Controlled incorporation of Mn in GaAs: Role of surface reconstructions

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A combined experimental and theoretical study on the incorporation of Mn in GaAs has been presented. We have successfully controlled the location of Mn atoms at GaAs(001) surfaces by changing the surface atomic geometry. While Mn atoms prefer to substitute Ga sites at a subsurface layer under the As-rich conditions, the incorporation into interstitial sites becomes more favorable as the surface As coverage is decreased. The present results provide a mechanism for the enhanced incorporation of substitutional Mn atoms in GaMnAs under low-temperature (i.e., As-rich) growth conditions.

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I. INTRODUCTION

The ferromagnetic behavior of III-V diluted magnetic semiconductors makes these materials very promising for applications in spintronic devices. In particular, Mn-doped GaAs has an obvious advantage over other candidate systems[1] because of an easy integration with the well-established III-V semiconductor technology. It is now generally accepted that substituted Mn atoms at Ga sites act as acceptors donating holes, mediating ferromagnetism.[2] According to the Zener mean-field model,[2] the Curie temperature is determined by the concentration of holes, p, and is roughly proportional to $p^{1/3}$, and the maximum value of ∼300 K has been predicted for $Ga_{0.875}Mn_{0.125}As$.[3] Despite considerable efforts, however, the maximum value of measured Curie temperature is 173 K at most for the substitutional Mn concentration of 6.8%,[4] and is too low for practical applications. Although $Ga_{1-x}Mn_xAs$ films with higher Mn concentration ($x \sim 0.2$) have been successfully grown by molecular-beam epitaxy (MBE) at low temperatures, their Curie temperatures are much lower than the value predicted by theoretical calculations.[5–7]

The improvement of ferromagnetic properties of GaMnAs is closely related with the removal of Mn-related defects such as MnAs precipitates and Mn atoms located at interstitial sites.[8] In particular, interstitial Mn atoms behave as electron-producing donors, destroying the free holes and hence hindering ferromagnetism.[9,10] Thus, in order to improve magnetic properties, it is necessary to address the issue of atomic configuration of Mn in GaAs.

To control the location of Mn in GaMnAs, it is essential to understand the initial incorporation processes of Mn in GaAs. Using the density functional theory (DFT), Erwin and Petukhov have shown that Mn adatoms tend to funnel into the interstitial site right beneath the As-As dimer on the GaAs(001) surface.[11] Zhang *et al.* have studied the stability of the reconstructed surface induced by the Mn adsorption on GaAs(001) and predicted that several types of (2 × 2) structures are formed depending on the surface composition.[12] This paper reports on a combined experimental and theoretical study on the incorporation of Mn in GaAs. We present the evidence that the location of Mn atoms on GaAs(001) surfaces could be controlled by changing the surface As coverage. Mn atoms are incorporated into the interstitial sites under the moderate As-rich conditions. On the other hand, the increase in the As coverage substitutes Mn atoms for Ga atoms at the subsurface layer. Structure models with substitutional and interstitial Mn atoms have been proposed, which account for the experimental data from reflection high-energy electron diffraction (RHEED), scanning tunneling microscopy (STM), and x-ray photoelectron spectroscopy (XPS), and are confirmed to be stable by first principles calculations.

II. EXPERIMENT

The experiments were performed in a system of interconnecting ultrahigh vacuum chambers for MBE growth and for on-line surface characterization by means of STM and XPS.[13] All the STM images were acquired at room temperature using electrochemically etched tungsten tips. XPS measurements were carried out by using monochromatic Al $K\alpha$ radiation (1486.6 eV). Nondoped and nominally on-axis GaAs(001) substrates were used for the RHEED and XPS measurements, while the Si-doped $N \approx (1\text{–}4) \times 10^{18}$ cm^{-3} substrates were employed for the STM experiments. Cleaned GaAs(001)-(2 × 4) surfaces were first obtained by growing an undoped homoepitaxial layer (∼0.5 μm) on a thermally cleaned GaAs(001) substrate. Mn atoms were deposited on the GaAs(001)-(2 × 4) surfaces at 550 °C under an As_2 flux with a beam-equivalent pressure of 2.5×10^{-7} Torr. The deposition rate was 0.0125 ML/s, which was calibrated by RHEED intensity oscillation measurements on the MnAs(1100) growth on GaAs(001). Here, 1 ML of Mn is defined as 6.26×10^{14} atoms/cm^2, which is the site-number density of the unreconstructed GaAs(001) surface.

III. CALCULATIONS

First-principles calculations[14] based on the density functional theory[15] with the generalized gradient approximation[16] were performed. A slab geometry was used for the simple calculation, which has the supercell consisting of nine atomic layers with surface dimers and of vacuum region (15 Å in thickness). The back side of the slab is terminated with 16 fictitious H atoms which eliminate artificial dangling bonds and prevent it from coupling with the front side. The wave functions were expanded in plane waves with a kinetic energy

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cutoff of 16 Ry. Eight and four k points were used for the integration in k space in the irreducible Brillouin zones of the (2×2) and $c(4 \times 4)$ surfaces, respectively.

IV. RESULTS AND DISCUSSION

When 0.25 ML of Mn was deposited on the GaAs(001)-(2×4) surface at 550 °C under the As flux, the (2×2) reconstruction was observed. Figure 1(a) shows a typical filled-state STM image taken from the Mn-induced (2×2) surfaces prepared by closing the As shutter at 450 °C. It is seen that bright spots are separated by ~8 Å along the $[1\bar{1}0]$ direction, while their positions are slightly (1–2 Å) shifted in the [110] or the $[\bar{1}\bar{1}0]$ direction. Similar to the case for the GaAs(001)-$c(4 \times 4)\alpha$ surface,[17] such STM features could be interpreted in terms of the coexistence of mixed Ga-As/As-Ga dimer structures, because only As atoms are usually imaged in the filled-state STM images of GaAs(001).

From the present STM observation, we propose the structure model for the Mn-induced (2×2) surface as shown in Fig. 2(a). The As coverage of this model is 1.0 ML, being consistent with our XPS results.[18] In this atomic geometry, the dangling bonds of Ga and As atoms of the Ga-As dimer and second-layer As atoms would have $\frac{3}{4}$, $\frac{9}{4}$, and $\frac{5}{4}$ electrons, respectively. To transform the As (Ga) dangling bond into s-type fully occupied (p_z-type empty) state, there is a deficiency of two electrons per (2×2) unit cell. Thus the surface could be electrically stabilized by the addition of one Mn atom at the interstitial site of the (2×2) unit (0.25 ML in coverage), because the interstitial Mn acts as a double donor.[9] Possible adsorption sites for Mn, which correspond to tetrahedral interstitial sites in bulk GaAs with four neighboring Ga atoms, are indicated by the letters A, B, C, and D. From the present STM observations, however, information about the location of Mn atoms could not be obtained. Thus, in order to study the relative stability of the proposed structure models with Mn adatoms at different sites, we performed first-principles calculations.

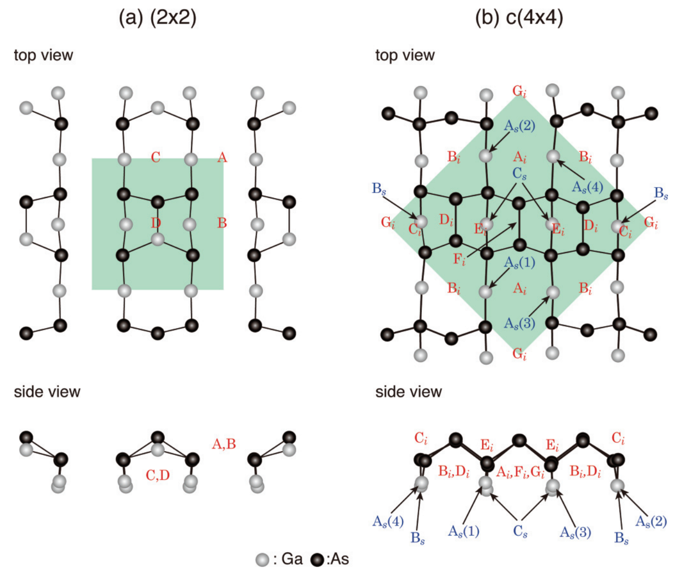

FIG. 2. (Color online) Structure model for the Mn-induced (2×2) (a) and $c(4 \times 4)$ reconstructions on GaAs(001). Possible adsorption sites for Mn are indicated by letters A, B, C, and D in (a), and A_i–G_i and A_s–C_s in (b).

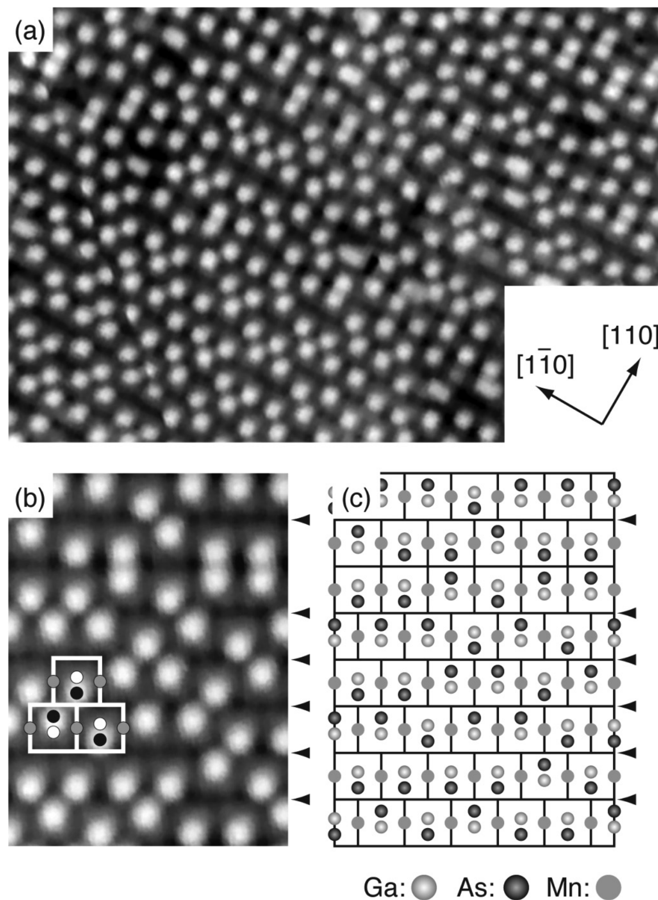

FIG. 1. (a) Typical filled-state STM image obtained from the Mn-induced (2×2) reconstructions prepared at 450 °C. (b) Magnified image of (a). Image dimensions are 120 Å × 180 Å (a) and 64 Å × 48 Å (b). The images were taken with a sample bias of −3.0 V. (c) Proposed Ga-As dimer model.

The calculations show that the adsorption of Mn at the B site is energetically most favorable. The A-, C-, and D-site models are higher in energy by 0.54 eV, 0.87 eV, and 0.42 eV, respectively. We also performed the calculations for the structure model with the Mn-As dimer instead of the Ga-As dimer and found that the Mn-As dimer structure is energetically unstable (see Fig. 5 below).

Further experimental evidence for the proposed structure model was obtained by RHEED rocking-curve analysis based on dynamical diffraction theory. RHEED rocking curves were measured using the extended beam-rocking facility (Staib, EK-35-R and k-Space, kSA400). The energy of the incident-electron beam was set at 15 keV. Integrated intensities of (0 0), (0 $\pm\frac{1}{2}$), (0 ±1), (0 $\pm\frac{3}{2}$), and (0 ±2) spots were measured along the $[1\bar{1}0]$ direction, and (0 0), ($\pm\frac{1}{2}$ 0), (±1 0), ($\pm\frac{3}{2}$ 0), and (±2 0) intensities were measured along the $[110]$ direction. RHEED intensities were calculated by the multislice method proposed by Ichimiya[19] using 10 fractional-order and 11 integer-order reflections for both the $[1\bar{1}0]$ and [110] electron-incidence azimuths. Parameters for the calculations, such as elastic and inelastic scattering potentials,

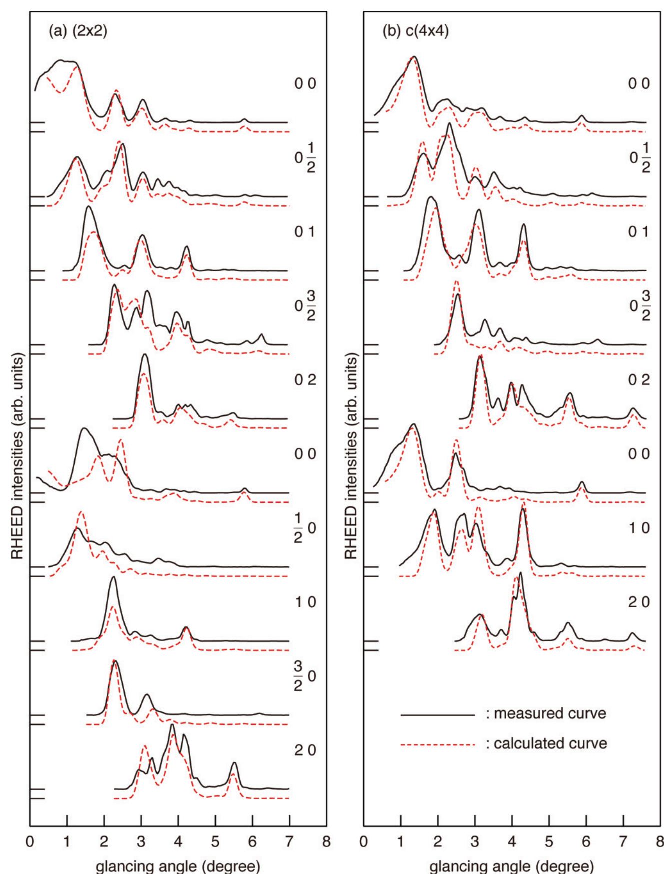

FIG. 3. (Color online) RHEED rocking curve (solid curves) measured from the Mn-induced (2×2) (a) and $c(4\times4)$ (b) surfaces. The dashed curves in (a) and (b) are calculated using the atomic coordinates obtained by first-principles calculations for the models with Mn atoms at the B site [Fig. 2(a)] and with the $A_s(1)$ and $A_s(4)$ sites [Fig. 2(b)], respectively.

and thermal vibrations, were derived in a similar way used in the structure analysis for GaAs surfaces.[13] In order to quantify the agreement between the measured and calculated rocking curves, the R factor defined in Ref. 20 was used.

Figure 3(a) shows the RHEED rocking curves measured from the Mn-induced (2×2) structure at 450 °C. Also shown by dashed curves in Fig. 3(a) are the calculated curves from the model in which the Mn atom is located at the B site, as shown in Fig. 2(a). The present analysis assumed a random distribution of the two types of asymmetric (2×2) unit cells with Ga-As and As-Ga dimers. The atomic coordinates used for the RHEED analysis were fixed at those obtained by first-principles calculations. The majority of features in the measured rocking curves are well reproduced by the calculations (R factor = 0.134) for the B-site model. On the other hand, the model with Mn adatoms located at the A, C, and D sites resulted in larger R factors of 0.334, 0.347, and 0.281, respectively. We have also found that the Mn-As dimer model gives a worse fit (R factor = 0.397). From the present RHEED analysis, we conclude that the Mn-induced (2×2) surface has the Ga-As dimer on the As-terminated surface with the Mn adatom located at the hollow site surrounded by four As atoms.

Here, it is interesting to note that the consecutive (2×2) unit cells along the [110] direction are often out of phase, as indicated by arrow heads in Figs. 1(b) and 1(c). On the other hand, such an antiphase boundary was hardly observed in the $[1\bar{1}0]$ direction. The formation of antiphase boundaries in the $[1\bar{1}0]$ direction results in the coexistence of A- and B-site structures, and, therefore, is energetically unfavorable, while the irregular phasing along the [110] direction does not affect the location of Mn atoms at the B site.

Previous DFT calculations have predicted that the Ga-As dimer in the (2×2) structure is replaced by the Ga-Ga dimer and the As-As dimer under more Ga-rich and As-rich conditions, respectively.[12] However, in the present experiments, the structure change from (2×2) to $c(4\times4)$ was observed as the substrate temperature was decreased below 450 °C under the As flux. Figure 4(a) shows a filled-state STM image of Mn-induced $c(4\times4)$ reconstructions prepared by closing the As shutter at 300 °C. While weak $c(4\times4)$ correlation was confirmed in RHEED patterns, several types of building blocks, such as (2×2), (2×3), (2×4), and $(2\times n)$ $(n>5)$, were observed in STM images. The (2×2), (2×3), and

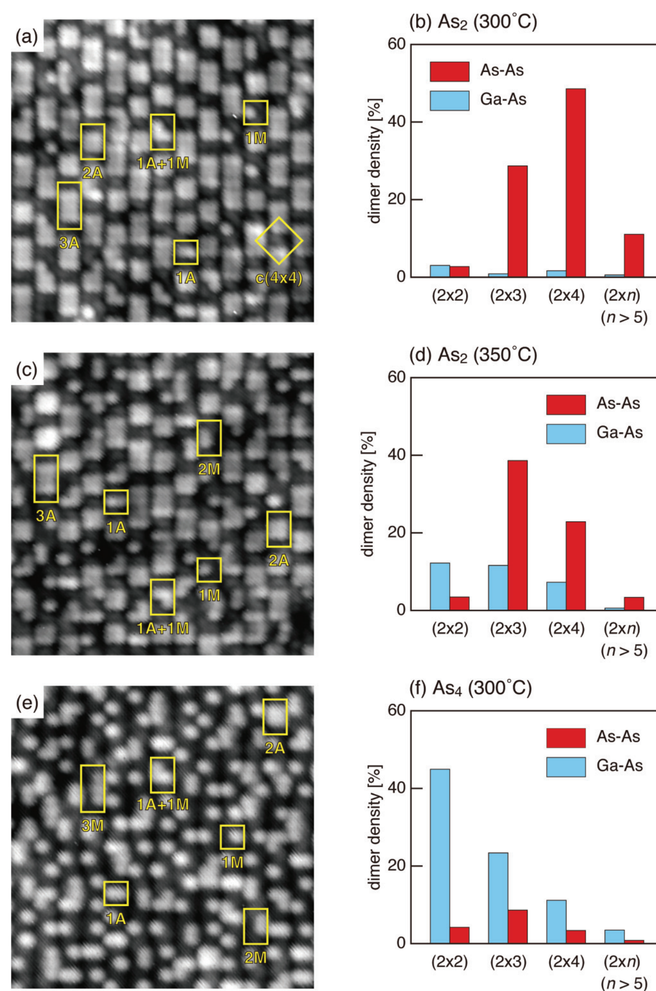

FIG. 4. (Color online) Typical filled-state STM images obtained from the Mn-induced $c(4\times4)$ reconstructions prepared at 300 °C (a) and 350 °C (c) using As_2 molecules. The surface in (e) was prepared at 300 °C using As_4 molecules. Image dimensions are 104 Å × 104 Å. The images were taken with a sample bias of −3.0 V. (b), (d), and (f) show distributions of As-As and Ga-As dimers in images (a), (c), and (e), respectively.

(2 × 4) units correspond to the structure with one, two, and three dimers, respectively. Figure 4(b) shows distributions of As-As and Ga-As dimers. Most of the unit cells have As-As dimers: the density of As-As (Ga-As) dimer is 94% (6%). The (2 × 3) and (2 × 4) units, consisting of two and three As-As dimers, respectively, constitute ∼80% of the surface area. On the other hand, the density of the (2 × 2) unit with one As-As dimer, which was predicted to be stable by previous first-principles calculations, is less than 5%.

In order to check whether the (2 × 2) As-As dimer structure is formed at intermediate states between (2 × 2) and $c(4 \times 4)$, the sample was prepared at 350 °C. As shown in Figs. 4(c) and 4(d), the increase in the preparation temperature does not significantly change the density of (2 × 2) units with single As-As dimer. We also prepared the samples using As_4 molecules, and found that the Ga-As dimer structures are dominant (>80%), as shown in Figs. 4(e) and 4(f).

Shown in Fig. 2(b) is the possible structure model for the $c(4 \times 4)$-Mn surface. For simplicity, we assumed that 0.25 ML of Mn atoms are incorporated into several substitutional (A_s, B_s, and C_s) and interstitial sites (A_i-G_i) of the (2 × 4) building block. Our XPS measurement revealed that the surface As coverage of the $c(4 \times 4)$-Mn surface is about 1.75ML, which is quite close to the value for the GaAs(001)-$c(4 \times 4)\beta$ structure. This value is also consistent with the As coverage estimated from STM observations.[21]

Figure 5 shows the relative formation energies of $c(4 \times 4)$ models with various Mn locations as a function of relative chemical potential of As ($\Delta\mu_{\mathrm{As}}$). When the Ga atoms at the A_s site was substituted by the Mn atoms, the surface becomes most stable at the As-rich limit. While the incorporation at $A_s(1)$ and $A_s(4)$ sites is found to be energetically most favorable, the difference in the energy with the model for $A_s(3)$ and $A_s(4)$ [$A_s(1)$ and $A_s(3)$] sites is only 0.027eV (0.030eV) per (1 × 1). On the other hand, the structure models with Mn atoms located at substitutional sites of B_s and C_s have higher energies of 0.84 eV and 1.08 eV, respectively, and all of the interstitial-site models (A_i-G_i) are found to be unstable. Another noteworthy finding is that the (2 × 2) As-As dimer structure is the most stable only at the boundary between the ranges of the As chemical potential where the $c(4 \times 4)$ and (2 × 2) Ga-As dimer structures are most stable.

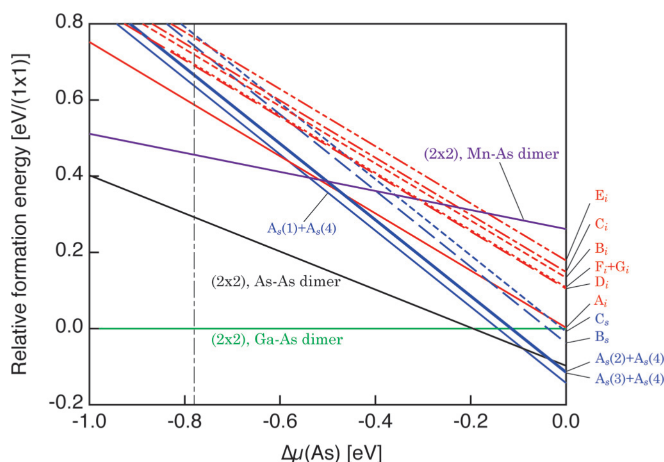

FIG. 5. (Color online) Relative surface energies for various Mn-induced surface reconstructions on GaAs(001) as a function of relative chemical potential of As. Thermodynamically allowed range is between −0.78 eV (Ga rich) and 0.00 eV (As rich).

The existence of Mn at the substitutional site was experimentally confirmed by the RHEED analysis. The present RHEED analysis assumed the (1 × 2) periodicity, because the 2× periodicity in the [110] direction is not clearly observed, owing to the coexistence of several (2 × n)-type units. As shown in Fig. 3(b), the structure models with Mn at the A_s site show a very good agreement with the experiments (R factor = 0.117-0.121). The B_s- and C_s-site models show larger R factors of 0.310 and 0.181, respectively, and the models with Mn interstitials also result in worse fits (R factors = 0.256-0.482). From these experiments and calculations, we conclude that the Mn atoms are located at the substitutional sites in the As-rich $c(4 \times 4)$ reconstruction. Although preferable incorporation of Mn in the substitutional site in GaAs under As-rich conditions has been predicted by Mahadevan and Zunger,[10] our analysis derived specific atomic configurations of Mn-induced surface reconstructions including information on atom location and bond length. Specifically, Mn atoms are incorporated into substitutional Ga sites at the third layer between the As-As dimer row [$A_s(1)$-$A_s(4)$ sites in Fig. 2(b)]. The incorporation of Mn in the A_s site is due to the local strain induced by the surface reconstruction: the formation of the As-As dimers at the outermost layer induces a compressive strain on the atomic sites beneath them (B_s and C_s site) and tensile strain on the neighboring A_s sites. Since the predicted Mn-As bond length in zinc-blende MnAs is 2.55-2.59 Å[1,22] and is larger than the value of the Ga-As bond in bulk (2.45 Å), substituting Mn in the Ga site causes compressive strain around the Mn atom. Thus, the Mn incorporation at the A_s site allows for the compensation of the tensile strain in the $c(4 \times 4)$ structure.

When the $c(4 \times 4)$ surface was heated to 450 °C with and without the As_2 flux, the $c(4 \times 4)$ surface rearranged to (2 × 2), indicating the diffusion of Mn atoms from substitutional to interstitial sites. On the other hand, cooling of the (2 × 2) surface below 300 °C without As_2 flux did not change the atomic geometry, leaving the Mn atoms at the hollow sites, as confirmed by reflectance difference spectroscopy and RHEED rocking-curve measurements. As mentioned in the beginning of this Letter, GaMnAs films with higher Mn concentrations of substitutional Mn atoms are grown by MBE at low temperatures (<300 °C), and the hexagonal MnAs phase is formed at typical growth temperatures for GaAs (>500 °C).[1,4–7] The MBE growth at low temperatures usually proceeds with the As-rich $c(4 \times 4)$ surface reconstructions. Thus, we conclude that the increase in the surface As coverage is essential to the preferential Mn incorporation into the substitutional site.

V. CONCLUSIONS

A combined experimental and theoretical study has demonstrated that the surface As coverage plays a crucial role in controlling the location of Mn atoms at the GaAs surface. Under the As-rich conditions, Mn atoms are favorably incorporated into Ga sites at third layer between the As-As dimer row in the $c(4 \times 4)$ reconstructions. As the surface becomes less As-rich, the $c(4 \times 4)$ surface reversibly changes to the (2 × 2) structure with Ga-As dimers and Mn atoms located at hollow sites.

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