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SOFT-X-RAY PHOTOEMISSION STUDY OF Mn/GaP(100) INTERFACE*

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The interface formation and electronic structures of the Mn/GaP(100) interface are studied with synchrotron radiation photoemission. At the early stage of Mn deposition, Mn covers the whole GaP(100) surface. With the increase of coverage, Ga atoms can be exchanged by Mn atoms and diffuse into the Mn overlayer. However, P atoms remain always near the interfacial region. A significant difference of the electronic structures is observed between the ultra-thin and the thick Mn films. The explanations for this are given in the text.

PACC: 7340; 7360D; 7330

I. INTRODUCTION

An understanding of the interface between transition metals and semiconductors is of both fundamental and technological importance. In very recent years, the study of thin magnetic metal films grown on non-magnetic metals[1-4] or semiconductors[5,6], has received much attention. For example, an uncommon behavior about oscillations in the exchange coupling between two transition metal ferromagnets separated by a non-magnetic transition metal spacer has been observed by many groups.[1-3] On the other hand, growth of magnets on semiconductors[5,6] has also attracted a fair amount of interest due to the possibility of coupling semiconductor logic with nonvolatile magnetic memory.

Among these transition metals, the transition metal Mn, which has a half-filled 3d shell, has very interesting properties. Drude *et al.*[4] declared in their experiment that the first layer of Mn deposited on Ag(100) surface at room temperature, showed the ferromagnetic behavior, despite the fact that the bulk α-Mn phase is non-magnetic at this temperature. Jin[5,6] also showed that the very thin Mn film grown on the GaAs(100) surface both at room temperature and at 400 K exhibits similar magnetic property. It seems that magnetism of

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thin film Mn could be intrinsic and very different from that of the bulk Mn. In addition, Hempsel[7] reported that magnetic properties of a few atomic layers turn out to be very sensitive to strain, interaction with substrate, and temperature. Therefore, in order to elucidate the relationship between the magnetic behavior and the substrate, one needs to know further the magnetic behaviors of the thin film Mn on other substrates. In this paper, we present the results concerning the electronic structure and core level studies of the Mn overlayers deposited on GaP(100) surface at room temperature.

II. EXPERIMENTS

The whole experiment was carried out at the photoemission beam line of the National Synchrotron Radiation Laboratory(NSRL), University of Science and Technology of China at Hefei. The photoelectron was collected and analyzed by a hemispherical analyzer in a Vacuum Science Workshop(VSW) chamber. The photon energy is 157 eV, whose resolution is estimated to be about 500 ($E/\Delta E$).

Before being introduced into the instrument, an n-type GaP(100) single crystal wafer was prepared by the ordinary chemical treatment. The single wafer was cleaned by several cycles of Ar ion bombardment followed by 550°C annealing in the ultrahigh vacuum(UHV) system, until no contamination of C and O was detected by X-ray photoemission spectroscopy(XPS), and a clear (1 × 1) low-energy electron diffraction (LEED) pattern was observed. During collection of data, the chamber pressure was kept lower than 1.5×10^{-10} Torr.

Mn was evaporated with an electron evaporator located ~ 10 cm from the sample. After extensive degassing, Mn could be evaporated below 5×10^{-10} Torr. The system operating pressure of ~ 1.5×10^{-10} Torr was regained within 1–2 minutes after each evaporation. The evaporation rate (0.2 nm/min) was measured with a quartz crystal monitor. During Mn deposition, the GaP(100) substrate was kept at room temperature. Overlayer thickness was expressed in monolayer. Conversion factor from monolayer(ML) to angstrom can be calculated assuming one site per semiconductor atom on the GaP(100) surface. This yields 1 ML=0.085 nm, relative to the GaP(100) surface atomic density of 6.73×10^{14} atoms·cm^{-2}.

III. RESULTS AND DISCUSSION

For a metal/semiconductor interface, a correct assessment of the adsorbate-substrate interaction is very important for the interpretation of the interface formation and the electronic structure of the interface. The measurement of the line-shape changes of core-level spectra of the substrate and the adsorbate is a good way to understand the interface interaction.

Figure 1 illustrates the sequential changes in the Ga 3d core-level spectra over a wide range of Mn coverage (0–23.4 ML). These spectra have been normalized to a constant height

to emphasize line-shape changes. Below 0.63 ML of Mn coverage, no changes of the line-shape of Ga 3d core levels are found in Fig. 1, because interface reaction at submonolayer is weak and the reacted component degenerates with the substrate component. With increasing thickness of Mn overlayers, a 'shoulder' appears at the higher kinetic energy side of the main peak of Ga 3d, and it gradually becomes a new peak. In other metal/semiconductor interfaces, a similar shift of the cations of the substrate has been observed.[5,6,8,9] This shift can be attributed to the final state effects as the Ga is diluted to the Mn host. So it is reasonable to conclude that Ga atoms can be exchanged with Mn atoms. However, at low coverage, this reaction is weak. For example, at 0.63 ML, after doing a simple calculation using the relative intensity of the reacted phase and taking into account the escape depth of the photoelectron, we finally obtain that the percentage of the reacted Ga atoms is about 8%.

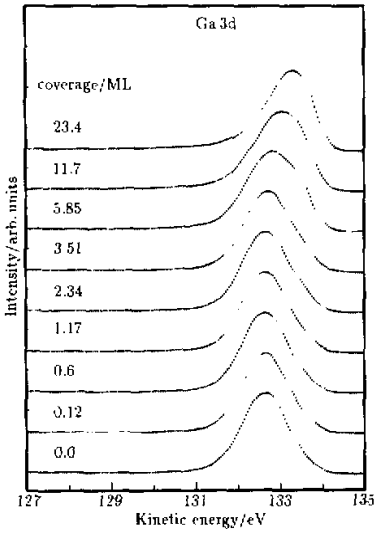

Fig. 1. Ga 3d core-level spectra as a function of Mn coverage for the Mn/GaP(100) interface.

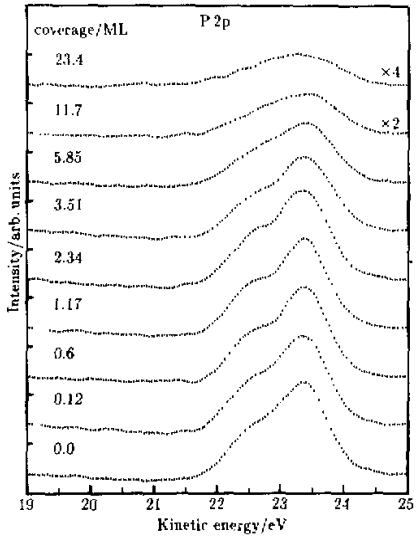

Fig. 2. P 2p core-level spectra as a function of Mn coverage for the Mn/GaP(100) interface.

Immediately, one think that the reaction process mentioned above might be indicated in the P 2p core-level spectra. In Fig. 2, the P 2p core-level spectra as a function of Mn coverage are used for this purpose. As expected, the change of P 2p line-shape has been found. For a clean surface, a clear spin-orbit split feature of P 2p can be observed. With increasing Mn coverage, the P 2p peak becomes a broadened hump with ill-defined structure and loses its original feature, indicating further that there is a chemical reaction in the Mn/GaP(100) interface. However, it is also found that the changes of the line-shape of P 2p are little at

low coverage of Mn, indicating that the interface reaction is weak again.

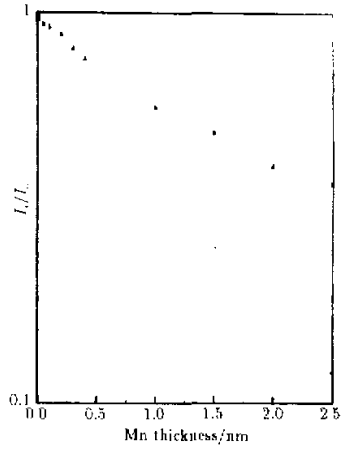

Fig. 3. Evolution of Ga(▲) and P(○) core intensities on a logarithmic scale as functions of Mn overlayer. For the Ga and P peaks, the core intensity is normalized to the value of clean InP surface.

Another factor affecting the interface formation and the electronic structures is the growth mode of Mn overlayer. Generally speaking, the determination of a growth mode of the overlayer using the photoelectron spectrum can be deduced from the attenuation of the substrate and the adsorbate core-level signals. Figure 3 shows a plot of the normalized core intensities of Ga 3d and P 2p as functions of Mn overlayer on a logarithmic scale. In Fig. 3, both of the Ga 3d and P 2p curves follow a nearly straight line at Mn coverage below 1.17 ML. That is to say, an exponential form of $e^{-x/\lambda}$ occurs for both P 2p and Ga 3d core levels below submonolayer. These results suggest the confinement of the Ga and P atomic species to the interfacial region or minimal diffusion of Ga and P into the Mn overlayers. LEED measurement of the 1.17 ML thick Mn sample shows hardly discrete reflections, indicating that the GaP(100) 1×1 surface is completely destroyed by the metal, and the first monolayer of Mn covers the whole GaP surface and no cluster forms. It should be mentioned that our assumption is reasonable, by comparing with the results by Jin *et al.*[5,6] In the Mn/GaAs(100) interface, they thought that the Mn growth mode is also layer by layer when the Mn coverage is below the monolayer. With increasing Mn coverage, Ga 3d deviates from the linear form or the exponential form $e^{-x/\lambda}$ and attenuates slowly and slowly. Even at a coverage greater than 2.5 nm the emission from the reacted Ga component persists. This indicates a diffusion into and through the Mn overlayers again. However, P 2p keeps its original linear form. In fact, P 2p signal is severely attenuated and cannot be detected at a coverage of 2.5 nm while the emission from the Ga 3d component can be detected, indicating the reacted P remains near the interfacial region. Therefore, the core-level results give evidence for the Mn-Ga exchange reactions and the confinement of P atomic species near the interfacial region.

It is emphasized here that no new LEED patterns are found after the disappearance of the original LEED pattern during the whole process of Mn evaporation. These results indicate that the Mn overlayer is disordered.

Figure 4 shows the typical energy distribution curves for the Mn/GaP(100) interface prepared at room temperature. With a few Mn atoms deposited on the substrate, we first notice a hump at the Mn coverage of $\theta \sim 0.12$ ML, whose binding energy is about 4.0 eV

(peak B). It becomes higher and more refined up to 1 ML and then decreases and finally disappears in the strong background of the main Mn 3d induced peak (peak A) at ~ 3 eV below E_F. At high Mn coverage, the feature of valence band is very similar to that of the valence band of α-Mn phase.

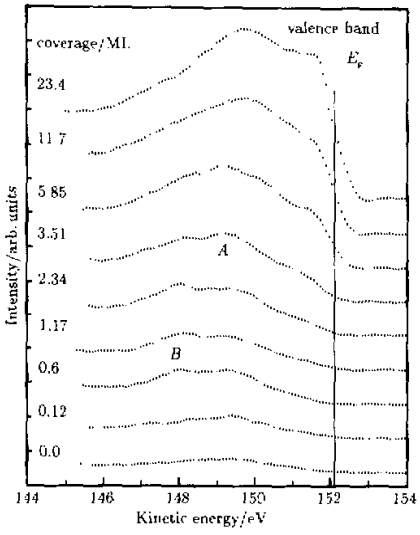

Fig. 4. Valence band photoelectron spectra for the Mn/GaP(100) interface as a function of Mn coverage.

Since the photo-ionization cross section of Mn 3d at photon energy of 157 eV is larger than that of GaP(sp)[9], the Mn 3d emission can be detected at the very early evaporation stage. Thus, the major structures in Fig. 4 are attributed to the Mn 3d emission. Here, according to the analysis by Jin *et al.*[5,6], we also assign the peak B feature coming from the magnetic Mn 3d emission and peak A from the non-magnetic Mn 3d emission. However, the Mn overlayer in our experiment is disordered, and it is very different from the results obtained by Jin *et al.*[5,6] An interesting question to ask is why the same magnetic Mn 3d emission appears in this disordered Mn overlayer. To answer this question, we must go back to the origin of the magnetism. When the applied field is zero, it is well understood that if the sign of the exchange integral (J) is positive, the matter exhibits magnetic feature. On the contrary, if $J < 0$, the matter exhibits no magnetic feature. One of the main factors affecting this sign of the exchange integral is the ratio of the distance between the neighboring Mn atoms to the radius of the electron subshell of the atom. At very low coverage, a Mn atom on the surface should have no coordinated Mn atoms around. That is to say, the interaction between the Mn atoms can be neglected, going back to a situation of an isolated Mn atom with the electron configuration of $3p^6 3d^5$. In this case, all 3d majority spin levels are occupied and all minority spin levels empty. With increasing Mn coverage, due to the adatom-adatom interaction, the electron structure of the Mn overlayer is not the same as that of the isolated Mn atom. However, the distance between the neighboring Mn atoms is still much bigger than the radius of the electron subshell. That is to say, the exchange integral is still positive, and the Mn overlayer is magnetic. Consequently, the Mn 3d emission is like the emission of isolated Mn atoms. When more Mn atoms are deposited, the distance between the neighboring Mn atoms becomes shorter and shorter, the sign of the exchange integral will change form positive to negative, i.e., the Mn overlayer exhibits non-magnetic feature,

and peak B disappears gradually. We think that the distance between the neighboring Mn atoms is the main factor affecting the transition from a magnetic phase to a non-magnetic phase of Mn overlayer in our experiments.

In addition, it is interesting to notice that the first layer of deposited Mn is magnetic on GaP(100), GaAs(100)[5,6] and Ag[4] substrates, though both the morphology and the interaction between Mn and substrates are different, which might indicate that the magnetic feature is an intrinsic property.

IV. CONCLUSIONS

In summary, according to the measurements of the core level and valence band of the Mn/GaP(100) interface, some conclusions can be obtained as the following:

1. Below submonolayer, Mn atoms will cover the whole GaP(100) surface, and the Mn overlayer is disordered. The ultra-thin Mn film exhibits magnetic feature, while the thick Mn film exhibits non-magnetic feature.

2. The distance between the neighboring Mn atoms is thought to be the main factor affecting the transition from the magnetic to non-magnetic phase of Mn overlayer in our experiments.

3. Like other metal/semiconductor interfaces, Ga atoms in the substrate can be exchanged with Mn atoms and diffuse into the Mn overlayer. Phosphorous atoms may bond with Mn and are kept near the interfacial region.

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