Epitaxial Growth of Vanadium-Doped ZnSe by MOVPE

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Vanadium-doped ZnSe, which is theoretically predicted to induce ferromagnetism above room temperature without carrier doping, was epitaxially grown on (100)GaAs substrate by metal-organic vapor phase epitaxial method in an atmospheric pressure. Vanadium concentration in the film obtained under the substrate and the vanadocene temperatures are 500 and 140°C, respectively, was 6.0 at% at maximum. The full width at half maximum (FWHM) of the peak diffracted from ZnSe(400) face increased with the increase of a vanadium concentration.

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1. Introduction

As a new material, diluted magnetic semiconductors (DMS) have attracted much interest and have been studied actively for the purpose of the use of both charge and spin of electrons in semiconductors with doping of magnetic elements. In some diluted magnetic materials, Curie temperature has been reported to be higher than room temperature and is given in several groups of semiconductors as follows; 285 K for Ge[1-x]Mn[1,1] in IV group, 300 K for Zn[1-x]Cr[2],Te[3] and Zn[1-x]N[1-x],O[3,4] in II–VI group, and 300 K for Ga[1-x]Mn[N[5,6] and Ga[1-x]Cr[N[6,7] and Al[1-x]Cr[N[7] in III–V group, respectively. However, Curie temperature for most of DMS is lower than room temperature so that it has been desired to get DMS with Curie temperature higher than room temperature for practical applications. Vanadium-doped ZnSe is expected as DMS inducing ferromagnetism above room temperature without carrier doping. ZnSe also has been investigated for a candidate to a blue light emitting diode and a blue laser one for a long time. Therefore, vanadium-doped ZnSe would have not only properties of both semiconductor and magnetic materials but also optical one so that vanadium-doped ZnSe has been expected as a device material having new functions. The purpose of this study is to fabricate vanadium-doped ZnSe films by using metal-organic vapor phase epitaxial method in an atmospheric pressure.

2. Experimental Procedure

Vanadium-doped ZnSe films were grown by metal-organic vapor phase epitaxial (MOVPE) method in an atmospheric pressure. Figure 1 illustrates the schematic view of the experimental apparatus. A reactor tube of the apparatus was horizontal and a substrate was heated by an infrared lamp. (100)GaAs single crystals were used as substrates. Dimethyl Se (DMSe, Se(CH₃)₂) and dimethyl Zn (DMZn, Zn(CH₃)₂) were used as source materials. Both materials were kept at 0°C in thermo-baths. The flow rates of DMSe and DMZn were 30 μmol/min and 12 μmol/min, respectively. The carrier gas was hydrogen at the flow rate of 200 ml/min. Vanadocene (V(C₅H₅)₂) was used as a dopant source for vanadium. The boat filled with vanadocene that is in solid state at room temperature was set into the reactor and was heated by a band-heater wrapped around the reactor. Figure 2 shows temperature sequences for the substrate and vanadocene.

Fig. 1 Schematic view of experimental apparatus.

Fig. 2 Temperature sequences for the substrate and vanadocene.

3. Results and Discussion

3.1 The dependence of vanadium concentration in ZnSe on vanadocene and substrate temperatures

Figure 3 shows the dependence of EDX spectra on the...
vanadocene temperature obtained at the constant substrate temperature of 500°C. There are only peaks due to zinc and selenium in undoped ZnSe. On the other hand, no peaks resulted from vanadium are seen in the vanadium doped sample grown at the vanadocene temperature of 130°C. At that of 140°C, the peaks resulted from vanadium were seen at 0.511 keV due to $L_1$-line, at 4.949 keV due to $K_{\text{II}}$-line, and at 5.426 keV due to $K_{\text{III}}$-line, respectively. At 150°C and higher temperatures, a surface of the film was covered with black powders and the film thickness was extremely thin so that results obtained at these conditions are excluded from here.

Next, the dependence of EDX spectra on the substrate temperature at the constant vanadocene temperature of 140°C is shown in Fig. 4. There are no peaks from vanadium for the sample grown at 450°C. This is the same for undoped ZnSe. Though the peaks from vanadium are seen in both 500°C and 550°C, the intensity of vanadium peaks in 550°C is relatively small in comparison with that in 500°C.

Figure 5 shows the vanadium concentration in ZnSe films depending on the vanadocene and the substrate temperatures. In the case where the substrate temperature was maintained at 500°C, the vanadium concentration increases with an increase of the vanadocene temperature. On the other hand, vanadium concentration increases up to 6.0 at% at maximum and then decreases by increasing of the substrate temperature at the constant vanadocene temperature of 140°C.

As a result, vanadium concentration in films takes maximum value of 6.0 at% at the condition where substrate and vanadocene temperatures are 500 and 140°C, respectively. It is theoretically predicted that ferromagnetism would be induced above room temperature if a vanadium concentration was higher than 5 at%.$^8$ In this study we have obtained vanadium concentration higher than 5 at%.

### 3.2 The effect of vanadium doping on crystallinity of ZnSe

The crystal quality of the ZnSe was investigated by the XRD measurement. ZnSe(400) peak was appeared regardless of vanadium doping, this experimental result indicated that ZnSe film was epitaxially grown on GaAs substrate. The relation between vanadium concentration and the FWHM of ZnSe(400) diffraction is shown in Fig. 6. The FWHM of undoped ZnSe was about 250 arc seconds. In the case vanadium doping, the FWHM increases rapidly up to 500 arc seconds and then increases gradually up to 600 arc seconds with an increase of vanadium concentration. The crystallinity of ZnSe became worse by vanadium doping, but it was found that vanadium doped ZnSe films were epitaxially grown on GaAs substrate regardless of vanadium doping.

Furthermore, the state of vanadium element in ZnSe crystal was investigated by the wide range X-ray diffraction measurement and the area scan with EDX showing distribution of vanadium element. No peaks except for ZnSe epitaxial layer and GaAs substrate were detected in all
samples investigated in this study. Also the area scan in the area of $5 \mu m \times 5 \mu m$ suggests that vanadium is distributed itself uniformly throughout the ZnSe crystal. These experimental results show that vanadium does not segregate locally in ZnSe.

4. Summary

Heavy doping of vanadium in ZnSe films at higher than 5 at% was successfully attained by MOVPE using vanadocene as the vanadium dopant source, where the substrate and the vanadocene temperatures were 500 and 140°C, respectively. ZnSe films were epitaxially grown on GaAs substrate regardless of vanadium doping. However, FWHM of X-ray diffraction peak of ZnSe(400) increased with an increase of vanadium concentration.

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REFERENCES