Interface formation and growth of ferromagnetic thin layers in the Mn:Ge(111) system probed by dichroic soft x-ray spectroscopies

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In this study, we provide evidence of surface ferromagnetism in a thin metallic Mn:Ge(111) layer displaying a $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction. Magnetic circular dichroism effects are observed in remanence below the Curie temperature in both x-ray absorption spectroscopy and valence-band photoemission spectra, the latter indicating that spin-polarized states are present within 2 eV below the Fermi edge.

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The discovery of ferromagnetism in Mn_xGe_{1-x} diluted alloys has triggered a large number of studies on the electronic and magnetic properties of these compounds in the form of bulk alloys, thin films, or Mn:Ge interfaces.[1–8] Among the Mn:Ge interfaces a considerable attention has been paid to the Mn:Ge(111) system, which is usually grown by evaporating Mn ions on a $c(2\times8)$ reconstructed Ge(111) surface. Subsequent annealing at about 300 °C of the unreacted interface yields a $(\sqrt{3}\times\sqrt{3})R30°$ reconstructed surface which is known to act as a seed layer for the growth of the metallic, ferromagnetic, Mn_5Ge_3 phase.[6] Due to the relatively high Curie temperature, the Ge-Mn_5Ge_3 interface is currently under investigation as possible candidate to develop spintronic devices. However, in spite of a large number of theoretical studies on the electronic properties, the experimental investigation of the electronic structure is still at the early stages, and few photoemission studies have been reported so far.[7,8] The major findings of these studies are the metallic nature of the interfaces down to a coverage of about 4 ML, and the presence of Mn-related states at the Fermi edge, as shown by resonant photoemission experiments.[8] These features make the Mn:Ge(111) annealed interface different from the bulk Mn_xGe_{1-x} alloys, which in turn should be regarded as a diluted magnetic semiconductor, with physical properties similar to those of $Ga_{1-x}Mn_xAs$ and $Zn_{1-x}Mn_xO$ diluted alloys.

Ordered Mn:Ge(111) alloy films, with a $(\sqrt{3}\times\sqrt{3})R30°$ unit cell relative to the unreconstructed Ge(111) surface, can be formed for very thick layers down to a few monolayers (MLs). Sangaletti *et al.* have reported on the magnetic properties of a rather thick (190 ML) Mn:Ge(111) ordered film produced by annealing Mn multilayers evaporated on a Ge(111) single crystal.[8] A broad ferromagnetic transition was detected in this film with a T_c of about 260 K, close to that reported for thicker layers[6,7] or bulk Mn_5Ge_3 single crystals,[5,9] which ranges from 296 to 304 K. In turn, ferromagnetism in thinner Mn:Ge(111) films has not yet been reported. Very thin layers (down to few MLs) are unaccessible to conventional bulk magnetometric techniques; therefore, evidence of ferromagnetic ordering should be searched for by using surface specific techniques, such as dichroic photoemission or x-ray magnetic circular dichroism (XMCD).

In this study, we provide evidence of surface magnetization of a metallic Mn:Ge(111) thin film (obtained after the deposition of about 14 ML of Mn) displaying a $(\sqrt{3}\times\sqrt{3})R30°$ low-energy electron diffraction (LEED) pattern. Absorption measurements at the Mn $L_{2,3}$ edge show XMCD effects below the Curie temperature, and dichroism is observed in valence-band photoemission spectra indicating the presence of spin-polarized states close to the Fermi level. The experiment was carried out at relatively high temperatures (245 and 250 K) in order to explore the magnetic properties at temperatures where ferromagnetic ordering had been probed for thick Mn_5Ge_3 layers, well above those so far reported for the Mn_xGe_{1-x} bulk alloy [i.e., $T_C=120$ K for $x=0.02$ (Ref. 1)].

XMCD and photoemission measurements have been carried out at the BACH beamline of the ELETTRA synchrotron radiation source in Trieste (Italy). Linearly and circularly polarized lights in the 35–1600 eV range are provided by two APPLE II helical undulators. The circular polarization rate over the full Mn $L_{2,3}$ edge was 100% using the first harmonic. The resolution of the monochromator was set to 0.24 eV at the Mn $L_{2,3}$-edge photon energy. X-ray absorption spectroscopy (XAS) and photoemission measurements have been carried out by using a modified 150 mm VSW hemispherical electron analyzer with a 16-channel detector.[10] Sample magnetization has been achieved by polarizing the surface with a permanent magnet which allowed us to apply a 0.30 T magnetic field 30° off with respect to the sample surface.

XMCD and dichroic photoemission measurements have been carried out at 245 and 250 K, respectively, in remanent magnetization. Both measurements have been carried out by changing the light polarization, with photon beam incidence angles of 15° and 30° with respect to the sample surface for XMCD and valence-band photoemission, respectively. Electrons emitted at 75° and 90° with respect to the sample surface for XMCD and valence-band photoemission, respectively, were collected.

A Ge(111) single crystal has been used as substrate for the deposition of the Mn atoms. The substrate preparation is described in Ref. 8. Mn layers were deposited *in situ* at room temperature by electron-beam evaporation from a Mo crucible, with a constant flux of Mn ions. The thickness of the deposited layers was measured by considering the attenuation length of photoemitted electrons. The surface structure we consider has been obtained after the evaporation of a

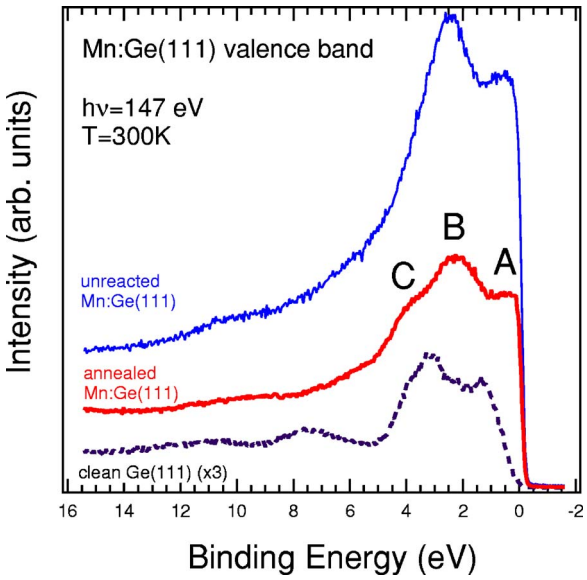

FIG. 1. (Color online) Valence-band photoemission spectra from the clean $c(2\times8)$ reconstructed Ge(111) surface (bottom, dotted line), and from the Mn:Ge(111) interface before (top, thin line) and after (middle, thick line) the annealing. The spectra have been measured at $T=300$ K with $h\nu=147$ eV photons and a total-energy resolution of 86 meV.

14-ML-thick Mn film on the (111) surface of a Ge single crystal. Postgrowth annealing was carried at 300 °C for 120 s to induce the surface alloy formation. Annealing at this temperature yields a single phase surface structure with a $(\sqrt{3}\times\sqrt{3})R30°$ LEED pattern. Oxygen contamination has been periodically controlled. New layers have been prepared when the oxygen signal exceeded the 0.5% of Mn signal, i.e., when the oxygen signal exceeded the mean fluctuation of the background signal.

In Fig. 1, the formation of the ordered Mn:Ge(111) thin layer on the Ge(111) surface is tracked by collecting at normal emission the valence-band spectra from the clean Ge, the unreacted interface after the Mn deposition, and from the alloy film after annealing at 300 °C. The spectra have been collected with a photon energy of 147 eV. The topmost spectrum of Fig. 1 corresponds to the unreacted interface after the evaporation of a 14-ML-thick Mn layer. As compared to the $c(2\times8)$-reconstructed Ge(111) substrate, two new features are clearly detectable, one at the Fermi edge (A) and the other at about 2.5 eV below the Fermi edge (B), which are characteristic of the Mn 3*d* density of states. In fact, this spectrum resembles the photoemission spectrum of Mn crystals and thick Mn films.[11] After annealing, the valence-band (VB) spectrum shows a new spectral feature at about 4.5 eV below E_F (C) that does not correspond to any of the VB features observed in the clean Ge(111) substrate or in the unannealed film. Peak C is characteristic of the reacted Mn:Ge(111) phase, in agreement with the analysis of Zeng *et al.* carried out on the valence band spectra of Mn_5Ge_3 films.[7] Moreover, the emission at the Fermi edge is still detected, which makes our reacted Mn:Ge(111) thin film metallic.

In the buildup of the Mn:Ge(111) ordered alloy, it is rather interesting the analysis of Ge 3*d* core lines, shown in Fig. 2.

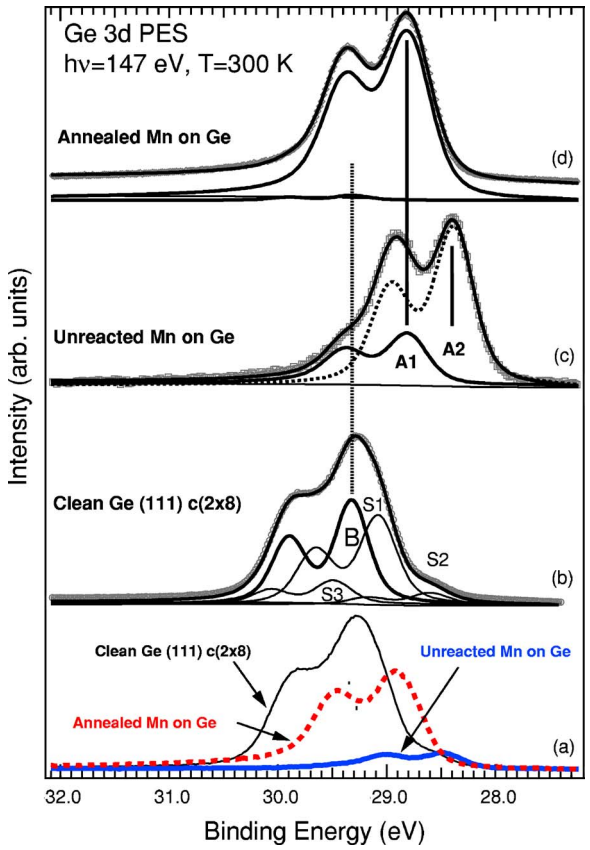

FIG. 2. (Color online) (a) Ge 3*d* photoemission spectrum collected from clean Ge substrate (thin line) from the unreacted Mn:Ge(111) interface (thick line) and from the reconstructed Mn:Ge(111) interface (dashed line). [(b)–(d)] Deconvolution of the shallow core-level spectra of the (b) clean Ge surface of the (c) unreacted Mn film on Ge and of the (d) reacted Mn layer. Spectra (b)–(d) have been normalized by setting a common value for the maximum intensity in order to clearly display the data deconvolution, whereas the spectra shown in (a) are normalized to the photon flux and are therefore directly comparable. The B label indicate the contribution form bulk Ge atoms, while A1 and A2 denote the contributions from Ge atoms after Mn deposition and prior to annealing. After annealing, the A1 component is found to prevalently contribute to the spectral weight. The spectra have been measured at $T=300$ K, with $h\nu=147$ eV photons in normal-emission conditions, with a total-energy resolution of 43 meV.

The Ge 3*d* photoemission spectrum of the clean substrate is that expected for a Ge(111)-$c(2\times8)$ reconstructed surface.[12] The deconvolution of the clean Ge 3*d* core line in terms of bulk, surface, adatoms, and rest-atom components is shown in Fig. 2(b). After Mn evaporation, the emission from the Ge 3*d* levels is quenched [Fig. 2(a)] and the spectral weight is shifted to lower binding energies. The Ge 3*d* spectrum just after the Mn deposition suggests the presence of at least two components. A tentative fit of these data using a pair of doublets is shown in Fig. 2(c). The two components are separated by about 0.4 eV and shifted by 0.42 eV (A1) and 0.86 eV (A2) to lower binding energy (BE) relative to the bulk Ge emission [B label in Fig. 2(b)], respectively.

After annealing, the intensity of the Ge 3*d* emission increases suggesting a migration of Mn and Ge atoms to form

TABLE I. Line-shape parameters resulting from the fitting shown in Fig. 2. For each component, the binding energy relative to the bulk emission (Rel. BE), the spin-orbit splitting (S-O), the branching ratio (BR), the Gaussian broadening (σ), and the lifetime broadening (Γ) are reported. For the alloy peaks, also the asymmetry parameter α is reported.

	Component	Rel. BE (eV)	S-O (eV)	BR (eV)	σ (eV)	Γ	α
Ge(111)	B	0	0.58	1.58	0.26	0.18	
	S1	−0.24	0.58	1.65	0.29	0.18	
	S2	−0.72	0.58	1.65	0.29	0.18	
	S3	0.17	0.58	1.65	0.29	0.18	
Unreacted	A1	0.53	0.58	1.65	0.32	0.18	0.09
	A2	0.94	0.58	1.65	0.32	0.18	0.01
Annealed	B	0	0.58	1.58	0.26	0.18	
	A1	0.53	0.58	1.51	0.38	0.18	0.06

a surface alloy [Fig. 2(a)] and the spectrum can be reproduced using a single spin-orbit split doublet with the same parameter of the A1 component. Therefore, the A1 component corresponds to Ge atoms surrounded by Mn atoms in the alloylike environment (reacted) and we tentatively assign the A2 component to the (unreacted) surface and subsurface Ge atoms at the Ge(111)/Mn interface affected by band bending. The used fitting parameters are reported in Table I. It is worth noting that for the reacted component A1, it is necessary to introduce a finite asymmetry parameter ascribed to the metallic character of the layer [Fig. 2(d)].

In Fig. 3(a), the Mn $2p$-$3d$ XAS (σ^+ and σ^-) spectra of the reacted thin layer are shown, along with the XMCD spectrum ($\sigma^+ - \sigma^-$). Here, σ^+ and σ^- represent the absorption intensity for the two photon helicities. For the Mn $2p_{3/2}$ component, a peak at about 642 eV with a tail toward higher photon energies is observed, while the Mn $2p_{1/2}$ component shows a peak at about 652 eV.

The line shape of these peaks is similar to that of Mn in metallic alloys, such as MnSb or Heusler alloys,[13] whereas the absence of a fine structure ascribed to Mn $2p^5 3d^6$ final state multiplet is assumed as an evidence of the lack strongly localized magnetic moments on Mn lattice sites.[14,15] The extent of metallic character can be qualitatively related to the width of the absorption bands within the same family of compounds. Indeed, recent studies have shown that the width of the Mn $2p$ XAS in Mn magnetic intermetallic compounds can be related to the band dispersion.[13] For instance, the larger width observed for MnSb with respect to PtMnSb is due to more delocalized Mn $3d$ electrons in the former compound.

These general features may help to qualitatively describe the electronic properties of the present layer. As compared to the XAS profile detected in the Mn:Ge(111) interface for a 1.3 ML thin film[16] and for a 4 ML thin film,[8] both displaying the $(\sqrt{3}\times\sqrt{3})R30°$ reconstructions the present thin film shows a larger width for both the L_3 and L_2 peaks in the XAS profile. In particular, as compared to the 1.3 ML thin film,

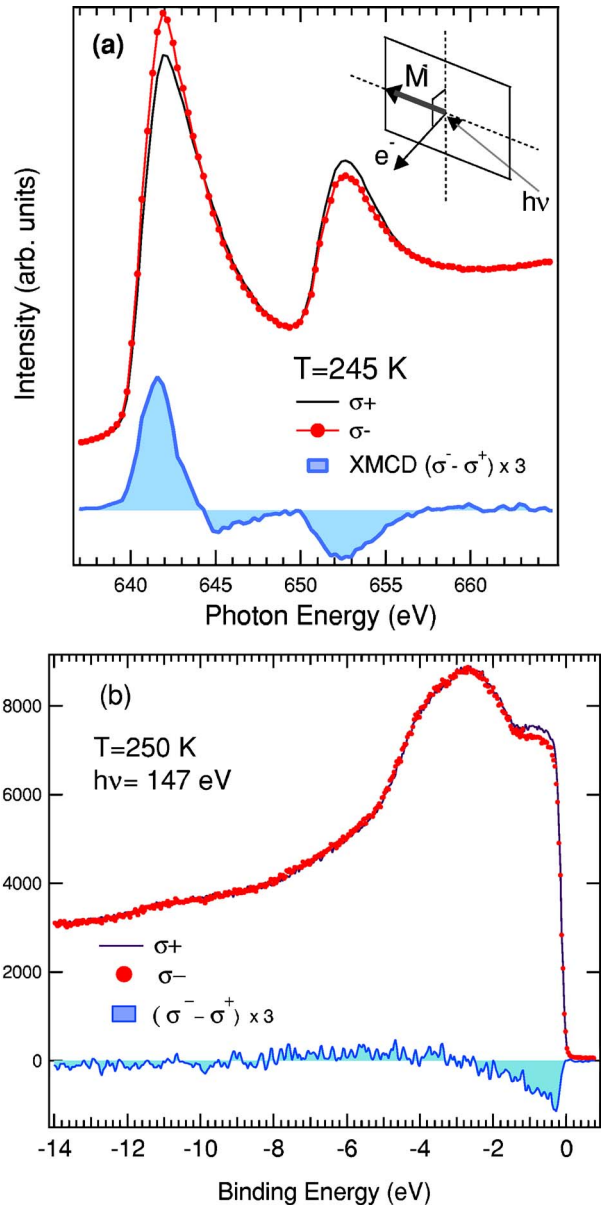

FIG. 3. (Color online) (a) XMCD spectrum measured at the Mn $2p$-$3d$ absorption edge of the Mn:Ge(111) $(\sqrt{3}\times\sqrt{3})R30°$ reconstructed interface (T=245 K). The drawing describes the experimental geometry for both XMCD and dichroic photoemission data. The energy resolution was set at 260 meV on the L_3 edge. (b) Magnetic circular dichroism spectrum of the valence band ($h\nu$ =147 eV, T=250 K). The dichroism spectra are obtained by calculating the difference between the spectra collected with left and right circularly polarized radiation (σ^-, dots and σ^+, thin line).

the present spectrum appears to be almost featureless, while the 1.3 ML film shows weak fine structure features that have been ascribed to Mn-Ge hybridization. Moreover, for the 1.3 ML thin film, the analysis of photoelectron diffraction (PED) patterns[16] has shown that Mn ions enter the Ge lattice as substitutional atoms. Because of this diffusion into the lattice, the innermost layers of the thinner interface can be regarded as an Mn_xGe_{1-x} diluted alloy. This also explains the weak fine structure detected in the XAS measurement. As the thickness of the evaporated Mn layer increases, the presence

of the metallic Mn_5Ge_3 phase hinders the contribution from the buried Mn_xGe_{1-x} interface and the XAS linewidth becomes closer to that of metallic Mn, as in the case of the present 14-ML-thick sample.

Indeed, the XMCD spectrum shown in Fig. 3(a) can be virtually superimposed to that measured in the intermetallic, ferromagnetic, Mn_5Ge_3 bulk single crystals,[5] where the line shape of XMCD was tentatively ascribed to a prevalent $3d^6$ configuration weight in the initial state of Mn atoms, yielding a $2p^53d^7$ final state multiplet, in fair agreement with atomic calculations. This finding can be regarded as an indication that the metallic character induces a redistribution of electrons within the *M* shell, with a possible transfer of charge from the 4*s* to 3*d* band.

Finally, we have also considered the possibility of having a ferrimagnetic ordering. Although we cannot rule out this possibility, we note that the ferromagnetic order in Mn_5Ge_3 thin layers is characterized by a remarkable anisotropy[6] with an in-plane ordering for layers as thick as 500 Å, in contrast with the bulk crystal where spin alignment along the hexagonal *c* axis has been observed. Being our layer much thinner than that prepared by Zeng *et al.*,[6] we expect a large anisotropy also for the present system, and the tendency to orient the magnetic moment along the *c* axis (i.e., perpendicular to the surface) should be more even more hindered.

Further evidence that our film is magnetic comes from the observation of magnetic circular dichroism in the valence-band photoemission spectra, as shown in Fig. 3(b). The spectra have been obtained at $T=250$ K, with a photon energy of 147 eV. A major dichroic effect is observed for states within about 2 eV from the Fermi level. Minor contributions could be present at higher BE but they are obscured by signal fluctuations.

In order to interpret this result, we refer to the available band-structure calculations on the Mn-Ge system by considering the cases of bulk Mn_xGe_{1-x} DMS alloy[17] and the metallic, Mn_5Ge_3 ferromagnetic phase.[18] The former case is considered because diffusion of Mn through the (111) surface of Ge may result in a DMS-like alloy at the early stages of deposition,[16] as already recalled in the discussion of the XAS data. From the calculations on the Mn_xGe_{1-x} alloy, a strong spin polarization results from the Mn-projected DOS at about BE=3 eV. This feature hardly accounts for the observed dichroism, and a better agreement is expected from the comparison with the calculations on Mn_5Ge_3. Indeed, band-structure calculations of the Mn_5Ge_3 phase[18] indicate that MnI (Ref. 19) states mainly contribute to the dichroism in a narrow energy range (2.0 eV) below the Fermi edge, with sharp peaks at 0.7 and 1.5 eV, i.e., in the energy range where we observe a clear spin polarization in our film. Magnetic circular dichroism should extend in a valence-band range as large as 6 eV due to the prevalent contribution of MnII atoms to the DOS far from E_F. Unfortunately, the signal fluctuations in this range do not allow us to identify a clear dichroic contribution, although we cannot exclude that a minor contribution could occur also in this region. The fact that we observe a clear dichroic effect in valence-band photoemission only for states within 2 eV below the Fermi level, reminiscent of the calculated behavior of MnI atoms in Mn_5Ge_3, suggests that we are probing the magnetic properties of an Mn_5Ge_3 layer, where only the MnI atoms contribute to the measured photoemission dichroic signal. Being our probe rather sensitive to the topmost layer, this finding is in agreement with recent scanning tunneling microscopy studies,[7] which have shown that the Mn_5Ge_3 thin layers are terminated by MnI atoms.

In conclusion, XMCD allowed us to detect ferromagnetic ordering of the metallic Mn:Ge(111) $(\sqrt{3}\times\sqrt{3})R30°$ thin film alloy that cannot be explored with conventional magnetic tools due to the reduced layer thickness. The present data have been interpreted by comparison with theoretical calculations on the Mn_5Ge_3 bulk phase and with XMCD from bulk single crystals. Our analysis shows that magnetism in the present thin film prevalently displays the characteristics of ferromagnetic Mn_5Ge_3.

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