MOCVD of RuO_2 Thin Films Using (η^6-benzene)(η^4-1,3-cyclohexadiene)Ru

Han-Na Hwang, Ki Chul Han, Ki-Seok An, Taek-Mo Chung, and Yunsoo Kim
Advanced Materials Division, Korea Research Institute of Chemical Technology, Yuseong P.O. Box 107, Daejeon 305-600, Korea

Ruthenium dioxide thin films have been deposited on Si(001) substrates using (η^6-benzene)(η^4-1,3-cyclohexadiene)Ru, Ru(bz)(chd), as a new Ru precursor by low pressure metal organic chemical vapor deposition. Dependence of the film qualities, such as the structural and electrical properties, on the substrate temperature and the oxygen flow rate were systematically investigated using X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy, and four-point probe resistivity measurements. Polycrystalline Ru thin films were deposited at the substrate temperature of 450 °C without oxygen, where the lowest carbon incorporation and resistivity were obtained. On increasing the oxygen flow rate with the substrate temperature kept at 350 °C, mixed films of polycrystalline Ru and RuO_2 were grown with increasing grain size, and, at the oxygen flow rate of 100 sccm, the films were completely converted to RuO_2 with the largest grain size.

Ruthenium dioxide, a transition metal oxide with the rutile structure, has attractive physical properties such as high electrical conductivity, high thermal and chemical stability, and effective interdiffusion barrier characteristics. These properties allow this material possibilities for very large-scale integration thick film resistors, a buffer layer for high T_c superconducting films on silicon, and an electrode in ferroelectric random access memory.

In this study, Ru and RuO_2 thin films were deposited on Si substrates by low pressure MOCVD using a newly synthesized precursor (η^6-benzene)(η^4-1,3-cyclohexadiene)Ru, Ru(bz)(chd). This precursor has been found to yield metallic Ru without O_2. Qualities of the films grown at various O_2 flow rates and substrate temperatures were systematically investigated by several structural and electrical characterization techniques, i.e., X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and four-point probe resistivity measurements.

The new Ru precursor (η^6-benzene)(η^4-1,3-cyclohexadiene)Ru, Ru(bz)(chd), was tested for the growth of Ru and RuO_2 thin films on Si(001) substrates by low pressure MOCVD with or without oxygen. The qualities of the films deposited at various O_2 flow rates and substrate temperatures were investigated by several characterization techniques such as XRD, SEM, XPS, and electrical resistivity measurements. Although the surface morphology is not significantly changed, the Ru thin film prepared at the substrate temperature of 450 °C without oxygen shows a well-developed XRD pattern of metallic Ru and little carbon incorporation with the resistivity of ~25 $\mu\Omega$ cm. With increasing the oxygen flow rate at the substrate temperature of 350 °C, XRD, SEM, and XPS results indicate that the increased film thickness and grain size up to 30 sccm of oxygen flow rate is mainly caused by the formation of a thin film of Ru rather than RuO_2. At 100 sccm of oxygen flow rate, a fully oxidized RuO_2 thin film is formed without the incorporation of metallic Ru. The film thickness is considerably decreased at high oxygen flow rates between 70 sccm and 100 sccm, which is mainly related to the formation of RuO_2. Finally, this study has shown that the new Ru precursor is suitable for MOCVD of both Ru and RuO_2.

References

1. G. J. Norga, L. Fè, D. J. Wouters, H. E. Maes, *Appl. Phys. Lett.*, **76**, 1318 (2000)
2. M. Prudenziati, B. Morten, F. Cilloni, G. Ruffi, *Sens. Actuators*, **19**, 401 (1989)
3. A. Dziedzic, L. Golonka, *J. Mater. Sci.*, **23**, 3151 (1988)
4. Q. X. Jia, W. A. Anderson, *Appl. Phys. Lett.*, **57**, 304 (1990)
5. P. Gopal Ganesan, M. Eizenberg, *Microelectron. Eng.*, **64**, 449 (2002)
6. Y. S. Huang, P. C. Liao, *Sol. Energy Mater. Sol. Cells*, **55**, 179 (1998)
7. Y. Gao, G. Bai, Y. Liang, G. C. Dunham, S. A. Chambers, *J. Mater. Res.* **12**, 1844 (1997)
8. Q. X. Jia, S. G. Song, X. D. Wu, J. H. Cho, S. R. Foltyn, A. T. Findikoglu, J. L. Smith, *Appl. Phys. Lett.*, **68**, 1069 (1996)
9. D.-J. Lee, S.-W. Kang, S.-W. Rhee, *Thin Solid Films*, **413**, 237 (2002)
10. J.-H. Lee, J.-Y. Kim, S.-W. Rhee, D. Y. Yang, D.-H. Kim, C.-H. Yang, Y.-K. Han, C.-J. Hwang, *J. Vac. Sci. Technol. A*, **18**, 2400 (2000)
11. M. L. Green, M. E. Gross, L. E. Papa, K. J. Schnoes, D. Brasen, *J. Electrochem. Soc.*, **132**, 2677 (1985)
12. P. Lu, S. He, F. X. Li, Q. X. Jia, *Thin Solid Films*, **340**, 140 (1999)
13. J.-H. Lee, J.-Y. Kim, S.-W. Rhee, *Electrochem. Solid-State Lett.*, **2**, 622 (1999)
14. J. M. Lee, J. C. Shin, C. S. Hwang, H. J. Kim, C.-G. Suk, *J. Vac. Sci. Technol. A*, **16**, 2768 (1998)
15. R.-s. Chen, Y.-s. Huang, Y.-l. Chen, Y. Chi, *Thin Solid Films*, **413**, 85 (2002)
16. S. Y. Kang, K. H. Choi, S. K. Lee, C. S. Hwang, H. J. Kim, *J. Korean Phys. Soc.*, **37**, 1040 (2000)
17. S. Y. Kang, K. H. Choi, S. K. Lee, C. S. Hwang, H. J. Kim, *J. Electrochem. Soc.*, **147**, 1161 (2000)
18. J. Choi, Y. Choi, J. Hong, H. Tian, J.-S. Roh, Y. Kim, T.-M. Chung, Y. W. Oh, Y. Kim, C. G. Kim, K. No, *Jpn. J. Appl. Phys.*, **41**, (2002) in print
19. K. S. Kim, N. Winograd, *J. Catal.*, **35**, 66 (1974)
20. Y. J. Kim, Y. Gao, S. A. Chambers, *Appl. Surf. Sci.*, **120**, 250 (1997)
21. J. Hrbek, D. G. van Campen, I. J. Malik, *J. Vac. Sci. Technol. A*, **13**, 1409 (1995)
22. H. Y. H. Chan, C. G. Takoudis, M. J. Weaver, *J. Catal.*, **172**, 336 (1997)