Epitaxial growth of a vacancy-ordered Ga_2Se_3 thin film on a vicinal Si(001) substrate

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Abstract

We have fabricated a vacancy-ordered Ga_2Se_3 epitaxial film by molecular beam epitaxy on a vicinal Si(001) surface tilted toward the $[110]$ direction by 4°. It is found by reflection high-energy electron diffraction observations that Ga_2Se_3 films grown around 470°C with Se/Ga flux ratios higher than 100 show excellent ordering of Ga vacancies. The vacancy ordering was not observed when the substrate temperature was higher than 490°C. In addition, polycrystalline film growth was dominant when the substrate temperature was lower than 450°C, and no vacancy ordering was observed when the Se/Ga ratio was 10. Only a poor crystallinity Ga_2Se_3 film was obtained on a nominal Si(001) substrate, which suggests that the single-domain 2×1 reconstruction on the vicinal Si(001) surface is essential to the growth of the vacancy-ordered Ga_2Se_3 film.

Keywords: A1. Reflection high-energy electron diffraction, A3. Molecular beam epitaxy, B1. Gallium compounds, B2. Semiconducting gallium compounds

1. Introduction

There is a growing interest in the III-VI compound semiconductor Ga_2Se_3 due to its unique optical properties. Ga_2Se_3 has been expected to show polarization dependent optical properties that are controlled by Ga vacancies [1, 2]. A bulk Ga_2Se_3 has a defective zincblende structure, in which one third of the Ga sites are vacant [3]. Ga_2Se_3 crystallizes into two forms, α and β; in the α-form, vacancies are disordered throughout the crystal, whereas the β-form has an ordered arrangement of vacancies [4, 5]. It has been also reported that there are two phases of the vacancy-ordering of β-Ga_2Se_3; monoclinic [5] and orthorhombic ones [6].

With regard to the thin film growth of Ga_2Se_3, vacancy-ordered epitaxial films have been grown on such III-V semiconductors as GaP [1, 7, 8] and GaAs [9, 10]. It has been also found that these vacancy-ordered films shows photon-polarization dependent optical anisotropies; optical absorption [1, 2], photoconductivity [2], Raman scattering [11] and photoluminescence [12]. Until now, however, there has been no report about the growth of an epitaxial Ga_2Se_3 film on a Si substrate, although Ga_2Se_3 and Si have very similar lattice constants (a triclinic substructure cell in monoclinic Ga_2Se_3: $a = b = 0.548$ nm, $c = 0.541$ nm [5], Si: $a = 0.543$ nm).

In this paper we report the first attempt to grow a vacancy-ordered epitaxial Ga_2Se_3 film on a Si(001) substrate. It is well known that monoatomic steps cause the double-domain 2×2 surface reconstruction on a nominal Si(001) [13, 14]. In the case of the heteroepitaxial growth of a compound semiconductor on a double-domain Si(001) surface, anti-phase domain boundaries are introduced into the grown film, and its crystallinity becomes poor [13, 14]. In order to grow a single-domain Ga_2Se_3 film with good crystallinity, we tried to use a vicinal Si(001) substrate whose surface is inclined toward the [110] direction by 4°. Bilayer-steps are stable on such a vicinal surface, so that every Si dimer row becomes parallel to the $[110]$ direction [14-16]. It is expected that Ga vacancies are ordered in the epitaxial film of Ga_2Se_3 even when it is grown on a non-polar Si surface, because the anisotropic 2×1 reconstruction of the substrate surface makes the Ga_2Se_3 film have a single-domain structure. It is also plausible that an epitaxial Ga_2Se_3 film with a unique crystallographic orientation will grow on the Si(001) substrate if it can most effectively accommodate the minor lattice mismatch between Si and Ga_2Se_3. Here we will report on reflection high-energy electron diffraction (RHEED) observations of Ga_2Se_3 films fabricated under several different growth conditions, and elucidate the best condition to obtain the vacancy-ordered Ga_2Se_3 film.

2. Experimental

Thin films of Ga_2Se_3 were grown on the 4°-off Si(001) substrates using a molecular beam epitaxy (MBE) chamber equipped with a RHEED system. A single crystalline Si(001) substrate (P-doped *n*-type wafer with 1.0 ~ 10 Ωcm resistivity) tilted toward the $[110]$ direction by 4° was cleaned by the direct current heating; overnight heating at 600°C, repeated flash heating from 900°C to 1200°C, and annealing at 900°C for several tens of minutes. Then the substrate temperature was set to the growth temperature (400°C ~ 500°C), at which clear 2×1 reconstruction could be seen in the RHEED pattern. Growth of Ga_2Se_3 was made using individual Ga and Se Knudsen cells with a beam pressure of Ga at 3.0 $\times 10^{-6}$ Pa. Se/Ga beam equivalent pressure ratio was varied in the range of 10 to 1000. At the beginning of the growth, only the Ga flux was irradiated onto the Si(001) surface for one minute. This procedure can prevent the excess reaction of Se atoms with the Si surface, which results in the formation of a disordered layer [17, 18]. The growth rate was about 70 nm/h for the substrate temperature of 470°C and the Se/Ga ratio of 100. For the comparison, a Ga_2Se_3 film was grown also on a nominal Si(001) substrate through the same cleaning and growth processes as on the vicinal Si(001) surface.

3. Results and discussion

Before the growth of a Ga_2Se_3 film, the vicinal Si(001) surface must show a well-ordered single-domain 2×1 reconstruction. Fig. 1(a) indicates a RHEED pattern of the Si(001)-2×1 surface at 470°C observed along the direction rotated around the surface normal by 4° from the $[110]$ crystal axis of Si. In this direction clear extra streaks could be seen between streaks of the 1×1 surface. In contrast, only faint extra streaks were seen in the RHEED pattern observed along the $[\bar{1}10]$ axis of Si, which means that the surface has the well-ordered 2×1 structure. A schematic view of the vicinal 2×1 surface is shown in Fig. 1(b). After the deposition of Ga for 1 minute, these extra streaks of the 2×1 reconstruction disappeared, and some faint streaks appeared between 1×1 streaks. Many types of the surface reconstruction are known for the Ga/Si(001) system [19], In the present work we didn't pursue control of the reconstruction, because it showed no effect on the subsequent growth process.

Figs. 2(a) and 2(b) show RHEED patterns observed after the irradiation of Se flux at the pressure of 3×10^{-4} Pa (Se/Ga ratio = 100) for 1 minute and 5 minutes, respectively. As shown in the figures, the streak pattern of the substrate changed into a clear spotty one. These spots reflect the growth of a film with a zincblende structure. After the deposition of Ga and Se flux for 1 hour, extra diffraction spots appeared between these preceding spots. Figs. 2(c) and 2(d) indicate RHEED patterns along the $[110]$ and $[\bar{1}10]$ azimuths of the Si(001) substrate, respectively, which were observed after 2 hours growth followed by cooling to room temperature. In addition to the spots of the zincblende structure, horizontally aligned extra spots with one-third periodicity can be seen only in the RHEED pattern observed along the [110] direction. These spots are considered to originate from the ordering of Ga vacancies, because these RHEED images are very similar to those of the vacancy-ordered Ga_2Se_3 film grown on a GaP or a GaAs substrate [7, 9, 10]. Therefore, we conclude that the grown film on the vicinal Si(001) is the vacancy-ordered Ga_2Se_3. At present it is not yet known whether this vacancy-ordered Ga_2Se_3 film has the monoclinic or the orthorhombic structure. In order to bring this problem to a settlement, structural analysis using high-resolution transmission electron microscopy is under the investigation [20].

The vacancy-ordered Ga_2Se_3 film could be obtained for the Se/Ga flux intensity ratio in the range of 100 to 1000. However, no extra spot with the one-third periodicity was observed when the Se/Ga ratio was lower than 100. Fig. 3(a) shows a RHEED pattern of the film grown for 2 hours at 470°C with the Se/Ga ratio of 10, in which only the spots of the zincblende structure appear. It is supposed that a vacancy-disordered α-Ga_2Se_3 film grows when the Se/Ga flux intensity ratio is as low as 10.

The substrate temperature also affects the crystallinity of the Ga_2Se_3 film. As shown in Fig. 3(b), many ring patterns were observed in the RHEED images when the Se/Ga ratio was 100 and the substrate temperature was lower than 450°C, which suggests the growth of polycrystalline Ga_2Se_3. At substrate temperatures higher than 490°C, on the contrary, extra spots coming from the ordered Ga vacancies disappeared, and only the spots of the zincblende structure remained in the RHEED pattern, as shown in Fig. 3(c). In the latter case the growth of vacancy-disordered α-Ga_2Se_3 is plausible.

As described in the previous section, a nominal Si(001) surface has a double-domain 2×2 structure, and was considered to be inadequate for the growth of a vacancy-ordered Ga_2Se_3 film. Fig. 3(d) indicates a RHEED image of the Ga_2Se_3 film grown on the

Si(001)-2×2 surface at the substrate temperature of 480°C and the Se/Ga ratio of 1000. Clear ring patterns in the RHEED image suggest the polycrystalline film growth, which could not produce the vacancy-ordered Ga_2Se_3 film. Therefore, it is concluded that the well-ordered 2×1 surface reconstruction of the Si(001) surface is essential for the growth of the vacancy-ordered Ga_2Se_3 epitaxial film.

From these results it is suggested that far excessive Se atoms are necessary for the growth of a vacancy-ordered Ga_2Se_3 film. When the Se/Ga ratio is low, amount of the Se atom is obviously deficient on the growing Ga_2Se_3 surface. When the substrate temperature is too high, residence time of incident Se atoms on the surface becomes short due to the high re-evaporation rate of Se, so that the amount of Se atoms contributing to the growth of Ga_2Se_3 film becomes poor. If the substrate temperature is too low, however, reaction or migration of incident atoms is insufficient so that the polycrystalline film growth becomes dominant. Therefore moderate substrate temperature around 470°C, in addition to the high Se/Ga ratio, is good for the vacancy ordering. The single-domain 2×1 reconstruction of the Si(001) surface is also indispensable to avoid the anti-phase domain boundary that degrades the crystallinity of the Ga_2Se_3 film.

4. Conclusions

We investigated the growth of a vacancy-ordered Ga_2Se_3 film on a nearly lattice-matched Si(001) substrate by MBE. In order to obtain a single-domain epitaxial film, use of a vicinal Si(001) surface tilted toward the $[110]$ direction by 4° was essential. Ga_2Se_3 films grown at the substrate temperature about 470°C and the Se/Ga flux ration higher than 100 showed the ordering of Ga vacancies. It was revealed that the well-ordered 2×1 reconstruction on the vicinal Si(001) surface is indispensable to the epitaxial growth of the vacancy-ordered Ga_2Se_3 film.

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Figure captions

Fig. 1 (a) A RHEED pattern of the single-domain 2×1 reconstruction of a vicinal Si(001) surface. The direction of the incident electron beam was rotated from the [110] crystal axis of Si around the surface normal by 4° in order to indicate extra streaks of the reconstruction clearly. (b) A schematic view of the vicinal Si(001)-2×1 surface. Pairs of black dots indicate dimer rows of Si on the (001) surface.

Fig. 2 RHEED patterns of a vacancy-ordered Ga_2Se_3 film grown on the vicinal Si(001)-2×1 surface. The incident electron beam was parallel to the [110] crystal axis of the Si substrate in (a, b, c) while it was parallel to the $[\bar{1}10]$ axis of Si in (d). The growth temperature was 470°C and the Se/Ga ratio was 100 at the Ga beam pressure of 3×10^{-6} Pa. (a) After 1 minute growth, (b) after 5 minutes growth, and (c, d) after 2 hours growth.

Fig. 3 RHEED patterns of Ga_2Se_3 films fabricated under different growth conditions from those for the sample shown in Fig. 2. The incident electron beam was parallel to the [110] crystal axis of the Si substrate, and the Ga beam intensity was fixed to 3×10^{-6} Pa for every sample. (a) Grown at 470°C with the Se/Ga ratio of 10, (b) grown at 450°C with the Se/Ga ratio of 100, (c) grown at 490°C with the Se/Ga ratio of 100, and (d) grown on a nominal Si(001)-2×2 surface at 480°C with the Se/Ga ratio of 1000.

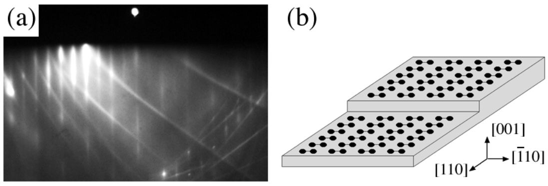

Fig. 1

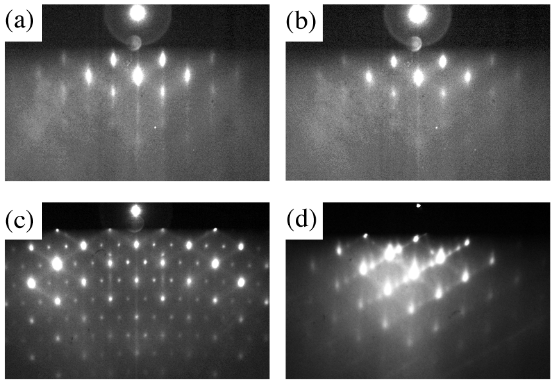

Fig. 2

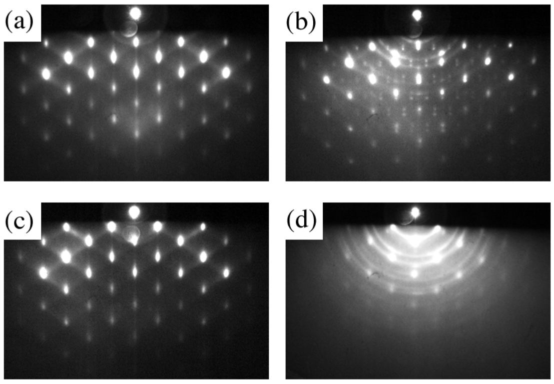

Fig. 3