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Zinc Phosphide Thin Films Grown by Molecular Beam Epitaxy

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Zinc phosphide (Zn_3P_2) thin films have been grown for the first time by molecular beam epitaxy (MBE) on GaAs substrates. Growth rate of Zn_3P_2 thin films was about 1 μm/h at V/II flux ratio of 13 and decreased as V/II flux ratio increased. The growth of Zn_3P_2 thin films is limited by Zn supply. Below the V/II flux ratio of 190, growth of Zn_3P_2 with Zn accumulation took place at growth temperature of 200°C, whereas above 190 the Zn_3P_2 films without Zn accumulation were observed to grow three dimensionally with large grains. The Zn_3P_2 films show n-type conductivity against the fact of usual p-type conductivity with mobility and carrier concentration of the order of 10^3 cm^2/Vs and 10^{10} cm^{-3} at room temperature, respectively. The temperature dependence of resistivity disclosed the existence of shallow (0.01 eV) and deep (0.7 eV) levels. Photoluminescence spectra show one broad peak near 1.41 eV at 20K ascribed to an acceptor level of 0.27 eV from the valence band.

1. INTRODUCTION

Zinc phosphide (Zn_3P_2), one of the II-V compound semiconductor, has attractive properties as an electronic material for several optoelectronic applications such as solar cells, infrared and ultraviolet sensors [1]. It has a direct bandgap near 1.5 eV [2], a large absorption coefficient, >10^4 cm^{-1}, and a long minority carrier diffusion length (10 μm) [1]. Because of its large optical absorption coefficient and an abundance of constituent elements, thin films of Zn_3P_2 have been fabricated for aiming solar cells.

Recently, there are several reports on Zn_3P_2 thin films grown by various techniques: vacuum evaporation [2,3], hot-wall deposition [4], rf sputtering [5], metalorganic chemical vapor deposition (MOCVD) [6-8], photo-assisted MOCVD [6-8], and ionized-cluster beam deposition (ICB) [9]. However, there happened a big problem of the occurrence of microcracks in Zn_3P_2 films during cooling process caused mainly by the large mismatch of thermal expansion coefficients between Zn_3P_2 (1.4×10^{-5} °C^{-1}) and various substrates [10]. Consequently, the Zn_3P_2 films prepared by above techniques were polycrystalline except by MOCVD and photo-assisted MOCVD [6-9], where low growth temperature was utilized.

This paper reports the first thin film growth of Zn_3P_2 by MBE onto GaAs (001) substrates at the low growth temperature of 200°C. The electrical and optical properties of Zn_3P_2 thin films have been characterized.

2. EXPERIMENTAL

An MBE system equipped with load-lock chamber and effusion cells of elemental zinc and red phosphorus (P_4) source was employed in this work. Growth temperature and the pressure-equivalent beam flux of

P_4 were fixed at 200°C and at 6.3×10^{-3} Pa, respectively, while the V/II flux ratio was varied from 13 to 300 by varying Zn flux. A GaAs (001) semi-insulating wafer was used as a substrate. The lattice mismatch between Zn_3P_2 and GaAs is about 1.3%.

The GaAs substrates were degreased, chemically etched in $H_2SO_4 : H_2O_2 : H_2O = 5:1:1$ solution for 30 s at 60°C, and then treated in $P_2S_5/(NH_4)_2S_x$ solution for 60 min at 60°C. The surface treatment of $P_2S_5/(NH_4)_2S_x$ solution was reported as an effective surface passivation technique [11]. After the passivation, the substrates were rinsed in pure water, and blown dry with N_2 gas. Prior to the growth, the GaAs substrates were heated at 300°C until the reflection high energy electron diffraction (RHEED) indicated streaky pattern.

3. RESULTS AND DISCUSSION

3.1 Growth of Zn_3P_2 thin films

Growth rate of Zn_3P_2 thin films was about 1 μm/h at V/II flux ratio of 13 and decreased as V/II flux ratio increased. In this work, solid red phosphorus was used as P source without cracking, so that the P source mainly supply tetramer which has a low absorption coefficient due to its high vapor pressure at growth temperature of 200°C. The growth of Zn_3P_2 thin film is, therefore, limited by Zn supply. The crystallinity of Zn_3P_2 was monitored *in situ* by the RHEED. A halo pattern was observed at V/II flux ratio of 13 and 35, while ring pattern was observed at V/II flux ratio of 80. Above V/II flux ratio of 190, extra diffraction spots appeared over the GaAs (001) diffraction pattern and a three dimensional epitaxial growth of Zn_3P_2 on GaAs substrates was confirmed. Surface morphology was also observed by a scanning-electron microscopy. The surface of Zn_3P_2 thin films grown at V/II flux ratio of 13 was rough with small grains of about 1 μm. The grain size decreased as V/II flux ratio increased to 80,

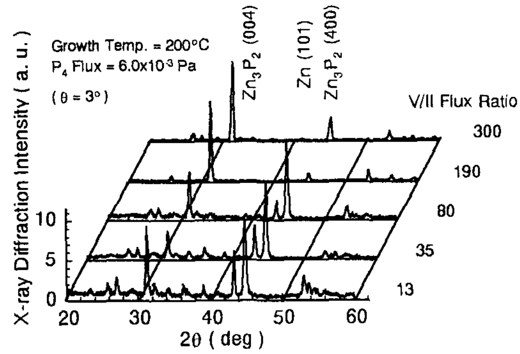

Fig.1 X-ray diffraction patterns of Zn_3P_2 thin films grown on GaAs substrates by MBE at growth temperature of 200°C and V/II flux ratio from 13 to 300.

and then increased again above 80 with smooth surfaces.

Figure 1 shows x-ray diffraction patterns of Zn_3P_2 thin films at the x-ray incident angle (θ) of 3°. Below the V/II flux ratio of 190, x-ray diffraction peaks of Zn_3P_2 and Zn were observed, suggesting that the growth of Zn_3P_2 with Zn accumulation took place. It was reported that thin films of Zn_3As_2, another II-V compound, were grown by MBE at growth temperature below 300°C, where the growth of Zn_3As_2 mixed with $ZnAs_2$ took place [12]. Although the compound from Zn and P has another phase ZnP_2, the ZnP_2 was not observed in our MBE growth. It should be noted that above V/II flux ratio of 190 the x-ray diffraction peaks from only Zn_3P_2 was observed. Since several diffraction peaks, i.e. (400), (004) etc., were observed, the Zn_3P_2 thin films were not epitaxially grown on entire GaAs surfaces.

Consequently, these results indicate that Zn_3P_2 films were grown three dimensionally with large grains on GaAs substrates at growth temperature of 200°C above V/II flux ratio of 190.

3.2 Electrical properties of Zn_3P_2 thin films

Resistivity measurement of Zn_3P_2 thin films was performed using van der Pauw method in the temperature range from 70 to 350K. The resistivity of all the films fabricated in this work indicated on the

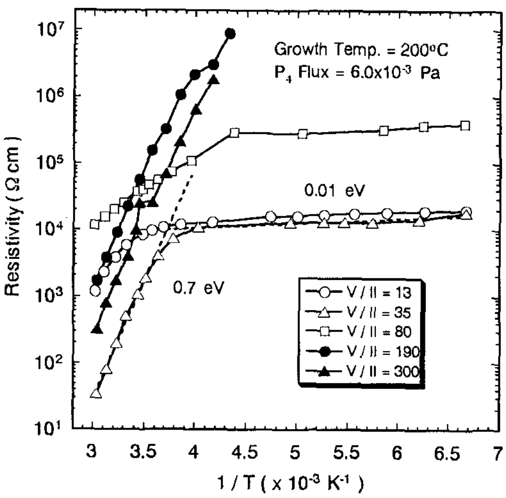

Fig.2 Temperature dependence of resistivity for Zn_3P_2 thin films grown by MBE at growth temperature of 200°C.

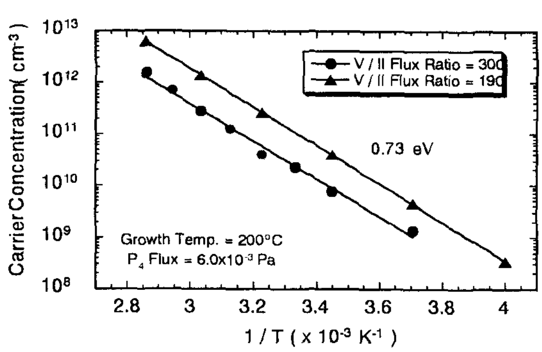

Fig.3 Temperature dependence of carrier concentration for Zn_3P_2 thin films grown by MBE at growth temperature of 200°C and V/II flux ratio of 190 and 300.

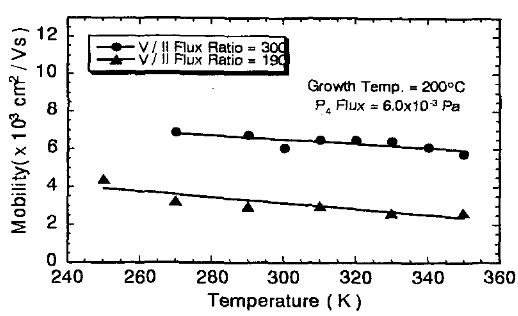

Fig.4 Temperature dependence of Hall mobility for Zn_3P_2 thin films grown by MBE at growth temperature of 200°C and V/II flux ratio of 190 and 300.

order of 10^3 Ωcm at room temperature and tended to increase as V/II flux ratio increased. The temperature dependence of resistivity for Zn_3P_2 films is shown in Fig. 2. The temperature dependence of the resistivity for Zn_3P_2 films grown below V/II flux ratio of 80 exhibits two exponential regions with activation energies of 0.01 and 0.7 eV, while that for Zn_3P_2 films grown above V/II flux ratio of 190 exhibits one exponential behavior with 0.7 eV.

Temperature dependences of Hall mobility and carrier concentration for Zn_3P_2 thin films grown at V/II flux ratio of 190 and 300, are presented in Fig. 3 and 4. Although as-grown Zn_3P_2 crystals show p-type conductivity due to its strong self-compensation effect and acceptor levels related to P-interstitials [13], those Zn_3P_2 films grown in this study show n-type conductivity. Hall mobility and carrier concentration are of the order of 10^3 cm^2/Vs and 10^{10} cm^{-3} at room temperature, respectively. The exponential behavior of carrier concentration is ascribed to the existence of donor level with activation energy of 0.7 eV. The Hall mobility decreased as the measurement temperature increased.

It is mentioned formerly that the growth of Zn_3P_2 is limited by Zn supply and the growth rate was small compared with other growth techniques. This implies that the most of P_4 tetramer may be re-evaporated without reacting with Zn. Therefore, producing P-interstitial and/or Zn-vacancies as an origin of acceptor levels, is suppressed. On the contrary, Zn interstitials and/or P-vacancies are probably the origin for the donor levels. The donor levels compensate the shallow acceptor levels resulting in the n-type conductivity. This assumption is supported by the low carrier concentration of 10^{10} cm^{-3}.

3.3 Photoluminescence

Photoluminescence was measured from 20 to 300K for Zn_3P_2 thin films. The samples were excited by the focused InGaAs semiconductor laser (λ=685 nm) with 20 mW power. The photoluminescence spectra obtained at 20K for a Zn_3P_2 thin film grown at V/II flux ratio of 300 and also for a GaAs substrate as a comparison, are presented in Fig. 5. A broad emission

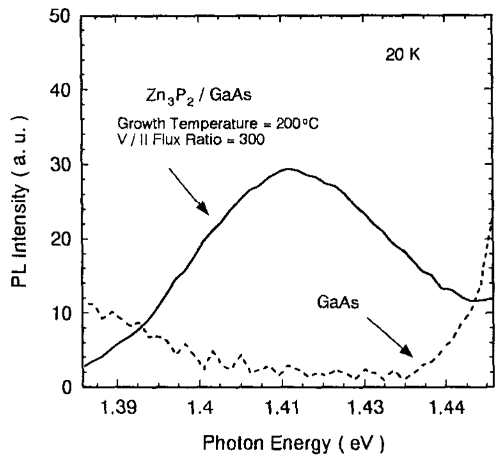

Fig.5 Photoluminescence spectra at 20K for Zn_3P_2 thin films grown by MBE at growth temperature of 200°C and V/II flux ratio of 300.

band appeared in the region 1.38 to 1.44 eV. The peak intensity was rapidly decreased above 150K. We assume this emission band to be associated with donor-acceptor pair (DAP) [14]: using the energy gap of 1.68 eV for Zn_3P_2 at 20K [15], an acceptor level is located at 0.27 eV above the valence band. The broad emission band and the temperature dependence of the peak intensity, however, indicate the additional existence of surface states.

4. CONCLUSION

Thin films of Zn_3P_2 have been grown by MBE at growth temperature of 200°C. Below the V/II flux ratio of 190, growth of Zn_3P_2 with Zn accumulation takes place, while above the V/II flux ratio of 190 the Zn_3P_2 films grow three dimensionally without Zn accumulation and with large grains. The Zn_3P_2 films show n-type conductivity against the fact of usual p-type due to strong self-compensation. A mobility and carrier concentration were obtained to be of the order of 10^3 cm^2/Vs and 10^{10} cm^{-3} at room temperature, respectively. Photoluminescence and Hall effect data suggest two levels at 0.27 eV from the valence band and about 0.7 eV from the conduction band.

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