

Structural and Electrical Properties of TiO₂ Films by Controlled Deposition of Sol-Gel Process

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ABSTRACT

Regarding to the material of high dielectric layers, the characteristic of current leakage is very important, and being worth to study. However, related works and researches are few, especially in preparation of TiO₂ nano thin film by the Sol-Gel method. In this paper, we studied the characteristics of TiO₂ nano thin film, with changes the pH value of TiO₂ solution formula, heat treatment temperature, film thickness and so on. And the TiO₂ was deposited on ITO glass by spin coating, following high temperature furnace tube annealing. Surface morphology and electric characteristic were investigated. The experiment included three parts (i) thin film surface microstructure analysis ; (ii) thin film device measurement ; (iii) thin film optics and penetration coefficient measurement. TiO₂ solution was prepared with titanium (IV) alkane oxygen compound (alkoxide) by Sol-Gel method. It was made from hydrolyzing of titanium-alkane oxide compound and water produced by esterification of acetic acid and IPA. This reaction may reduce the hydrolysis rate of the mellow oxygen compound to avoid fast precipitates, which led to produce homogeneous phase. By means of the TEM and SEM investigation, Sol-Gel pellets were 15-25nm in size, and the surface was extremely smooth. Brookite structure distinguished XRD. After annealing at 550 °C, preferential crystallized texture and structure were formed. Al was taken as the point electrode of thin film device in I-V and C-V measurement. In order to study relation between leakage current, annealing temperature, and film thickness, different annealing temperature(200 °C to 600 °C), film thickness and pH value of solution has been involved. As the result, there was a minimum leakage current $1.2 \times 10^{-8}A$ with 7.53um thickness (4 layers) after 550 °C annealing. It might be attributed to the better crystallization and smooth surface. On the other hand, we also found that annealing can reduce the leakage current of TiO₂ effectively, due to the compensation of oxygen left vacancy during prepare process. Titanium dioxide not only has stable chemical and physical properties, but also has excellent optical property. (photo-conductivity, reflectivity, refractive index and so on.) Besides, titanium dioxide also has good penetration coefficient. The penetration coefficient of TiO₂ thin film is 80% measured by UV-Vis.

Keywords : Sol-Gel ; titanium dioxide ; thin film ; leakage current ; Dielectrics

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REFERENCES

- 參考文獻 【1】 Fujishma, A.Honda, " Electrochemical photolysis of water at s semiconductor electrode ", Nature, 238, (1972)37 【2】 電工材料 吳朗 編著 滄海書局 【3】 Takashi Fuyuki and Hiroyuki Matsunami, " Electronic Properties of Interface between Si and TiO₂ Deposited at Very Low Temperature " Japanese Journal of Applied Physics, 25, 1288-1291(1986) 【4】 Takashi Fuyuki and Hiroyuki Matsunami, " Electronic Properties of Interface between Si and TiO₂ Deposited at Very Low Temperature " Japanese Journal of Applied Physics, 25, 1288-1291(1968) 【5】 G. Blondeau, " Influence of Copper Addition on Optical Properties of TiO₂ " J. Electrochem. Soc., 126, 1592(1979) 【6】 Hirofumi Takikawa, " Properties of titanium oxides film prepared by reactive cathodic vacuum arc deposition " thin Solid Films, 348, 169-178(1995) 【7】 K. S. Yeung and Y. W. Lan, " A simple chemical vapor deposition method for depoiting thin TiO₂ film Thin Solid Films ", 109, 169-178(1983) 【8】 H. J. Frenck, " Deposition of TiO₂ thin film by plasma enhanced decomposition of teraiopropya titanate " Thin Solid Films, 201, 327-335(1991) 【9】 K. S. Yeung and Y. W. Lan, " A simple chemical vapor deposition method for depoiting thin TiO₂ films " Thin Solid Films, 109, 169-178(1983) 【10】 K. S. Yeung and Y. W. Lan, " A simple chemical vapor deposition method for depoiting thin TiO₂ films " Thin Solid Films, 109, 169-178(1989) 【11】 Kiichiro Kamata, " Rapid formation of TiO₂ films by plasma enhanced decomposition of teraiopropya titanate " Thin Solid Films, 201, 327-335(1991) 【12】 Carl. P. Fictorie, " Kinetic and mechanistic study of the chemicalvapor deposition of titanium dioxide thin films using tetrakis-(isopropoxo)-tit-nium(IV) " J. Vac.Sci. Technol.A12, 1108-1113(1994) 【13】 R. B. van Dover, Appl. Phys. Lett., 74(20), pp 3041-3043(1999) 【14】 陳繼仁, TiO₂陶瓷的燒結、電性及晶界偏析理論模型之研究, 清華大學材料所博士論文(1989) 【15】 W. D. Brown, W.W. Grannemann, Thin Solid Films, 51, pp 119-132(1978) 【16】 Yu.D. Dolmatov, Priklad, Zh., 42, 8, (19669)1275 【17】 Z. Jerman, Collect. Czech. Chem. Commun., 31, (1966)3270 【18】 Yoldas.B.E, " Hydrolysis of titanium alkoxide and effects of hydrolytic polycondensation parameters ", J.Mater.Sci., 21, (1986)1087 【19】 K. Terabe, K.Kato, H. Miyazaki, S. Yamaguchi, A. Imai, Y. Iguchi, " Microstructure and crystallization behaviour of TiO₂ Precursor prepared by the sol-gel method using metal alkoxide ", J. Mater. Sci., 29, (1994)1617-1622 【20】 K. P. Kumar, and K. Keizer, " Effect of Peptization on Densification and Phase-Transformation Behavior of Sol-Gel-Derived Nanostructured Titania ", J.Am.Ceram.Soc., 77(5), (1994)1396-1400 【21】 K. Kamiya, S. Sakka, " Thermal expansion of TiO₂-SiO₂ and TiO₂-GeO₂ glasses ", J. Non-Cryst. Solids.52, (1982)357 【22】 J. Livsge, S. Doeuff, M.Henry and C.Sanchez, " Hydrolysis of titanium alkoxides: Modification of the molecular precurar precursor by acetic acid ", J. Non-cryst. Solids, 89, (1995)206-216 【23】 R. W. Jones, Fundamental principles of sol-gel technology, The institute of metals(1989) 【24】 S. Sakka and K. Kamiya, " Glasses from metal alcoholates ", J. Non-Cryst. Solids, 42, (1980)40 【25】 Kamiya, K. Tanimoto and T. Yoko, " Presparation ofTiO₂ fibers by hydrolysis and polycondensation of Ti(O-i-C₃H₇)₄ ", J. Mater. Sci. Lett., 5, (1986)402 【26】 J. Livage, in " Sol-Gel Science and Technology ", eds. by M. A. Aegeter, M. Jr. Jafellicci, D.F.Souza and E. D. Zanotto, World Scientific, Singapore(1989)103 【27】 H. L. M. Pulker, G. Paesold, and E. Ritter, Refractive indices of TiO₂ films produced by reactive evaporation of various titaniumm-oxygen phases APPLIDE OPTICS, 15, 2986-2991(1976). 【28】 Properties as a Function of Processing Temperature J. Electrochem. Soc. :SOLID-STATE SCIENCE AND TECHNOLOGY, 119, 735-739(1972) 【29】 Feng Zhang, Highly oriented rutile-type TiO₂ films synthesized by ion beam enhanced deposition J. Vac. SCI. Technol. A 15, 1824-1827(1997) 【30】 Kiichiro Kamata, Rapid formation of TiO₂ films by a conventional CVD method journal of Materials Science Letters, 9, 316-319 (1990) 【31】 A. C. Ting and S. Y. Chen, J. Appl. Phys., 88(8), pp 4628-4633 (2000) 【32】 Mills A. and S. L. Hunte, " An overview of semiconductor photocatalysis ", J. Photochem. & photobio. A: Chemistry, 108, pp 1-35(1995) 【33】 B. R. Weinberger and R. B. Garber, Appl. Phys. Lett., 66(18), pp2409-2411(1995) 【34】 J. D. Deloach and C. R. Aita

, J. Vac. Sci. Technol. A , 16(3) , pp1963-1968(1998) 【35】 O. Carpa,* C.L. Huismanb , A. Rellerb ,Photoinduced reactivity of titanium dioxide ,Progress in Soid State Chemistry 32 (2004) 33-177 【36】 O. Treichel , V. Kirchoff , Surface and Coating Technol. , 123 , pp268-272 (2000) 【37】 Jang , S. W. Whangbo , H. B. Kim , K. Y. Im , Y. S. Lee , I. W. Lyo , and C. N. Whang , J. Vac. Sci. Technol. A , 18(3) , pp917-921(2000) 【38】 K. Yokota , T. Yamada , F. Miyashita , K. Hirai , H. Takano and M. Kumagai , Thin Solid Films , 334 , pp109-112(1998) 【39】 C. Byun , J. W. Jang , I. T. Kim , K. S. Hong and B. W. Lee , Materials Research Bulletin , 32 (4) , pp431-440(1997) 【40】 N. Rausch and E. P. Burte , J. Electrochem. Soc. , 140(1) , pp145-149(1993) 【41】 Y. H. Lee , K. K. Chan , and M. J. Brady , J. Vac. Sci. Technol. A , 13(3) , pp 596-601(1995) 【42】 A. Watanabe , Y. Imai , Thin Solid Films , 348 , pp63-68(1999) 【43】 T. Kamada , M. Kitagawa , M. Shibuya , and T. Hirao , Jphys. , 30(12B) , pp 3594-3596(1991) 【44】 C. Chaneliere , S. Four , J. L. Autran , R. A. B. Devine and N. P. Sandler , properties of amorphous and crystalline Ta₂O₅ thin film deposited on Si from a Ta(OC₂H₅)₅ precursor J. Appl. Phys. , Vol 83 , Number9 , 1998 , p.4823-p.4828 【45】 Wai Shing Lau , et al. he Superiority of N₂O plasma Annealing over O₂ plasma Annealing for Amorphous Tantalum Pentoxide (Ta₂O₅) Films Jpn. J. Appl. Phys.Vol.3 【46】 M. S. Tsai , S. C. Sun , and T. Y. Tseng , Effect of oxygen to argen ratio on properties of (Ba , Sr)TiO₃ thin films prepared by radio-frequency magnetron sputtering J.Appl.Phys.82(7) , 1 October 1997 , p.3482-p.3487 【47】 陳啟明 , 以磁控濺鍍法製備二氧化鈦薄膜電容器及電性分析 , 清華大學電子所碩士論文(2000)