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The growth of ZnSe by photo-assisted metalorganic chemical vapor deposition (MOCVD)

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Abstract

ZnSe epitaxy layers were grown on (1 0 0)GaAs substrates by photo-assisted MOCVD using DMZn and DMSe as group II and VI sources, respectively. Irradiation can improve the growth rate efficiently, but the irradiation intensity influences the growth rate and the crystalline quality negligibly in a large range. Due to an oxidation reaction on the surface of ZnSe, the growth rate and the flow ratio of group II and VI sources influence the crystalline quality. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

ZnSe base wide gap II–VI compound semiconductors have potential applications for visible light emitting devices [1,2]. However, because of self-compensation or residual impurities, it is very difficult to realize a p–n junction, which is the most significant structure for light-emitting diodes. One of the effective methods to solve this problem is to lower material growth temperature in order to suppress intrinsic defects. For this reason, in metalorganic chemical vapor deposition (MOCVD) processes, dialkyl compounds such as dimethylzinc (DMZn) or diethylzinc (DEZn) and hydrides such as H_2Se or H_2S are used as group II and group VI sources, respectively. But the combination of these sources easily causes premature reaction in the gas phase and results in predeposition on the chamber well.

Using dialkyl compounds such as dimethylselenium (DMSe) for group VI sources, instead of hydrides, can avoid the problem of premature reaction. However, the decomposed temperature of dialkyl compounds is much higher than that of hydrides, which will introduce native defects. For the reason of lowering the growth temperature, photo-assisted MOCVD is used, and considered as a new kind of low temperature epitaxy method [3–5].

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Usually, most dialkyl compounds have optical absorption bands in ultraviolet range, and they can be decomposed by irradiation whose energy is larger than the dialkyl compounds' absorption bands. Actually, the growth rate in the MOCVD process is markedly increased when the irradiation photon energy is higher than the band gap of growing materials at the growth temperature. Under this condition, the irradiation cannot decompose dialkyl compounds directly, but there is a photocatalysis phenomena, which makes oxidation or reduction reaction happen on the surfaces of the growing materials [4].

In this paper, we report the growth of ZnSe layers by photo-assisted MOCVD and analyse the growth process. In addition, the crystalline qualities of ZnSe epitaxy layers are discussed.

2. Experimental procedure

ZnSe epitaxy layers were grown on (1 0 0)GaAs substrates using DMZn and DMSe as the sources by photo-assisted MOCVD shown in Fig. 1. H_2 was used as the gas carrying the sources, and the total flow rate was kept at 2.3 l/s.

A high pressure mercury lamp was used as an irradiation source, which has been proved to be an effective one [6,7], and 365 nm irradiation was selected by a 365 nm filter to irradiate on surfaces of the substrates. The irradiation intensity was tuned from 5 to 90 mW/cm^2 by a neutral filter. The irradiation window was cleaned by a window purge of H_2 in order to prevent it from clouding due to the deposition products and from decreasing the irradiation intensity. Because of the difficulty to grow ZnSe layer using DMSe directly on GaAs substrate at low temperature (350°C), the growth process was divided into two steps, the first one was to grow ZnSe at 600°C in order that DMSe can be decomposed by pyrolysis directly; the second one was, after the first step, the growth temperature was lowered to 350°C, then continued to grow ZnSe layer with photo-assistance. The quality of the ZnSe epitaxy layers was characterized by the method of X-ray diffraction spectra using a D/max-RA X-ray diffractometer with a Cu target, and the surfaces of the epitaxy layers were studied by a KYKY 1000B scanning electron microscope.

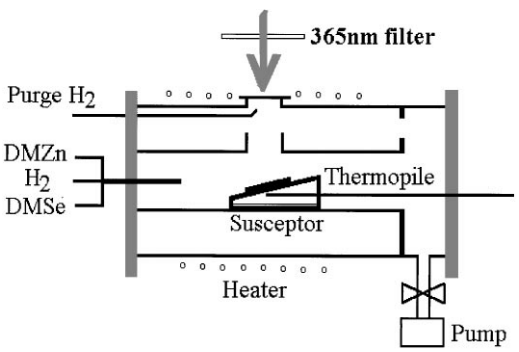

Fig. 1. Schematic diagram of the photo-assisted MOCVD apparatus.

3. Results and discussion

3.1. Growth rate

Fig. 2 shows the dependence of the growth rate on the irradiation intensity (the flows of II, VI group sources were 5.6×10^{-5} and 5.7×10^{-5} mol/min, respectively, and the reactor pressure was kept at an atmosphere pressure). It is found that the irradiation can improve the growth

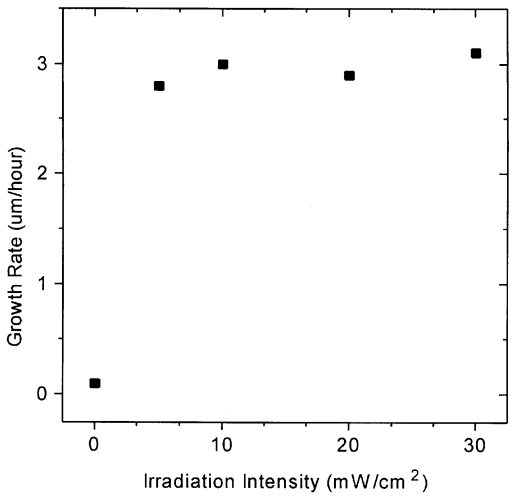

Fig. 2. Dependence of the growth rate on the irradiation intensity.

rate efficiently, but the growth rate does not change with the irradiation intensity in a wide range (from 5 to 30 mW/cm^2), in other words, the irradiation intensity does not influence the growth rate any more after the growth rate reaches a certain value. The similar phenomenon in the growth rate with the irradiation intensity has been observed by Yoshikawa et al. [5] and Irrine et al. [8]. It has been proved that the reason that the growth rate can be improved by photo-assistance is the generation of free carriers excited by photons in the growth material [5]. At growth temperature (350°C), the energy of the 365 nm light is larger than the band gap of ZnSe (2.43 eV), therefore, free carriers can be excited by photons. On the other hand, at the growth temperature, the electrons are not so stable as those at room temperature, and they are easy to be excited, so the quantum yield for producing free carriers by photons is high. Consequently, at the low irradiation intensity, the free carriers excited by photons are enough to support the reaction that improves the decomposition of dialkyl compounds on the surface of the growth material. Increasing the irradiation intensity, the free carries will be more than those needed, and the extra carriers will combine by some ways.

3.2. Crystalline quality

Fig. 3 shows the X-ray diffraction spectra of ZnSe epitaxy layers grown by photo-assisted MOCVD, keeping the growth rate at 3 μm/h with the irradiation intensity at 5 and 30 mW/cm^2, respectively. From the figure, we find that crystalline qualities are similar under different irradiation intensities, implying that the effect of irradiation on the crystalline quality is negligible. The spectra are dominated by a strong diffraction peak on (1 1 1) orientation, and the diffraction peak on (2 0 0) orientation is weak (the substrate's orientation is (1 0 0)), which shows poor crystalline quality even at a very low irradiation intensity.

Fig. 4 shows the X-ray diffraction spectrum of a ZnSe epitaxy layer grown by photo-assisted MOCVD with a low growth rate (1 μm/h) and a irradiation intensity of 5 mW/cm^2. The growth rate was lowered by reducing the flow rates of the sources (The flow rate of DMZn was changed from

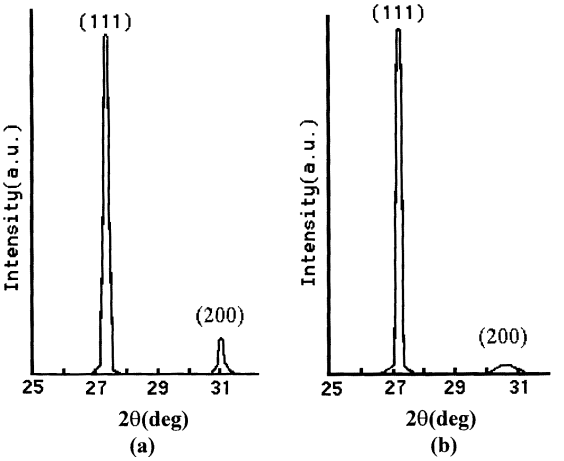

Fig. 3. X-ray diffraction pattern of ZnSe films deposited by photo-assisted MOCVD under different irradiation intensities: (a) 5 mW/cm^2, (b) 30 mW/cm^2.

5.6×10^{-5} to 2.8×10^{-5} mol/min, while the flow rate of DMSe was changed from 5.7×10^{-5} to 2.9×10^{-5} mol/min.) and reducing the reactor pressure from an atmosphere pressure to 150 Torr. There is a diffraction peak on (2 0 0) orientation dominating the spectra, and only a very weak (1 1 1) peak in the spectra. Comparing Figs. 4 and 3, it is easy to get the conclusion that the crystalline quality is influenced by the growth rate efficiently and can be improved by lowering the growth rate. Further evidence can be found from the surfaces of ZnSe epitaxy layers by SEM (shown in Fig. 5). It is obvious that the epitaxy layer is made up with polycrystal at a higher growth rate, while the crystalline quality is improved at a lower growth rate.

Another factor that influences the crystalline quality is the flow ratio of II, VI group sources (II/VI). Fig. 6 shows the X-ray diffraction patterns of ZnSe epitaxy layers grown by different II/VI. From the figure we see that the half-maximum width of the diffraction peak of (4 0 0) orientation for the sample grown at the II/VI about 1/2 (flow rates of DMZn and DMSe are 2.8×10^{-5} and 5.7×0^{-5} mol/min, respectively) is narrower than that for the sample grown at the II/VI about 1/1 (flow rates of DMZn and DMSe are 2.8×10^{-5} and 2.9×0^{-5} mol/min, respectively), which implies the crystalline quality is improved at lower II/VI.

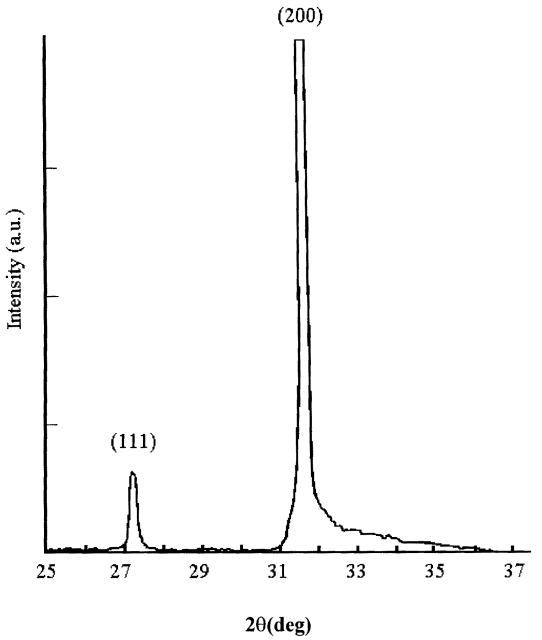

Fig. 4. X-ray diffraction pattern of ZnSe films deposited by photo-assisted MOCVD with a low growth rate.

3.3. Photo-assisted growth mechanism

The photo-assisted growth mechanism has been studied before [5], and it was attributed to photo-induced excess holes. When a ZnSe surface is irradiated by photons with energy larger than the band gap of ZnSe at growth temperature, the electrons are excited and electron–hole pairs are generated, then the holes are transferred to the surface. The oxidation number of Se in DMSe is -2 while that of Zn in DMZn is $+2$, and both the oxidation numbers of elemental Se and Zn are 0, so DMSe may be decomposed by positive holes excited by irradiation with an oxidation reaction. Now we will further discuss how the irradiation influences the crystalline quality. Because of the low decomposed temperature of DMZn, it will be decomposed first and Zn^{2+} will chemisorb at the growth surface. On the other hand, the bonding angle of C–Se–C is 100.6° in DMSe [5], thus DMSe has a finite dipole moment and Se in the molecules has a negative charge. Therefore, the active Zn bonds on the growth surface attract DMSe which will adhere to the surface. As a result, charges of holes transfer from the surface to the adsorbed DMSe and then the oxidation reaction takes place in DMSe helping it decomposed, and strong Zn–Se bonds are formed.

According to Volmer–Weber growth model [9], the growth is a three-dimensional nucleation process at a high growth rate. In different growth directions, the bond structures are different, which induces different attractions for DMSe. Therefore, the normal growth process is disturbed and some directions or planes grow prior to others; thus in this process, the crystalline quality is poor. However, the growth is a two-dimensional nucleation process at a low growth rate, and the crystalline quality is improved.

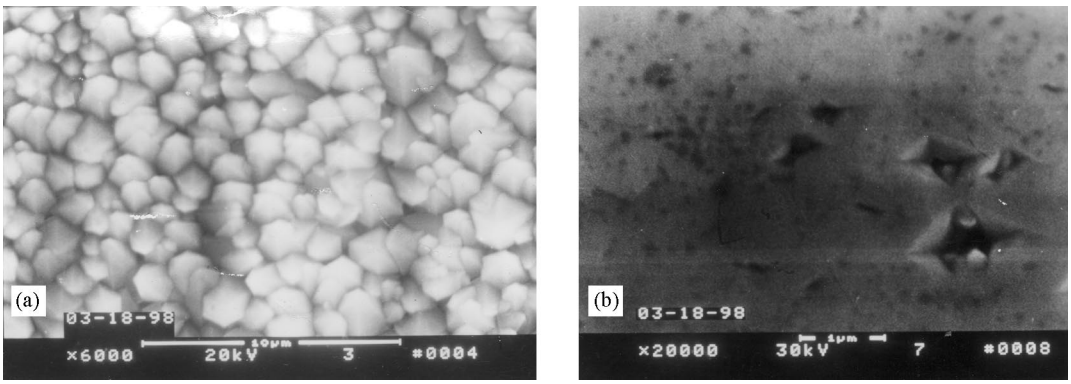

Fig. 5. Surface morphology of ZnSe films grown by photo-assisted MOCVD with different growth rates observed by SEM: (a) 3μm/h, (b) 1 μm/h.

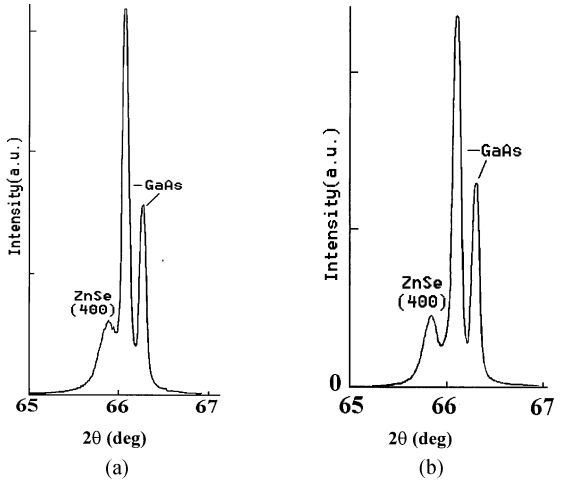

Fig. 6. X-ray diffraction pattern of ZnSe films deposited by photo-assisted MOCVD with different flow ratio of II and VI sources (II/VI), (a) II/VI is about 1/1; (b) II/VI is about 1/2.

As discussion in Section 3.2, another factor influencing the crystalline quality is the flow ratio of II and VI group sources. The source partial pressures are changed by the II/VI ratio, and then the number of the dialkylate molecular decomposed is different with the II/VI ratio. Usually when the number of DMZn molecular decomposed is larger than that of DMSe, a Zn-rich surface is formed, otherwise, a Se-rich surface is formed. Growth surface reconstruction has been reported for ZnSe(1 0 0), in which a (2×1) Se-rich surface and a $c(2 \times 2)$ Zn-rich surface were obtained [10–12]. It has been proved that the (2×1) Se-rich surface is terminated with Se-dimerized pairs and the $c(2 \times 2)$ Zn-rich surface is terminated with a half-monolayer of undimerized Zn atoms. According to the study of Tomiya et al. [13], a stable island structure on the Zn-$c(2 \times 2)$ surface is perpendicular to that on the Se-dimer (2×1) surface. The surface morphology is determined by the competition between development of the islands and the steps of the islands. For the Se-dimer surface, the direction that the islands extend is perpendicular to that the steps extend, however, for the Zn-$c(2 \times 2)$ surface, the islands extend in the same direction with that the steps do. Therefore, different surface morphologies are formed. In addition, the dangling bond structures are different between the two kinds of surfaces, which induces the different distributions of the charge-density between the two kinds of surfaces [14]. Considering the two reasons discussed above, the capacity of transferring the photo-induced holes to the surface and that of the surface attraction for the DMSe are different, which induces the different crystalline qualities.

4. Conclusions

ZnSe epitaxy layers have been grown on (1 0 0)GaAs substrates using DMZn and DMSe as the sources by photo-assisted MOCVD. It has been shown that irradiation can improve the growth rate efficiently, but the irradiation intensity influences the growth rate and the crystalline quality negligibly. However, the crystalline quality is influenced by the growth rate and the flow ratio of the group II and VI sources. The reason is the oxidation reaction of DMSe on the growth surface. Therefore, under a certain irradiation intensity, to lower the growth rate and to select an appropriate flow ratio of the group II and VI sources may be helpful for improving the crystalline quality.

Acknowledgements

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References

[1] S. Taniguchi, T. Hino, S. Itoh, K. Nakano, N. Nadayama, A. Ishibashi, M. Ikeda, Electron. Lett. 32 (1996) 552.
[2] E. Kato, H. Noguchi, M. Nagai, H. Okuyama, S. Kijima, A. Ishibashi, Electron. Lett. 34 (1998) 282.
[3] H. Ando, H. Inuzuka, M. Konagai, K. Takahashi, J. Appl. Phys. 58 (1985) 802.
[4] Sz. Fujita, Sg. Fujita, J. Crystal Growth 117 (1992) 67.
[5] A. Yoshikawa, Physica B 185 (1993) 50.
[6] T. Yasuda, Y. Koyama, J. Wakitani, J. Yoshino, H. Kukimoto, Jpn. J. Appl. Phys. 28 (1989) L1628.
[7] H. Kukimoto, J. Crystal Growth 101 (1990) 953.

[8] S.J.C. Irvine, M.U. Ahmed, P. Prete, J. Electron. Mater. 27 (1998) 763.
[9] M. Volmer, A. Weber, Z. Phys. Chem. 119 (1926) 277.
[10] H.H. Farrell, J.L. deMiguel, M.C. Tamargo, J. Appl. Phys. 65 (1989) 4084.
[11] M. Vos, F. Xw, S.G. Anderson, J.H. Weaver, H. Cheng, Phys. Rev. B 39 (1989) 10744.
[12] T. Yao, Z.Q. Zhu, K. Vesugi, S. Kamiyama, M. Fujimoto, J. Vac. Sci. Technol. A 8 (1990) 997.
[13] S. Tomiya, R. Minatoya, H. Tsukamoto, S. Itoh, K. Nakano, E. Morita, A. Ishibashi, J. Appl. Phys. 82 (1997) 2938.
[14] C.H. Park, D.J. Chadi, Phys. Rev. B 49 (1994) 16467.