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Formation of Cr-rich columnal regions in magnetic semiconductor (Zn,Cr)Te

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1. Introduction

In the search for novel semiconducting materials exhibiting high-T_C ferromagnetism, a broad class of diluted magnetic semiconductors (DMSs) have been studied. So far, some of them have been claimed to be room-temperature ferromagnetic semiconductors [1,2], but the intrinsic nature of ferromagnetism has sometimes been controversial, with both positive and negative experimental results reported even for the same materials. Recently, it has become realized that the distribution of magnetic elements in the host crystal is a key dominating the magnetic properties of DMSs [3,4]. Indeed, the aggregation of magnetic elements and the resultant enhancement of ferromagnetism have been reported in various DMSs [5-8]. In our recent study on (Zn,Cr)Te [7], it has been demonstrated that the Cr distribution can be controlled by the co-doping of donor impurity; Cr-rich regions in nanometer scale are formed coherently in the zinc-blende (ZB) host crystal co-doped with iodine (I) as a donor impurity.

In the present study, we investigate structural, chemical and magnetic properties of I-doped (Zn,Cr)Te films grown by molecular beam epitaxy (MBE) under various growth conditions. We reveal that the formation of Cr-rich regions depends sensitively on the substrate temperature during the MBE growth. With the increase of the substrate temperature, the shape of Cr-rich regions changes from isolated clusters into one-dimensional columnal regions. In this article, we report on the detailed study on the formation of these Cr-rich nanocolumns and the magnetic properties.

2. Experimental methods

The growth of I-doped (Zn,Cr)Te was performed using solid-source MBE. Thin films with a thickness around 300 nm were grown on GaAs(001) or (111) substrates. In a series of I-doped $Zn_{1-x}Cr_xTe$ films studied in this work, the average Cr content was fixed at around $x \sim 0.2$ and the growth parameters such as the substrate temperature during the growth, the growth rate and the crystallographic orientation of the substrate were changed. Structural and chemical characterizations were performed using high resolution transmission electron microscope (HRTEM) for cross-sectional pieces with a thickness ~100 nm cut from the grown films using focused ion beam (FIB). The composition of constituent elements was investigated using energy-dispersive X-ray emission spectroscopy (EDS) and the Cr distribution in nanometer scale was surveyed by mapping the intensity of Cr K_α emission in the scanning TEM mode. The magnetization of grown films was measured using superconducting quantum interference device (SQUID) magnetometer in the reciprocating sample measurement mode with magnetic fields applied perpendicular or parallel to the film plane. From the dependences of magnetization on temperature and magnetic field *M(T,H)*, we deduced characteristic temperatures describing magnetic properties; the apparent ferromagnetic transition temperature $T_C^{(app)}$ was determined from the Arrott plot analysis of *M-H* curves and the blocking temperature T_B was determined from a peak position of *M-T* curves measured in the zero-field-cooled process.

3. Experimental results and discussions

The Cr distribution was investigated by the EDS mapping for a series of the films which were grown under various growth parameters. Figure 1 (a), (b) shows the Cr mapping images of the films grown at different substrate temperatures of T_S = 300°C and 360°C. These two films were grown on the GaAs (001) surface at a growth rate around 1 Å/sec. Though the Cr distribution is inhomogeneous in the both images, the shape of Cr-rich regions changes with the increase of T_S; the Cr-rich regions take the form of isolated clusters in the film grown at T_S = 300°C, while they take the form of stripes in the film grown at T_S = 360°C. In the latter case, the width of Cr-rich stripes is ~10 nm and their interval is 10~20 nm. These stripes are slanted against the growth direction with an angle around 55 degree. These stripes in the Cr mapping image indicates that Cr-rich regions are formed as one-dimensional (1D) columns in the crystal. From the observed direction of Cr-rich nanocolumns, it is suggested that Cr atoms have a tendency to aggregate along the {111} plane of the ZB structure. In order to investigate the dependence on the growth rate, the Cr distribution was examined on the films grown at different growth rates. As a result, it is found that the formation of Cr-rich nanocolumns does not exhibit significant variation with the growth rate; the Cr mapping images of the films grown at smaller growth rates down to about 0.1 Å/sec present almost a similar appearance. In the films grown in a different crystallographic orientation, the Cr-rich nanocolumns are formed in a different direction. In Fig. 1 (c), the Cr mapping image of a film grown on the GaAs (111) surface is shown. This film was grown at a substrate temperature T_S = 360°C and at a growth rate around 1 Å/sec.

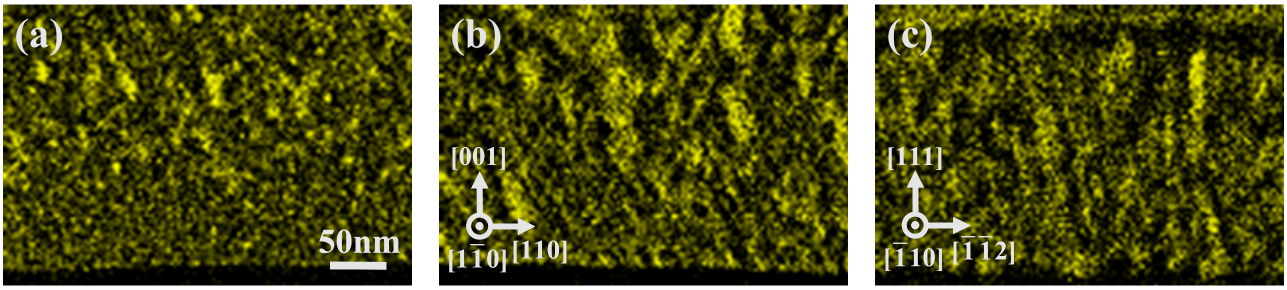

Fig. 1 The Cr mapping images in $Zn_{1-x}Cr_xTe$:I films ($x \sim 0.2$) grown (a) at a substrate temperature T_S = 300°C on the (001) surface, (b) at T_S = 360°C on the (001) surface, (c) at T_S = 360°C on the (111) surface.

Cr-rich nanocolumns are also formed in this film and the direction of these nanocolumns is almost vertical to the surface. This result is consistent with the tendency of the Cr aggregation along the {111} plane of the ZB structure.

In the magnetization measurements, it is revealed that the magnetic properties are different according to the shape of Cr-rich regions formed in the films. When we compare the film containing Cr-rich clusters and the one containing Cr-rich nanocolumns, the superparamagnetic features are more pronounced in the film containing nanocolumns; the blocking temperature T_B is higher in the film shown in Fig. 1 (b) than the one shown in Fig. 1 (a), though the apparent ferromagnetic transition temperature $T_C^{(app)}$ is not much different. The enhancement of the superparamagnetic features due to the formation of Cr-rich nanocolumns can be understood considering that the energy barrier due to the magnetic anisotropy is larger in the Cr-rich nanocolumns with a larger volume than clusters [9]. In addition, the films containing Cr-rich nanocolumns exhibit anisotropic magnetization depending on the relation between the magnetic field direction and the film plane. In particular, in the film grown on the (111) surface shown in Fig. 1 (c), in which Cr-rich nanocolumns are formed in the almost vertical direction, *M-H* and *M-T* curves exhibit different behaviors under magnetic fields perpendicular and parallel to the plane. The hysteresis loop in the *M-H* curves becomes larger under perpendicular magnetic fields than under parallel fields. This anisotropy suggests that the easy magnetization axis is along the axial direction of the nanocolumns. This is reasonable because the demagnetization field in such a columnal shape is larger when magnetic fields are applied along the axial direction.

The transformation of the Cr-rich regions from 0D clusters into 1D columns by increasing substrate temperature can be interpreted as a result of the enhancement of migration of the impinging atoms on the growing surface. According to a theoretical simulation [10], the aggregation of magnetic impurities in the layer-by-layer growth mode results in the formation of 1D columnal regions containing magnetic impurity in rich contents. It is considered that the enhanced migration on the growing surface promote the aggregation of Cr atoms in such areas where Cr-rich areas are already formed in the layer just below the surface. As a result, Cr-rich areas in the respective layers are piled up and Cr-rich regions form themselves into 1D columns.

4. Conclusions

We have studied the formation of Cr-rich nanocolumns in I-doped $Zn_{1-x}Cr_xTe$ films with a relatively high value of the Cr average content $x \sim 0.2$. It is found that the shape of Cr-rich regions is transformed from isolated clusters into one-dimensional nanocolumns with the increase of the substrate temperature during the MBE growth. The direction of the nanocolumns changes according as the films are grown on the (001) or (111) surface, suggesting that Cr atoms tend to aggregate along the {111} plane of the zinc-blende structure. In the magnetization measurements, anisotropic properties are observed in the films containing Cr-rich nanocolumns depending on the relation between the direction of the nanocolumns and the applied magnetic fields.

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