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Molecular-beam epitaxy of MnAs in the presence of atomic hydrogen

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Abstract

Effects of atomic hydrogen ($H^{\cdot}$) on the molecular-beam epitaxy of MnAs/GaAs heterostructures were investigated. X-ray diffraction and reflection high-energy electron diffraction characterizations revealed that the growth was along the $[\bar{1}\,1\,0\,0]$ direction for the hexagonal MnAs epilayer grown with $H^{\cdot}$, and along both the $[\bar{1}\,1\,0\,0]$ and $[\bar{1}\,1\,0\,1]$ directions for the epilayers grown with/without hydrogen molecules (H_2). Atomic force microscope (AFM) images showed that the faceted mounds elongated along the GaAs$[1\,1\,0]$ direction were only observed for the epilayers grown with $H^{\cdot}$. On the other hand, large three-dimensional (3D) islands were observed on the elongations along the GaAs$[\bar{1}\,1\,0]$ direction for the epilayers grown with/without the supply of H_2. The results indicate that the irradiation of $H^{\cdot}$ enhances the growth of MnAs epilayers along the single direction and improves the surface smoothness. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Ferromagnet/semiconductor heterostructures are attracting much attention because of their potential application in fabricating new devices integrating magnetic, electronic and optical properties [1]. Recent progress in the molecular-beam epitaxy (MBE) technique has demonstrated that CuAu-type ferromagnetic compounds such as MnGa and MnAl [2,3], as well as NiAs-type ferromagnetic compounds such as MnSb and MnAs [4–8] can be grown on III–V substrates such as GaAs and InAs. We have also elucidated the effects of the substrate orientation and the growth temperature on the structure and magnetic properties of MnAs epilayers grown by MBE [9]. However, the surface smoothness was not of sufficient quality for device applications.

In the MBE growth of lattice-mismatched systems, it is well known that surfactants can suppress three-dimensional (3D) island growth and enhance two-dimensional (2D) layer-by-layer growth, even when the film thickness exceeds the critical layer thickness [10–14]. Copel et al. have first reported the surfactant effect using As in a Ge/Si heterostructures [10]. Chun et al. have used atomic

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hydrogen ($\mathrm{H}^{\cdot}$) in the InAs/GaAs and GaAs/InP heterostructures [14]. We have also used $\mathrm{H}^{\cdot}$ in the hot-wall epitaxy (HWE) of MnSb on GaAs substrates, and shown that the irradiation of $\mathrm{H}^{\cdot}$ improves the surface smoothness [15]. In this letter, we report on the considerable effect of $\mathrm{H}^{\cdot}$ not only on the surface smoothness but also on the growth direction in the MBE growth of MnAs/GaAs heterostructure.

2. Experimental procedure

MnAs MBE growth was carried out in a conventional III–V MBE machine with Mn effusion cell. The growth apparatus used in the present experiment was described in a previous paper [9]. Briefly, the substrates were n-type (0 0 1)GaAs. After growing a 70 nm thick undoped GaAs buffer layer on the substrates at 600°C, the substrate temperature (T_s) was lowered to 250°C. During the cooling process, the As_4 shutter was closed at T_s of about 480°C. A $c(4\times4)$ reconstruction was observed from the GaAs surface after closing the As shutter.

$\mathrm{H}^{\cdot}$ was generated by flowing H_2 through a tungsten (W) filament cell heated at about 1600°C. As described in a previous paper, although the cracking efficiency of H_2 was presumed to be extremely low, a small amount of $\mathrm{H}^{\cdot}$ was sufficient to improve the surface smoothness in the hot-wall epitaxy of MnSb on GaAs substrates [15]. The $\mathrm{H}^{\cdot}$ and H_2 BEP of 2.0×10^{-6} Torr, measured by an ion gauge, were controlled by a needle valve. MnAs layers were grown under the following conditions: A Mn beam equivalent pressure (BEP) was fixed at about 8×10^{-8} Torr on a beam-flux monitor, and the As_4/Mn BEP ratio was kept constant at about 50. MnAs layers with thicknesses of about 600 nm were grown on (0 0 1) substrates with a growth rate of about 300 nm/h, while T_s was kept constant at about 250°C, as measured by an infrared pyrometer.

The growth direction and the crystal structure of MnAs epitaxial layers were studied by reflection high-energy electron diffraction (RHEED) and X-ray diffraction (XRD). The microscopic surface features were observed by an atomic force microscope (AFM).

3. Results and discussion

Fig. 1 shows XRD patterns for MnAs epitaxial layers grown without the supply of $\mathrm{H}^{\cdot}$ (a), and with the supply of $\mathrm{H}^{\cdot}$ (b). As shown in Fig. 1a, besides a GaAs(0 0 2) peak at 31.6° and a huge GaAs(0 0 4) peak at 66.0°, two peaks were observed at 27.7° and 57.2° in the epilayer grown without the supply of $\mathrm{H}^{\cdot}$, corresponding to $(\bar{1}\ 1\ 0\ 0)$, $(\bar{2}\ 2\ 0\ 0)$ reflection of hexagonal MnAs, respectively. Moreover, a small $(\bar{1}\ 1\ 0\ 1)$MnAs peak was observed at the shoulder of the GaAs(0 0 2) peak ($2\theta = 31.9°$). Almost the same tendency was observed regarding the XRD patterns for the epilayer grown with the supply of H_2. These results indicate that the introduction of H_2 gas leads to no change in the growth direction of MnAs epitaxial layers.

On the other hand, a $(\bar{1}\ 1\ 0\ 1)$MnAs peak was not observed in the epilayers grown with the supply of $\mathrm{H}^{\cdot}$ (Fig. 1b), even though $(\bar{1}\ 1\ 0\ 0)$ and $(\bar{2}\ 2\ 0\ 0)$MnAs peaks were also observed, indicating that the $\mathrm{H}^{\cdot}$ introduction suppresses the growth of MnAs epitaxial layers along the $[\bar{1}\ 1\ 0\ 1]$ direction

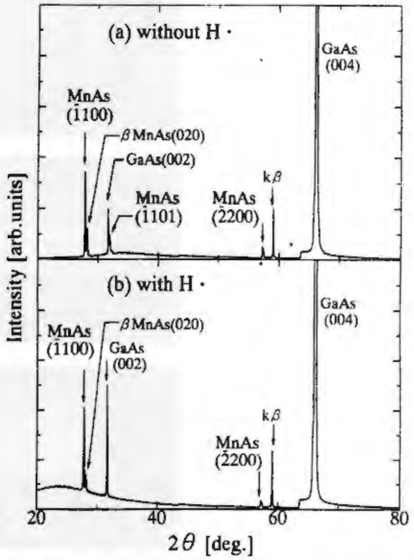


Fig. 1. XRD patterns for MnAs epitaxial layers grown without the supply of $\mathrm{H}^{\cdot}$ (a) and with the supply of $\mathrm{H}^{\cdot}$ (b).

and enhances the growth along the $[\bar{1}\,1\,0\,0]$ direction.

The full-width at half-maximum (FWHM) of the MnAs peaks was less than 0.1° for the epilayers grown with the supply of $H^{\cdot}$. The value was about half the width of the epilayers grown with/without the supply of H_2, showing that high-quality epilayers were grown with the supply of $H^{\cdot}$.

In the present MnAs epilayers, the orthorhombic paramagnetic β-MnAs coexisted with hexagonal ferromagnetic α-MnAs at room temperature, although the dominant phase was α-MnAs, independent of the results with/without the supply of $H^{\cdot}$. The difference in the structures between the MnAs epilayer and GaAs substrate is considered to cause the existence of the β-MnAs below the Curie temperature (40°C). However, it is not possible to clarify how the β-MnAs is formed at present.

Fig. 2 shows a set of RHEED patterns of the epilayers grown without the supply of $H^{\cdot}$ (a) and with the supply of $H^{\cdot}$ (b) together with those just before the growth of MnAs along the [1 1 0] and $[\bar{1}\,1\,0]$GaAs directions. By measuring the interval between the integral-order streaks, the lattice constant in the layer plane of MnAs epilayers was estimated: The estimated atomic distances along the various directions were in good agreement with those of bulk hexagonal MnAs. It was also found that the in-plane relationship between the $(\bar{1}\,1\,0\,0)$MnAs epilayer and the GaAs substrate is MnAs$[\bar{1}\,\bar{1}\,2\,0]\|$GaAs[1 1 0] and MnAs$[0\,0\,0\,1]\|$GaAs$[\bar{1}\,1\,0]$, which agrees with that reported for the MBE growth of MnAs on (0 0 1)GaAs at T_s of about 250°C [6]. On the other hand, although we cannot determine the in-plane relationship between the $(\bar{1}\,1\,0\,1)$MnAs epilayer and GaAs substrate because the growth directions were along both the $[\bar{1}\,1\,0\,1]$ and $[\bar{1}\,1\,0\,0]$ directions for the epilayer grown without the supply of $H^{\cdot}$ in the present experiment, we found that the in-plane structure of

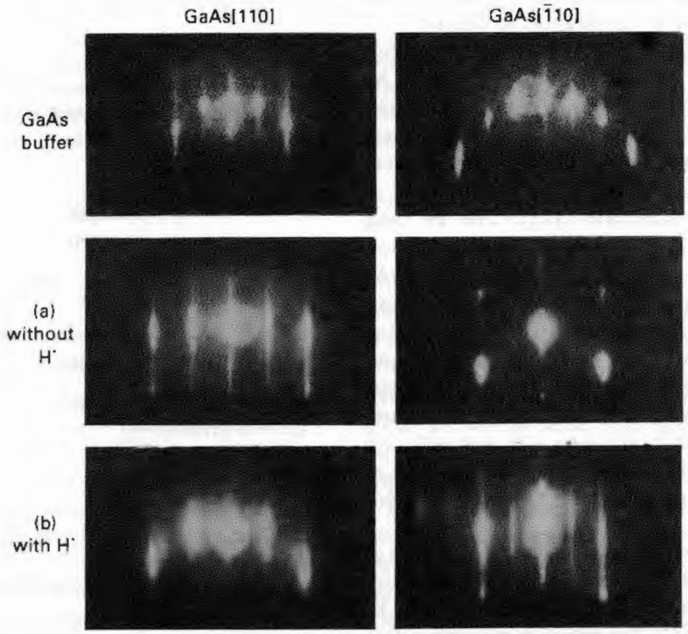


Fig. 2. RHEED patterns of the epilayers grown without the supply of $H^{\cdot}$ (a) and with the supply of $H^{\cdot}$ (b) along the [1 1 0] and $[\bar{1}\,1\,0]$GaAs directions.

$(1\,\bar{1}\,0\,1)$MnAs epilayers is MnAs$[1\,\bar{1}\,0\,2]\|$GaAs$[1\,1\,0]$ and MnAs$[\bar{1}\,\bar{1}\,2\,0]\|$GaAs$[\bar{1}\,1\,0]$ in our previous work [9].

In the case of the growth without the supply of $H^{\cdot}$, a spotty RHEED pattern was observed from a MnAs surface along the $[\bar{1}\,1\,0]$GaAs direction, although a streaked one along the $[1\,1\,0]$GaAs direction, which may suggest that the mounds elongated along the $[\bar{1}\,1\,0]$GaAs direction cover the surface. On the other hand, in the case of the growth with the supply of $H^{\cdot}$, a spotty RHEED pattern was observed from a MnAs surface along the $[1\,1\,0]$GaAs direction. Moreover, the fundamental streaks became extended. The extended angles were measured to be about ±15°, corresponding to the $[\bar{2}\,2\,0\,1]$ and $[\bar{2}\,2\,0\,\bar{1}]$MnAs directions. These results suggest that the $(\bar{2}\,2\,0\,1)$ and $(\bar{2}\,2\,0\,\bar{1})$ faceted mounds, elongated along the $[1\,1\,0]$GaAs direction, were formed on the surface during MBE with the supply of $H^{\cdot}$.

Fig. 3 shows AFM images observed for the epilayers grown without the supply of $H^{\cdot}$ (a) and with the supply of $H^{\cdot}$ (b). As shown in Fig. 3a, large 3D islands were observed on the mounds elongated along the GaAs$[\bar{1}\,1\,0]$ direction for the epilayer grown without the supply of $H^{\cdot}$. Almost the same tendency was observed regarding the surface morphology for the epilayer grown with the supply of H_2. On the other hand, large 3D islands were not observed for the epilayers grown with $H^{\cdot}$, even though the faceted elongations along the GaAs$[1\,1\,0]$ direction were also observed (Fig. 3b). These results suggest that a suppression of 3D island growth of MnAs can be achieved by adsorbed $H^{\cdot}$.

The facets of elongations along the $[1\,1\,0]$GaAs direction formed certain angles with the surface for the epilayer grown with the supply of $H^{\cdot}$. The average of the measured angle was $16 \pm 2°$, coinciding with the extension angle of the RHEED streaks. The extension of the fundamental RHEED streaks can therefore be explained by these faceted mounds.

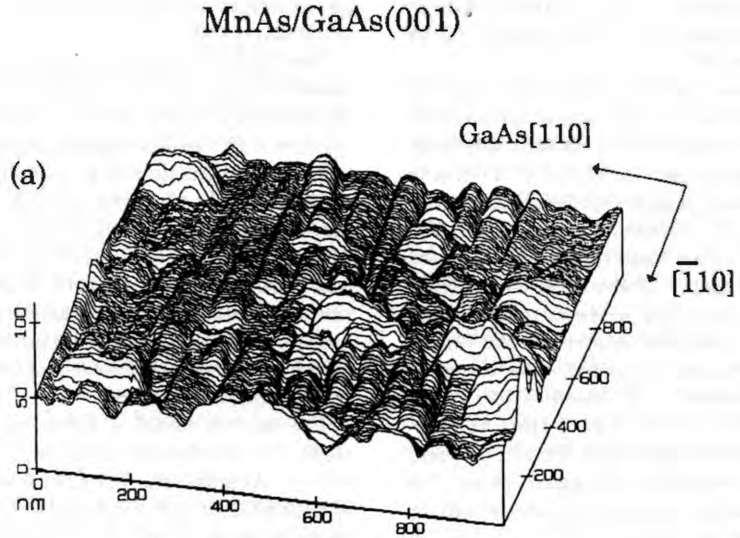
Improvement of surface morphology for the epilayers grown with $H^{\cdot}$ is not caused by an increase in the substrate temperature due to heat irradiation from a W-filament cell heated at about 1600°C. Hence, an increase in the substrate temperature during MBE without the introduction of $H^{\cdot}$ led to no change in surface morphology of MnAs epitaxial layers [9].

Two kinds of models are therefore considered to explain the improvement of surface morphology for the epilayers grown with $H^{\cdot}$. One is due to the increase in the surface diffusion length during MBE with the introduction of $H^{\cdot}$. In the case of MBE growth of GaAs on GaAs surfaces, it was reported that the surface diffusion length of Ga adatoms with $H^{\cdot}$ was about 1.2 times larger than that in the case of MBE without $H^{\cdot}$ [16]. If the surface diffusion length is enhanced sufficiently in the case of the growth of MnAs with $H^{\cdot}$, then incoming atoms can migrate over long distances and consequently flat surfaces can be obtained.

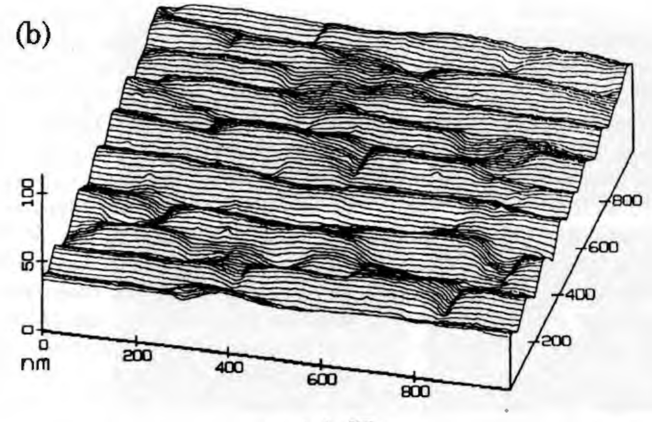
The second model is based on the surfactant effect, as described regarding the MBE of InAs/GaAs and GaAs/InP [14] as well as the HWE of MnSb/GaAs with the supply of $H^{\cdot}$ [15]. $H^{\cdot}$ always covers the top-most surface of the epilayer as metallic hydrides via surface segregation, and act as surfactants which limit the kinetic movement of adatoms on the growing surface, resulting in a suppression of 3D island growth of MnAs.

In order to investigate the role of $H^{\cdot}$ on the growing surface in more detail, further AFM observations were performed for the epilayers grown at the As_4/Mn BEP ratio of 10 under $H^{\cdot}$ pressure. The substrate temperature of 250°C and film thickness of 600 nm were not changed, compared to the conditions described above. Many islands were observed for the case of a low As_4/Mn BEP ratio, while a very flat surface was observed for a high As_4/Mn BEP ratio. The root-mean-square roughness was about 50 and 5 nm for the As_4/Mn BEP ratio of 10 and 50, respectively. Moreover, as described above, an increase in the substrate temperature from 250 to 350°C during MBE without $H^{\cdot}$ led to no change in surface morphology of MnAs epilayers [9]. These results indicate that the effect of $H^{\cdot}$ on surface morphology appears clearly under the conditions such as high As_4/Mn BEP ratio and low substrate temperature that suppress the surface diffusion of growing atoms. Thus, among the two models, the second model based on the surfactant effect is preferable.

The model readily explains a suppression of the growth of MnAs epilayer along the $[\bar{1}\,1\,0\,1]$



without H·



with H·

Fig. 3. AFM images observed for the epilayers grown without the supply of H· (a) and with the supply of H· (b).

direction. The supply of 1 ML of Mn as a template before the growth of MnAs was reported to change the growth direction from [$\bar{1}$ 1 0 0] to [$\bar{1}$ 1 0 1] direction [6]. Surfactants are therefore considered to prevent the intermixing/interchanging between the supplied Mn atoms and the top-most As atoms covered on GaAs surfaces, just after the initiation of the growth of MnAs.

The discrepancy between the directions of elongations observed for epilayers grown with/without

H˙ is considered to be due to the difference in the binding energies of surfactants to topmost atoms at atomic step normal to the [$\bar{1}$ 1 0]GaAs direction and to those at atomic step normal to the [1 1 0]GaAs direction. Although it is very difficult to evaluate the bonds of hydrogen with other atoms on the surface, investigations about the reaction process are desired in order to understand the detailed mechanisms of improvement of surface morphology for the epilayers grown with H˙.

4. Summary

MnAs epitaxial layers were grown by MBE with the supply of atomic H. The growth direction of hexagonal MnAs epitaxial layers with the supply of atomic H˙ was along the [$\bar{1}$ 1 0 0] direction, although the growth directions were along both the [$\bar{1}$ 1 0 0] and [$\bar{1}$ 1 0 1] directions for the epilayers grown with/without the supply of H_2. In the case of growth with the supply of H˙, the faceted mounds elongated along the GaAs[1 1 0] direction were formed during the growth. On the other hand, large 3D islands were also grown on the mounds elongated along the GaAs[$\bar{1}$ 1 0] direction for the epilayers grown with/without the supply of H_2. Two possible explanations have been proposed. One is that the increase in the surface diffusion length during MBE with the introduction of H˙ results in improvement of surface morphology. The second one is that metallic hydrides act as surfactants which suppress the 3D island growth of MnAs.

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