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Effect of Post-annealing on Magnetic Properties of Ternary Transition-metal Chalcogenide $(Cr,Fe)_{1-\delta}Te$ thin films grown by MBE

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Abstract

We fabricated ternary transition metal telluride compound hexagonal-$(Cr,Fe)_{1-\delta}Te$ films by molecular beam epitaxy (MBE). We have investigated the effect of post-annealing process on the magnetic property of a $(Cr,Fe)_{1-\delta}Te$ film grown at 150 ºC. We found that structural and magnetic properties were varied by changing the annealing temperature. Especially, the film annealed at 450 ºC, which is the highest annealing temperature in this study, showed quite different ferromagnetic property from other films with a ferromagnetism, which could be maintained from low temperature to higher temperature up to 300 K, and much larger magnetization around room temperature than others.

1. Introduction

A binary transition metal compound chromium telluride ($Cr_{1-\delta}Te$) has been energetically studied as one of the promising materials for realization of future semiconductor spintronics devices, because of its ferromagnetic character with a ferromagnetic transition temperature (T_c) above room temperature (RT); T_c ~ 340 K was reported for the most stable bulk phase of stoichiometric CrTe with the NiAs-type crystal structure [1], and structural compatibility with III-V and II-VI conventional semiconductor materials. Therefore $Cr_{1-\delta}Te$ has been expected to be applied to injectors of a spin-polarized current into semiconductor devices. In our earlier study, we fabricated thin films of hexagonal $Cr_{1-\delta}Te$ (hex- $Cr_{1-\delta}Te$), which is derived from the stoichiometric NiAs-type CrTe by introducing Cr deficiencies, on II-VI semiconductor ZnTe(001) and CdTe(001) surfaces by molecular beam epitaxy (MBE) under various growth conditions [2]. We found that the hex-$Cr_{1-\delta}Te$ layers grew with its *c*-plane parallel to the growth plane at small Cr/Te flux ratios. Magnetic-field dependence of the magnetization (*M-H*) curves measured for the hex-$Cr_{1-\delta}Te$ film with the magnetic field perpendicular to the film plane showed a square-shaped hysteresis curve with a large coercive force. Such a large perpendicular magnetic anisotropy of the film is considered to be useful for application to spintronics devices. However, the Curie temperature (T_C) of the hex-$Cr_{1-\delta}Te$ is about 210 K at highest, which must be too low for a practical use.

In our previous study, in order to fabricate hex-$Cr_{1-\delta}Te$-based thin films with higher ferromagnetic transition temperature, we investigate the magnetic properties of a ternary transition-metal chalcogenide (Cr,Fe)Te [3]. We grew several hex-$(Cr_{1-x}Fe_x)_{1-\delta}Te$ films with various composition ratios between Cr and Fe. And we found that the hex- $(Cr_{1-x},Fe_x)_{1-\delta}Te$ with Fe composition x ranging in $0.45 < x < 0.6$ exhibited ferromagnetic property at above RT ($T_c > 350$ K).In this study, in order to realize further improvement of the ferromagnetic character of the hex-$(Cr,Fe)_{1-\delta}Te$ films ($x \sim 0.5$), we fabricated films with various post-annealing temperatures.

2. Experimental

The growth of (Cr,Fe)Te thin film was performed by MBE using solid sources of Zn, Te, Cr, and Fe. A piece of GaAs(111)A wafer was used as a substrate. Firstly a buffer layer (~ 600 nm) of ZnTe was grown on the substrate, then a (Cr,Fe)Te layer was grown at 150 ºC. After the (Cr,Fe)Te growth, we grew a ZnTe cap layer (~ 20 nm) to prevent the deterioration. We prepared the (Cr,Fe)Te layer grown under flux ratio of Fe : Cr : Te = 0.03 : 0.03 : 1, to fabricate a hexagonal-$(Cr_{1-x},Fe_x)_{1-\delta}Te$ with $x \sim 0.5$. After the sequence of the MBE growth, we annealed the sample for 10 hours under high vacuum condition in another chamber. In order to investigate the post annealing-temperature dependence, we prepared four kinds of samples: as-grown and 200 ºC, 350 ºC, 450 ºC annealed samples, respectively.

Sample surface during the MBE growth was monitoring *in situ* using reflection high-energy electron diffraction (RHEED) to estimate flatness and symmetry of surface of the layer. The crystal structure analyses of the films were performed using X-ray diffraction (XRD). The magnetic properties of the films were investigated using superconducting quantum interference device (SQUID) magnetometer with magnetic fields applied perpendicular to the film plane.

3. Results and Discussion

The result of RHEED observation during the MBE growth of the (Cr,Fe)Te layer was very similar to that observed for hex-$Cr_{1-\delta}Te$; the RHEED image exhibited six-fold in-plane rotational symmetry and clear streaky images were observed both at the GaAs[110] and $[1\bar{1}0]$ azimuths. In addition, the spacing between the observed

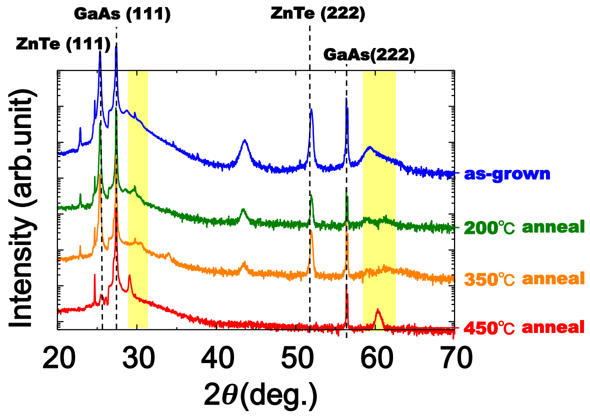

Fig.1 Profiles of XRD $2\theta/\theta$ scans of (Cr,Fe)Te thin films annealed at various temperature (as-grown, 200 °C, 350 °C, 450 °C). Peaks in yellow-colored region correspond to diffractions from the (0002) and (0004) planes of the hexagonal structures.

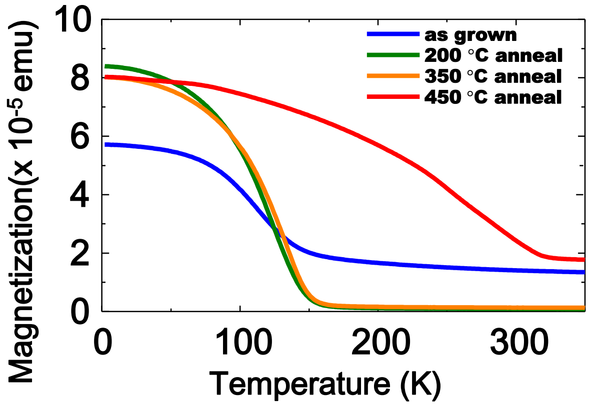

Fig.2 Temperature dependence of magnetization (*M-T*) curves of the (Cr,Fe)Te thin films annealed at various temperature. External magnetic field was 500 Oe.The direction of magnetic field was perpendicular to the film plane.

streaks was almost same as that in the growth of hex-$Cr_{1-\delta}Te$. Figure 1 shows the profiles of XRD $2\theta/\theta$ scan for (Cr,Fe)Te films. As shown in the figure, all (Cr,Fe)Te thin films have peaks at ~29º and ~60º, whose values are very close to the peak positions expected from diffractions by the (0002) and (0004) planes of NiAs-type CrTe; this result indicates that the (Cr,Fe)Te films with hexagonal crystal structure was grown in the direction along the [0001] orientation. Furthermore, as indicated by the change of the shape of these peaks, we could find that the crystal property of the hexagonal was varied by each post-annealing process. The peak split at 60º observed for samples post-annealed at 200 °C and 350 °C, comparing with the as-grown sample, indicates the occurrence of a crystalline phase separation induced by the post-annealing processes. On the other hand, the sharp peak shape of the sample post-annealed at 450 °C suggests the formation of the relatively homogeneous hexagonal crystalline film.

Figure 2 shows temperature dependence of magnetization (*M-T*) curves of the (Cr,Fe)Te films measured with 500 Oe magnetic field perpendicular to the film plane. As shown in the figure, the magnetic character of the films changed by the post-annealing processes; while the as-grown film exhibit some RT ferromagnetism, which should be attributed to the magnetic property of the solid-solution hex-$(Cr_{1-x},Fe_x)_{1-\delta}Te$[3], but *M-T* curves of the films annealed at 200 ºC and 350 ºC were very similar to that of hexagonal-$Cr_{1-\delta}Te$ observed in our earlier study and didn't show any ferromagnetic character at RT. On the other hand, the film which annealed at 450 ºC shows a quite different ferromagnetism, which could be maintained from low temperature to higher temperature (~ 300 K) than other films and exhibited the largest magnetization at RT. Considering with the result of XRD, these results suggest that annealing at 200 ºC and 300 ºC induced a phase separation from the solid-solution hex-$(Cr_{1-x},Fe_x)_{1-\delta}Te$ into two hexagonal phases: Cr-rich (CrTe-like) and Fe-rich (FeTe-like, which should exhibit antiferromagnetic or paramagnetic character). And the 450 ºC annealing formed homogenous crystalline film consisting of another hexagonal phase, whose detailed character is not clear at present, with relatively large ferromagnetic character around RT. However, since such enhancement of the ferromagnetic character was not observed for the hexagonal-$Cr_{1-\delta}Te$ film annealed at 450 ºC, this change must be closely connected with the coexistence and interaction between Cr and Fe atoms in short-range region.

4. Conclusions

In this study, we investigated effect of post-annealing process on structural and magnetic properties of ternary transition metal telluride compound hexagonal-$(Cr_{1-x},Fe_x)_{1-\delta}Te$ (x ~ 0.5) thin films grown by MBE at 150 ºC. Our experimental results suggest that phase separation into Cr-rich and Fe-rich hexagonal regions was induced by annealing at 200 ºC and 300 ºC. Moreover, the film annealed at 450 ºC, which was the highest annealing temperature in this study, exhibited most homogeneous hexagonal crystalline structure and showed quite different magnetic property with a ferromagnetism maintained from low temperature to RT and much larger magnetization at RT than those of other films. These results indicate that a post-annealing process for a transition metal chalcogenide film is very effective to vary the characteristics of the film and we may improve the magnetic property of the hexagonal (Cr,Fe)Te thin film by further optimization of the post-annealing process in the future.

References

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