Effect of thermal annealing on the properties of narrow-bandgap ZnSnAs$_2$ epitaxial films on InP(001) substrates

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Abstract

ZnSnAs$_2$ epitaxial film has been grown on epi-ready semi-insulating InP(001) substrates by low-temperature molecular beam epitaxy (LT-MBE) technique. The MBE-grown sample was then cleaved into pieces, three of which were subjected to low-temperature annealing at different temperatures of 300°C, 320°C and 340°C which are equal or slightly higher than growth temperature using face-to-face proximity capping by GaAs wafers to simulate arsenic atmosphere. HR-XRD measurements showed that increasing annealing temperature decreases the lattice constant towards the bulk value. This suggests that indeed the relatively higher lattice constant of ZnSnAs$_2$ epitaxial films is partly, if not wholly, due to defects consequence of low temperature growth. For the as-grown control sample, resistivity of $4.31 \times 10^{-2}$ $\Omega$-cm, mobility of 17.7 cm$^2$/V-s and hole concentration of $8.18 \times 10^{18}$ cm$^{-3}$ were obtained at room temperature. After annealing at 340°C, the resistivity was increased to $21.0 \times 10^{-2}$ $\Omega$-cm, the mobility increased to 60.9 cm$^2$/V-s, and the hole concentration was decreased to $4.88 \times 10^{17}$ cm$^{-3}$.

Keywords: ternary semiconductor, MBE, annealing, transport properties

1. Introduction

The ternary ZnSnAs$_2$ with a bandgap energy of 0.73 eV is a member of the II-IV-$V_2$ compound semiconductors, which are promising materials for thermo-photovoltaic solar cells, nonlinear optics, and infrared detectors [1,2]. In our previous works, we have reported on the room temperature ferromagnetism in Mn-doped ZnSnAs$_2$ epitaxial films [3,4]. In the course of our investigation of the properties of ZnSnAs$_2$ epitaxial films grown on nearly lattice matched InP(001) substrates, we have found out that the lattice constants of the ZnSnAs$_2$ thin films are slightly greater than those of their bulk counterparts. For instance, in one of our previous reports [5], we obtained a free-standing lattice constant $a$ of 5.88 Å in as-grown ZnSnAs$_2$ thin films. In comparison, the reported values of lattice constant of bulk ZnSnAs$_2$ are 5.8520 Å in chalcopyrite phase (CP) and 5.8537 Å in sphalerite phase (SP). We have hypothesized that this slight difference in lattice constant could be due to point defects such as vacancies, antisites, and interstitial atoms which are naturally occurring in most LT-MBE grown epitaxial films. To test this hypothesis, we studied the effect of thermal annealing on the lattice constant of ZnSnAs$_2$ thin films grown by LT-MBE technique.

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2. Experiment

The undoped ZnSnAs₂ epitaxial film was grown on epi-ready semi-insulating InP(001) substrates by LT-MBE technique to enable the deposition of Zn atoms whose sticking coefficient increases with decreasing substrate temperature [6-7]. After degassing at 300°C, the substrate was heated to 500°C for thermal cleaning with impinging As₄ flux. Using the optimum substrate temperature of 300°C and Zn:Sn:As₄ beam equivalent pressure ratio (BEPR) of 24:1:52 described in [2-3], ZnSnAs₂ epitaxial films were grown on the semi-insulating InP(001) substrates. The entire growth was monitored in-situ by reflection high-energy electron diffraction (RHEED) pattern observation. After the confirmation of the sample stoichiometry using Electron Probe Micro Analysis (EPMA), this sample was then cleaved with three pieces annealed at different temperatures of 300°C, 320°C and 340°C using face-to-face proximity capping by GaAs wafers to simulate arsenic atmosphere in order to inhibit surface degradation. To determine the lattice constants of ZnSnAs₂ epitaxial films, 0-20 HR-XRD scans were performed. We also investigated the annealing effects on the transport properties by performing Hall effect measurements.

3. Results and Discussion

The RHEED patterns observed after growth are shown in figure 1. Long and streaky RHEED patterns were observed during the growth, suggesting two-dimensional growth mode resulting into flat and smooth surfaces. EPMA revealed that the epitaxial film is nominally stoichiometric with an average Zn:Sn:As composition ratio of 1.00: 0.96: 2.30.

The result of the HR-XRD wide scan measurements is shown in figure 2. Aside from the peaks assignable to ZnSnAs₂ which appeared to the lower angle side of the InP diffraction peaks, no other prominent peaks were observed. This result is very similar to the one we obtained in ref [3] for the undoped ZnSnAs₂.

![Fig. 1 RHEED patterns taken along the (a) [110] and (b) [110] azimuths of the InP substrates after the growth of the ZnSnAs₂ epitaxial film.](image1.png)

![Fig. 2 HR-XRD 0-20 wide scan profiles of the as-grown and annealed ZnSnAs₂.](image2.png)
Figure 3 shows the HR-XRD narrow scan around the InP (004) ... temperature (°C)
Lattice constant (Å)
Fig. 4 Variation of the lattice constant with annealing temperature.

![Graph showing lattice constant variation with annealing temperature]

Figure 3 shows the HR-XRD narrow scan around the InP (004) diffraction peak of the as-grown and annealed samples. The intensity oscillations or Pendellosung fringes around the ZnSnAs$_2$ diffraction peaks were clearly observed for each of the XRD profiles. The values of the free-standing lattice constant calculated from this data, assuming that the epitaxial film was pseudomorphic with the InP substrate, are plotted against annealing temperature in Fig. 4. It can be seen from the figure that annealing at higher temperatures shifts the ZnSnAs$_2$ diffraction peak towards higher Bragg angle, indicating the decrease of the lattice constant towards the bulk value. This suggests that indeed the relatively higher lattice constant of ZnSnAs$_2$ epitaxial films is partly, if not wholly, due to defects consequence of low temperature growth. From the Pendellosung fringes the film thickness was calculated to be 100 nm, and appears not to vary with annealing temperature.

A summary of the transport data measured at room temperature is given in Table 1. The room temperature values of as-grown sample compare well with those values reported in bulk ZnSnAs$_2$[8,9] For instance, our resistivity of $4.31 \times 10^{-2}$ Ω-cm is almost equal to $4.3 \times 10^{-2}$ Ω-cm from bulk chalcopyrite ZnSnAs$_2$ of ref [8], our mobility of 17.7 cm$^2$/V-s at hole concentration of $8.18 \times 10^{18}$ cm$^{-3}$ is in between those mobility of 14.6 cm$^2$/V-s at hole concentration of $5.4 \times 10^{18}$ cm$^{-3}$ from bulk sphalerite ZnSnAs$_2$ of ref [9] and 130 cm$^2$/V-s at hole concentration of $1.2 \times 10^{18}$ cm$^{-3}$ from bulk chalcopyrite ZnSnAs$_2$ of ref [8]. These results led us to speculate that both the chalcopyrite and sphalerite phases are indeed present in our sample. It should be mentioned that the values presented here are values of apparent mobility as the conduction in ZnSnAs$_2$ is due to holes in the valence and impurity bands [10,11]. However, since the mobility values given in Table 1 are measured at room-temperature where the valence band conduction is dominant, the mobilities can also be considered as good approximation of the valence band hole mobilities.

| Table 1. Summary of room temperature transport properties. |
|----------------------------------------------------------|
| as-grown | $T_a=300$ °C | $T_a=320$ °C | $T_a=340$ °C |
| resistivity $\rho$ [Ω-cm] | $4.31 \times 10^{-2}$ | $8.99 \times 10^{-2}$ | $1.47 \times 10^{-1}$ | $2.10 \times 10^{-1}$ |
| hole concentration $p$ [cm$^{-3}$] | $8.18 \times 10^{18}$ | $2.37 \times 10^{18}$ | $8.51 \times 10^{17}$ | $4.88 \times 10^{17}$ |
| mobility $\mu$ [cm$^2$/V-s] | 17.73 | 29.35 | 50.13 | 60.85 |
Figure 5 shows the annealing temperature dependence of transport properties of as-grown and annealed ZnSnAs$_2$ thin films. Resistivity and apparent hole mobility increase, while hole carrier concentrations decreases with increasing annealing temperature. The decrease in the hole concentration with annealing temperature could be due to the reduction of vacancy-type defects. This lowering of the hole concentration in turn lead to the decrease of resistivity and partly the increase in mobility.

4. Conclusion

In summary, ZnSnAs$_2$ epitaxial film was grown on epi-ready semi-insulating InP(001) substrates by low-temperature molecular beam epitaxy (LT-MBE) technique and subjected to low-temperature annealing at different temperatures of 300°C, 320°C and 340°C which are equal or slightly higher than growth temperature using face-to-face proximity capping by GaAs wafers to simulate arsenic atmosphere in order to inhibit surface degradation. HR-XRD measurements showed that increasing annealing temperature decreases the lattice constant towards the bulk value. This suggests that indeed the relatively higher lattice constant of ZnSnAs$_2$ epitaxial films is partly, if not wholly, due to defects consequence of low temperature growth. Consequently, it was also observed that resistivity and apparent hole mobility increase, while hole carrier concentrations decreases with increasing annealing temperature.

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References

1) J.L. Shay, and J. H. Wernick, Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications (Pergamon, New York, 1975) p.1.
2) G.A. Seryogin, S.A. Nikishin, H. Temkin, R. Schlaf, L.I. Sharp, Y.C. Wen, B. Parkinson, V.A. Elyukhin, Yu. A. Kudriavtsev, A.M. Mintairov, N.N. Falace, M.V. Baidakova, J. Vac. Sci. Technol. B 16 (1998) 1456.
3) J.T. Asubar, A. Kato, T. Kambayashi, S. Nakamura, Y. Jinbo, N. Uchitomi, J. Cryst. Growth 301-302, (2007) 656.
4) J.T. Asubar, Y. Jinbo, N. Uchitomi, J. Cryst. Growth 311, 929 (2009).
5) J.T. Asubar, A. Kato, Y. Jinbo, N. Uchitomi, Jpn. J. Appl. Phys. 47 (2008) 657.
6) S. Heun, J.J. Paggel, S. Rubini, and A. Franciosi, J. Vac. Sci. Tech. 14 (1996) 2908.
7) J.T. Asubar, S. Sato, Y. Jinbo, N. Uchitomi, Phys. Status Solidi A 203, 11 (2006) 2778.
8) K. Masumoto, and S. Isomura, J. Phys. Chem. Solids 26 (1965) 163.
9) D.B. Gasson, P.J. Holmes, I.C. Jennings, B.R. Marathe and J.E. Parrot, J. Phys. Chem. Solids 23 (1962) 1291.
10) J.T. Asubar, Y. Jinbo, N. Uchitomi, Phys. Status Solidi C 6 (2009) 1158.
11) S. Isomura, Phys. Status Solidi A 66 (1981) K157.

Fig. 5 Anneal temperature dependence of transport property parameters of ZnSnAs$_2$ films.