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MBE Growth of Diluted Magnetic Semiconductor Gadolinium-doped GaAs

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We prepared diluted-magnetic semiconductors (DMSs) Gd doped GaAs on GaAs (001) substrates by means of molecular beam epitaxy (MBE) method and their magnetic and structural properties were investigated. Samples with different Gd concentration were obtained from different growth conditions of vapor flux rates of Gd and Ga. Reflection high-energy electron diffraction (RHEED), cross-sectional transmission electron microscopy (TEM) show that GaAs:Gd DMSs were grown epitaxially on GaAs buffer layer. X-ray diffraction (XRD) profiles indicate that there are two phases, GdAs compounds and GaAs matrix with slightly doped Gd. The lattice constant around a Gd atom seems to be larger than GaAs one. From the result of magnetization measurement, GaAs:Gd DMS shows a ferromagnetic-like behavior at room temperature.

Key words: Molecular beam epitaxy, Diluted-magnetic semiconductor, Gadolinium doped GaAs, Cross-sectional TEM, Rare earth

1. INTRODUCTION

DMSs have been much attractive materials from both the next-generation spintronics devices and the fundamental physics. For viable applications using DMSs such as spin LED [1-2] or spin transistor [3-4], it is necessary to make DMSs with higher Curie temperature (Tc) above the room temperature and with better lattice matching with general semiconductors. DMSs which include transition metals as magnetic elements are extensively studied. Especially, hole-mediated ferromagnetism in Mn doped GaAs (hereafter abbreviated to GaAs:Mn,) leads to important concepts of electrical controllability of magnetism in spintronics devices[5], though the Tc of GaAs:Mn has been lower than room temperature[6-7]. Most recently some groups have reported the growth and the magnetic properties of DMSs of rare earth doped III-V semiconductors [8-11]. S.Dhar *et al.* were reported that GaN:Gd has colossal magnetic moment and ferromagnetism above the room temperature. On the other hand, there are few report about DMSs of GaAs:Gd [9]. In this report, we investigate GaAs:Gd DMSs, which is grown on GaAs (001) substrate by means of MBE method. Crystal structures of the samples were studied by the cross-sectional transmission electron microscopy (TEM) observation and x-ray diffraction (XRD). The magnetic properties were characterized by macroscopic magnetization measurements.

2. EXPERIMENTAL

GaAs:Gd DMSs were grown in ultra-high vacuum chamber by means of MBE method, on GaAs (001) buffer layer which was pre-grown on substrate. Substrate temperature was set at 500 ~ 550 °C, and As evaporation cell were set at around 200 °C, respectively. We controlled the Gd flux with changing the temperature of Gd evaporation cell from 1350 °C to 1450 °C in steps of 50 °C. In Table I, growth conditions of Gd cell temperature and growth rates are tabulated. We measured deposition rates of DMSs using a quartz crystal monitor. For all samples, thickness of DMS layer are designed to be approximately 1μm, which were capped with 100~200nm GaAs. During MBE growth, we observed *in-situ* RHEED pattern. Crystal structures of samples were studied by cross-sectional TEM observation (JEOL JEM-3010) with 300 kV high voltages and XRD measuremsnts (Shimazu XRD-6100). Magnetizations of samples were measured using a superconducting quantum interference device (SQUID, Quantum Design, MPMS-5S).

3. RESULTS AND DISCUSSIONS

Figure 1 shows in-situ RHEED patterns during MBE growth of GaAs:Gd at Gd cell 1350 °C, sample C. The image of (a) is obtained before the growth of GaAs:Gd layer, and (b) is after the growth. In the image (a), we observed brilliant streak pattern, and in the (b), spot-like pattern is observed. RHEED patterns of other samples show the similar feature. This means that GaAs:Gd layers in all samples have been grown epitaxially on GaAs buffer layer, however, the surface of GaAs:Gd layer tends to be rough at the end of the growth.

Table I Growth conditions of GaAs:Gd DMS samples in MBE method.

Sample	Temperature of Gd-cell	Growth Rate (Å/sec)	Growth Time (min)
A	1450°C	2.0	82
B	1400°C	2.2	76
C	1350°C	1.5	120

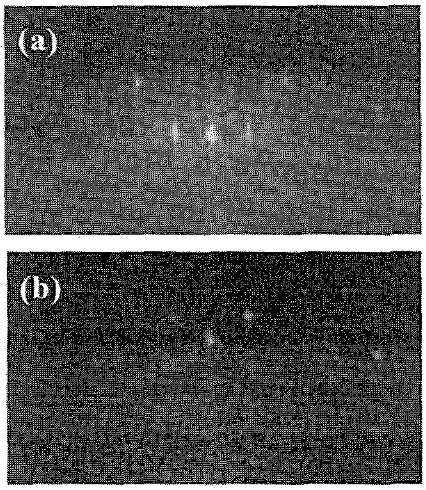

Fig.1 *In-situ* RHEED pattern obtained during the growth of sample (C) grown at Gd cell 1350 °C. (a) before the growth of GaAs:Gd DMS layer, (b) after the growth of GaAs:Gd DMS layer.

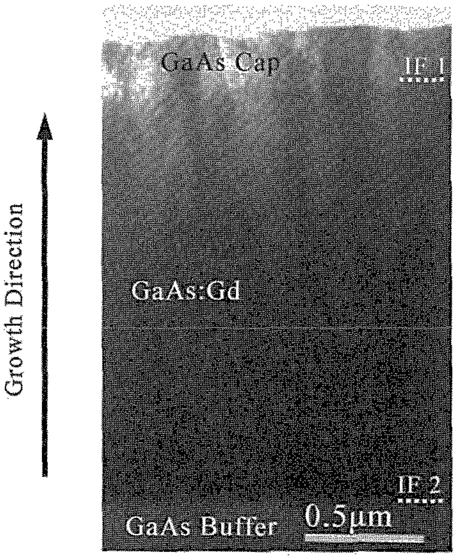

Fig.2 Cross-sectional TEM image GaAsGd of sample C. Interfaces of between GaAsGd and buffer layer (IF 2), and between GaAs:Gd and cap layer (IF 1) are observed.

Figure 2 shows the cross-sectional TEM images of whole GaAs:Gd DMS layer in sample C. Similar images were observed from sample A and sample B. From the figure 2, we shows successful growth of GaAs:Gd on GaAs (001). GaAs:Gd DMS layer is slightly dark compared to either GaAs buffer layer or GaAs cap layer in figure 2. Interface (I.F.) between the cap layer and GaAs:Gd DMS layer has less flatness than I.F. between the buffer and DMS layer. This coincides with the spotty RHEED pattern after the growth of DMS. There are some longitudinal stripe patterns in the upper area of DMS layer in figure 2. We think these stripes are due to lattice distortions which is caused by Gd doping.

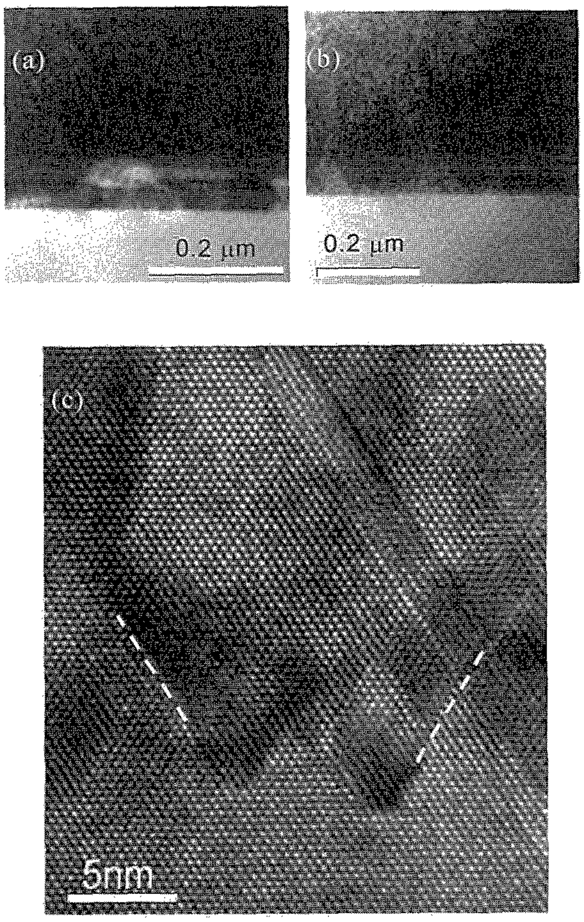

Fig.3 (a) Close-up TEM image at interface between GaAs:Gd DMS and buffer layer of sample A, (b) of sample C. (c) High-resolution TEM image of GaAs:Gd of sample B. Dashed line indicate dislocations along (111) plane.

TEM images at interfaces between GaAs:Gd layer and GaAs buffer of sample A and B are shown in figures 3(a) and 3(b), respectively. In Fig.3(a), there exists black and white region near the interface, which are Gd-rich and Gd-lean region, respectively. This means, when the temperature Gd-cell is high, doped Gd makes inhomogeneity of Gd concentration. We found little inhomogeneity in Fig.3(b). Fig.3(c) shows a high-resolution TEM image of GaAs:Gd DMS in sample B. GaAs:Gd DMS has crystal dislocations along (111) plane. This crystal dislocation was observed at all samples.

Figure 4 shows XRD profiles of all GaAs:Gd samples. A profile of GaAs substrate is also shown as a reference in Fig.4. Three sharp peaks from GaAs (002), (004) and (006) are observed in all profiles. We think there are two types of Gd; one is Gd atom randomly dispersed in GaAs matrix as substitutional or interstitial atom, which should make broad peaks much close to the GaAs substrate peaks, and the other is NaCl type GdAs. In the profile A and B, we found peaks of rocksalt GdAs. GaAs has zinc-blend structure, however, lattice constants of these two structures are very close and so these two structure can have lattice matching in the direction of (001).

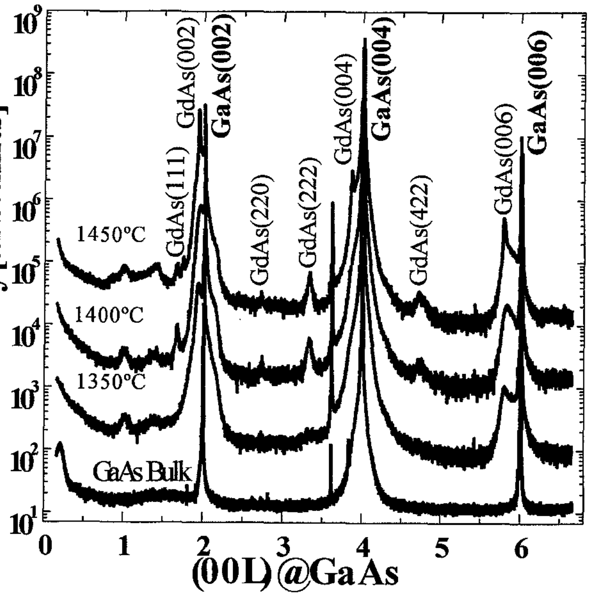

Fig.4 XRD profiles of GaAsGd DMSs grown at Gd cell temperature from 1350 °C to 1450 °C, and GaAs bulk substrate.

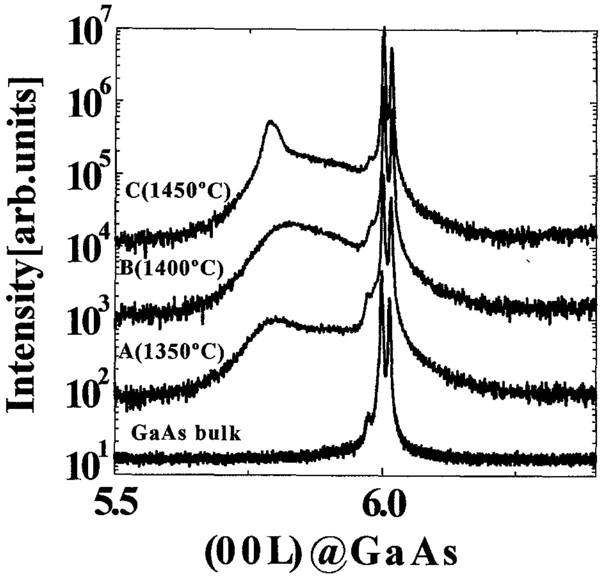

Fig.5 XRD profiles around GaAs (006) of GaAsGd DMSs grown at Gd cell of 1350 °C ~ 1450 °C , and GaAs bulk substrate.

Figure 5 shows XRD profiles around GaAs (006) peak. In each profiles, except for GaAs substrate, a broad peak exists at a little lower than GaAs peak, which is due to the first type phase as mentioned above: randomly Gd-doped GaAs. In the profile of sample C, another peak superimposed on the broad peak is clearly observed. This peak is supposed to be from the second type phase: the rocksalt GdAs. From the position of broad peaks, the lattice mismatch against GaAs buffer is estimated to be 3.7%, 2.9%, and 3.4% for sample A, B, and C, respectively. In order to estimate Gd concentration in samples, we perform following analysis. (i) First, we evaluated Gd concentration in sample A using Gd flux ratio, which were obtained from monitoring other growth of Gd metal films in the same MBE system. (ii) Next, we analyzed the lattice distortion of randomly doped GaAs:Gd phase in sample A, on the assumption of Vegard's law, and estimated lattice constant of rocksalt GdAs as 5.86Å. (iii) Finally, using the lattice constant of GdAs, we obtained Gd concentration of first phase GaAs:Gd in sample B, and C, from the lattice distortion. The obtained value of Gd atomic concentration is 5.8 %, 4.7%, and 5.5%, for sample A, B, and C, respectively.

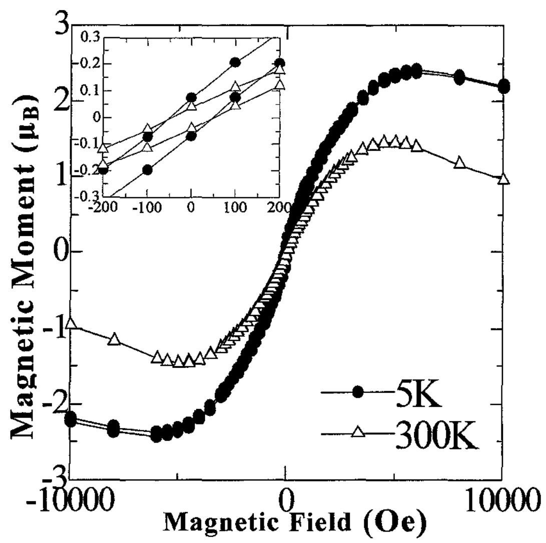

Fig.6 Magnetization versus magnetic field curves of sample (B) grown at Gd cell 1400 °C. The inset is a close-up around origin.

Figure 6 shows the result of magnetization measurements of GaAs:Gd DMS of sample B, where data are not calibrated in terms of a diamagnetism of GaAs substrate. A magnetic field was applied in the sample plane. In figure 6, magnetization of both temperature 5K and 300K saturate around 5000 Oe. As shown in the inset of figure 6, magnetic hysteresis was observed for both temperatures, which comes from ferromagnetic phase in the sample. Rocksalt GdAs phase has been reported as antiferromagnetic in stoichiometric sample [12]. If not stoichiometric, GdAs phase might have ferromagnetic coupling. However it is expected to be in low temperature, less than 20K [13]. Therefore, the hysteresis in our sample comes from the magnet moment per randomly dispersed Gd atom in GaAs matrix, which has ferromagnetic coupling at even the room temperature. From the Gd concentration, the distance between each Gd atom is estimated to be as 8 ~ 10 Å. This distance is slightly long for directly magnetic coupling. Some spin-polarized carriers in GaAs matrix might mediate the ferromagnetic interaction between Gd atoms. The magnetic moment per Gd atom, which is evaluated assuming all Gd atoms are ordered ferromagnetically, comes close to 1.5 μ_B at high field at 300K. This saturation moment is large as compared to other Gd compounds, but not so large as reported in [14]. We expect that less concentration of Gd may increase spin-polarized carriers around one Gd atom, and may lead to larger magnetic moment. More careful measurements of magnetization using samples with more wide range of Gd concentration is necessary to reveal role of spin carriers in magnetic couplings.

4. CONCLUSION

We have successfully grown GaAs:Gd DMSs on GaAs(001) by MBE method, where temperature of Gd evaporation cell is ranging from 1350°C to 1450°C. From, cross-sectional TEM observation, we found that GaAs:Gd DMSs have flat interface however samples have fluctuation of Gd concentration. When the temperature Gd cell is high, there are Gd-rich region and Gd-lean region. From high resolution TEM image, we found that GaAs:Gd DMSs have dislocation along (111) and there is some inhomogeneity of Gd concentration at around interface between DMS and buffer layer in sample A. Gd concentration of the DMSs in our samples were evaluated to be approximately 5.3 %. From magnetization measurements, GaAs:Gd DMSs show soft ferromagnetic behavior at both 5K and 300K.

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