Electronic structure, growth, and structural and magnetic properties of magnetic semiconductor Fe/GaAs heterostructures

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In this article we describe a study of the magnetic semiconductors of Fe/GaAs, undertaken theoretically and experimentally. We discuss the structural advantage of body-centered-cubic-Fe structure lattice matching to GaAs (001). Theoretical calculations using the self-consistent linear augmented-plane-wave method indicate the existence of an energy state of the quantum well in Fe layers in a GaAs/Fe/GaAs double heterostructure. We then present the preparation of Fe/GaAs heterostructures by using molecular beam epitaxy. α-Fe and δ-Fe could be grown epitaxially on (001) GaAs at a substrate temperature of 290 and 580 °C, respectively, which was confirmed from the results of reflection high energy electron diffraction and x-ray diffraction measurements. We also found that, in order to obtain α-Fe/GaAs, a low-temperature GaAs growth must be induced before the Fe growth can occur. Differences in magnetic properties were observed in the magnetic measurements, indicating that α-Fe dominates the ferromagnetic state, while the δ-Fe shows relatively slight ferromagnetic behavior.
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I. INTRODUCTION

Studies of the formation of artificial lattices and multilayer structures have been widely conducted in order to develop novel functional materials and devices. For instance, in the field of magnetics, when multilayer structures were formed, several interesting behaviors such as giant magnetic resistivity,[1] oscillation due to interaction between magnetic layers,[2] and perpendicular magnetic anisotropy[3] were found.

Until recently, MnAs/GaAs magnetic semiconductors have been demonstrated using molecular beam epitaxy (MBE).[4,5] This method was proved advantageous as a result of MBE, which enabled the growth of different materials having different physical properties and crystal structures under low-temperature nonequilibrium growth conditions. The results proved that magnetic-semiconductor-multilayer structures can produce controlled magnetism via changes in the number of magnetic layers and the direction of spin momentum. However, as pointed out by Tanaka *et al.*,[4] MnAs a hexagonal NiAs structure, differs from the zinc-blende GaAs structure such that the formation of the multilayer structure is restricted because of the large lattice strain between magnetics and semiconductors.

Considering this, we selected the Fe–GaAs heterostructure system as a novel magnetic-semiconductor material. Its merits are as follows. (i) Fe is one of the most abundant magnetic metals in the earth and has its own ferromagnetic properties; (ii) GaAs is the most widely used compound semiconductor and offers excellent optical and electronic properties by fabricating heterostructures and changing dopant impurity concentrations (e.g., high optical emission efficiency and high speed electron mobility); and (iii) the Fe/GaAs system offers lattice matching conditions.

In this work, we report the structural advantages of the Fe/GaAs system and discuss the quantum size effect on Fe/GaAs heterostructures. The energy band structures of GaAs and Fe layers were calculated using the linear augmented-plane-wave (LAPW) method. We then present the preparation of Fe on GaAs using MBE. The structural and magnetic properties are also described.

Notably, some previous reports have been made about the crystal growth of α-Fe epilayers on GaAs.[6,7] However, to our knowledge, these reports primarily corroborated that obtained Fe films are ferromagnetic, and included little information regarding magnetization. Specifically, the preparation of δ-Fe and its physical properties have not been previously reported. We attempt to obtain a new interpretation about magnetic semiconductor Fe/GaAs heterostructures.

II. THEORETICAL DETAILS

A first-principle electronic structure calculation was made using the self-consistent LAPW method.[8] For a periodic bulk crystal, all space is partitioned into two types of regions: nonoverlapping muffin-tin spheres centered on each atom and the remaining interstitial space between these spheres. $\Psi_{\mathbf{k},\varepsilon}$ satisfies the Schrödinger equation,

$$-\frac{\hbar}{2m}\nabla^2\Psi_{\mathbf{k},\varepsilon}(\mathbf{r})+V(\mathbf{r})\Psi_{\mathbf{k},\varepsilon}(\mathbf{r})=\varepsilon(\mathbf{r})\Psi_{\mathbf{k},\varepsilon}(\mathbf{r}), \tag{1}$$

and

$$V(\mathbf{r})=\begin{cases} V(|\mathbf{r}-\mathbf{R}_n|)=V(r) & \text{(the atomic region)},\\ V(r_0)=0 & \text{(the interstitial region)},\end{cases} \tag{2}$$

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where r_0 is taken to be half the nearest-neighbor distance. For any reciprocal lattice vector $\mathbf{G}_j$, the $\varphi_{\mathbf{k}_j}(\mathbf{r})$ satisfies the Bloch condition with wave vector $\mathbf{k}$, and therefore the expansion of $\Psi_j(\mathbf{r})$ will be of the form

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{j=1}^{N} C_j(\mathbf{G}_j)\varphi_{\mathbf{k}_j}(\mathbf{r}), \quad \text{with } \mathbf{k}_j = \mathbf{k} + \mathbf{G}_j, \tag{3}$$

and

$$\varphi_{\mathbf{k}_j}(\mathbf{r}) = \begin{cases} \displaystyle\sum_{l=0}^{\infty} \sum_{m=-l}^{l} A_{l,m}(\mathbf{k}_j) Y_{l,m}(\theta,\phi) R_l(\mathbf{r}) \\ \quad \text{(the atomic region)}, \\ e^{i\mathbf{k}_j \cdot \mathbf{r}} \quad \text{(the interstitial rigion)}, \end{cases} \tag{4}$$

where N is the number of unit cells of volume, $R_l(\mathbf{r})$ are solutions of the radical Schrödinger equation within the inscribed sphere of radius r_0, $A_{l,m}(\mathbf{k}_j)$ are the arbitary coefficients, and $Y_{l,m}(\theta,\phi)$ are spherical harmonics. Because the eigenvalues are necessary for solving the radical Schrödinger equation, eigenvalues and eigenfunctions must be determined self-consistently.

III. EXPERIMENTAL DETAILS

The growth system was a molecular beam epitaxy system in which chamber pressure for the idle running reached 10^{-10} Torr. Ga and As_4 with a purity of 7 N (99.99999%) were used as sources. Ga and As fluxes were $3.1–7.3 \times 10^{13}$ and $1.9–3.4 \times 10^{13}$ number/cm^2/s, respectively, with a V/III ratio that varied from 1 to 4. Fe fluxes were changed from 6.8×10^{13} to 9.1×10^{13} number/cm^2/s. GaAs and Fe were grown at the substrate temperature T_s ranging from 290 to 580 and 150 to 580 °C, respectively.

The surface condition was checked by reflection high energy electron diffraction (RHEED). Magnetic properties were investigated by magnetic measurements. In order to ignore the diamagnetism of the GaAs substrate, the substrates were scraped to a thickness of less than 100 μm.

IV. RESULTS AND DISCUSSIONS

As stated in Sec. I, the Fe/GaAs system provides lattice matching conditions. Fe is known to be form three types of crystal structure: body-centered-cubic (bcc)-α, face-centered-cubic (fcc)-γ, and bcc-δ structures, as shown in Fig. 1. The lattice constants of the α-Fe, γ-Fe, and δ-Fe phases along the [001] direction were 2.866, 3.674, and 2.932 Å, respectively.[9] If α-Fe and δ-Fe (001) are grown epitaxially on the (001) GaAs surface ($a_0 = 5.6533$ Å), the values of the lattice mismatch at α-Fe/GaAs and δ-Fe/GaAs are 1.4% and 3.7%, respectively. In contrast, on the lattice of γ-Fe on GaAs would become forced due to the large lattice mismatch value which is estimated to be 35%. Therefore, the use of bcc-Fe structures (α-Fe and δ-Fe) is preferable for forming heterostructures to that of the fcc-Fe structure (γ-Fe).

To clarify the nature of the energy states and spin interaction of electrons between Fe and GaAs, we calculated the electronic structures of Fe and GaAs along the [001] growth direction from first principles (Fig. 2). Since GaAs is a III–V compound semiconductor with a direct energy gap, no such state occurred in the energy gap at the Γ point, as shown in Fig. 2 (left side). In contrast, the bcc-Fe element is a ferromagnetic metal. The electron bands crossed the Fermi level, and the energy dispersion curves showed different curves, depending on the direction of spin (Fig. 2, right).

Here, based on the concept of quantum well states of magnetic and nonmagnetic metal superlattices,[10,11] we assumed a structure in which Fe layers are sandwiched by GaAs layers. As seen in the energy band structure of Fe, electrons in the $\Delta_5\uparrow$ bands having up spin could be freely injected into GaAs layers because the same energy state of electrons in the Δ_5 band existed in the GaAs layers. In contrast, regarding the energy state of electrons in the $\Delta_5\downarrow$ band in the Fe layers, only electrons below the Fermi level could be connected to that in the Δ_5 band in the GaAs layers. The electrons that remained at the energy state over the Fermi

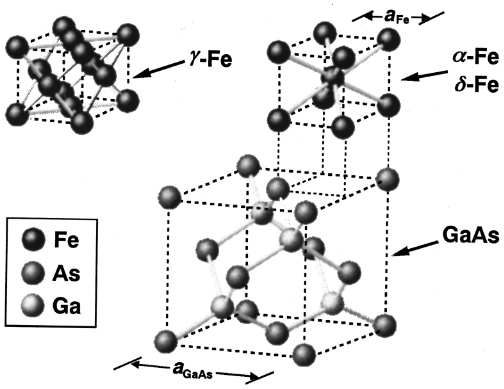

FIG. 1. Crystal structures of Fe and GaAs. α-Fe, γ-Fe, and δ-Fe have bcc, fcc, and bcc structures, respectively. GaAs has a zinc-blende structure.

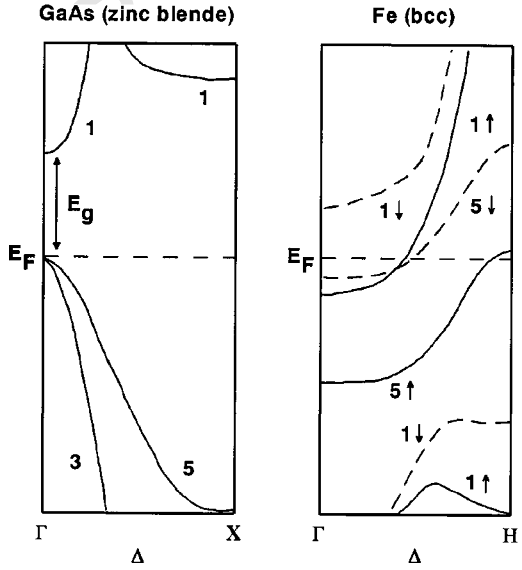

FIG. 2. Band structures of GaAs (zinc-blende structure) and Fe (body-centered-cubic structure). The bands are plotted from the center of $\mathbf{k}$ space to the points on the zone surface along the [001] direction. The horizontal broken lines mark the Fermi energy.

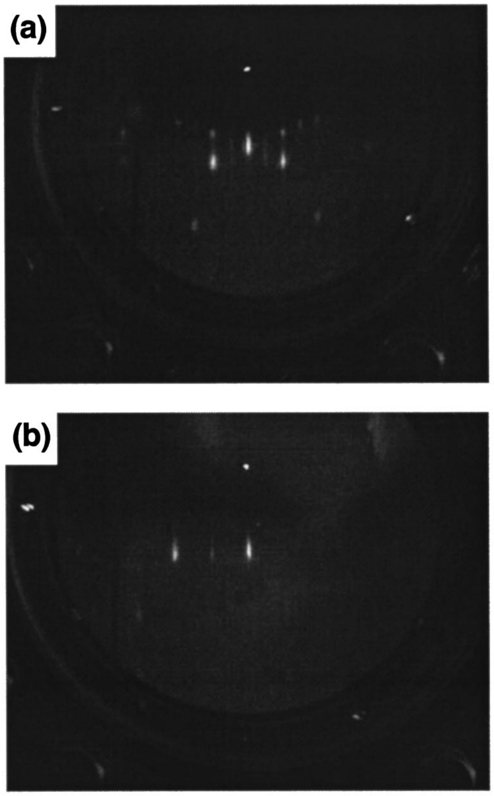

FIG. 3. RHEED patterns along the [110] azimuth obtained from (a) GaAs buffer layers and (b) Fe epilayers on the GaAs (001) substrate at $T_s = 580\,°\mathrm{C}$.

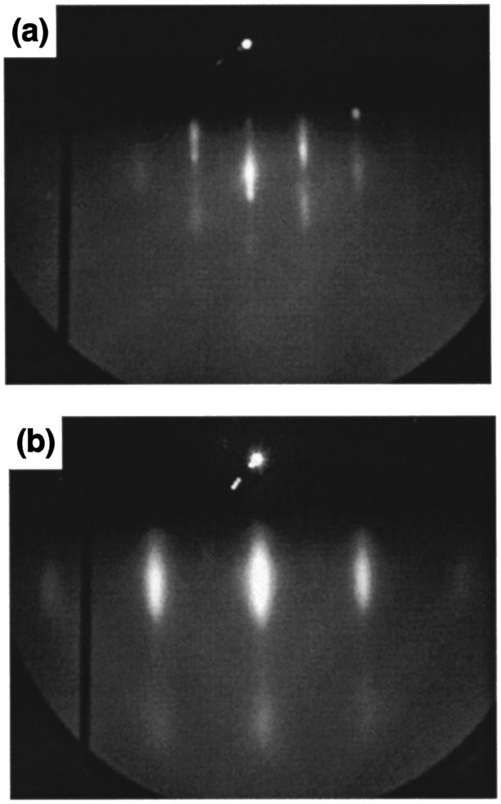

FIG. 4. RHEED patterns along the [110] azimuth obtained from (a) GaAs buffer layers at $T_s = 290\,°\mathrm{C}$ and (b) Fe epilayers on the GaAs (001) substrate at $T_s = 150\,°\mathrm{C}$.

level were reflected at the Fe/GaAs interfaces; therefore, quantum well states were formed in the Fe layers. This phenomenon is ascribed to the prohibited existence of electrons in the Δ_5 band in the GaAs layers. We believe that, as is the case in metal magnetic and nonmagnetic superlattices, the energy level of the quantum well $\Delta_5\downarrow$ band in the Fe layers can be decreased with decreasing Fe layer thickness in Fe/GaAs heterostructure. The calculation result indicates that the energy state of electrons in the Fe layers makes it possible to control magnetism by changing the Fe layer thickness in the GaAs/Fe/GaAs double heterostructure.

MBE growths of Fe were performed on GaAs (001) substrates. The GaAs substrate set on the holder was deoxided by thermal treatment for 10 min at a substrate temperature of 580 °C. Then, Ga and As beams were irradiated to grow GaAs buffer layers on the GaAs (001) substrate. The RHEED pattern of the surface showed a 2×4 GaAs surface with sharp streak lines, indicating that a well-ordered GaAs surface was formed [Fig. 3(a)]. After the Ga and As shutters were closed, the Fe shutter was opened to deposit Fe atoms at a growth rate of 24 nm/h, during which time the substrate temperature of 580 °C was maintained. The RHEED pattern showed a somewhat diffused surface pattern compared to the original pattern of the GaAs surface [Fig. 3(b)]. The line separation for the Fe surface was two times that for GaAs, indicating that the lattice constant of Fe layers was half that of the GaAs layers. This suggests that epitaxial Fe growth was realized on GaAs (001) at $T_s = 580\,°\mathrm{C}$.

In contrast, after a 100-nm-thick undoped GaAs buffer layer growth had occurred on the GaAs (001) substrate at $T_s = 580\,°\mathrm{C}$, we cooled T_s down to 290 °C and simultaneously decreased the As flux while sustaining the Ga flux. A clear and streaky 1×1 pattern of GaAs grown at $T_s = 290\,°\mathrm{C}$ was observed [Fig. 4(a)], while the RHEED pattern for GaAs buffer layers indicated 2×4 GaAs surface configuration. Then the Fe shutter was opened to allow Fe growth. During Fe growth at a growth rate of 15 nm/h, a 1×1 RHEED pattern for the Fe surface was observed, as shown in Fig. 4(b). This indicates that Fe was epitaxially grown on GaAs (001), and the surface of Fe was observed to be very smooth. We noticed that the pattern of streak line separations appeared to have twice as many as that for the GaAs 2×4 patterns. The lattice constant of Fe was half that of GaAs, as was to be expected at this temperature.

X-ray diffraction (XRD) measurements revealed the crystallinity of the obtained Fe films. Figure 5 shows the x-ray spectra of MBE-grown Fe films on the (001) GaAs substrates at $T_s = 580\,°\mathrm{C}$. Two main peaks appeared. One peak, located at 66.05°, was the peak originating from the GaAs (001) substrate. The other peak appeared at 63.128°, which position was consistent with that for theoretically calculated values for the δ-Fe epilayer on GaAs (001). Therefore, we can assume that Fe epilayers grown at $T_s = 580\,°\mathrm{C}$ are δ-Fe.

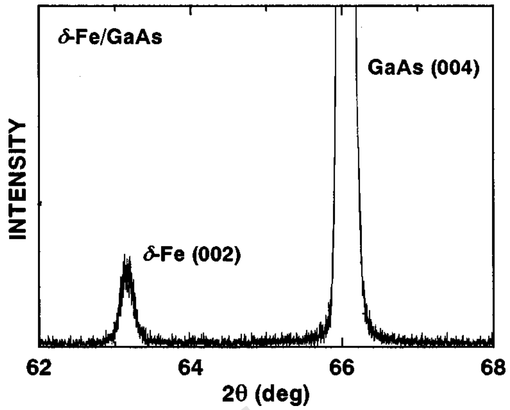

FIG. 5. X-ray diffraction patterns of δ-Fe epilayers on the (001) GaAs substrate.

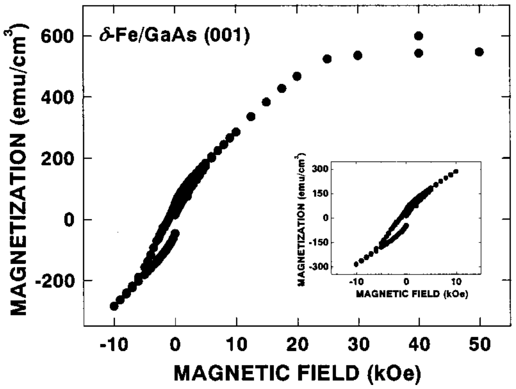

FIG. 7. Magnetization curves for δ-Fe grown on the GaAs (001) substrate at $T_s = 580\,°\mathrm{C}$. The inset shows a magnified view of the area near the zero magnetic field.

In contrast, by adopting a pattern of low-temperature LT growth of GaAs prior to the Fe growth, XRD data for Fe films grown at $T_s = 290\,°\mathrm{C}$ were significantly different from those at $T_s = 580\,°\mathrm{C}$. In addition to the main peak originating from the GaAs (001) substrate, only one peak originating from the epilayer was clearly observed, as seen in Fig. 6, indicating that the obtained Fe film was single crystalline and epitaxially grown on GaAs (001). Moreover, the peak originating *from* the epilayer showed a lattice spacing of $d = 0.32\,\mathrm{nm}$, corresponding to the (001) reflection of α-Fe. Consequently, we proved that two different single crystalline Fe epilayers (α-Fe and δ-Fe) can be epitaxially grown on GaAs (001) by selecting the growth conditions.

The results of the magnetization measurement are displayed in Figs. 7 and 8. The inset shows the magnified view of each figure. In the case of the δ-Fe/GaAs, the magnetization dependence of the magnetic field showed ferromagnetic order, suggesting that δ-Fe/GaAs may be ferromagnetic (Fig. 7). The magnetization was increased with increases in the applied magnetic field. When the magnetic field was larger than 30 kOe, the magnetization was saturated at 550 emu/cm^3.

In the α-Fe/GaAs sample, strong ferromagnetic behavior was observed (Fig. 8). The hysteresis loop was found to be a clear square. The value of remanent magnetization M_r and coercive field H_c were 1100 emu/cm^3 and 20 Oe, respectively. Comparing these results with those of other ferromagnetics/semiconductor structures such as Co/GaAs and MnAs/GaAs, M_r and H_c for Fe/GaAs were extremely high and low values, respectively. In principle, the characteristics of high M_r and low H_c with squareness in the hysteresis are very attractive for inclusion in magnetic digital memory devices.

It should be noted that the formation of Fe_2As and FeAs at the Fe/GaAs interfaces should be prevented because Fe_2As and FeAs are considered to be antiferromagnetic materials.[12] Such formation would be a significant problem when growing heterostructures in which GaAs and Fe are grown alternately; changes in the periodicity of the crystal would occur in the growth direction. However, it was confirmed that the introduction of a process consisting of 1 min irradiation of Ga atoms (without As atoms and before the Fe growth) makes it possible to prevent the decrease of magnetization even when the thickness of Fe layers is decreased. This result is encouraging; MBE growth under specific growth conditions can unify rather poor agreement among the results of previous research, in which disagreement reflects the diffi-

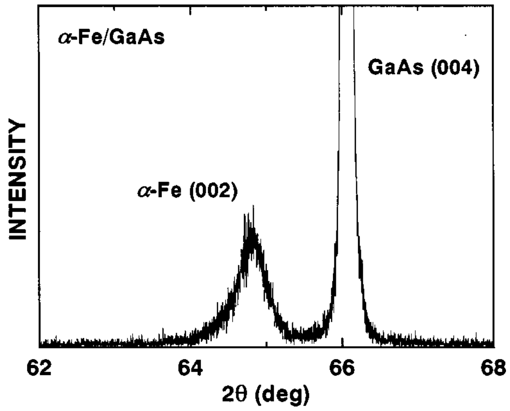

FIG. 6. X-ray diffraction patterns of α-Fe epilayers on the (001) GaAs substrate.

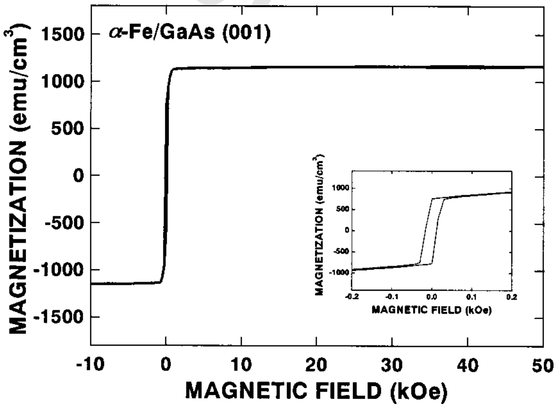

FIG. 8. Magnetization curves for α-Fe grown on the GaAs (001) substrate at $T_s = 290\,°\mathrm{C}$. The inset shows a magnified view of the area near the zero magnetic field.

culty of attaining proper growth conditions. Details of magnetization in Fe/GaAs multilayer structures will be described elsewhere.

V. CONCLUSIONS

We demonstrated the structural advantages of the Fe/GaAs system, and discussed the quantum size effects in the Fe/GaAs heterostructure based on the results derived by the self-consistent LAPW method. Then we demonstrated that α-Fe and δ-Fe layers are epitaxially grown on GaAs (001) at substrate temperatures of 290 and 560 °C, respectively. We emphasize that a low-temperature GaAs buffer layer growth was necessary in order to achieve the growth of α-Fe on GaAs. RHEED observations and XRD measurements of these films confirmed the formation of single crystalline α-Fe/GaAs and δ-Fe/GaAs. Magnetization measurements revealed that the α-Fe and δ-Fe were ferromagnetic materials. Although quantum size effects were not confirmed in this investigation, we have provided valuable information relating to the epitaxial growth of Fe/GaAs multilayer structures.

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