MOCVD Growth of ZnO

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Introduction

ZnO can be considered as an 'old' semiconductor. It has been compelling research attention for a long time because of its applications in many scientific and industrials areas such as piezoelectric transducers, optical waveguides, acoustooptic media, conductive gas sensors, transparent conductive electrodes, varistors. It has now received increasing attention and recognized as a promising candidate for applications related to its optoelectronic possibilities in the UV range and also to its piezoelectric properties to develop SAW filters to be integrated in future analog circuits for portable electronic for which there is a strong need. These potential applications have boosted research related to the growth of high quality ZnO thin films by various techniques among which MOCVD occupies a significant place.

The aim of this communication is, after summing up the main physical properties of ZnO, to review the MOCVD growth of ZnO in its various aspects of growth modes, precursors and their reaction chemistry, substrates, assessment of the layers. We will keep constantly in mind some key issues for device application of ZnO in optoelectronic, surface acoustic filters and spintronics, such as the growth of high quality epitaxial layers of both n– or p–type conductivity, and the possibility of incorporating transition elements in the ZnO lattice.

ZnO physical properties

Among the most significant characteristics of ZnO, let us cite a large band gap of 3.37 eV @ RT; a unique combination of piezoelectric, conducting, thermal and optical properties; the largest exciton binding energy of all classical II–VI and III–V semiconductors. High quality ZnO substrates are now produced by a variety of techniques, meaning that the ZnO homoepitaxy is now possible. The ternary system CdO–ZnO–MgO covers a larger band gap range than nitrides with a smaller variation of the lattice parameter. ZnO has a large shear modulus of ~ 45.5 Gpa, parameter which expresses the stability of the crystal. P–type conductivity of ZnO remains a problematical issue but preliminary encouraging results have been reported. Furthermore, it has been suggested that the incorporation of transition elements like Co or Mn in ZnO could lead to a ferromagnetic phase transition close to room temperature, This should pave the way to the realization of devices based on the control of the spin state (spintronics) like quantum computers. ZnO has finally the same crystallographic structure as GaN, with a lattice mismatch < 1.8%, and can then act as an alternative substrate for GaN.

ZnO MOCVD Growth

Two distinct periods can be clearly distinguished in the MOCVD growth of ZnO depending on the applications envisaged. During the first period, roughly from 1964 to 1999, the films were mainly dedicated to such applications as solar cell transparent electrodes, piezoelectric devices, SAW filters. After 1998, given the hope of p–type doping, the main application aimed was photonic devices. During the first period, the epitaxial quality of the films was not as crucial as it was after 1998. The evolution of the number of communications versus time shows clearly an increasing interest from 1998.

Premature reaction between the Zn metal–organic compounds and the oxidants, leading to the deposition of particulates upstream from the susceptor, has been the main problem to which the MOCVD growth of ZnO has been faced. To solve this key issue, not only various Zn metal–organic compounds, in combination with various oxidants, but also some adducts and some single source precursors have been used, according to different growth modes such as low pressure MOCVD, photo–enhanced or laser–induced MOCVD with separate inlets to inject the metal–organic compound and the oxidant, with various carrier gases, in different geometries, horizontal or vertical

reactor, high speed rotation reactor…

Precursors

The main criteria which have guided the choice of precursors have been their cost, safety, purity, availability, the key problem of premature reactions and the growth rate of the layers.

DEZn, $(C_2H_5)_2Zn$, has been and remains the most used Zn precursor [4–8,12,15,19,21,22,24,26,31–39, 43–48,50,53–62,64,65,69]. Because of premature homogeneous reactions with some oxidants in the gas phase, which severely limit the process, several other metal–organic compounds have been used as well : zinc propionate [1–3]($Zn(C_3H_5O_2)_2$), dimethyl zinc [9–11,13,18,63] ($Zn(CH_3)_2$), dimethyl zinc triethylamine [35,68], zinc acetate [17,23,30] ($Zn(CH_3COO)_2$), zinc acethylacetonate [2,3,20,42,52] ($Zn(AA)_2$) $Zn(C_5H_7O_2)_2$ considered as low cost and easy to handle and some adducts like DMZ–THF or DEZ–THF [16].

As an oxidant, in addition to the very reactive oxygen [1,2,4,5,8,9,15,18,20,29–31,34,36–39,42–44, 46,47,52,58,59,64,65], alternative less reactive compounds such as CO_2 [6,7,18,40,41,53,62], H_2O [16,20,21,24,25,27,30,32,33,55], H_2O_2 [27], N_2O [6,10,26,56,57,60,63], NO_2 [10,15,19,45,48,57], NO [69], the heterocyclic furan [11] (C_4H_4O), tetrahydrofuran [11] (C_4H_8O), tetrahydrophyran [11] ($C_5H_{10}O$) and alcohols, mainly tBuOH [12,35,49,54,61], and i–PrOH [50,51,61,63] have been used. The advantages of tBuOH over i–PrOH have been demonstrated [61]. The low deposition rates obtained with such oxidants as CO_2, N_2O, NO_2 or H_2O are often enhanced by an excitation by plasma [18,26,29,40,41,47,58,59,62,64,65] or UV light [3,7,10,15,19,24,32,33].

Alkylzinc alkoxides like methylzinc isoprotoxide [28], $MeZn(OPr^i)$, and methylzinc tert–butoxide [28], $MeZn(OBu^t)$, Zn acetate [17,23,70,71] and Zn acethylacetonate [72] have been shown to be single source precursors for the growth of ZnO films, i.e. allowing the growth of ZnO without any added oxygen source and hence to get rid of premature reactions. At the present time, DEZn as a Zn precursor and O_2, CO_2, N_2O or tBuOH as oxygen sources are mostly used in a separate injectors configuration.

For doping, B_2H_6 [24,32,33], $Al(C_5H_7O_2)_2$ [25,27] and TEGa [31,35] have been used as a B, Al and Ga source respectively, and NO [53,69], NH_3 [39,46,65] or diallylamine [68] as a N source.

Substrates

During the first period mentioned above, the main substrates used have been Corning 7059 glass, and sometimes *R*– or *c*–sapphire. After 1998, in order to get epitaxial layers, such substrates as a– [45,48], *c*–[40,41,43,45,47,49–51,53–55,58–61,64,71], and *R*– [36,37,39–42,46,52] sapphire, (001)–GaAs [9,38,45], –GaP [11,45], –Si [9,16,26,62,70,71) and –InP [72], (111) Si [72], GaN/c–Al_2O_3 [51], GaN/(111)Si [63] and finally more recently ZnO [51,60] or ZnO/a–Al_2O_3 [48], ZnO/sapphire [56], ZnO/Si [56,57] have been used. C–plane sapphire remains still today the most used substrate.

Layer characteristics

During the first period, c–axis oriented polycrystalline films have been essentially obtained for layers grown on glass. Some epitaxial films have been reported when the growth occurred on c– and R–sapphire templates. Transmission, reaching 90%, and electrical properties have been essentially reported for these layers. Resistivities ranging from 10^{-2} to 10^{8} ohm.cm have been measured on as–grown layers, depending on the growth conditions (VI/II ratio, temperature, nature of precursors) and on eventual post–growth annealing (under O_2 pressure), and resistivities ranging from 2×10^{-4} to 6×10^{-3} ohm.cm for films doped with B, Al or Ga. Electron concentrations in the 10^{17} to 3.6×10^{20} cm^{-3} are reported with mobilities ranging from 4 to 60 cm^2 /Vs. It has been found that the layers show a better morphology but poorer electrical properties when grown on R– rather than on c–sapphire.

From 1999, the FWHM of band edge emissions, generally bound exciton lines (D^0 X), have been reported. 1.1 meV at 2.1K for heteroepitaxial layers on sapphire [61] and 0.5 meV at 9K for homoepitaxial films [60] are among the best values reported so far. Rocking–curve FWHM of 255 arsec and 100 arcsec have been measured respectively on heteroepitaxial layers grown on c–Al_2O_3 and homoepitaxial layers [51]. Electron concentrations ranging from 1.8×10^{15} to 10^{18} cm^{-3} with mobilities ranging from 20 to 100 cm^2 /Vs have been reported.

Doping

It has been shown that hydrogen behaves essentially as a shallow donor in ZnO [65] and has hence to be carefully considered in view of *p*–type doping. The inevitable presence of hydrogen in the MOCVD growth of ZnO, either coming from the carrier gas or from the organic radicals of Zn precursors, could make the MOCVD technique unfavorable for *p*–type doping. But hydrogen could have the beneficial effect of increasing the acceptor solubility [66] and suppressing compensation by native defects.

Attempts to achieve *p*–type doping of MOCVD grown ZnO layers have not been so far very successful. Using N from NH_3 as a dopant, Wang et al. [67] have obtained a hole concentration ~ 10^{16} cm^{-3} , but this *p*–type conductivity turned out to be unstable as a function of time. A two step strategy for achieving *p*–type doping has been developped by Rommeluère *et al.* [68]. N has been incorporated using diallylamine $(CH_2=CHCH_2)_2NH$ as a dopant source in ZnO layers grown on sapphire substrates. The concentration of N has been found to depend on several parameters such as precursor nature, VI/II ratio r, carrier gas nature, growth temperature, dopant pressure. It could reach more than 10^{21} cm^{-3} for $r < 1$, indicating that N is likely incorporated in oxygen sites. When [N] increases, [e] decreases up to a minimum value no = 5 x 10^{14} cm^{-3} for [N] = 10^{21} cm^{-3} . A hole concentration reaching 6.5×10^{17} cm^{-3} has been obtained by post–growth annealing under high pressure conditions stemming from the decomposition of NH_4NO_3 . Using NO as an oxidant and DEZn as a Zn precursor, Li *et al*. [69] obtained *p*–type polycrystalline films with p ranging from 1.0×10^{15} to 1.0×10^{18} cm^{-3} and μ ~ 0.1cm^2/Vs.

Conclusions

Very promising results have already been obtained in the MOCVD growth of ZnO films. As usual, the best layers have been obtained by homoepitaxy, but their quality remains limited by the quality of the substrates and by the difficult preparation of the ZnO surface. Concerning the key issue of p–type doping, the compensation of acceptors as a result of the inevitable presence of residual hydrogen donors could be balanced by an increase of the solubility of acceptors. Encouraging results demonstrate the possibility of *p*–type doping using nitrogen. As far as the incorporation of transition elements in the ZnO lattice in view of spintronics applications is concerned, the thermodynamic conditions of the MOCVD mechanism, close to the equilibrium, make it this technique less favourable than out of equilibrium techniques such as MBE or laser ablation.

References

1. Ya.S. Savitskaya and L.A. Ryabova, Zh. Prikl. Khim. 37 (1964) 796.

2. L.A. Ryabova, Ya. S. Savitskaya, R.N. Sheftal’, Izv. Akad. Nauk SSSR Neorg. Mater. 4 (1968) 602.

3. V.F. Korzo, P.S. Kireev, G.A. Lyashchenko, Neorg. Mater. 5, 2 (1969) 367.

4. W. Kern, R.C. Heim, J. Electrochem. Soc. 117, 4 (1970) 562.

5. S.Z. Ghandi, R.J. Field, Appl. Phys. Lett. 37, 5 (1980) 449.

6. C.K. Lau, S.K. Tiku, K.M. Lakin, J. Electrochem. Soc. 127, 8 (1980) 1843.

7. T. Shiozaki, T. Yamamoto, M. Yagi, A. Kawabata, Appl. Phys. Lett. 39, 5 (1981) 399.

8. A.P. Roth, D.F. Williams, J. Appl. Phys. 52, 11 (1981) 6685.

9. F.T.J. Smith, Appl. Phys. Lett. 43, 12 (1983) 1108.

10. R. Solanki, G.J. Collins, Appl. Phys. Lett. 42, 8 (1983) 662.

11. P.J. Wright, R.J.M. Griffiths, B. Cokayne, J. Crystal Growth 66 (1984) 26.

12. S. Oda, H. Tokunaga, N. Kitajima, J–I Hanna, I. Shimuzu, H. Kokado, Jpn. J. Appl. Phys. 24, 12 (1985) 1607.

13. S. Bethke, H. Pan, B.W. Wessels, Appl. Phys. Lett. 52, 2 (1988) 138.

14. P. Souletie, S. Bethke, B.W. Wessels, H. Pan, J. Crystal Growth 86 (1988) 248.

15. M. Shimuzu, H. Kamei, M. Tanizawa, T. Shiosaki, A. Kawabata, J. Crystal Growth 89 1988) 365.

16. Th. Kaufmann, G. Fuchs, M. Webert, Cryst. Res. Technol. 23, 5 (1988) 635.

17. O.F.Z. Khan, P. O'Brien, Thin Solid Films 173 (1989) 95.

18. T. Maruyama, A. Nakai, Jpn. J. Appl. Phys. 28, 3 (1989) L 346.

19. M. Shimuzu, T. Takayama, Y. Tanaka, T. Shiosaki, A. Kawabata, J. Crystal Growth 101 (1990) 171.

20. M.F. Ogawa, Y. Natsume, T. Hirayama, H. Sakata, J. Mat. Sci. Lett. 9 (1990) 1351.

21. W.W. Wenas, A. Yamada, M. Konagai, K. Takahashi, Jpn. J. Appl. Phys. 30, 3B (1991) L 441.

22. J. Hu, R.G. Gordon, J. Appl. Phys. 71, 2 (1992) 880.

23. T. Maruyama, J. Shionoya, J. Mat. Sci. Lett. 11 (1992) 170.

24. M. Yoshino, W.W. Wenas, A. Yamada, M. Konagai, K. Takahashi, Jpn. J. Appl. Phys. 32, (1993) 726.

25. T. Minami, H. Sato, H. Sonohara, S. Takata, T. Miyata, I. Fukuda, Thin Solid Films 253 (1994) 14.

26. Y.J. Kim, H.J. Kim, Mat. Lett. 21 (1994) 351.

27. H. Sato, T. Minami, T. Miyata, S. Takata, M. Ishii, Thin Solid Films 246 (1994) 65.

28. J. Auld, D.J. Houlton, A.C. Jones, S.A. Rushworth, M.A. Azad, P.O'Brien, G.W. Critchlow, J. Mater. Chem. 4,8 (1994) 1249.

29. T.V. Tabenskaya, V.P. Ovsyannikov, E.A. Mazurenko, J. Phys. IV 4 (1995) C5–711.

30. K. Kobayashi, T. Matsubara, S. Matsushima, S. Shirakata, S. Isomura, G. Okada, J. Mat. Sci. Lett. 15 (1996) 457.

31. Y. Li, G.S. Tompa, S. Liang, C. Gorla, Y. Lu, J. Doyle, J. Vac. Sci.Technol. A 15, 3 (1997) 1063.

32. B. Sang, A. Yamada, M. Konagai, Jpn. J. Appl. Phys. 37 (1998) L1125.

33. B. Sang, A. Yamada, M. Konagai, Jpn. J. Appl. Phys. 37 (1998) L206.

34. S. Liang, C.R. Gorla, N. Emanetoglu, Y. Liu, W.E. Mayo, Y. Lu, J. Electron. Mater. 27, 11 (1998) L72.

35. B. Hahn, G. Heindel, E. Pschorr–Schoberer, W. Gebhardt, Semicond. Sci. Technol. 13 (1998) 788.

36. M. Wraback, H. Shen, S. Liang, C.R. Gorla, Y. Lu, Appl. Phys. Lett. 74, 4(1999) 507.

37. C. R. Gorla, N.W. Emanetoglu, S. Liang, W.E. Mayo, Y. Lu, J. Appl. Phys. 88, 5 (1999) 2595.

38. A.B.M.A. Ashrafi, A. Ueta, A. Avramescu, H. Kumano, Y.–W. Ok, T.–Y. Seong, Appl. Phys. Lett. 76, 5 (2000) 550.

39. Y. Liu, C.R. Gorla, S. Liang, N. Emanetoglu, Y. Lu, S. Shen, M. Wraback, J. Electron. Mater. 29, (2000) 69.

40. K. Haga, M. Kamidaira, Y. Kashiwaba, T. Sekiguchi, H. Watanabe, J. Crystal Growth 214/215 (2000) 77.

41. T. Sekiguchi, K. Haga, K. Inaba, J. Crystal Growth 214/215 (2000) 68.

42. Y. Kashiwaba, F. Katahira, K. Haga, T. Sekiguchi, H. Watanabe, J. Crystal Growth 221 (2000) 431.

43. W.I. Park, G.–C. Yi, J. Electron. Mater. 30,10 (2001) L32.

44. W.I. Park, G.–C. Yi, H.M. Jang, Appl. Phys. Lett. 79, 13 (2001) 2022.

45. K. Ogata, K. Maejima, Sz. Fujita, Sg. Fujita, J. Electron. Mater. 30,6 (2001) 659.

46. S. Liang, H. Sheng, Y. Liu, Z. Huo, Y. Lu, H. Shen, J. Crystal Growth 225 (2001) 110.

47. X. Wang, S. Yang, J. Wang, M. Li, X.Jiang, G. Du, X. Liu, R.P.H. Chang, J. Crystal Growth 226 (2001) 123.

48. K.–I. Ogata, T. Kawanishi, K. Maejima, K. Sakurai, Sz. Fujita, Sg. Fujita, Jpn. J. Appl. Phys. 40 (2001) L657.

49. V. Sallet, J.F. Rommeluere, A. Lusson, A. Rivière, S. Fusil, O. Gorochov, R. Triboulet, Phys. Stat. Sol. (B) 229, 2 (2002) 903.

50. Th. Gruber, C. Kirchner, K. Thonke, R. Sauer, A. Waag, Phys. Stat. Sol. (A) 192, 1 (2002) 166.

51. Th. Gruber, C. Kirchner, A. Waag, Phys. Stat. Sol. (B) 229, 2 (2002) 841.

52. Y. Kashiwaba, K. Haga, H. Watanabe, B.P. Zhang, Y. Segawa, K. Wakatsuki, Phys. Stat. Sol. (B) 229, (2002) 921.

53. J. Ye, S. Gu, . Zhu, T. Chen, L. Hu, F. Qin, R. Zhang, Y. Shi, Y. Zheng, J. Crystal Growth 243 (2002) 151.

54. V. Sallet, C. Thiandoume, J.F. Rommeluere, A. Lusson, A. Rivière, J.P. Rivière, O. Gorochov, R. Triboulet, Mat. Lett. 53 (2002) 126.

55. Sho Shirakata, Keisuke Saeki, Tomoaki Terasako, J. Crystal Growth 237−239 (2002) 528.

56. K.−I. Ogata, T. Kawanishi, K. Maejima, K. Sakurai, Sz. Fujita, Sg. Fujita, J. Crystal Growth 237−239 (2002) 553.

57. K. Ogata, S.−W. Kim, Sz. Fujita, Sg. Fujita, J. Crystal Growth 240 (2002)112.

58. X. Wang, S. Yang, J. Wang, X. Jiang, G. Du, X. Liu, R.P.H. Chang, Optic. Quant. Electron. 34 (2002) 883.

59. J.−Z. Wang, G.−T. Du, X.−Q. Wang, Y.−C. Chang, W. Yan, S.−R. Yang, Y. Ma, H.−S. Wang, D.−S. Gao, X. Liu, H. Cao, J.−Y. Xu, R.P.H. Chang, Chin. Phys. Lett. 19, 4 (2002) 581.

60. K.−I. Ogata, K. Maejima, Sz. Fujita, Sg. Fujita, J. Crystal Growth 248 (2003) 25.

61. C. Kirchner, Th. Gruber, F. Reuss, K. Thonke, A. Waag, Ch. Giessen, M. Heuken, J. Crystal Growth 248 (2003) 20.

62. B.S. Li, Y.C. Liu, D.Z. Shen, J.Y. Zhang, Y.M. Lu, X.W. Fan, J. Crystal Growth 2489 (2003) 179.

63. N. Oleynik, M. Adam, A. Krtschil, J. Bläsing, A. Dadgar, F. Bertram, D. Forster, A. Diez, A. Greiling, M. Seip, J. Christen, A. Krost, J. Crystal Growth 248 (2003) 14.

64. G.−T. Du, J.−Z. Wang, X.−Q. Wang, X. Jiang, S.−R. Yang, Y. Ma, W. Yan, D.− S. Gao, X. Liu, H. Cao, J.−Y. Xu, R.P.H. Chang, Vacuum 69 (2003) 473.

65. C.G. Van de Walle, Phys. Stat. Sol. (b) 229, 1 (2002) 221.

66. A. Karchner, U. Haboeck, Martin Strassburg, Mathias Strassburg, G. Kaczmarczyk, A. Hofmann, C. Thomsen, A. Zeuner, H.R. Alves, D.M. Hofmann, B.K. Meyer, Appl. Phys. Lett. 80, 11 (2002) 1909.

67. J.−Z. Wang, private communication.

68. J.F. Rommeluère, L. Svob, F. Jomard, J. Mimila−Arroyo, A. Lusson, V. Sallet, Appl. Phys. Lett., to be published

69. X.Li, Y.Yan, T.A. Gessert, C. DeHart, C.L. Perkins, D. Young, T.J. Coutts, Electrochem. and Solid−State Lett. 6 (2003) C56.

70. M.H. Koch, A.J. Hartmann, R.N. Lamb, M. Neuber, M. Grunze, J. Phys. Chem. B 101 (1997) 8231.

71. J. Lu, Z. Ye, J. Huang, L. Wang, B. Zhao, Appl. Surf. Sci. 207 (2003) 295.

72. M. Purica, E. Budianu, E. Rusu, M. Danila, R. Gavrila, Thin Solid Films 403−404 (2002) 485.