been considered. An analysis of the Mn 2p X-ray photoemission core line shows that the former interface can be described by a single-configuration Mn 3d⁶ initial state, while the latter presents satellite features typical of Mn-based diluted magnetic semiconductors, characterized by relevant ligand-to-metal charge transfer effects.

1. Introduction
Since the discovery of ferromagnetism in the MnₙGe₁₋ₙ diluted magnetic semiconductor (DMS) [1], the Mn-Ge system as played a central role for possible applications in the field of spintronics. This role has been recently tested with devices based on MnₓGe₁₋ₓ quantum dots [2]. The Mn-Ge system includes a large set of compounds, ranging from the MnₓGe₁₋ₓ diluted alloy (x < 0.05) [1], to the MnGe₅ nanocolumns [3], and from Mn:Ge(100) or Mn:Ge(111) interfaces [4,5] to amorphous, ferromagnetic (FM), Mn-Ge thin films [6].

In the present study we compare the electronic properties of an ordered metallic Mn:Ge(111) thin interface with those of a MnₓGe₁₋ₓ diluted alloy, that can be regarded as a DMS. Our attention is focused on the DMS, as core level photoemission data on this kind of system are virtually missing, in spite of a large set of X-ray absorption data collected at the Mn L-edge. In many respects, the two compounds represent the end-points of the Mn-Ge system: while the former is FM and metallic, the latter is semiconducting and, in the present case, weakly paramagnetic.

2. Experimental
The samples have been prepared by e-beam evaporation of Mn contained in a Mo crucible in ultrahigh-vacuum conditions, at a base pressure better than 1x10⁻⁹ mbar. The metallic sample is obtained by annealing at 400 °C a Mn layer (5 ML) evaporated onto a c(2x8) reconstructed Ge(111) surface. This annealing induces the formation of an ordered surface layer, which can be regarded as the seed layer for the growth of thicker MnₙGeₓ thin films. The surface ordering after annealing (a (√₈×√₈)R30° reconstruction [5]) has been checked by low-energy electron diffraction. The DMS alloy is obtained
by evaporating at room temperature a thin Mn layer on a sputtered Ge(111) surface. The sputtering prevents the formation of an ordered metallic layer, and favors the formation of a diluted alloy through the diffusion, already at room temperature, of Mn atoms into the Ge host lattice. Photoemission spectroscopy data ruled out oxygen contaminations in both samples.

X-ray photoemission (XPS) data have been obtained by exciting the sample with the Al ke line of a twin-anode X-ray source and by collecting the spectra with a VG-Sciencta R3000 electron spectrometer. Static magnetization (M) was measured at 1000 Oe in field cooling regime from 350 K to 2 K with a SQUID Quantum Design Magnetometer. For the metallic sample, magnetization loops were collected at 50 K for magnetic fields ranging between 0 and ±2000 Oe.

3. Results and Discussion

3.1. Electronic properties

Figure 1-a shows the Mn 2p XPS spectrum of the ordered surface alloy, with the expected Mn 2p_{1/2} and Mn 2p_{3/2} spin-orbit split peaks, with a binding energy (BE) of 638 and 649 eV, respectively. The lineshape is quite similar to that measured on a reference thick (0.2 µm) Mn film (Figure 2-d), obtained by e-beam evaporation on a silicon substrate. Following Ref.7, the Mn 2p XPS lineshape was calculated on the basis of a single configuration Mn 3dⁿ initial state (Figure 1-b). This was done under the assumption that the metallic character of the sample yields a 3dⁿⁿ⁺¹ electron configuration in the outer shell of the Mn ion, i.e. that the overlap between the 3d and 4s/4p bands increases by one unit the count of 3d electrons of atomic Mn. The results show that the lineshape of Mn 2p can be well described by the present single configuration atomic approach, which fully accounts for multiplet effects arising from the coupling of the core hole with the 3dⁿ electron shell, while the 3dⁿ⁻¹ atomic calculations (Figure 1-c) fail in reproducing the main features of the experimental data.

Figure 2 shows the Mn 2p core levels of the Mn₂Ge₁₋ₓ DMS. The spectrum of the as-grown film (Figure 2-a) shows a manifold of features, ascribed to both metallic Mn and Mn diluted in the Ge lattice. In fact, a comparison with the Mn 2p XPS core line from metallic Mn (Figure 2-d) indicates that the Mn features (marked by dashed vertical lines) can be ascribed to metallic Mn. These features are progressively quenched with annealing treatments (Figure 2-b,c), indicating that the annealing induces a diffusion of Mn into the Ge lattice, rather than a clustering of Mn on the Ge(111) surface. After the second annealing treatment (Figure 2-c), the spectrum can be described by two broad peaks (A and C) separated by the spin-orbit interaction. The width of each peak is ascribed to disorder effects, related to both surface sputtering effects and diffusion of Mn into the Ge lattice. On the high BE side of these peaks, two satellites, B and D are also detected. These satellites are often found in Mn-based DMS, such as Cd₁₋ₓMn₆Te (Figure 2-e), Zn₁₋ₓMn₆S and Ga₁₋ₓMn₆As [8, 9], and are ascribed to charge transfer (CT) effects from the ligand anions (Te, S or As, respectively) to the 3dⁿ electron shell of atomic Mn. The results show that the lineshape of Mn 2p can be well described by the present single configuration atomic approach, which fully accounts for multiplet effects arising from the coupling of the core hole with the 3dⁿ electron shell, while the 3dⁿ⁻¹ atomic calculations (Figure 1-c) fail in reproducing the main features of the experimental data.

The Mn 2p spectral weight for a Mn₂Ge₁₋ₓ impurity in a Ge matrix is shown in Figure 1-d and compared with the DMS alloy spectrum of Figure 2-c. The calculated curve (shaded area) has been obtained by setting Δ=1.0 eV, the on-site Coulomb repulsion Uₐd = 3.3 eV, T = 1.0 eV and the Mn 2p-3d Coulomb interaction Qₐd = 4.4 eV. These findings are consistent with those obtained on Mn-doped DMS [8, 9]. As expected, the CT energy is rather low as compared to other DMS systems, as it roughly scales with the energy gap of the host crystal, that for Ge is smaller than for CdTe and GaAs.

Therefore, for the Mn₂Ge₁₋ₓ DMS, the observed lineshape indicates that CT-related configurations contribute to the XPS spectrum, resulting in the B and D satellites shown in Figure 2. In turn, the
metallic surface alloy virtually shows a single configuration behavior. In principle, the ground state of an itinerant transition metal is assumed to be described by a broad distribution of different d weights which converge towards a single d count when electron localization is increased by the effects of the $U_{dd}$ correlation energy (see Ref.[10], and Refs. therein). Large electronic correlations are supposed to quench charge fluctuations and limit the number of d weights. These effects have been invoked to explain the suppression of valence fluctuations observed for the ground state of Mn in MnSi [11].

**Figure 1.** Mn 2p XPS spectrum of the Mn:Ge(111) ordered surface alloy (a). Calculated Mn 2p XPS spectra of single-configuration Mn 3d$^0$ (b) and Mn 3d$^5$ (c) electron systems. CI calculation of the Mn 2p XPS spectrum for a Mn$^{2+}$ impurity in a Ge matrix (shaded area, d). Calculations are compared to XPS data obtained from Figure 2-c after background subtraction (thick line, d).

**Figure 2.** Mn 2p XPS spectra of the Mn$_x$Ge$_{1-x}$ DMS. (a) as grown; (b) after the first annealing at 473 K for 15'; (c) after the second annealing at 473 K for 30'. Mn 2p XPS spectrum of a metallic thick Mn film (d) and of a Cd$_{1-x}$Mn$_x$Te DMS [e], from Ref.8).

### 3.2 Magnetic properties

The magnetization curves of both samples are shown in Figure 4 and Figure 5. The ordered surface alloy shows a dependence of magnetization on temperature (Figure 4) characteristic of a ferromagnetic (FM) ordering established just about 300 K. The inset of Figure 4 shows the magnetization loop measured at 50 K. This behavior is consistent with that observed in similar metallic surface alloys [5]. For the Mn$_x$Ge$_{1-x}$ DMS, the main features of the M vs. T curve (Figure 5) are: (i) an overall Curie-like behavior, revealing the presence of paramagnetic ions (substitutional Mn in the Ge host), (ii) a broad maximum in the 200-250 K range, that could be ascribed to the effects of Mn$_x$Ge$_{1-x}$ nanoparticle inclusions [12], and (iii) a magnetization increase above 270 K. A similar behavior was observed for Mn$_{0.06}$Ge$_{0.94}$ thin films grown on a Ge(100) substrate [12]. For a higher Mn content, a FM behavior is expected [12]. The lack of a dominant FM contribution in the present sample indicates that the density of Mn atoms diffused into the Ge bulk lattice is still too low to yield a long-range FM behavior.
4. Conclusions
Mn evaporation on Ge(111) may yield quite different surface alloys, depending on the surface preparation prior to Mn deposition. The difference in surface ordering significantly affects the magnetic and electronic properties. The Mn 2p photoemission core level data provide evidence of Mn-Ge hybridization effects in the DMS alloy. These effects can be accounted for in the frame of a CI model by assuming CT from Ge to Mn. In turn, the metallic, FM surface alloy is virtually described by a single 3d$^6$ configuration, suggesting that electronic correlations among 3d electrons are large enough to suppress the 3d charge fluctuations expected in metallic systems.

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