

## Synchrotron-radiation study of the electronic structure of fcc Mn thin films grown on a GaAs(001) surface

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(Received 30 June 1994; revised manuscript received 28 November 1994)

The epitaxial growth of metastable fcc Mn thin films on a GaAs(001) surface has been achieved at a substrate temperature of 400 K. The development of the fcc Mn thin films as a function of coverage is studied by photoemission with synchrotron radiation. The electronic density of states below the Fermi edge of the bulk fcc Mn phase is measured experimentally. A significant difference of the electronic structures is observed between the metastable fcc Mn phase and the thermodynamically stable  $\alpha$ -Mn phase. Possible mechanisms are proposed to account for the experimental result.

### INTRODUCTION

Epitaxial growth of various stable and metastable phases of 3d transition metals on lattice-matched substrates has opened a field of experimental and theoretical physics.<sup>1</sup> Of the 3d transition metals, Mn provides the most varied family of crystallographic phases.<sup>2</sup> Besides the room-temperature stable  $\alpha$ -phase, a complex cubic structure with 58 atoms per unit cell, there are three high-temperature phases as well, i.e., the  $\beta$ ,  $\gamma$ , and  $\delta$  phases, where the  $\gamma$  and  $\delta$  phases are simple face-centered-cubic and simple body-centered-cubic structures, respectively. A number of theoretical works in recent years have dealt with the electronic structures and magnetic properties of the metastable  $\gamma$  and  $\delta$  phases, and some interesting predictions have been made awaiting<sup>3-5</sup> further experimental verification. Meanwhile, considerable efforts have been made to stabilize the metastable Mn phases at low temperature by the epitaxial growth of Mn on various lattice-matched substrates.<sup>6-14</sup> For example, the metastable body-centered-tetragonal phases of Mn were grown both on the Pd(001)<sup>10</sup> and Ag(001) surfaces,<sup>11</sup> with lattice constants of  $a = 0.389$  nm and  $c = 0.343$  nm for the former and  $a = 0.409$  nm and  $c = 0.331$  nm for the latter, and they might be regarded as tetragonal distorted versions of the fcc phase. It was also reported that the Mn structure in the (Mn/Ag)<sub>n</sub>/Ag(001) superlattices with 3-ML Mn layers was nearly fcc.<sup>12</sup>

As far as we know, no experimental studies have been done revealing the electronic structure of the fcc Mn phase, even for the distorted fcc phases. In this paper, we first show direct evidence of the achievement of preparing

single-crystalline fcc Mn films on a GaAs(001) surface using the molecular-beam epitaxy (MBE) technique, then the electronic structure of the fcc Mn thin films as a function of coverage is measured by photoemission with synchrotron radiation. A significant difference between the fcc Mn phase and the room-temperature stable  $\alpha$  phase is observed. Possible mechanisms are proposed to explain the difference.

### EXPERIMENT

The experimental data presented in this paper were taken in two different systems. The *in situ* reflection high-energy electron-diffraction (RHEED) characterization as well as the x-ray photoemission spectroscopy (XPS) measurements were carried out in a VG-ESCALAB-5 electron spectrometer system connected with a MBE growth chamber at Fudan University in Shanghai. The other data were collected 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 an estimated resolution of  $E/\Delta E \sim 500$ . All the photoemission spectra were measured by an angle-integrated analyzer located at the normal emission position.

The Te-doped GaAs(001) single-crystal wafers were polished and prepared by an ordinary device cleaning process before being loaded into the UHV systems. The final substrate cleaning in UHV was achieved by several cycles of 800-eV argon bombardment followed with 500°C annealing until a clear ( $4 \times 1$ ) low-energy electron-diffraction (LEED) 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  $2 \times 10^{-8}$  Pa in measurement, and lower than  $1 \times 10^{-7}$  Pa during Mn deposition. The Mn ovens were operated at 800 °C, yielding a flux of 0.2 nm/min, according to the quartz-crystal monitors. In this paper, the coverage of Mn are expressed in monolayers (ML) with 1 ML=0.08 nm relative to the GaAs(001) surface-atomic density of  $6.3 \times 10^{14}$  atoms  $\text{cm}^{-2}$ .

## RESULTS AND DISCUSSIONS

First, the achievement of the metastable fcc Mn phase on top of the GaAs(001) surface at a substrate temperature of 400 K is obtained by *in situ* RHEED observation. Figure 1(a) shows the RHEED pattern for a clean surface of GaAs(001) when the incident electron beam was along the  $[1\bar{1}0]$  direction. Figure 1(b) shows the pattern at a Mn coverage of 8 nm, with the incident electron beam along the  $[1\bar{1}0]$  direction. In fact, the spotlike RHEED pattern is the projection of a three-dimensional reciprocal lattice along the  $[1\bar{1}0]$  direction. By comparing the spot spaces with those of a clean GaAs(001) surface, it was easily obtained that the lattice constants of the Mn thin film along the  $[110]$  (in the surface plane) and  $[001]$  (out of surface plane) directions were about 0.368 nm. The fact that the pattern after a 90° rotation along the surface normal was exactly the same as Fig. 1(b) leads to the conclusion that the single-crystalline Mn epilayer has a cubic structure. In addition, Fig. 1(c) shows a pattern after a 45° rotation around the surface normal, so that the electron beam was along the  $[100]$  direction. It can clearly be deduced from this pattern, together with that of Fig. 1(b), that the diffraction spots of the Mn thin film in reciprocal space form a body-centered-cubic lattice. Correspondingly, the real-space Bravais lattice of the epilayer forms a face-centered-cubic structure with a lattice constant of 0.368 nm. Furthermore, this Bravais lattice actually corresponds to the atomic structure of the metastable fcc Mn phase itself; otherwise one would expect at least a factor of 2 change for the atomic density relative to that of  $\alpha$  phase, which is very unlikely to happen for metals.

It should also be mentioned that a lattice constant of 0.362 nm is obtained independently by x-ray-diffraction measurement, which agrees well with the above RHEED result; meanwhile the unrotated bcc structure can be excluded unambiguously.<sup>15</sup>

It is recognized immediately after obtaining the metastable fcc Mn phase that it will be very interesting to explore its electronic structure, since the interplay between the crystallography and the electronic structures is always important. Figure 2 shows a series of valence-band photoelectron spectra of Mn/GaAs(100) interfaces prepared at 400 K, taken with a photon energy of 98 eV by synchrotron radiation as a function of Mn coverage. It should be noted that the absolute intensity for each spectrum is not important, but the relative intensity change among these spectra reflects the change of the density of states near the Fermi edge. According to Yeh and Lindau,<sup>16</sup> the photoionization cross section of Mn  $3d$  at this photon energy is larger than those of GaAs( $4sp$ ) and Mn( $4sp$ ) by a factor of two orders of magnitude, so the Mn  $3d$  contribution starts to show up at a very early stage and becomes dominant before the Mn coverage reaches one monolayer. This can clearly be seen on the enlarged curves at the right upper corner of Fig. 2 from which an additional state at 3.9 eV below  $E_f$  is observed even at a coverage of  $\theta \leq 0.13$  ML. When the Mn coverage is further increased, the intensity of the peak becomes stronger and is gradually mixed with the density of states appearing near the Fermi edge. It is found that the line shape of the valence-band spectra at  $\geq 25$  ML remains unchanged, which indicates that the distribution of the electronic density of states near the Fermi edge at about 25 ML reaches to that of a bulk fcc Mn phase.

A comparison is now made for the valence-band spectra between the above fcc Mn bulk phase prepared at 400 K and the  $\alpha$ -Mn bulk phase prepared at 300 K (room temperature). Figure 3 shows the two valence-band spectra, between which a significant difference in line shape is observed. Compared with the  $\alpha$ -Mn bulk phase, the fcc Mn phase has an electronic density of states lower at the Fermi edge and far higher below the Fermi edge. Since it is reasonable to believe that the  $3d$  electron configurations of Mn  $3d^5$  remain the same from the  $\alpha$ -Mn metal phase to the fcc Mn metal phase, the result

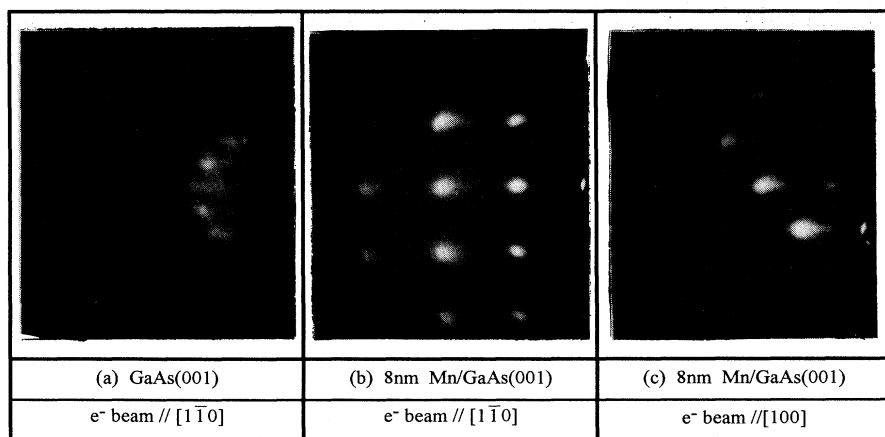


FIG. 1. RHEED patterns for a GaAs(001) clean surface, and an 8-nm fcc Mn thin film grown on a GaAs(001) substrate.

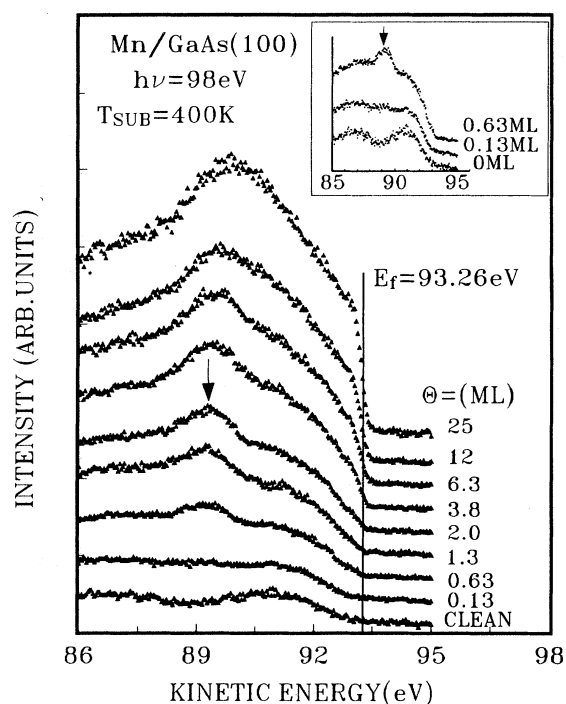


FIG. 2. Valence-band photoelectron spectra for the fcc Mn/GaAs(100) interface as a function of Mn coverage,  $h\nu=98$  eV.

simply indicates the fact that a redistribution of the electronic density of states below the Fermi edge occurs; i.e., a downward shift of the occupied  $3d$  electron density of states for the fcc Mn phase. Meanwhile, an upward shift of the unoccupied  $3d$  electron density of states above the Fermi edge for the fcc Mn phase should also be expected, because the density of states at the very Fermi edge has a

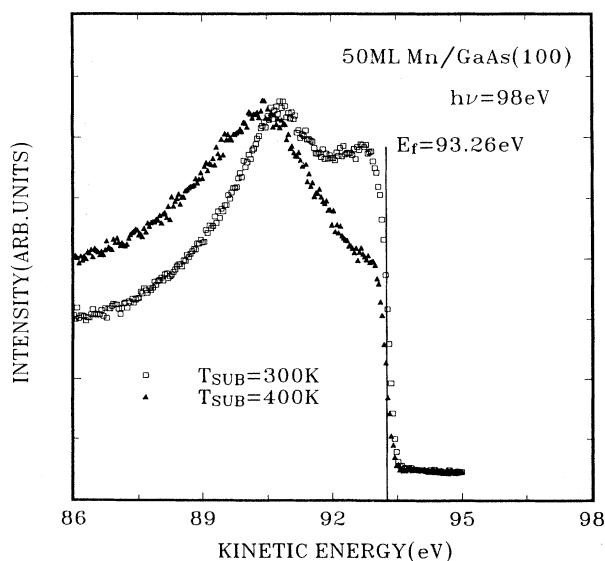


FIG. 3. Comparison of the valence-band spectra for the fcc Mn bulk phase and the  $\alpha$ -Mn bulk phase.

single value both for unoccupied and occupied states. An interesting question to ask at this point is what mechanisms are responsible for the splitting of the occupied and unoccupied  $3d$  states. Among numerous possibilities, three are proposed here because they are perhaps better defined and can be checked later on by further experiments and theoretical calculations. The first possibility could be due to the fact that the electron localization occurs during the fcc Mn phase, no matter whether it is caused by one-particle-type or Mott-Hubbard-type mechanisms.<sup>18</sup> However, it is very unlikely that such a localization can occur in a bulk metal. The second possibility could be due to the fact that changing the lattice symmetry between the  $\alpha$ -Mn and fcc Mn phases leads to a redistribution of electron density of states near the Fermi edge. It is certainly not unlikely in principle, but needs to be confirmed by further theoretical calculations to account for such a large change. The third possibility could be due to Stoner's exchange splitting of the  $3d$  majority- and minority-spin bands. In fact, the overall features of the experimentally measured fcc Mn valence-band spectrum agree qualitatively with the calculated density of states for a magnetically ordered fcc Mn phase,<sup>5</sup> while a quantitative agreement between absolute peak positions is not expected since the lattice constant used in the calculation is much larger than what we observed here in experiment. Again, a direct magnetic measurement *in situ* is needed to verify the magnetic properties of the fcc Mn thin films.

In addition to the significant difference found between the metastable bulk fcc Mn phase and the thermodynamically stable bulk  $\alpha$ -Mn phase, it is also interesting to compare the development of the valence-band photoemission as a function of coverage between the 400- and 300-K prepared Mn/GaAs(001) interfaces. It is noted in Fig. 2 that, similar to the room-temperature case,<sup>17</sup> much of the density of states appears far below the Fermi edge at the initial stage of the Mn deposition, and that the Fermi edge emission starts only after the coverage exceeds 2 ML. However, the difference begins to develop as the Mn coverage increases. For the 300-K prepared Mn/GaAs(001) interface, on the one hand, the main features of the experimental valence-band spectra change quickly to the  $\alpha$ -Mn situation, while on the other hand, for the 400-K prepared Mn/GaAs(001) interface, the main features remain similar as the Mn coverage increases.

To achieve a better understanding of the 400-K prepared fcc metastable Mn thin films on the GaAs(001) surface, it is important and necessary to know in some detail about the interface formation and the interface chemistry. It should be emphasized first that the contamination in the UHV chamber during the experiment can be ruled out, based on the facts that not only can no traces of carbon and oxygen contamination be seen by Auger electron spectroscopy, but also that no traces of an O  $2p$  contribution are observed in the valence-band spectra at about 6 eV below the Fermi edge, which is very sensitive to the oxidation of the Mn thin films—a common problem when working on the  $3d$  transition-metal ultrathin films.

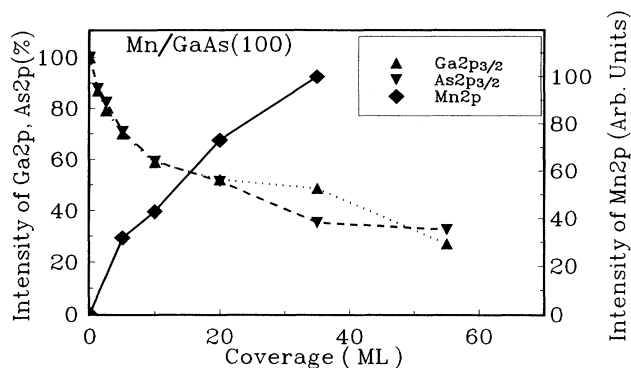


FIG. 4. As  $2p$ , Ga  $2p$ , and Mn  $2p$  core-level photoelectron spectra for the fcc Mn/GaAs(100) interface as a function of Mn coverage,  $h\nu=1486.6$  eV.

For the 300-K case, it was demonstrated by surface states decay both from ultraviolet photoemission spectroscopy (UPS) and electron-energy-loss spectroscopy (EELS) that the first-layer growth of Mn on GaAs(001) was in a layerwise mode,<sup>17</sup> and that there was no strong evidence of clustering at the later stage.<sup>19</sup> On the other hand, for the 400-K case, the layerwise mode for the first-layer growth of Mn was also realized,<sup>20</sup> but strong evidence of a cluster growth mode at the later stage is obtained both from RHEED results shown above and the intensity change as a function of Mn coverage for core-level photoelectron spectra of As  $2p$ , Ga  $2p$ , and Mn  $2p$ . Since RHEED patterns for the fcc Mn thin films are spotlike instead of streaklike from a quite early stage (at least  $\sim 4$  ML), this is clearly an indication that the deposited Mn atoms form clusters and that the surface is rough. As shown in Fig. 4, the intensities of the substrate

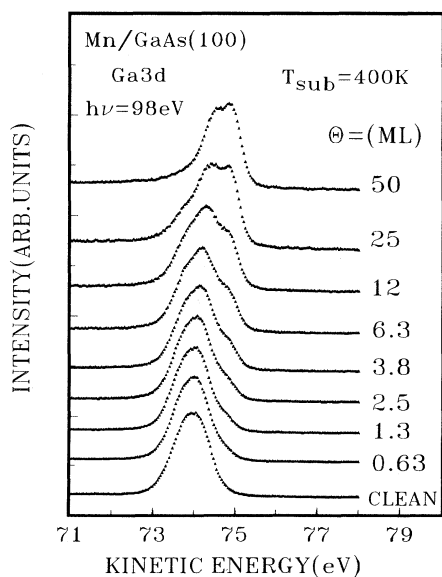


FIG. 5. Ga  $3d$  core-level photoelectron spectra for the fcc Mn/GaAs(100) interface as a function of Mn coverage,  $h\nu=98$  eV.

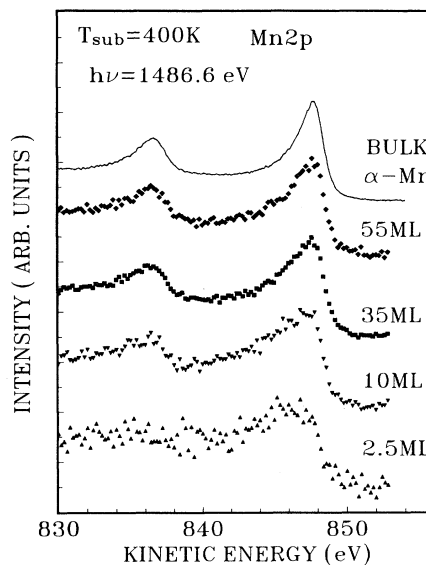


FIG. 6. Mn  $2p$  core-level photoelectron spectra for the fcc Mn/GaAs(100) interface as a function of Mn coverage,  $h\nu=1486.6$  eV.

core-level photoelectron spectra of As  $2p$  and Ga  $2p$  decay much more slowly than an exponential form as a function of coverage, which also strongly suggests that the growth is not a layer-by-layer mode but a cluster growth mode.

Due to the fact that the photoionization cross section of Mn  $3d$  at a photon energy of 98 eV is larger than that of GaAs( $4sp$ ) and Mn( $4sp$ ) by a factor of two orders of magnitude, the dominated contribution of Mn  $3d$  in the valence-band spectra cannot be affected by the cluster growth mode. However, on the other hand, the interface

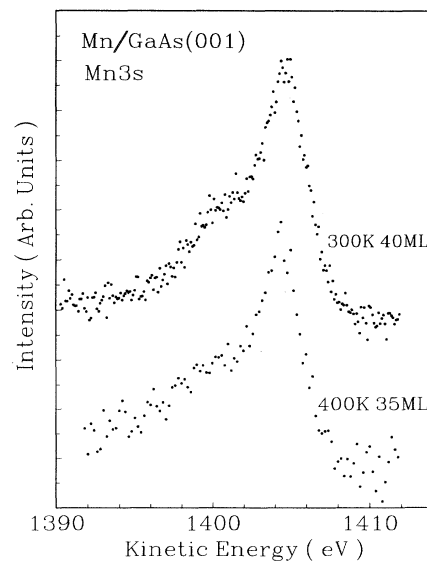


FIG. 7. Comparison of the Mn  $3s$  core-level spectra for the fcc Mn bulk phase and the  $\alpha$ -Mn bulk phase.

chemistry can certainly affect whether the valence-band spectra reflects information about a metallic fcc Mn thin film or just a complicated Mn/GaAs interface.

In Fig. 5, the Ga 3*d* core-level spectra, as a function of Mn coverage, are used for this purpose. As expected, a chemical reaction is indeed found at the interface, corresponding to a shoulder appearing and developing at the higher-kinetic-energy side. Therefore, the Mn/GaAs(001) interface is very complicated for the early stage of Mn deposition. However, instead of dealing with such a complicated early stage interface, we are mostly interested in the property of the bulk fcc Mn thin films at an Mn coverage of about 50 ML. It will be demonstrated in what follows that the interface reaction is no longer an important issue. In Fig. 6, Mn 2*p* photoelectron spectra as a function of Mn coverage are shown to confirm the above argument. It is clearly seen that the Mn 2*p* spectra have become bulklike at 35 ML and do not show any sign of reacted components. This result corroborates the statement that the valence-band spectrum given in Fig. 3 are representative of unreacted fcc Mn phase.

Although there is still a lack of a complete understanding of the correlation between the magnetic orderings (long range or short range) of a material with its 3*s* core-level photoelectron spectra, here in Fig. 7 we still provide

the Mn 3*s* spectra for the bulk fcc Mn and bulk  $\alpha$ -Mn phases as an experimental result. We would rather say that no significant difference is found from the spectra.

In conclusion, we have reported the achievement of fcc metastable Mn thin films grown on a GaAs(001) surface at a substrate temperature of 400 K. The electronic density of states below the Fermi edge of the fcc Mn phase is measured by experiment. A significant difference of the electronic density of states is observed between the metastable fcc Mn phase and the thermodynamically stable  $\alpha$ -Mn phase. Even though the valence-band spectra of fcc Mn and  $\alpha$ -Mn are very different, it is found in experiment that the core-level data (Mn 2*p* and Mn 3*s*) appear almost identical.

#### ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China. Partial supports from the State Education Foundation for Ph.D. Training, the State Education Commission Foundation for Young Faculty at Universities, the State Education Commission Foundation for Returned Overseas Chinese, and the Shanghai Foundation for Returned Overseas Chinese are acknowledged.

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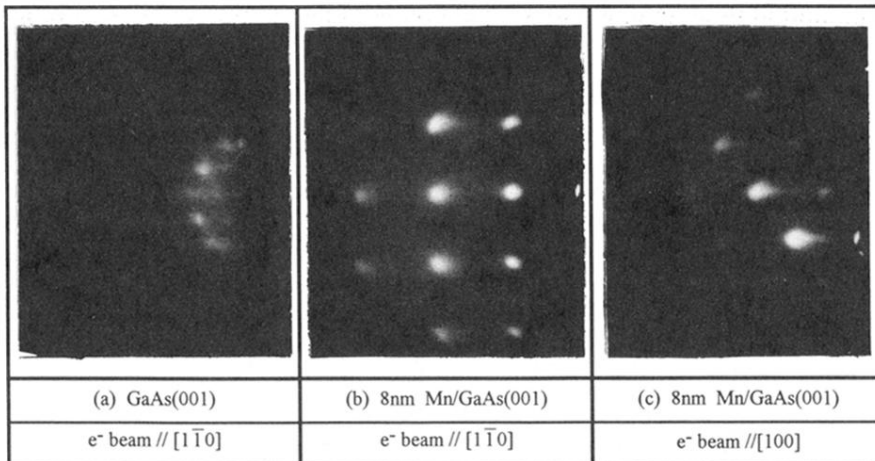


FIG. 1. RHEED patterns for a GaAs(001) clean surface, and an 8-nm fcc Mn thin film grown on a GaAs(001) substrate.