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Identification of different electron screening behavior between bulk and surface of (Ga,Mn)As

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We report x-ray photoemission spectroscopy results on (Ga,Mn)As films as a function of both temperature and Mn doping. Analysis of Mn 2p core level spectra reveals the presence of a distinct electronic screening channel in the bulk, hitherto undetected in more surface sensitive analysis. Comparison with model calculations identifies the character of the Mn 3d electronic states and clarifies the role, and the difference between surface and bulk, of hybridization in mediating the ferromagnetic coupling in (Ga,Mn)As.

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The extensive effort in understanding the mechanisms at the origin of ferromagnetic order in diluted magnetic semiconductors (DMS) has resulted in a wealth of new concepts in spintronics [1–4]. In the case of (Ga,Mn)As – the prime representative of a DMS material – recent advances have demonstrated that the properties of the first few atomic layers play a fundamental role for possible spintronics applications [5, 6]. Manipulation of the carrier density, and consequently of the magnetic properties, has been demonstrated via electrical gating [7, 8]. Efficient spin injection from (Ga,Mn)As into GaAs and room temperature ferromagnetism of thin layers of (Ga,Mn)As have been achieved in engineered heterostructures [9] or in hybrid structures comprising of ferromagnetic overlayers grown on DMS [10, 11]. Although many experimental and theoretical efforts have been focused on reaching a reliable control and description of surface and interface effects of (Ga,Mn)As, a basic understanding of the differences between surface and bulk electronic properties is still lacking [12–14] and fundamental open questions persist regarding the spatial homogeneity of the coupling between Mn ions and the role, understanding and control of the reduced carrier density at interfaces [7]. A meaningful experimental investigation of these important properties requires on the one hand the ability to probe the electronic and magnetic properties with chemical sensitivity and on the other hand an adequate control over the depth information. Photoemission spectroscopy (PES), and in particular x-ray based PES, is a powerful method that possesses these prerequisites. Reports of PES on DMS, however, are scarce [15, 16], which is mainly due to the extreme surface sensitivity of this technique, which in turn requires surface preparation methods, often producing a severe modification of the surface and interface electronic properties [17, 18].

Here we report on high resolution hard x-ray PES (HAXPES) data obtained on (Ga,Mn)As films. Owing to the unusually high achievable bulk sensitivity, with probing depth $\geq 100 \, \text{Å}$, we are able to deduce striking differences in electron screening between surface and bulk. We observe the presence of extra features in the Mn 2p core level spectra: using model calculations we can ascribe these changes to the electron screening process, which highlights the importance of the d-electron hybridization with respect to the ferromagnetic properties. Mn 2p HAXPES spectra vs. temperature and vs. Mn doping reveal details of the carrier properties in terms of localized vs. itinerant behavior.

The ferromagnetic (Ga,Mn)As films (Mn 1%, 5% and 13% doping with 50 nm, 35 nm and 18 nm of thickness, respectively) were grown by molecular beam epitaxy (MBE) using a modified Veeco Gen II system. A description of the (Ga,Mn)As sample growth, preparation and characterization is found in Ref.[18, 19]. For the present experiment, contamination free surfaces were obtained by HCl etching [17]. The magnetic characterization, before and after the chemical etching procedure, was performed using x-ray magnetic circular dichroism, superconducting quantum interference device magnetometry and magneto-optical Kerr effect on pieces of the very same samples, revealing i) the complete removal of Mn oxide from the surface after chemical etching, and ii) stable long-range ferromagnetic order with $T_c \leq 4 \, \text{K}$, 60 K and 80 K for 1%, 5% and 13% Mn doping, respectively. Post-annealing of the sample has been purposely avoided, in order to exclude MnAs cluster segregation on the sur-
Figure 1. (Color online). (a) Mn 2p PES of (Ga,Mn)As (5% Mn) after HCl chemical etching. The overall energy resolution was set to 250 meV (hv = 900 eV) and 400 meV (hv = 5953 eV). Spectra have been aligned to the same relative BE scale without background subtraction. (b) Calculated evolution of the Mn 2p HAXPES spectral features as a function of the hybridization parameter \( V \). Spectra (offset for clarity) are convoluted with a Lorentzian (\( \Gamma = 0.25 \) eV (leading peak), 0.5 eV (rest)) and Gaussian (\( \sigma = 0.15 \) eV) to account for lifetime and experimental resolution, respectively. Inset: energy level diagram of the \( d \)-states in the initial and final state before hybridization and without crystal field and multiplet structure.

The energy of each possible final state depends on how effective the core hole is screened by the valence electrons.

The inset in Figure 1 shows the schematic energy level diagram for the Mn 3d configurations in (Ga,Mn)As in the initial and final states of the PES process in the absence of hybridization (\( V=0 \)) and without multiplet structure. In the initial state, \( d^{5} \) is the lowest configuration, but with significant mixing of \( d^{4} \) and \( d^{6} \), where \( \hbar \) denotes a combination of appropriate symmetry of states characterizing a hybridized valence band hole near the Fermi level. Although the \( d^{5} \) and \( d^{6} \) configurations are close in average energies, the lowest energy levels in the initial state are mainly \( d^{5} \), because the multiplet structure is...
much broader for $d^6$. In the final states, the $c d^6 h^2$ configuration, where $c$ denotes the core hole, is pulled down in energy (i.e. towards lower BE) by an amount $Q$ due to the core-valence Coulomb interaction compared to the $cd^5 h$ configuration. An essential point to note, is that the relative energy positions of the $d^6$ and $d^5$ configurations are reversed in the final states compared to the initial state. Turning on the hybridization between the configurations, the $cd^6$ peak increases in intensity. Thus this low-BE peak corresponds to the well-screened state, which has an extra $d$ electron. Figure 1(b) shows the calculated Mn $2p$ PES for different $V$. Keeping the energies of the $d$ levels fixed, $V$ varied between 1 and 4 eV. For large hybridization the spectrum reflects mainly $cd^6$ final states. Upon decreasing the hybridization, the $cd^5$-like final states, seen up to 6 eV above the main peak, strongly gain in relative intensity. By comparing the calculations with the experimental data in Fig. 1(a) we are now able to unambiguously assign the extra peak at the low BE side of the Mn $2p$ HAXPES spectrum to the well-screened $cd^6$-like peak, whereas the broader peak at 1-2 eV higher BE is the well-screened peak which is a mixture of $cd^6$ and $cd^5$ final states, which in addition shows multiplet structure. The experimental HAXPES spectra agree best with a mixing of $V \approx 2.5$ eV. The absence of the well-screened peak in the low photon energy PES spectrum of Fig. 1(a), and by implication a small value of $V$, indicates a more localized electronic environment in the vicinity of the surface. This finding is in full agreement with the results presented in Ref. 7 where it was shown that a significant carrier depletion layer exists at the surface of (Ga,Mn)As. For the given values of $\Delta$ and $U$ the multiplet calculations with different $V$ give the $d^n$ weights in the initial state, as shown in Table I. The meaning of the hybridization parameter $V$ becomes clear from the corresponding $d^n$ weights (in %), e.g., a larger $V$ results in a broader spread over the $d$-levels.

Figure 2 shows the Mn $2p$ HAXPES spectra of (Ga,Mn)As (13% Mn, $T_c = 80$ K) vs. temperature. One observes that the relative intensity of the well-screened peak compared to the poorly-screened peak increases significantly for a temperature below $T_c$. The redistribution of spectral weight is better seen in Fig. 2(b-d), where the differences between three low temperature spectra (100 K, 50 K, 20 K) and the room temperature one are shown, in the Mn $2p_{3/2}$-spectral region. One observes a clear redistribution of spectral weight, where the intensity of the well screened peak increases when lowering the temperature while the peak located around BE $\approx 640$ eV looses spectral weight. From the comparison between experiments and calculations we are able to clarify that: i) a higher relative intensity of the well-screened peak means a larger hybridization, i.e., the Mn $d$ states become less localized; ii) a change in hybridization and a redistribution of the $d$-weight in the electron screening is observed upon crossing $T_c$, i.e., the hybridization increases when ferromagnetic order settles in (Ga,Mn)As. The one-to-one correspondence between the intensity change of the well-screened peak and the collective electronic behavior is confirmed in Fig. 2(e), where Mn $2p$ HAXPES spectra from a (Ga,Mn)As sample with 1% Mn doping are compared vs. temperature. In this case $T_c \leq 4$ K, and within our detection limit, no intensity change is observed down to 20 K. This suggests further that the hybridized $d^6$ electronic character is mainly responsible for mediating the ferromagnetic coupling among the localized substitutional Mn atoms.

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Table I. Calculated ground state $3d$ weights (in %) of Mn atoms vs. hybridization parameter $V$ (in eV). In bold, the $d^6$ configuration, responsible for the observed extra peak in Mn $2p$ HAXPES.
The difference in the screening ability between surface and bulk is schematically illustrated in Fig. 3, where in panel (a) we present the zincblende structure of GaAs (blue and green spheres for Ga and As, respectively) with randomly substituted (10%) Mn atoms (red spheres) on the Ga sites. Each Mn atom carries a cloud of partially localized d electrons, represented as yellow spheres in panel (b). A difference in the spatial extension of the electronic cloud at the surface and in the bulk, as derived by the calculation, is obtained for different screening length (hybridization): near the surface (top side) the d electrons are more localized than in the bulk (bottom side), which is indicated by a smaller (larger) radius of the spheres. In panel (c), a cross section of panel (b) shows that only in the bulk the d electrons will percolate through the lattice, i.e. a sizeable overlapping of electronic clouds is found, giving rise to long-range ferromagnetic ordering below $T_c$.

In conclusion, we have performed bulk sensitive PES of the Mn 2p core level of (Ga,Mn)As: the presence of a strong feature at the low BE side of the 2p$_{3/2}$ peak reveals that the electronic structure of the bulk and the surface of (Ga,Mn)As are profoundly different. This feature shows a noticeable increase for temperatures below $T_c$ and is strongly related to the ferromagnetic phase of (Ga,Mn)As. Anderson impurity model calculations establish electron screening as its origin, which is strongly suppressed close to the surface. This result is expected to help to understand and to control the electronic and magnetic surface properties of (Ga,Mn)As, which are of importance in spintronics applications.

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