Magnetic ordering of Mn overlayers on GaAs(100)

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Growth of Mn on GaAs(100) is studied by photoemission and electron-energy-loss spectroscopy. We find that the first layer of Mn grows on GaAs(100) in a two-dimensional mode, where about 10% of the Mn atoms take part in the chemical reaction with the substrate. The electronic structure of the ultrathin film of Mn is found to be very different from that of bulk α-Mn, and the possibility that magnetic ordering exists in the ultrathin overlayer of Mn is proposed.

Magnetism of thin films has been an exciting and controversial area. Magnetic properties of a few atomic layers turn out to be very sensitive to strain, interaction with substrate, and temperature.[1] Therefore, one hopes it might be possible to tailor the magnetic behavior of atomic layer films and superlattices in the future, when their growth can be brought under complete control. On the other hand, growth of ferromagnets on semiconductors has attracted a fair amount of interest, due to the possibility of coupling semiconductor logic with nonvolatile magnetic memory.[2] The transition metal Mn, which has a half-filled $3d$ shell, has very interesting properties. The magnetic structures depend strongly on the corresponding crystallography,[3] and it is believed that the detailed study of Mn should be helpful to establish the general interplay between crystallography and magnetic structures.

Due to the translation symmetry breaking as well as the overlayer-substrate interaction, the magnetism of Mn thin films might be very different from that of bulk Mn. Consequently, it is important and interesting to explore thin-film magnetism of Mn. In fact, Drude and Himpsel declared in their experiment that the first layer of Mn deposited on a Ag(100) surface at room temperature showed ferromagnetic behavior,[4] despite the fact that bulk α-Mn phase is nonmagnetic at this temperature. However, it will be also interesting to address the same problem for the ultrathin film of Mn prepared on semiconductor substrates such as GaAs, because the overlayer-substrate interaction could be very different. Such kinds of studies will be useful to understand and even to separate the intrinsic (due to the broken translation symmetry) and the extrinsic (due to the overlayer-substrate interaction) contributions in the ultrathin film magnetism of Mn. In this paper, we report the results concerning the electronic structure of the ultrathin film of Mn, deposited on a GaAs(100) surface at room temperature. The possibility that the magnetic ordering exists in the ultrathin overlayer of Mn is recognized.

The experimental data presented in this paper were taken in two different systems. One was at the VG ESCALAB-5 system, connected with a molecular-beam epitaxy growth chamber, at Fudan University in Shanghai. The valence-band spectra were taken with a photon energy of 21.2 eV from a He lamp with an estimated resolution of 0.2 eV. The electron energy-loss spectra were taken with electron energy of 200 eV with the estimated resolution of 1 eV. The other was at the photoemission beam line of the National Synchrotron Radiation Laboratory, University of Science and Technology of China at Hefei. The photon energy used was from 70 to 160 eV with the estimated resolution of $E/\Delta E \sim 500$. The Te-doped GaAs(100) single-crystal wafers were polished and prepared by ordinary device process before being inserted into the UHV systems. Final cleaning was achieved by several cycles of 800-eV argon bombardment followed with 500 °C annealing in UHV, until a clear (4×1) low-energy electron diffraction pattern was observed. The Auger spectra and the x-ray photoelectron spectra show no evidence of either carbon or oxygen contamination. In both systems, the background pressures were lower than 2×10^{-8} Pa in measurement, and it was lower than 1×10^{-7} Pa during Mn deposition. The Mn ovens were operated at 800 °C yielding a flux of 2 Å/min, according to the quartz crystal monitors. In this paper, the coverage of Mn is expressed in monolayers (ML) with 1 ML=0.8 Å relative to the GaAs(100) surface atomic density of 6.3×10^{14} atoms/cm^{-2}.

The determination of the growth mode of a Mn overlayer on a GaAs(100) surface is an essential step to a full assessment of its electronic structure. It is the submonolayer region we are mostly interested in here. The experimental method used is to follow the As dangling-bond-induced surface-state emission as a function of Mn coverage—a well-accepted and widely used method, regarded as a fingerprint in determining the growth modes in a submonolayer region on III-V semiconductor surfaces.[5] Figure 1 shows the valence-band photoemission spectra taken with photon energy of 21.2 eV from a He

lamp as a function of the coverage of Mn. Because this photon energy is sensitive in detecting the substrate GaAs signals according to Yeh and Lindau,[6] the attenuation of the surface states of GaAs(100) can be clearly followed. In the spectrum of a clean GaAs(100) surface marked by "clean," the surface states caused by the surface As dangling bonds are superimposed on the background of bulk GaAs sp^3 states. The peak position of the surface states was determined to be at ~ 1.2 eV below the Fermi edge by hydrogen adsorption. The attenuation of the surface state emission as a function of Mn coverage is plotted at the right upper corner of Fig. 1, from which it can be clearly seen that the surface-state emission disappears completely at the Mn coverage $\theta < 1$ ML. This result indicates that almost all the surface As dangling bonds are disturbed during the first-layer Mn deposition, i.e., the two-dimensional growth mode of Mn on GaAs(100). In other words, if the initial growth were in a cluster mode, some of the As dangling bonds would be undisturbed, and the decrease of the surface state peak in Fig. 1 would be much slower.[5] The growth mode of Mn on GaAs(100) in an early stage has also been determined by the electron-energy-loss spectroscopy, where the attenuation of the surface-state emission induced by the surface Ga dangling bond of GaAs(100) is obtained and the layerwise growth mode in the first layer of the Mn deposition is verified again. It is therefore concluded that the first layer of Mn grows in a layerwise mode on the GaAs(100) surface.

For the Mn/GaAs(100) interface, the assessment of the overlayer-substrate interaction is also important for the later interpretation of the electronic structure of the Mn overlayer. In Fig. 2, the Ga 3*d* core-level spectra, as a function of the Mn coverage, are used for this purpose, while the As 3*d* spectra are omitted because of little changes found in the submonolayer region. As expected, the chemical reaction is indeed found at the interface; corresponding to the shoulder and appearing and developing at the higher kinetic energy side. It is the change in the submonolayer region that we are interested in, and the percentage of the reacted Mn atoms in the first layer will be estimated. At the right upper corner is shown the spectrum of 1.3 ML, which is decomposed to two peaks, corresponding to the unreacted and the reacted phases, respectively. Thus, the relative intensity of 4% for the reacted phase is easily obtained. After doing a simple calculation using this value by taking into account the escape depth of the photoelectron, we finally obtain that the percentage of the reacted Mn atoms is less than 10%. Of course, it is assumed in the simple calculation that the chemical reaction happens only on the top layer of GaAs and the interface diffusion is neglected. It should be mentioned that our estimation above is reasonable, by comparing with the result of Stiles *et al.*,[7] where they showed both the spectra of Ga/GaAs(110) and Mn/GaAs(110). It was obvious from their results that the reacted Ga signal at the Mn/GaAs(110) interface in submonolayer region was much smaller than that at the Ga/GaAs(110) interface for the same coverage. Thus, we come to the conclusion that only a small part of the first-layer Mn atoms on the GaAs(100) surface takes part in the chemical reaction with the substrate and that most of the deposited Mn atoms are unreacted and can still be regarded as an Mn overlayer.

After considering the growth mode and the overlayer-substrate interaction, we are now exploring the electronic structure of the ultrathin overlayer of Mn on the GaAs(100) surface. Figure 3 shows a series of valence-band photoelectron spectra of Mn/GaAs(100) interface taken with a photon energy of 98 eV by synchrotron radiation as a function of Mn coverage. According to Yeh and Lindau,[6] the photoionization cross section of Mn 3*d* at this photon energy is larger than that of GaAs(4*sp*) and Mn(4*sp*) by a factor of 2 orders of magnitude, so the contribution from Mn 3*d* can be detected at a very early stage and is dominant over all the Mn coverage. This is

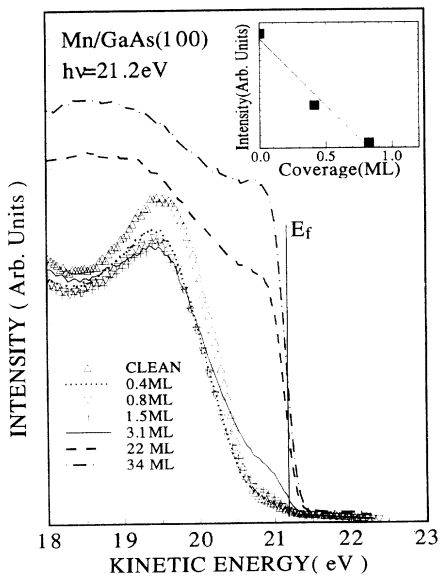

FIG. 1. Valence-band photoelectron spectra for the Mn/GaAs(100) interface as a function of Mn coverage, $h\nu = 21.2$ eV.

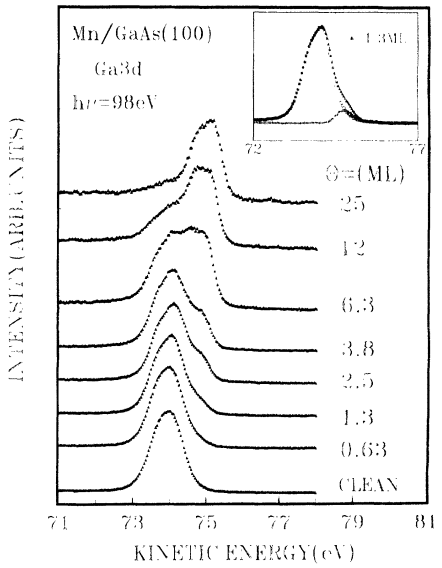

FIG. 2. Ga 3*d* core-level photoelectron spectra for the Mn/GaAs(100) interface as a function of Mn coverage, $h\nu = 98$ eV.

clearly seen by the enlarged curves at the right upper corner of Fig. 3, from which a state at 3.9 eV below Fermi level (E_f) is shown even at the coverage of $\theta < 1.3$ ML. When the Mn coverage is further increased, the intensity of the new peak becomes stronger at first ($\theta < 2$ ML), then remains almost unchanged ($\theta < 3.8$ ML), and finally disappears in the strong background of the α-Mn $3d$ induced peak (at ~ 3 eV below E_f). Because of the significant difference between the valence-band spectra of the ultrathin films of Mn and that of bulk α-Mn, it is thus clear that the electron structure of the ultrathin overlayer of Mn on the GaAs(100) surface is very different from that of bulk α-Mn. We are going to show in the following that the origin of the 3.9-eV peak is caused most likely by the majority-spin band of Mn $3d$.

As pointed out, the growth of Mn on a GaAs(100) surface is in a two-dimensional mode for the Mn coverage $\theta < 1$ ML. Consequently, using an average for the Mn coverage as low as $\theta \sim 0.13$ ML, a Mn atom on the surface should have no coordinated Mn atoms around it. It turns out that the electronic structure in such a case must lie in between the following two extreme cases. One of the extremes is that the interaction between the Mn atom and the GaAs(100) substrate can be neglected entirely, going back to a situation of an isolated Mn atom with the electron configuration of $3p^6 3d^5$, which has all the $3d$ majority-spin (or up-spin) levels occupied and all of the minority-spin (or down-spin) levels empty. This corresponds to a high-spin state of ^6S, or a magnetic ordering state with a net magnetic moment. The other extreme is that the interaction between Mn and the substrate is so strong that the Mn atom replaces a Ga atom in GaAs, with the Mn atom locating in a tetrahedral environment of As atoms. Similar to the result of $A^{II}_{1-x}Mn_xB^{VI}$,[8] the Mn $3d$ induced levels are superimposed on the band structure of GaAs, and are also split into two manifolds, i.e., the occupied majority-spin band and the unoccupied minority-spin band. This is again a magnetic ordering state. Thus, as a case lying in between the two extremes, the peak which appeared at 3.9 eV at $\theta \sim 0.13$ ML must be from the Mn $3d$ majority-spin band as well.

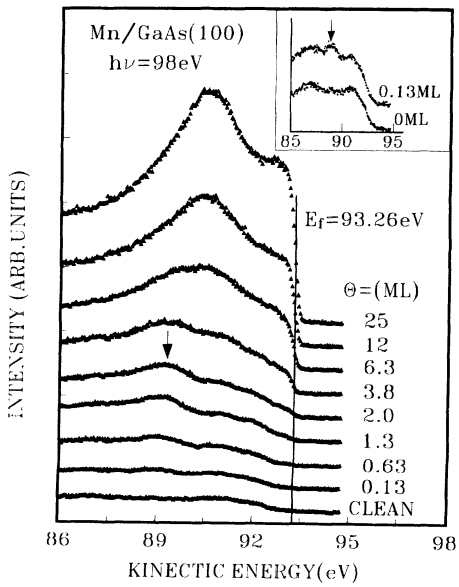

FIG. 3. Valence-band photoelectron spectra for the Mn/GaAs(100) interface as a function of Mn coverage, $h\nu = 98$ eV.

However, as the Mn coverage increases, due to the adatom-adatom interaction, the electronic structure of the Mn overlayer does not necessarily lie in between the above two extremes. However, the main features of the experimental valence-band spectra are found to be almost the same as the Mn coverage increases up to 1.3 ML. One explanation is that the Mn adatom-adatom interaction is weak so the same mechanism for the $\theta = 0.13$ ML still plays the role. The other explanation, however, is that the Mn adatom-adatom interaction is not weak but is different from that in the nonmagnetic bulk α-Mn phase, resulting in the possibility of the Stoner's exchange splitting of the majority- and minority-spin bands with the former shifting downwards and the latter upwards. This also corresponds to a magnetic ordering state. It is evident from Fig. 3 that the spectrum weight for the submonolayer Mn on GaAs(100) does shift downwards from the Fermi level, compared to the situations for the higher Mn coverage of $\theta > 2$ ML. This is consistent with the above model, because the adatom-adatom interaction for the higher Mn coverage resembles the bulk α-Mn phase which is nonmagnetic. On the other hand, for a half-filled $3d$ band, it is unlikely to have such a large downward shift of the $3d$ density of states, while still maintaining a nonmagnetic state. Similar results were also revealed (without explanation) by Stiles *et al.* at the Mn/GaAs(110) interface prepared at low temperature (80–100K),[7] where the chemical reaction was strongly limited. However, it can also be well explained by the above ideas.

An interesting question to ask is when or at what coverage the similarity between the ultrathin overlayer of Mn and the bulk α-Mn phase shows up, or the magnetic ordering to nonmagnetic ordering happens. To answer this question, we subtract the clean spectra from that of $\theta = 1.3$ and 2 ML, respectively, and obtain the contributions of the Mn ultrathin films themselves, which are now shown in Figs. 4(a) and 4(b). Besides, we subtract the spectrum of $\theta = 1.3$ ML from that of $\theta = 2$ ML, and get the contribution of the addition of 0.7 ML of Mn, as shown in Fig. 4(c). Furthermore, also given in 4(d) is the spectrum representing bulk α-Mn for comparison. From the similarity of 4(c) and 4(d), it is immediately recognized that there are already some α-Mn phases formed on the surface, while no trace is found in the spectra below $\theta = 1.3$ ML. After $\theta > 2$ ML, the α-Mn contribution becomes more dominant. Because there does not exist a critical coverage beyond that where the α-Mn phase appears, there is no well-defined transition point. Anyway, roughly speaking, most of the Mn atoms deposited on the GaAs(100) surface below $\theta < 2$ ML exist in the magnetic ordering phase instead of the nonmagnetic phase. Finally, it needs to be mentioned that the transition observed here is not a phase transition.

It is also realized that the intensity of the electron density of states at the Fermi edge is strongly correlated with the above magnetic-nonmagnetic transition, as it is ex-

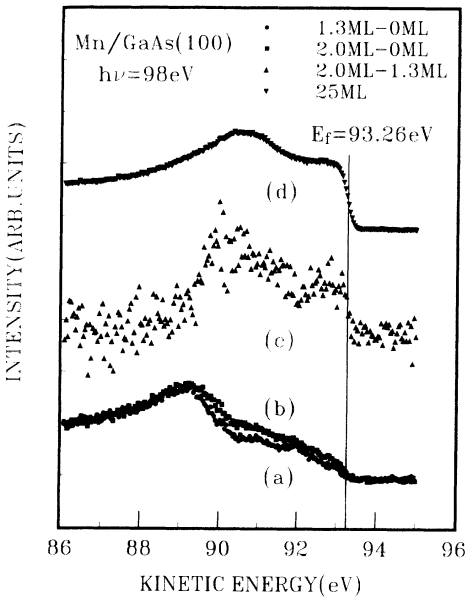

FIG. 4. Valence-band photoelectron spectra, (a) the subtracted spectrum of 1.3 ML of Mn on GaAs(100) from that of clean surface; (b) the subtracted spectrum of 2 ML of Mn/GaAs(100) from that of clean surface; (c) the subtracted spectrum of (b) from (a); (d) α-Mn-like spectrum as a reference, $h\nu=98$ eV.

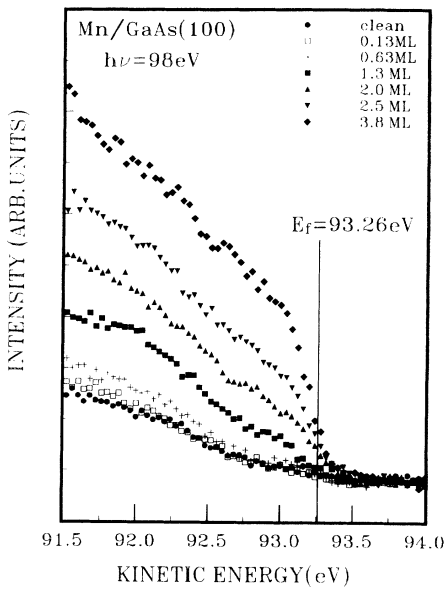

FIG. 5. Valence-band photoelectron spectra near the Fermi edge as a function of Mn coverage, $h\nu=98$ eV.

pected by the Stoner's exchange splitting model for a half-filled $3d$ band of Mn. In Fig. 5, the changes of the density of states at the Fermi edge are clearly shown. It is evident from this figure that no distinct increase of the density of states was found at the Mn coverage $\theta \leq 1.3$ ML, but the situation changes significantly after $\theta > 2$ ML. This result is indeed consistent with the picture given previously. At $\theta < 1.3$ ML, because of the magnetic ordering of the Mn ultrathin films, the Mn $3d$ majority and minority bands are split into two manifolds with the occupied band peaked at 3.9 eV below E_f and the unoccupied band peaked above E_f, leading to the lower density of states at the Fermi level. On the other hand, after $\theta > 2$ ML, the exchange splitting collapses, resulting in the high density of states at the Fermi level as expected for a half-filled $3d$ band.

Finally, it needs to be mentioned that the Mn coverage used above was based on a calculation relative to the surface atomic density of the GaAs(100) substrate (1 ML=0.8 Å). In fact, the bulk atomic density of Mn is much larger than that of GaAs, which could lead to the higher surface atomic density of Mn on the GaAs(100) surface. It is reasonable to assume that the first layer of Mn atoms covers the GaAs(100) surface in the γ-Mn phase.[9] In this case, the above Mn coverage of $\theta=1.5$ ML means actually almost one monolayer of γ-Mn atoms on GaAs(100). It is thus clear that the first layer of deposited Mn on GaAs(100) is magnetic. It is interesting to notice that the first layer of Mn is magnetic both on Ag (Ref. 4) and GaAs substrates, although the interactions between Mn and these two substrates are very different. It might indicate that the magnetic ordering is an intrinsic property of the Mn ultrathin film itself. In other words, the translation symmetry breaking from the three-dimensional (3D) Mn system to the quasi-2D system might change the electron-electron interaction, then cause the magnetic ordering in the ultrathin film of Mn.

In conclusion, it is identified in the experiment that Mn grows on GaAs(100) in a two-dimensional mode in the first layer. Meanwhile, it is found that the ultrathin film of Mn on a GaAs(100) surface exhibits the magnetic ordering. It is proposed that the 3D to 2D symmetry breaking plays an important role in establishing the magnetic structure of the ultrathin Mn overlayer.

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