Spatial Chemical Inhomogeneity and Local Electronic Structure of Mn-Doped Ge Ferromagnetic Semiconductors


1Department of Physics, The Catholic University of Korea, Puchon 420-743, Korea
2Department of Physics, University of Ulsan, Ulsan 680-749, Korea
3Department of Physics, Gyeongsang National University, Chinju 660-701, Korea
4Pohang Accelerator Laboratory (PAL), POSTECH, Pohang 790-784, Korea
5Department of Material Physics, Graduate School of Engineering Science, Osaka University, Osaka 560-8531, Japan
6Department of Physics, University of Ulsan, Ulsan 680-749, Korea

(Received 2 September 2004; published 11 April 2005)

We have investigated the chemical distributions and the electronic structure of potential diluted magnetic semiconductor Ge$_{0.94}$Mn$_{0.06}$ single crystals using scanning photoelectron microscopy (SPEM), x-ray absorption spectroscopy (XAS), and photoemission spectroscopy (PES). The SPEM image shows the stripe-shaped microstructures, which arise from the chemical phase separation between the Mn-rich and Mn-depleted phases. The Mn $2p$ XAS shows that the Mn ions in the Mn-rich region are in the divalent high-spin Mn$^{2+}$ states but that they do not form metallic Mn clusters. The Mn $3d$ PES spectrum exhibits a peak centered at $-4$ eV below $E_F$ and the negligible spectral weight near $E_F$. This study suggests that the observed ferromagnetism in Ge$_{1-x}$Mn$_x$ arises from the phase-separated Mn-rich phase.

DOI: 10.1103/PhysRevLett.94.147202
PACS numbers: 75.50.Pp, 68.37.Xy, 79.60.-i

One promising strategy to achieve spin injection into nonmagnetic semiconductors in spintronics is to use a diluted magnetic semiconductor (DMS), prepared by substituting $3d$ transition-metal (TM) ions, such as Cr, Mn, Fe, Co, and Ni, into nonmagnetic semiconductors. Interest in DMS materials has been reinvoked with the discovery of spontaneous ferromagnetic (FM) order in Ga$_{1-x}$Mn$_x$As [1] exhibiting the Curie temperature $T_C$ up to 110 K. Theoretically, mean-field calculations of a Zener model [2] predicted that the FM order can be stabilized in Mn-doped semiconductors with sufficiently high hole carriers. Recent experiments show that both Ge films [3,4] and bulk single crystals [5] doped with Mn ions exhibit the FM ordering at $T_C \approx 116$ K and at $T_C \approx 285$ K, respectively. Also the FM ordering at $T_C \approx 270$ K was reported for Co and Mn-doped Ge epitaxial films [6].

The origin of the ferromagnetism in DMSs is still controversial, and the reproducibility of the FM order in DMSs is questionable, as found in contradicting reports on Zn$_{1-x}$Co$_x$O [7–9] and anatase Ti$_{1-x}$Co$_x$O$_2$ [10]. One of the key issues in this field is whether there is no phase separation of dopants in DMSs. Therefore it is very important to investigate the possibility of the phase separations in DMSs in the micrometer ($\mu$m) or nanometer scale, and to investigate the electronic structures of doped TM impurities. In this aspect, scanning photoelectron microscopy (SPEM) is a powerful method for studying the chemical distribution of dopant elements in sub-$\mu$m scale [11]. In SPEM, x rays are focused through a focusing lens (or a zone plate) to a sub-$\mu$m scale spot. By scanning a sample at a characteristic photon energy $h\nu$ corresponding to a certain element, one can obtain the spectral image for the chemical distribution of that element [11]. No SPEM study on DMS materials has been reported so far. On the other hand, photoemission spectroscopy (PES) and x-ray absorption spectroscopy (XAS) are the essential experimental tools for providing direct information on the electronic structures and the valence states of TM ions in solids [12,13]. Only a few experimental PES/XAS studies have been reported on potential DMS materials [14–17], but not on Ge$_{1-x}$Mn$_x$.

In this Letter, we have investigated the sub-$\mu$m scale chemical distribution and the electronic structure of Ge$_{0.94}$Mn$_{0.06}$ single crystals by combining SPEM, XAS, and PES methods in order to understand the nature and the origin of ferromagnetism in Mn-doped Ge. Single-crystalline Ge$_{1-x}$Mn$_x$ samples were made by using high-purity (99.999%) Ge and Mn powders of the particle size less than $<200$ mesh. The details of the sample preparation and characterization are described in Ref. [5]. In the x-ray diffraction (XRD) analysis of these samples, no impurity phases were detected within the experimental detection limit. Caution is needed, however, since the presence of nanoscale impurity phases within the host matrix cannot be completely excluded by the standard XRD technique. The Laue diffraction patterns showed that these samples were single crystals with diamond structures, and the lattice constant increased linearly with increasing Mn concentration. Both results indicate that Mn ions were substituted properly for the host Ge sites. These crystals exhibited the paramagnetic to FM transition at $T_C \approx 285$ K and the FM to antiferromagnetic transition at $T_C \approx 150$ K (see Fig. 3 in Ref. [5]).

SPEM, PES, and XAS measurements were performed at the 8A1 undulator beam line of the Pohang Accelerator Laboratory. A 50 $\mu$m pinhole is placed between the zone...
plate and the sample, resulting in the size of the focused x rays on the sample to be about 0.5 μm in diameter [11]. Topographic SPEM images are constructed either by the total intensity over 16 channels in the photoelectron detector arrays or by employing the total electron yield method (sample current). The latter method is known to be more bulk representative owing to the longer probing depth. Before samples were introduced into the SPEM chamber, they were polished by using the abrasive papers and diamond powders up to 1 μm in size. The SPEM images were obtained first from the as-is surfaces. Then samples were sputtered mildly with Ne ions to remove carbons (C) on sample surfaces but to minimize the possible artifacts caused by sputtering. All the measurements were done at room temperature, and with the pressure better than 4 × 10^{-10} Torr. All the spectra were normalized to the incident photon flux. XAS spectra were obtained by employing the total electron yield method, with the photon energy resolution of ~100 meV at the Mn 2p absorption threshold (hν = 640 eV).

Mn 2p → 3d resonant PES (RPES) experiments were performed at the twin-helical undulator beam line BL25SU of SPring-8 equipped with a SCIENTA SES200 analyzer. Samples were fractured and measured in vacuum better than 3 × 10^{-10} Torr at T ≈ 20 K. The Fermi level EF and the FWHM of the system were determined from the valence-band spectrum of a scraped Pd in electrical contact with samples. PES data were obtained in the transmission mode, with the FWHM of about 100 meV at hν ~ 600 eV. All the spectra were normalized to the photon flux.

The top left of Fig. 1 shows the SPEM image of Ge_{0.94}Mn_{0.06}. The scan area and the step size of this SPEM image were 1000 μm × 1000 μm and 20 μm × 20 μm, respectively. In obtaining the SPEM image, the photon energy was set at the Mn 2p_{3/2} absorption peak (hν = 640 eV, see Fig. 3), and SPEM images were constructed by employing the total electron yield method. Thus this SPEM image represents the chemical distributions of Mn ions, and the brightness is proportional to the relative Mn concentration. Further, this SPEM image can be considered to represent the bulk features of the measured samples [18]. The SPEM image reveals the stripe-shaped bright regions with a width of a few tens μm and a length of a few hundreds μm. The bright (B) and dark (D) spots in the image correspond to the Mn-rich and Mn-depleted region, respectively, as confirmed in the survey PES spectra on the right.

The top right of Fig. 1 shows the survey PES spectra of Ge_{0.94}Mn_{0.06}, obtained at the bright (B) spot and the dark (D) spot, respectively, and with hν = 640 eV. The survey spectrum for a dark spot is essentially the same as that for pure Ge, indicating that the average Mn concentration in the dark region is very low. In contrast, the survey spectrum for a bright spot reveals the large Mn-derived features, such as the Mn 3d peak and Mn LMM Auger peaks. Therefore these survey PES spectra provide evidence that the bright (B) and dark (D) regions in the SPEM image correspond to the Mn-rich and Mn-depleted phases, respectively. We note that the magnetic properties of Ge_{0.94}Mn_{0.06} [5] are similar to those of Ge_{8}Mn_{11} [19]. It is thus likely that the Mn-rich phase in Ge_{0.94}Mn_{0.06} actually consists of several Ge_{Mn} alloys, including Ge_{5}Mn_{11} [19,20]. This finding suggests that preparing homogeneous Ge_{1−x}Mn_{x} DMS samples is very difficult. This may be the reason why very few works have been reported on the Ge_{1−x}Mn_{x} system so far, either bulk [5] or films [3,4]. By comparing the magnetization data between our Ge_{0.94}Mn_{0.06} crystal [5] and Ge_{8}Mn_{11} [19], we have roughly estimated the volume fraction of the impurity phase of ~2% in our sample, which implies that some of the doped Mn ions form Mn-rich alloys, and the rest of them are substituted for the Ge sites.

The bottom of Fig. 1 shows the survey images of Ge_{0.99}Cr_{0.01} and Ge_{1−x}Fe_{x} (x = 0.05) [21], which were obtained at the Cr and Fe 2p_{3/2} absorption peaks, respectively, and constructed from the total electron yields. These images also exhibit the stripe-shaped bright regions. The survey spectra show [22] that the bright and dark regions in the SPEM images correspond to the Cr(Fe)-rich and Cr(Fe)-depleted phases. Therefore these observations provide evidence that Ge_{1−x}T_{x} (T = Cr, Mn, Fe) crystals consist of the microstructures with very different T concentrations.

Figure 2 compares the Mn 2p XAS spectrum of Ge_{0.94}Mn_{0.06} to those of reference Mn compounds having formal Mn valences of 2+ (MnS [23], MnO [24]) and 4+ (MnO_{2} [24]), and that of Mn metal [25]. The peak positions and the line shape of the Mn 2p XAS spectrum depend on the local electronic structure of the Mn ion, and provide the information on the valence state and the ground-state symmetry of the Mn ion [12,13]. The Mn 2p XAS spectrum of
ions in Ge0.94Mn0.06 calculated metal. This observation suggests that the valence states of Mn ions in Ge0.94Mn0.06 are nearly divalent (Mn2+) but not tetravalent (Mn4+), and that the formation of the Mn metal cluster in our Ge0.94Mn0.06 samples is ruled out.

In order to confirm this effect, we have included the calculated Mn 2p XAS spectrum for a Mn2+ (3d5) ion in the tetrahedral (Td) symmetry (reproduced from Ref. [13]) at the bottom of Fig. 2. The calculation is based on the cluster model which includes the effects of the multiplet interaction, the crystal field, and the hybridization with the ligand orbitals. The Mn2+ (3d5) configuration and the small Td crystal field energy of 10Dq = 0.5 eV yields a good fit for the measured Mn 2p XAS spectrum of Ge0.94Mn0.06. The small value of 10Dq = 0.5 eV implies that Mn ions are in the high-spin (HS) states. The similarity between the measured Mn 2p XAS spectrum and the calculated 2p XAS spectrum indicates that the doped-Mn ions in Ge0.94Mn0.06 are in the HS divalent Mn2+ (d5) states with the total spin of S = 5/2. This analysis also reveals [13] that the line shapes of the XAS spectra for small 10Dq are very similar between the O6 (octahedral) and Td symmetries.

Figure 3 shows the valence-band PES spectra of Ge0.94Mn0.06 near the Mn 2p3/2 absorption edge, obtained at T ≈ 20 K. The inset shows the corresponding Mn 2p3/2 XAS spectrum of Ge0.94Mn0.06. The off-resonance valence-band PES spectrum (A) is similar to the valence-band x-ray photoemission spectroscopy spectrum for pure Ge [26], as expected from the small average Mn concentration (~6%) in Ge1−xMnx in addition to the smaller photoionization cross sections of Mn 3d electrons (by an order of magnitude) than those of Ge 3d electrons. Then the enhanced features near ~4 eV binding energy at the Mn 2p → 3d absorption energy (C) represent the resonating Mn 3d electron emission. Therefore the difference between the on-resonance and off-resonance spectra can be considered to represent the bulk Mn 3d partial spectral weight (PSW) distribution [27].

Figure 4 presents the extraction procedure of the Mn 3d PSW for Ge0.94Mn0.06. As a first approximation, it is taken as the difference (dotted line) between the Mn 2p → 3d on-resonance spectrum (solid line) and off-resonance spectrum (gray line). The extracted Mn 3d PSW exhibits a peak centered at ~4 eV binding energy with the FWHM of ~4 eV and a weak tail to the high binding energy side (up to ~12 eV). The Mn 3d PSW for Ge0.94Mn0.06 shows that Mn 3d states are located well below E_F, indicating that the doped-Mn 3d electrons occupy the very deep levels.

The extracted Mn 3d PSW of Ge0.94Mn0.06 is compared to that of Ga0.93Mn0.06As film (Ref. [15]) at the bottom of Fig. 4. The position of the main peak for Ge0.94Mn0.06 is the same as that for Ga0.93Mn0.06As. However, the spectral weight between E_F and ~2 eV binding energy is negligible in the Ge0.94Mn0.06 crystal, but clearly observable in the Ga0.93Mn0.06As film [28]. In the cluster model analysis [15], the Mn 3d PSW for Ga1−xMnx,As was interpreted to represent the Mn2+ valence state, and the spectral weight between E_F and ~2 eV binding energy arose mainly from the d5L1 final-state component (L: a ligand hole). Similarly, our Mn 3d PSW for Ge0.94Mn0.06 can be interpreted to represent the Mn2+ valence state, but to have the negligible d5L1 final-state component. The presence of the d5L1 final-state component in PES of Mn-doped GaAs film occurs when there is charge transfer from neighboring metals.

![FIG. 2. Comparison of the Mn 2p XAS spectrum of Ge0.94Mn0.06 to those of MnS (Mn2+) (Ref. [23]), MnO (Mn2+) (Ref. [24]), MnO2 (Co3+) (Ref. [24]), and Mn metal (Ref. [25]). At the bottom is shown the calculated Mn 2p XAS spectrum for a Mn2+ (3d5) ion (Ref. [13]).](image)

![FIG. 3. Valence-band PES spectra of Ge0.94Mn0.06 near the Mn 2p3/2 → 3d absorption edge. Inset: The Mn 2p3/2 XAS spectrum of Ge0.94Mn0.06. Arrows denote hν’s where the valence-band PES spectra were obtained.](image)
As 4p electrons to Mn 3d electrons, which requires substantially large hybridization between Mn 3d and As 4p states. Therefore the negligible \( d^3 L^1 \) final-state component in Ge\(_{0.94}\)Mn\(_{0.06}\) suggests that the hybridization between Mn 3d and Ge 4p orbitals is much weaker than that between Mn 3d and As 4p states in Ga\(_{0.93}\)Mn\(_{0.07}\)As. Finally, the Mn 3d PSW with the main peak at \( \sim 4 \text{ eV} \) is quite different from the Mn 3d partial density of states of the local density approximation (LDA) band results for Mn-doped Ge [29,30], which exhibit the Mn 3d peaks at \( \sim 2 \text{ eV} \). One can attribute this difference to the Coulomb correlation effect between Mn 3d electrons, which is not properly described in the LDA scheme. In fact, the LDA + U calculation for Mn-doped GaAs, incorporating the Coulomb interaction \( U = 4 \text{ eV} \), yields the peak position in agreement with that of the Mn 3d PSW, reflecting the importance of Mn 3d correlation effects [31].

In conclusion, the present study by using SPEM, XAS, and PES indicates that the Ge\(_{0.94}\)Mn\(_{0.06}\) crystal is chemically phase separated into the Mn-rich and Mn-depleted phases. The stripe-shaped bright regions are observed in the SPEM images of Ge\(_{0.94}\)Mn\(_{0.06}\) crystals, reflecting the inhomogeneous distribution of Mn concentrations. The simultaneous PES measurements provide more information that the bright and dark regions in the SPEM images correspond to the Mn-rich and Mn-depleted phases, respectively. The Mn 2p XAS spectrum of Ge\(_{0.94}\)Mn\(_{0.06}\) indicates that Mn ions are in the divalent states, but that they do not form pure metal clusters. This finding is consistent with the Mn 3d PSW, determined from Mn 2p \( \rightarrow 3d \) RPES. This study indicates that the ferromagnetism observed in Ge\(_{1-x}\)Mn\(_{x}\) (\( x \ll 1 \)) systems [3–5] may not be an intrinsic nature of DMSs, but arises from the magnetic properties of the Mn-rich phases in phase-separated Ge\(_{1-x}\)Mn\(_{x}\).

We thank V. Kryukhin for helpful discussions. This work was supported by the KRF (KRF-2002-070-C00038) and by the KOSEF through the CSCMR at SNU and the eSSC at POSTECH. The PAL is supported by the MOST and POSCO in Korea.

FIG. 4 (color online). Top: Comparison of the on-resonance (solid line) and off-resonance valence-band spectra (gray line) in Mn 2p \( \rightarrow 3d \) RPES. The difference curve between two spectra is shown as a dotted line. Bottom: Comparison of the extracted Mn 3d PSW of Ge\(_{0.94}\)Mn\(_{0.06}\) to that of Ga\(_{0.93}\)Mn\(_{0.07}\)As (Ref. [15]).

---

*Electronic address: kangis@catholic.ac.kr

[18] SPEM measurements were also done for the samples that were scraped in situ. We still observed the inhomogeneous regions, even though the images were not very clear due to the rough surfaces after scraping. This finding indicates that the observed inhomogeneous images are not due to the surface segregation nor due to the artifact caused by sputtering.
[28] The Mn 3d PSW for Ga\(_{0.93}\)Mn\(_{0.07}\)As was determined by using the surface-sensitive Mn 3p \( \rightarrow 3d \) RPES technique, while our Mn 3d PSW for Ge\(_{0.94}\)Mn\(_{0.06}\) is determined by using more bulk-sensitive Mn 2p \( \rightarrow 3d \) RPES (see Ref. [27]).