Growth of Ge Homoeptaxial Films by Metal-Organic Chemical Vapor Deposition Using t-C₄H₉GeH₃

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Ge homoeptaxial films are grown at low growth temperature of 320°C by metal-organic chemical vapor deposition (MOCVD) using tertiarybutylgermane (t-C₄H₉GeH₃). We also performed ab initio calculations in order to reveal the chemical reaction for the epitaxial growth. As a result, we revealed that the t-C₄H₉GeH₃ was most likely decomposed into germane (GeH₄) and isobutene \([\text{CH}_2\text{C}=\text{C(CH}_3)_2]\) through the \(\beta\)-hydrogen elimination. We considered that this chemical nature allowed the growth temperature as low as that obtained by GeH₄ precursor with sufficiently suppressed C impurity incorporation.

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Furthermore, we discuss the reaction mechanisms of MOCVD epitaxial growth using t-C₄H₉GeH₃ precursor. We calculated the decomposition energies of t-C₄H₉GeH₃ by ab initio calculations using Becke3LYP (B3LYP) density functional theory with 3–21G basis set. The calculated chemical reaction paths are decompositions from t-C₄H₉GeH₃ into GeH₂ and CH₃CH(CH₃)₂, GeH₃ and CH₃C(CH₃)₂, and GeH₄ and CH₂=CH(CH₃)₂. The reaction energies were calculated to be approximately 170, 330 and 150 kJ/mol, respectively. The lowest reaction energy path seemed to be the decomposition into GeH₄ and CH₂=CH(CH₃)₂ (isobutene) through β-hydrogen eliminations. We considered that the growth species are GeH₄ molecules, and CH₂=CH(CH₃)₂ is pumped out without any chemical reactions. The low growth temperature, as low as that obtained with GeH₄, should be achieved through the GeH₄ generation by the β-hydrogen eliminations, although the t-C₄H₉GeH₃ is stable enough at the room temperature. Moreover, we considered that CH₂=CH(CH₃)₂ generated through the β-hydrogen eliminations is stable enough to prevent from more chemical reactions. So, we considered this is the reason why the C impurity incorporation was sufficiently suppressed.

We also evaluated the activation energies of the epitaxial growth using t-C₄H₉GeH₃. Figure 4 shows the Arrhenius plot between 320 and 380°C. Here, the growth at 380°C may be under the supply limited conditions. Therefore, we calculated the activation energy between 320 and 360°C. As the result, the activation energy using t-C₄H₉GeH₃ was approximately 160 kJ/mol. In the literature, it is reported that the activation energy using GeH₄ is approximately 140 kJ/mol. So, we could reveal that the activation energy using t-C₄H₉GeH₃ was almost as low as that using GeH₄. This result is consistent with the simulation results by ab initio calculation. The growth rate at 310°C is calculated as approximately 8.0 nm/h from the activation energy, which cannot be recognized as practical. Therefore, we conclude the epitaxial temperature should be practically more than 320°C under the present conditions. Further effort should be needed to lower the epitaxial temperature such as controlling the atmospheric pressure or changing the carrier gas during the growth.

In conclusion, we demonstrated the experimental results and discussed the mechanism of the low temperature Ge homoepitaxial growth using novel safe precursor, t-C₄H₉GeH₃. We have achieved to grow the Ge homoepitaxial films at low temperature of 320°C and the deposited epitaxial films had no obvious contaminations such as C and O, at least which should be less than the XPS detection limit of approximately 1 at.%. Moreover, we discussed the growth mechanism based on the ab initio calculations. As the result, we found that t-C₄H₉GeH₃ decomposes into GeH₂ and CH₂=CH(CH₃)₂ through the β-hydrogen eliminations. We considered that GeH₂ as a product of the β-hydrogen elimination contributes the low temperature growth, and CH₂=CH(CH₃)₂ contributes the low C impurity incorporation. We have also shown that the activation energy using t-C₄H₉GeH₃ is almost the same as that using GeH₄. This result is consistent with the simulation results by ab initio calculation. So we believe that the Ge MOCVD using t-C₄H₉GeH₃ is more appropriate than traditional GeH₄ and Ge₂H₆ for the safe epitaxial growth applicable for both the scientific experiment and commercial mass production.

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References

1. S. Zaima, Jpn. J. Appl. Phys. 52, 030001 (2013).
2. K. Morii, T. Iwasaki, R. Nakane, M. Takenaka, and S. Tskagi, IEEE Electron Device Lett. 31(10), 1092 (2010).
3. C. H. Lee, T. Nishimura, T. Tabata, S. K. Wang, K. Nagashio, K. Kita, and A. Toriumi, IEDM Tech. Dig., 2010, 18.1.1 (2010).
4. Y. J. Yang, W. S. Ho, C.-F. Huang, S. T. Chang, and C. W. Liu, Appl. Phys. Lett. 91, 102103 (2007).
5. T. Krishnamohan, D. Kim, T. V. Dinh, A.-T. Pham, B. Meinerzhagen, C. Jungemann, and K. Saraswat, IEDM Tech. Dig., 2008, 1 (2008).
6. K. Suda, S. Ishihara, N. Sawamoto, H. Machida, M. Ishikawa, H. Sudoh, Y. Ohshita, and A. Ogura, ECS Trans. 64 (6), 697 (2014).
7. K. Suda, T. Uno, T. Miyakawa, M. Ishikawa, H. Sudo, Y. Ohshita, and A. Ogura, ECS Trans. 53 (1), 245 (2013).
8. S. Gupta, R. Chen, B. Magyari-Kope, H. Lin, B. Yang, A. Nainani, Y. Nishi, J. S. Harris, and K. C. Saraswat, IEDM Tech. Dig., 2008, 16.6.1 (2008).
9. S. Takeuchi, Y. Shimura, T. Nishimura, B. Vincent, G. Eneman, T. Clarysse, J. Demeulmeester, A. Vantomme, J. Dekoster, M. Caymax, R. Loo, A. Sakai, O. Nakatsuka, and S. Zaima, Solid-State Electron. 60, 53 (2011).
10. V. R. D'Costa, C. S. Cook, A. G. Birdwell, C. L. Littler, M. Canonico, S. Zollner, J. Kouvetakis, and J. Menéndez, Phys. Rev. B 73, 125207 (2006).
11. R. A. Soref and L. Friedman, Superlattices Microstruct. 14, 189 (1993).
12. J. F. Liu, D. D. Cannon, K. Wada, Y. Ishikawa, S. Jongthammanurak, D. T. Danielson, J. Michel, and L. C. Kimerling, Appl. Phys. Lett. 84, 660 (2004).
13. M. Nakamura, Y. Shimura, S. Takeuchi, O. Nakatsuka, and S. Zaima, Thin Solid Films, 520, 3201 (2012).
14. H. Lin, R. Chen, W. Lu, Y. Hsu, T. I. Kamins, and J. S. Harris, Appl. Phys. Lett. 100, 102109 (2012).
15. H. Fujisawa, K. Kita, M. Shimizu, and H. Niu, Jpn. J. Appl. Phys. 40, 5551 (2001).
16. B. S. Kwak, E. P. Boyd, and A. Erbil, Appl. Phys. Lett. 53, 1702 (1988).
17. M. P. Singh, C.-S. Thakur, K. Shalni, N. Bhat, and S. A. Shivashankara, Appl. Phys. Lett. 83, 2889 (2003).
18. Y. Shimura, N. Tsutsumi, O. Nakatsuka, A. Sakai, and S. Zaima, Thin Solid Films, 518, S2 (2010).
19. K. Suda, S. Ishihara, N. Sawamoto, H. Machida, M. Ishikawa, H. Sudoh, Y. Ohshita, and A. Ogura, Jpn. J. Appl. Phys. 53, 110301 (2014).
20. K. Suda, T. Uno, T. Miyakawa, N. Sawamoto, H. Machida, M. Ishikawa, H. Sudoh, Y. Ohshita, and A. Ogura, Jpn. J. Appl. Phys. 52, 128006 (2013).
21. H. Machida, S. Hamada, T. Horike, M. Ishikawa, A. Ogura, Y. Ohshita, and T. Ohba, Jpn. J. Appl. Phys. 49, 05FF06 (2010).
22. T. Horike, S. Hamada, T. Uno, H. Machida, M. Ishikawa, H. Sudo, Y. Ohshita, and A. Ogura, Proc. Non-Volatile Memory Technology Symposium, 2011, 1 (2011).
23. S. Hamada, T. Horike, T. Uno, H. Machida, M. Ishikawa, H. Sudo, Y. Ohshita, and A. Ogura, Proc. Materials Science Forum, 725, 289 (2012).
24. S. Su, B. Cheng, D. Zhang, G. Zhang, C. Xue, and Q. Wang, ECS Trans. 50(9), 903 (2012).
25. B. Vincent, F. Gencarelli, H. Bendir, C. Merckling, B. Douhard, D. H. Petersen, O. Hansen, H. H. Hentrichsen, J. Meerschaert, W. Vandervorst, M. Heyns, R. Loo, and M. Caymax, Appl. Phys. Lett. 99, 152103 (2011).
26. S. Wirths, D. Buca, A. T. Tiedemann, B. Hollander, P. Bernardy, T. Stoica, D. Gruutmacher, and S. Mantl, ECS Trans. 50(9), 885 (2012).
27. N. Ueno, M. Sakuraba, J. Murota, and S. Sato, Thin Solid Films, 557, 31.
28. J. Margetis, S. A. Ghetmiri, W. Dub, B. R. Conley, A. Mosleh, R. A. Soref, G. Sunc, L. Domulevicz, H. A. Naseem, S.-Q. Yu, and J. Tolle, ECS Trans. 64(6), 711 (2014).
29. P. Ponath, A. B. Posadas, R. C. Hatch, and A. A. Demkov, J. Vac. Sci. Technol. B 31, 031201 (2013).
30. J. Murota, M. Kato, R. Kircher, and S. Ono, J. Phys. IV 02, C2 (1991).
31. B. Cunningham, J. O. Chu, and S. Akbar, Appl. Phys. Lett. 59, 3574 (1991).