Photoemission studies of $Ga_{1-x}Mn_xAs$: Mn concentration dependent properties

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Using angle-resolved photoemission, we have investigated the development of the electronic structure and the Fermi level pinning in $Ga_{1-x}Mn_xAs$ with Mn concentrations in the range 1%–6%. We find that the Mn-induced changes in the valence-band spectra depend strongly on the Mn concentration, suggesting that the interaction between the Mn ions is more complex than assumed in earlier studies. The relative position of the Fermi level is also found to be concentration dependent. In particular we find that for concentrations around 3.5%–5% it is located very close to the valence-band maximum, which is in the range where metallic conductivity has been reported in earlier studies. For concentrations outside this range, larger as well as smaller, the Fermi level is found to be pinned at about 0.15 eV higher energy.

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I. INTRODUCTION

The possibility to include magnetic impurities at relatively high concentrations in GaAs by means of low-temperature molecular beam epitaxy (LT-MBE) has opened new exciting prospects of combining magnetic phenomena with high-speed electronics and optoelectronics. The numerous investigations of $Ga_{1-x}Mn_xAs$ alloys that have been carried out so far have revealed interesting material properties, the most notable being carrier-induced ferromagnetism, with reported Curie temperatures as high as 110 K.[1] Other interesting properties are the anomalous Hall effect, negative magnetoresistance, and photoinduced ferromagnetism. Although there is general consensus concerning the importance of Mn-induced holes, the detailed mechanisms behind the ferromagnetic ordering of the Mn spins remain a subject of debate.[2–7] The electronic state of the Mn ions in samples with high Mn content is also discussed, though at low concentrations (below 1%) the d^5+hole configuration is established.[8] Also the role of As antisites has been discussed extensively.[9,10] It is clear that further spectroscopic studies related to these problems are strongly motivated. In the present work we have used photoemission to study two key features in the electronic structure of $Ga_{1-x}Mn_xAs$ alloys for a range of Mn concentrations: the Mn-related modifications of the electronic structure and the Fermi level position relative to the valence-band maximum (VBM).

II. EXPERIMENT

The experiments were performed on the toroidal grating monochromator beamline (BL 41) at the MAX I storage ring of the Swedish National Synchrotron Radiation Center MAX-lab, where a dedicated system for MBE is attached to the photoelectron spectrometer. This configuration allows samples to be transferred between the growth and analysis chambers under UHV conditions. In the transfer system the vacuum was in the low-10^{-9}-torr range and in the electron spectrometer in the low-10^{-10}-torr range. The ability to transfer samples means that no post-growth treatment was needed to prepare the surfaces for the photoemission measurements. This is a point worth stressing in the present context, as the samples are prepared under rather extreme conditions and change their properties with annealing even at temperatures well below that at which MnAs segregates.[11] Indeed, the spectra presented here are somewhat different from those obtained on sputtered and annealed surfaces.[12]

The MBE system contains six sources, including an As_2 valved cracker. It is also equipped with a 10 keV electron gun for reflection high-energy electron diffraction (RHEED). The samples were approximately 10×10 mm^2 pieces of epiready *n*-type GaAs(100) wafers, which were In glued on tranferrable Mo holders. Each sample preparation started with a 1000 Å buffer, grown at a substrate temperature (T_s) of 590 °C; T_s was then lowered to the growth temperature of LT-GaAs and GaMnAs, which was typically 220 °C. At low temperature the growth started always with a 200–300 Å LT-GaAs buffer layer. The As_2/Ga flux ratio was maintained at values around 10. During deposition of this layer the LT-GaAs growth rate was measured by recording RHEED intensity oscillations. After opening the Mn shutter the RHEED oscillations were observed again during the GaMnAs growth.[13] At this low growth temperature the reevaporation of Mn and Ga from the surface is negligible, so the growth rate increase is proportional to the Mn content. The Mn concentrations quoted below are estimated to be accurate within 0.5%.

Immediately after transfer the surfaces were checked with low-energy electron diffraction (LEED). All Mn-containing samples exhibited 1×2 reconstructed surfaces in RHEED as

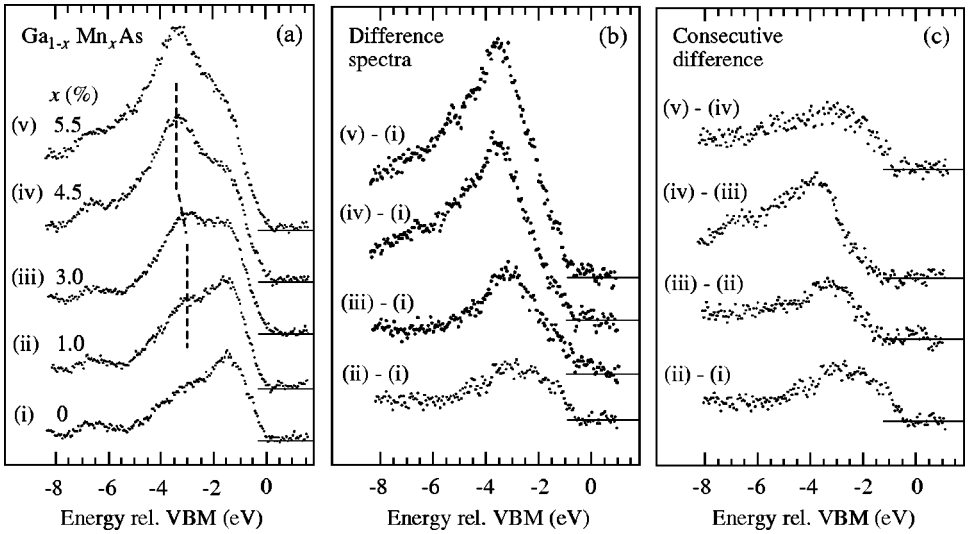

FIG. 1. (a) Normal emission valence-band photoemission from $Ga_{1-x}Mn_xAs$ with different Mn concentrations, aligned at the valence-band maximum. The spectra were excited with 81 eV photons. (b) Difference spectra obtained by subtracting the LT-GaAs spectrum (i) from the respective $Ga_{1-x}Mn_xAs$ spectra in (a). (c) Difference spectra obtained by subtracting consecutive spectra in (a).

well in LEED, while the clean reference GaAs sample displayed a $c(4\times4)$ LEED pattern with sharp integer order and less distinct fractional order spots. Photoemission was excited with mainly *p*-polarized light incident at 45° relative to the surface normal, the samples being oriented with the [110] azimuth (i.e., the onefold periodicity) in the plane of incidence. The electron energy distribution curves were obtained using a hemispherical electron energy analyzer with an angular resolution of 2°, and the overall energy resolution was around 0.3 eV. A clean Ta foil, in contact with the sample holder, was used to determine the Fermi level position in each case. The counting rates were normalized to the incident beam intensity by means of photocurrent from a gold mesh in the beam path.

A superconducting quantum interference device (SQUID) was used to estimate the paramagnetic-to-ferromagnetic phase transition temperature (T_c) for some of the samples used in the photoemission experiments. T_c was defined as the temperature at which the nonzero magnetization onset appeared on cooling the sample from liquid nitrogen to liquid helium temperatures.

III. RESULTS AND DISCUSSION

Considering the intrinsic surface sensitivity of photoemission and that surface compositions in alloy systems often deviate from those in the bulk, it is well motivated to start with a brief comment on this point. The fact that clear and actually unusually persistent RHEED oscillations are observed during growth of GaMnAs shows that the atoms are still mobile in the surface layer despite the low-temperature conditions. However, once accommodated in lattice sites, further mobility that would lead to phase separation is efficiently inhibited under the low-temperature growth conditions. Thus, it is well motivated to expect that the sample compositions are uniform, including the first atomic layers. We should mention, however, that applying secondary-ion mass spectroscopy (SIMS) as well as Auger microprobe analysis on samples exposed to atmospheric pressure, we have observed pronounced enrichment (by a factor of 2) of Mn in the surface layer (and a corresponding depletion in the underlying region), which is clearly associated with oxidation. Typically these redistributions range over a thickness of around 150 Å. This clearly emphasizes the significance of carrying out surface-sensitive experiments on *in situ* prepared samples.

Photoemission from Mn $3d$ states in dilute systems like $Ga_{1-x}Mn_xAs$ is easily identified via resonant enhancement of the $3d$ cross section at the $4p$ excitation threshold, which occurs at 50 eV photon energy. Since the spectral shape changes quite much in this energy range and since our aim is to compare spectra recorded from a series of different samples, we have chosen to use a photon energy well above this resonant range (81 eV). Although the absolute cross section of Mn $3d$ is smaller at 81 eV than that just above 50 eV photon energy, the cross sections of the GaAs valence states are also reduced in a similar way and therefore the Mn $3d$-induced spectral features are still readily detected. Figure 1(a) shows a set of such valence-band spectra from samples with different Mn contents, together with a reference spectrum from clean LT-GaAs. It is worth pointing out that just like the GaMnAs, such LT-GaAs contains large concentrations of point defects (mostly As antisites) and that spectra from such layers are found to be somewhat different relative those obtained from MBE layers grown at high temperature.[14] Considering that until now only one independent valence-band photoemission study of such materials has been published[12] and that the samples are produced under rather extreme growth conditions, it is well motivated to start the discussion with a direct comparison between the present data and the published ones. We note then that the data contain some similarities, but also some significant differences. The main Mn-induced feature is the peak at 3.4 eV below the VBM for the most Mn-rich samples. Its Mn origin is clearly revealed by the resonant enhancement mentioned above. A similar resonant structure was found in Ref. 12, but at a binding energy of 4.5 eV relative to the Fermi level. Since the Fermi level is located about 0.13 eV above the VBM (see below), there seems to be a discrepancy of almost 1 eV between the two results. Furthermore, the spectra in Ref. 12 contain a second pronounced peak at about 2.5 eV larger binding energy. This structure is completely missing in our

data. The weak asymmetric peak seen in all spectra around 6.5–7 eV in Fig. 1(a) reflects the X_3 critical point emission. Such density-of-states (DOS) structures are seen at all photon energies and all emission angles due to diffuse elastic scattering of the direct interband excitation of this state. Altogether we thus find that the present spectra are significantly different from those found in the literature, and although the reason for these deviations is not clear, it is natural at this point to suspect that the different surface preparations could be the cause. This would then underline the importance of carrying out these experiments on *in situ* grown samples.

It is immediately clear in Fig. 1 that the Mn-induced spectral changes vary with Mn content. To examine this variation in some more detail, we have generated difference spectra, as displayed in Figs. 1(b) and 1(c). The first spectrum in this sequence shows that with 1% Mn the spectral intensity is increased over a range 1–4 eV below the VBM, with a peak centered around 3 eV and a shoulder at 1 eV below the VBM. The main increase coincides with weak structures in the clean GaAs spectrum (around 3 eV and 4 eV below the VBM). As these structures are due to excitations at the high DOS regions at the X_5 and Σ_1^{min} points, one could suspect that the Mn-induced changes are in this case caused by disorder-related increase of diffuse scattering. However, from the fact that no corresponding increase is seen for the X_3 critical point emission and from the following development of the 3-eV peak, we can safely conclude that these spectral changes do indeed reflect Mn-derived states. The low-Mn-concentration spectrum does in fact resemble closely the theoretical energy distribution of majority spin states ($e+t_2$ orbitals) derived in local density approximation (LDA) calculations[15] of $Ga_{1-x}Mn_xAs$ in the diluted limit. With the Mn content raised to 3% we see that the incremental change is somewhat different than the initial one. The peak at 3 eV is increased further, but the range around 1 eV remains essentially unchanged. Increasing the Mn content further results in another change: the main additional spectral contribution appears as an asymmetric peak around 3.8 eV below the VBM, i.e., clearly shifted relative to that found at lower concentrations. Thus, the peak observed at 3.4 eV in the corresponding full spectrum [Fig. 1(a)] can be concluded to represent an average of several contributions. Finally, the additional spectral changes with further increase of Mn content are found to be less distinct, the intensity is increased rather uniformly over a range 2–6 eV below the VBM.

The reason behind the downwards shift of the Mn 3*d* states is not clear at this point. In very recent experiments[16] we have found that similar shifts may be induced by low-temperature annealing (250–300 °C). Since annealing at high temperatures is known to result in phase separation and formation of MnAs clusters, it is natural to ascribe the annealing-induced changes in our experiments to displacement of Mn atoms from the substitutional sites. In view of the spectral similarities, it is then tempting to assume that the present observations of concentration dependence reflects an increasing fraction of Mn atoms residing in nonsubstitutional sites as the Mn concentration is increased. Such sites could for instance be interstitials. In this case the Mn 3*d* states should be more localized than for the substitutional sites, and

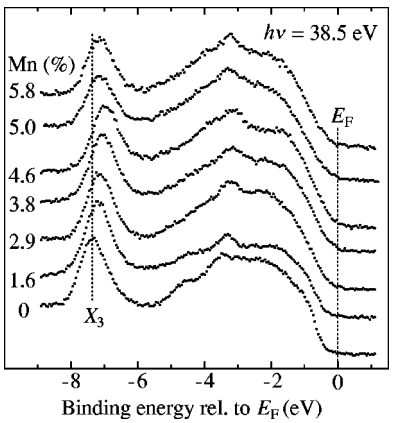

FIG. 2. Normal-emission valence-band photoemission from $Ga_{1-x}Mn_xAs$ with different Mn concentrations, aligned at the Fermi level. The spectra were excited with 38.5 eV photons.

the shifts towards higher binding energies could be an effect of increased correlation energy, as found in LDA calculations[17] on $Ga_{1-x}Mn_xAs$.

The important conclusion from the data in Fig. 1 is that the character of the Mn states in $Ga_{1-x}Mn_xAs$ depends on the Mn concentration. Since supplementary x-ray diffraction analysis of our samples shows a high degree of perfection in the layers, we have no reason to suspect that the variations seen here are due to varying sample structure quality, but ascribe them to the different Mn contents. No such dependence has been reported in any of the earlier studies. A previous analysis of Mn 3*d* partial DOS in GaMnAs with 6.9% Mn was successful in modeling the observed spectrum using a configuration interaction model involving Mn 3*d* and ligand states in a $MnAs_4$ cluster.[12] Obviously, this kind of model cannot account for concentration-dependent properties like those reported here. With an average distance between two impurities of around 10 Å, it is clear that the explanation must be based on a model in which long-range interactions are taken into account. A possible cause for the spectral variations discussed here is Mn-concentration-dependent *p-d* exchange. Such dependence has been suggested previously on the basis of magnetic circular dichroism experiments.[18]

GaMnAs is also known to exhibit unusual conductivity characteristics:[19] at low Mn concentrations the system is semiconducting; around 4%–5% Mn metallic conductivity is reported, and with a further increase of the Mn content the material becomes again insulating. Interestingly enough, the Curie temperature also exhibits a maximum around the same Mn concentration. These two observations suggest that the density of holes is actually decreasing with Mn concentrations above 5%, and this might be directly reflected by the Fermi level position relative the VBM. In Fig. 2 we show a set of valence-band spectra from samples with varying Mn contents, aligned at the Fermi level. The photon energy used in this case was 38.5 eV, chosen to probe the phase space region around the X_3 point. This emission is reflected by the prominent peak around 7.5 eV. Considering the high density of defects in LT-GaAs and in GaMnAs (in the range of $10^{20}/cm^2$) it is reasonable to assume that the surface Fermi

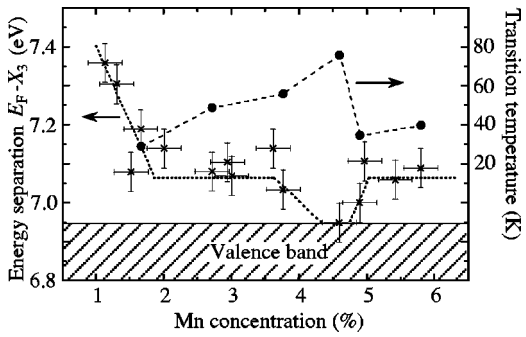

FIG. 3. Fermi level position relative the X_3 critical point as a function of Mn concentration in $Ga_{1-x}Mn_xAs$. Included are also the measured paramagnetic-to-ferromagnetic phase transition temperatures (T_c) for some of the samples (solid circles). The dashed region represents the valence band.

level does not deviate from that in the bulk. This assumption is supported by the fact that no additional spectral broadening that could be expected due to emission from a very narrow band bending region was detected in any spectra. Focusing on the X_3 emission we see that its position is changing with Mn content. This variation is shown more clearly in Fig. 3, where we have plotted the energy separation $E_F - X_3$ for a larger set of samples. Starting at a value of 7.35 eV for clean LT-GaAs, it is reduced and settles at a value of 7.1 eV around 1.5% Mn concentration. This pinning position remains stable for Mn concentrations up to around 3.5% and is likely due to the Mn acceptor level known to be located 113 meV above the VBM.[7] With this interpretation we deduce the VBM to be located around 6.95 eV above the X_3 point, a value well in the range of literature data[20] (6.70–7.1 eV) based on angle-resolved photoemission and x-ray photoemission. A very interesting feature is observed around 4%–5% Mn concentrations, where E_F appears to drop to a position close to the VBM. As already mentioned, samples in this concentration range are reported to exhibit metallic conductivity. The present observations are fully consistent with such behavior. We also note that the low position of E_F implies an increased density of holes, which in turn may be the explanation for the relatively high Curie temperatures previously found in this range of Mn concentrations. This is also verified in the present experiment as seen in Fig. 3. The fact that the maximum T_c is observed in the most metallic samples (i.e., those for which the Fermi level is close to the VBM) is in good agreement with existing theories describing magnetism in GaMnAs. We note that the maximum T_c value of the samples shown in Fig. 3, close to 80 K, is lower than the 110 K reported by Ohno *et al.* (see Ref. 1). We attribute this to the influence of As antisites on T_c. The growth temperature of all the samples shown in Fig. 3 was close to 220 °C and no post growth annealing was performed after the MBE growth. Thus the maximum T_c value can be expected to be smaller than the values for annealed samples reported by Ohno *et al.* (110 K) and by other groups.[11,21] The most intriguing observation is the shift of E_F back into the band gap region with further increased Mn content. This is consistent with the reported metal-insulator transition,[19] though the present results suggest that the reason for the insulating properties is not impurity scattering, but rather a true reduction of charge carriers. It is possible that this could be related to the growing density of As antisite defects within GaMnAs with increasing Mn concentration. An increase of the As antisite density should influence the Fermi level position in the observed direction (due to their donor character). Furthermore, it has been found[22] that inclusion of Mn in the GaAs host matrix leads to a higher As antisite density even if the growth conditions are otherwise the same.

IV. CONCLUSIONS

The present investigations of valence-band photoemission from $Ga_{1-x}Mn_xAs$ compounds show two new effects. First, we find that the spectral changes induced by the Mn atoms depend on the Mn concentration, and second, we observe that the position of the Fermi level also changes with Mn content. None of these features has been reported previously. The varying shape of the Mn-induced valence-band structures directly shows that the Mn-host interaction cannot be treated with a local model. As to the Fermi level variations, we note that the minimum observed around 3.5%–5% Mn content coincides with previously reported metallic conductivity and also with the range of maximum paramagnetic-ferromagnetic transition temperatures.

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