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Impact of the Precursor Conditions on the Solid-phase Crystallization of Amorphous GaAs Thin Films on Glass and Plastic Substrates

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Abstract

We investigated the solid-phase crystallization (SPC) of GaAs mainly focusing on the amorphous precursor film conditions. The deposition temperature (T_d) and the atomic ratio of Ga to As ($R_{Ga/As}$) strongly influenced the subsequent SPC of GaAs. The precise control of T_d and $R_{Ga/As}$ enlarged the grain size to the sub-μm order, which is more than an order of magnitude larger than that of conventional polycrystalline GaAs layers. These findings will be highly essential and useful for controlling the crystallization process of various compound semiconductor thin films

1. Introduction

The technology of polycrystalline thin films is the key to expanding the versatility of III-V compound semiconductors. We have recently reported that, in the SPC of Ge, the grain size can be dramatically increased by densifying amorphous layers by controlling the deposition temperature [1] or doping elements [2,3]. This significantly suppressed the grain boundary (GB) carrier scattering and improved the hole mobility of the polycrystalline Ge [4]. This approach was also effective for alloys such as SiGe [5] and GeSn [6,7]. In this study, we focused on the GaAs precursor, which will have the great effect on subsequent SPC.

2. Experimental Procedures

The 200-nm-thick GaAs precursors were deposited on glass and plastic substrates using a Knudsen cell for Ga and As in a molecular beam deposition system. The crucible temperature of the Ga Knudsen cell was fixed at 925 °C, while that of the As Knudsen cell ranged from 220 to 245 °C to modulate $R_{Ga/As}$. $R_{Ga/As}$ was obtained using energy dispersive X-ray (EDX) spectroscopy, which was calibrated using a standard GaAs sample. T_d ranged from 25 °C to 125 °C. The samples were then loaded into a conventional tube furnace under a N_2 (99.9%) atmosphere and annealed at 400 °C for 25 h. The samples were evaluated using Raman scattering spectroscopy, scanning electron microscopy (SEM) analysis, electron backscatter diffraction (EBSD) analysis, and transmission electron microscopy (TEM) analyses with an EDX spectrometer and a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM).

3. Results and Discussion

We examined the influence of $R_{Ga/As}$ and T_d on the state of as-deposited GaAs layers using the Raman spectroscopy. Figure 1(a) shows that the sample with $R_{Ga/As} = 1.3$ exhibits small peaks corresponding to the transverse optical (TO) mode (~270 cm^{-1}) and the longitudinal optical (LO) mode (~290 cm^{-1}) of crystalline GaAs, while the samples with $R_{Ga/As} \leq 1.1$ exhibit broad peaks corresponding to amorphous GaAs. These results indicate that, for high $R_{Ga/As}$, the GaAs layer crystallizes during deposition even at room temperature. Figure 1(b) shows that the samples for $T_d \geq 100$ °C exhibit peaks corresponding to crystalline GaAs, while the samples for $T_d \leq 75$ °C exhibit broad peaks corresponding to amorphous GaAs. These results indicate that the GaAs layer becomes easier to crystallize as T_d increases. From the Raman study, the state of the as-deposited GaAs layers is comprehensively summarized in Fig. 1(c). The state of GaAs strongly depends on both $R_{Ga/As}$ and T_d: the higher $R_{Ga/As}$ and T_d induce the crystallization of GaAs more significantly. Because the crystalline state is more energetically stable than the amorphous state, the more prominent atomic migration makes the deposited film more crystallized. When $R_{Ga/As}$ is high, liquid phase Ga is considered to be present. The atomic migration is generally significant in liquid phase, which may induce the crystallization even at room temperature. Conversely, higher T_d gives the atoms higher energy and more promotes the migration, which also promotes the crystallization of the GaAs layer.

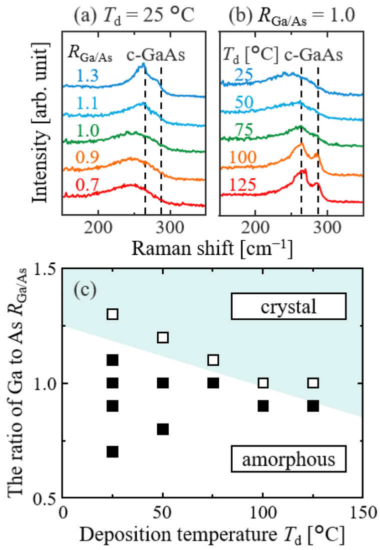

Fig. 1. Raman spectroscopy study of the as-deposited GaAs layers. (a,b) Raman spectra. (c) Influence of $R_{Ga/As}$ and T_d on the crystalline state: closed squares show amorphous and open squares show crystalline.

We examined the sample surface after annealing at 400 °C for 25 h using SEM. Figure 2 shows that the sample surface strongly depends on $R_{Ga/As}$: the surface is rough for

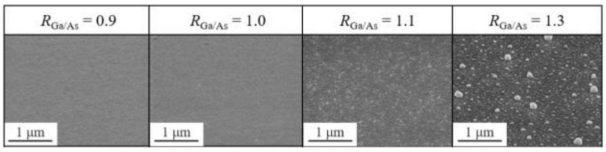

Fig. 2. Surface SEM images of the T_d = 25 °C samples annealed at 400 °C for 25 h with various $R_{Ga/As}$, where the samples are 70 ° tilted.

$R_{Ga/As} \geq 1.1$, while flat for $R_{Ga/As} \leq 1.0$. The Ga-rich samples have the particles on the surface, which are likely excess Ga.

The inverse pole figures (IPFs) images in the GaAs layers formed by SPC were obtained using the EBSD analyses. Figure 3 shows that both grain size and crystal orientation dramatically vary with $R_{Ga/As}$ and T_d. We note that $R_{Ga/As}$ = 1.0 is not necessarily optimal for obtaining large-grained GaAs layer. For the samples crystallized during deposition (Fig. 1), the GaAs layers after annealing are nanocrystalline below the detection limit of the EBSD system for all T_d (Figs. 3(a), (e), (h), (j) and (l)). This behavior is attributed to the formation of numerous crystalline nuclei during deposition. For the samples that were amorphous before annealing (Fig. 1), the grains are identified by IPF images (Figs. 3(b), (c), (d), (f), (i), (k) and (m)) after annealing, except for $R_{Ga/As} \leq$ 0.8 (Fig. 3(g)). These results indicate that the SPC of amorphous layers produces larger grains than the crystallization during deposition, while As clusters in As-rich samples inhibit the lateral growth of GaAs grains. Especially, Figs. 3(b), (f) and (i) exhibit large grains with sub µm orders. The preferential (111) orientation likely reflects the surface energy minimization of heterogeneous nucleation at the interface. In these samples, $R_{Ga/As}$ and T_d are just before the conditions where crystallization occurs during deposition. Therefore, the amorphous GaAs layers for these samples may have a high atomic density close to that of crystalline GaAs. In the previous study about SPC of group IV semiconductors, we reported that the densification of the amorphous layer promotes the lateral growth and increases the grain size. This phenomenon may be applied to GaAs as well. Further, the

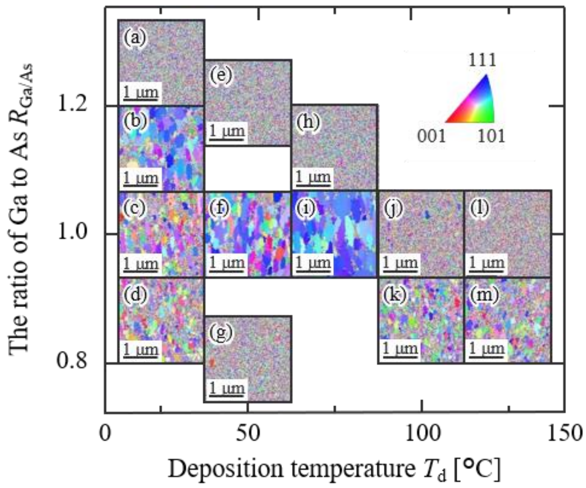

Fig. 3. (a)–(m) IPF images of the samples annealed at 400 °C for 25 h with various $R_{Ga/As}$ and T_d. The coloration in the IPF images indicates the crystal orientation according to the legend inserted in the figure.

grain size in the GaAs layers formed by SPC depends on $R_{Ga/As}$ in addition to T_d. $R_{Ga/As}$ = 1.0 and T_d = 75 °C are the approximate optimum conditions for obtaining high quality GaAs layer.

Since the GaAs layer can be synthesized at 400 °C, we fabricated that the under optimum conditions ($R_{Ga/As}$ = 1.0 and T_d = 75 °C) on a plastic substrate. Figure 4(a) shows that the grain size of the sample on the plastic substrate is slightly smaller than that on glass. This behavior is common in other semiconductor layers, which was explained that the film strain due to the substrate bending increases the nucleation frequency. Figure 4(b) shows that a flat surface GaAs layer is formed uniformly on the substrate. Figures 4(c)–(e) show that the GaAs layer, that is stoichiometric composition ($R_{Ga/As}$ = 1.0) on macroscopic EDX observation. Figure 4(f) shows that the crystal grain of GaAs contains dislocations. The grain size is a few hundred nm, which is consistent with the EBSD results (Fig. 4(a)). Figure 4(g) shows that there are no extended defects in the vicinity of the grain boundary, which may have been formed by the collision of the grains by the lateral growth.

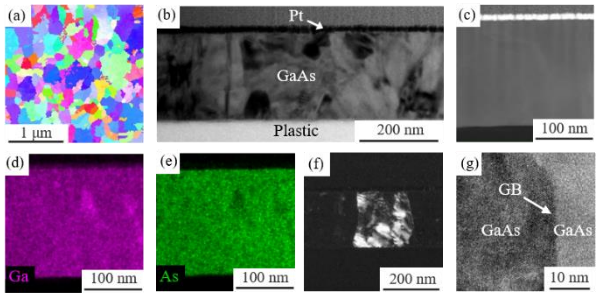

Fig. 4. Characterization of the cross-section of the GaAs layer on a plastic substrate annealed at 400 °C for 25 h with T_d = 75 °C, $R_{Ga/As}$ = 1.0. (a) IPF image. (b) Bright-field TEM image. (c) HAADF-STEM image. EDX elemental maps of (d) Ga and (e) As. (f) Dark-field TEM image. (g) High-resolution lattice images showing a GB.

4. Conclusions

The deposition conditions of the GaAs precursor had a great influence on the SPC of the GaAs layers on insulators. Both high T_d and $R_{Ga/As}$ formed nanocrystalline GaAs layer during deposition. By controlling T_d and $R_{Ga/As}$ just before the crystallization conditions of as-deposited GaAs, the grain size of the GaAs layer after SPC reached the sub-µm order, likely due to the precursor densification effect. Although there is still much room for improving crystallinity, the adaptability of low-temperature process will be useful for flexible electronics.

References

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