Effect of Vanadium Doping on Structure and Properties of ZnSe Films Prepared by Metal-Organic Vapor Phase Epitaxy

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Vanadium-doped ZnSe films were epitaxially grown on (100) GaAs substrates by metal-organic vapor phase epitaxy. The crystal structure and the state of vanadium in the ZnSe crystal were investigated using X-ray diffractometry, infrared absorption, and photocurrent. It was revealed that zinc sites in the ZnSe crystal were substituted by vanadium atoms on the basis of the results of infrared absorption which peaked around 2200 nm as a result of the presence of V$^{2+}$, and the photocurrent which peaked at 860 nm as a result of the internal transition between V$^{2+}$ and V$^{3+}$. The magnetic properties were measured by using a superconducting quantum interface device at room temperature, and it was found that the magnetization curve of ZnSe was markedly changed by vanadium doping.

Keywords: vanadium, ZnSe, metal-organic vapor phase epitaxy (MOVPE)

1. Introduction

Recently, diluted magnetic semiconductors (DMSs) which display both semiconducting and ferromagnetic properties have attracted considerable research interest as new functional device materials. Since the discovery of carrier-induced ferromagnetism in Mn-doped InAs in 1989$^1$ and in Mn-doped GaAs in 1996,$^2$–$^4$ many studies have sought to identify and explore DMS materials. Several materials have been reported to exhibit ferromagnetism in IV-IV,$^5$ II-VI,$^6$–$^8$ and III-V,$^9$–$^{11}$ compound semiconductors. However, the synthesis of DMS materials with high Curie temperature (at or above room temperature) has proven difficult. In the search for new DMS materials, we doped ZnSe crystals with a 3d-transition element, namely vanadium, in order to induce spin polarization. Sato and Katayama-Yoshida also predicted that vanadium-doped ZnSe exhibits ferromagnetism at room temperature without carrier doping.$^{12,13}$ As the mother material of vanadium-doped ZnSe, ZnSe is a compound semiconductor which has a direct band gap of 2.7 eV at room temperature and which is a candidate for use in optical devices such as blue light emitting diodes. In addition, the lattice mismatch between ZnSe and GaAs is 0.3%, and therefore ZnSe layers can be grown epitaxially on GaAs substrates. Thus, vanadium-doped ZnSe might be a useful material for devices with multiple functions owing to its magnetic, electric, and optical properties.

We previously reported the effects of vanadium doping on the crystallographic and magnetic properties of ZnSe crystals grown on a (100) GaAs substrate by metal-organic vapor phase epitaxy (MOVPE) under atmospheric pressure. As a preliminary experiment for examining vanadium doping, vanadocene, which is a purple-colored solid at room temperature, was used as a dopant source. Heavy doping (greater than 5%) of vanadium in ZnSe was successfully achieved by this method. However, the supply rate of vanadocene was strongly dependent on its heating temperature, and as a result it was difficult to control its supply rate. Thus, we adopted triethoxovanadyl, which is a yellow-colored liquid at room temperature, as a new dopant source of vanadium. The advantage of this source is that its supply rate is precisely controlled by the mass flow rate of the carrier gas.

In the present study, we investigated the effects of vanadium doping on the crystal structure of ZnSe, as well as the optical and magnetic properties of vanadium-doped ZnSe at room temperature.

2. Experimental Procedure

Vanadium-doped ZnSe growth was carried out by MOVPE under atmospheric pressure. Figure 1 indicates the schematic view of the experimental apparatus. Dimethylzinc (DMZn), dimethylselenide (DMSe), and triethoxovanadyl (TEV) were used as source materials for zinc, selenium, and vanadium, respectively. The materials were introduced into the reactor using hydrogen as carrier gas. The substrate was semi-insulating (100) GaAs, which was etched in a solution of $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 3 : 1 : 1$ for 1 min at 70°C. A carbon susceptor, on which the substrate was mounted, was heated inductively by an RF heater. The growth temperature was 500°C, and the growth duration was 1 h. The supply rate of DMSe and TEV was maintained at $10\,\mu\text{mol}/\text{min}$ and 0.01 $\mu\text{mol}/\text{min}$, respectively, and that of DMZn was changed from 5 to 10 $\mu\text{mol}/\text{min}$. In other words, the molar supply ratio of DMSe to DMZn (VI/II ratio) was changed from 1 to 2.

The lattice constant of ZnSe was investigated using a four-crystal X-ray diffractometer. The concentration of vanadium in the ZnSe film was obtained with energy dispersive X-ray spectrometry (EDX). The state of vanadium in the ZnSe crystal was estimated by three methods: infrared absorption, photocurrent and Hall Effect measurements. The magnet-
ization curve of each sample was characterized using a superconducting quantum interface device (SQUID) magnetometer.

3. Results and Discussion

3.1 Effects of vanadium doping on crystal structure of ZnSe

Figure 2 shows the lattice constants of vanadium-doped and undoped ZnSe films, where the VI/II ratio was taken as a parameter. The lattice constant of undoped ZnSe was 0.5668 nm regardless of the VI/II ratio. On the other hand, in the case of vanadium doping, the lattice constant of vanadium-doped ZnSe increased linearly with increasing VI/II ratio and approached a saturation value of 0.5671 nm for values of the VI/II ratio of 1.5 and above. Figure 3 shows the relationships between the VI/II ratio and vanadium concentration in vanadium-doped ZnSe films. The concentration of vanadium increased with increasing VI/II ratio, and the gradient of the vanadium concentration to the VI/II ratio changed when the value of the VI/II ratio was between 1.2 and 1.5, in which the vanadium concentration was 0.2%.

The tendency shown by the lattice constant with respect to the VI/II ratio in Fig. 2 was similar to that of the vanadium concentration with respect to the VI/II ratio in Fig. 3. In other words, the gradients of both the lattice constant and the vanadium concentration with respect to the VI/II ratio changed when the VI/II ratio was between 1.2 and 1.5. The crystal structure was also changed by vanadium doping. In previous studies, we reported that the crystal growth condition of ZnSe was changed from epitaxial growth to polycrystal growth at a VI/II ratio between 1.2 and 1.5, as determined from the results of structural analysis using X-ray diffractometry with a 2θ scan.18,19) In other words, this region where the VI/II ratio is between 1.2 and 1.5 corresponds to the transition region, which is divided into the epitaxial and polycrystal growth regions. The limit of vanadium concentration that could maintain the epitaxial growth condition was considered to be about 0.2%. Furthermore, the crystallinity of each sample was estimated by the full width at half maximum (FWHM) of the diffraction peak corresponding to the (400) plane of ZnSe, which is the epitaxial growth orientation of ZnSe on (100) GaAs substrate. In the epitaxial growth region, the FWHM was increased with increasing VI/II ratio. On the other hand, in the polycrystal region, the peak corresponding to (400) disappeared and thus the FWHM could not be estimated.

3.2 Effects of vanadium doping on optical and magnetic properties of ZnSe

For the measurement of the magnetic properties of ZnSe, we fabricated thick films of vanadium-doped ZnSe. The supply rates of DMZn and DMSe were maintained at 10 and 8.3 μmol/min, respectively. More specifically, the molar supply ratio of DMSe to DMZn (VI/II ratio) was set to 1.2, which is the epitaxial growth condition.18,19) The supply rate of TEV was maintained at 0.01 μmol/min. The growth temperature was 500°C, and the growth duration was extended from 1 to 5 h. The thickness of the undoped and the vanadium-doped sample was 25 and 22 μm, respectively.

X-ray diffractometry analysis (2θ scan) showed that strong peaks corresponded to only the (200) and (400) planes of both ZnSe and GaAs regardless of vanadium doping. In addition, the FWHM of the diffraction peak corresponding to ZnSe (400) of undoped ZnSe was 68 arcsec. In contrast, the crystallinity of ZnSe became worse in the case of vanadium doping, and the FWHM of the vanadium-doped ZnSe sample was 670 arcsec. In other words, epitaxial growth of the crystal was confirmed regardless of vanadium doping. The vanadium concentration in the vanadium-doped ZnSe was 0.2%.

It is necessary for vanadium atoms to substitute zinc atoms at zinc sites in order to produce ferromagnetism.12,13) The substitution of zinc by vanadium was confirmed by three methods: infrared absorption, photocurrent and Hall effect measurements. In the case where a zinc atom is substituted by a vanadium atom at a zinc site, splitting of the ground states...
of the 3d electrons in the point group $T_d$ crystal field occurs, and the $^4F$ ground state of $V^{2+}$ splits into three levels: $^4T_1$, $^4T_2$, and $^4A_2$ excited states. The emission band centered near 2300 nm due to the $^3T_2 \rightarrow ^4T_1$ transition of $V^{2+}$ was experimentally observed.\(^{20}\) Figure 4 shows absorption spectrum of vanadium-doped ZnSe. Vanadium-doped ZnSe exhibited broad optical absorption, peaking at 2220 nm at room temperature, while undoped ZnSe showed no such absorption. This peak corresponds to the transition from $^4T_1$ to $^4T_2$. Furthermore, vanadium atoms become amphoteric impurities, that is, they form the donor level ($V^{3+}/V^{2+}$) below 1.43 eV from the bottom of the conduction band, and the acceptor level ($V^{2+}/V^{+}$) above 1.91 eV from the top of the valence band.\(^{21}\) These transitions were identified from photocurrent measurements, in which indium metal contacts were evaporated onto the surface of each sample as ohmic electrodes and a halogen lamp was used as the light source. The measured photocurrent was normalized by illuminating photons in order to correct the illumination efficiency of the light source and the diffraction efficiency of the spectroscope. Figure 5 shows the photocurrent measurement of vanadium-doped ZnSe. The rise of the photocurrent starts from 880 nm and shows maximum value at 860 nm (1.44 eV), when the light was scanned from a longer wavelength. This fact indicates that the photocurrent originated from electrons excited from the donor level of $V^{2+}$. However, the photocurrent does not show whether the carriers are electrons or holes. Then, Hall measurements were conducted under the illumination of light corresponding to levels below the bandgap of ZnSe, which clarified that the carriers generated by the light are electrons. These experiments support the hypothesis that vanadium atoms act as substitutes at zinc sites. Considering both the state of vanadium in the ZnSe crystal, as described above, and the effects of vanadium on the lattice constant, as described in 3.1, it was revealed that the lattice constant was extended by substituting zinc sites in the ZnSe crystal with vanadium atoms owing to the difference in bond length between zinc and vanadium. By doping the ZnSe crystal with larger amounts of vanadium, higher than 0.2%, it was found that vanadium atoms markedly distort the lattice, inhibiting epitaxial growth in favor of polycrystal growth.

Figure 6 shows the magnetization curves as functions of the magnetic field, which was applied in a direction parallel to the substrate plane, at 20 °C. The magnetization curve of each sample was obtained by using a superconducting quantum interface device (SQUID) magnetometer. The diamagnetic contribution from the substrate was subtracted from the experimental curves. The magnetization curve of undoped ZnSe, as shown in the upper left corner of Fig. 5, indicates diamagnetic behavior. The magnetic susceptibility of undoped ZnSe as calculated from the slope of the magnetization curve was found to be $-1.73 \times 10^{-6}$ emu/cm$^3$, which agrees with the values reported in the literature.\(^{22–24}\) In the case of vanadium doping, the behavior of the magnetization curve changed markedly from diamagnetic to ferromagnetic, although metal vanadium exhibits paramagnetic properties. The magnetization curve of vanadium-doped ZnSe also shows a hysteresis loop with a coercive field of 85 Oe, as shown in the lower right corner of Fig. 5. The origin of ferromagnetism is considered to be induced by the ferromagnetic double-exchange interaction, as predicted in Refs. 12 and 13, on the basis of the experimental result that zinc sites in the ZnSe crystal were substituted by vanadium atoms.

4. Conclusions

We fabricated vanadium-doped ZnSe on a (100) GaAs substrate by MOVPE. From the results of infrared absorption, which peaked around 2200 nm as a result of the presence of $V^{2+}$, and the photocurrent measurements, which peaked at 860 nm as a result of the internal transition between $V^{2+}$ and $V^{3+}$, it was found that zinc sites in the ZnSe crystal were substituted by vanadium atoms. The crystal growth condition of ZnSe was notably affected by vanadium doping.
In regions with low concentration of vanadium, the lattice was extended by substituting zinc sites in the ZnSe crystal with vanadium. By doping the ZnSe crystal with larger amounts of vanadium, the lattice was notably distorted as a result of the doping, leading to the inhibition of epitaxial growth. Vanadium-doped ZnSe fabricated under epitaxial growth conditions exhibited ferromagnetic behavior at room temperature.

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REFERENCES