行政院國家科學委員會補助專題研究計畫成果報告

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※ 12吋矽晶圓半導體CVD製程設備及BST介 ※

※ 電薄膜成長研究（I）－子計畫四：利用 ※

※ CVD法成長BST薄膜與特性分析 ※

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共同主持人：

本成果報告包括下列應繳交之附件

- □赴國外出差或研習心得報告一份
- □赴大陸地區出差或研習心得報告一份
- □出席國際學術會議心得報告及發表之論文各一份
- □國際合作研究計畫國外研究報告書一份

執行單位：國立交通大學電子工程學系

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12吋矽晶圓半導體CVD製程設備即BST介電薄膜成長研究（Ⅰ）-子計劃四：利用CVD法成長BST薄膜與特性分析

國科會編號：
NSC 89-2212-E009-040
主持人：曾俊元
國立交通大學電子工程系所

一．中文摘要（關鍵詞：鈦酸鍶鋇，薄膜，溶液，液相化學汽態沈積法）

流動膠體或溶液可藉液相化學汽態沈積法，旋轉法或噴霧法來製備薄膜。本研究發展了兩種溶液的製備法，並利用來在石英和氧化鋁單晶基板上製備鈦酸鍶鋇薄膜，並探討相形成的特性。另方面並報導於氧氣和笑氣的氣氛中，濺鍍的鈦酸鍶鋇薄膜快速退火處理對其電性與介電性質之影響。

二．英文摘要（Key Words：$(Ba_{1-x}Sr_x)TiO_3$，thin films，solution，LSCVD）

The fluid sol or solution is ideal for preparing thin films by the processes such as liquid source chemical vapor deposition，spinning or spraying . Two methods have been used for the preparation of solution，hydroxide alkoxide precursor and acetate-alkoxide precursor . BST thin films have been deposited on quartz and sapphire substrates using these solutions . The phase formation characteristics have been investigated . In addition，we present the effect of rapid thermal annealing treatment in O_2 and N_2O ambient on the properties of rf-sputtered BST thin films .

三．結果與討論

The hydroxide-alkoxide precursors method uses the inexpensive $Ba(OH)_2 8H_2O$ and $Sr(OH)_2 8H_2O$ as Ba- and Sr- sources materials . The processing method is outlined in Flow Chart 1 (Fig.1) . Precursor solutions were prepared using high purity Ba-，Sr-hydroxides and titanium (ⅠV) isopropoxide ($Ti(OC_3H_7)_4$) . For a desired composition，the required amounts of Ba-，Sr- hydroxides were separately mixed in 2-methoxy ethanol and refluxed at 120˚C . Similarly，stoichiometric amount of Ti-isopropoxide was mixed 2-methoxy ethanol separately and refluxed at 120˚C for 3h to form a homogeneous mixture of BST-precursor . The films were prepared by spin coating using the solution on sapphire substrates . These films were then prebaked to evaporate the solvent at 120˚C followed by baking at 400˚C to pyrolize the organics . Film of required thickness is obtained by repeating the spin coating-prebaking-baking several times before final annealing process . The phase formation characteristics are probed using X-ray diffraction . Figure 2 shows the pattern of BST (x = 0.5) deposited using this method on sapphire substrate . Interesting observation is that crystalline film is obtained at 550˚C and the film shows a (101) preferred orientation up to an annealing temperature of 650˚C . Film thickness of 650˚C annealed

sample is 100 nm . Highly crystalline films were obtained after annealing at higher temperature without presence of a second phase .

The BST-precursor solution preparation using acetate-alkoxide precursor and film preparation procedure is outlined in Flow Chart II (Fig.3) . BST-precursor solution of required concentration (0.3-0.8M) is prepared by dissolving appropriate molar ratios of Ba- , Sr-acetate in 90°C heated glacial acetic acid followed by the addition of stoichiometric amount of Ti-isopropoxide and ethylene glycol and refluxing as outlined in flow chart . The reaction of acetic acid to ethylene glycol is critical as it determines how low the crystallization temperature of BST can be brought down . Lowest crystallization temperature is obtained for an acetic acid to ethylene glycol ratio of 3/1 . Figure 4 shows the XRD pattern of BST (x = 0.5) on quartz substrate . The 500°C annealed sample is amorphous and a crystalline film is obtained at 600°C . In order to understand the effect of post-annealing on the rf-sputtered BST thin films after deposition . The film was annealed with RTA treatment in O_2 and N_2O ambient . The annealing profile about the RTA in O_2 or N_2O treatments is shown in Fig.5 . Figures 6 and 7 show the XRD patterns of the 10% OMR BST thin films deposited on Pt bottom electrodes at 600°C and afterward annealed for 3 min at 500 , 600 and 700°C in O_2 and N_2O ambient . The (110) peak intensity of the BST thin films increases with increasing annealing temperature in the RTA temperature range of 500~700°C in O_2 ambient . When BST film is annealed at 500 , 600 and 700°C in N_2O ambient , the (110) peak intensity of the BST thin film is slightly increased with increasing temperature . It could find from Figs.6 and 7 that crystallinity of these films was improved by using RTA process . The composition of BST film deposited at 600°C wad determined from ICP-AES . The composition of BST film annealed at 500 , 600 and 700°C in O_2 or N_2O ambient was substantially equal to the target compositions within an error of 2.2% (Ba/Sr = 0.47/0.52) . The composition of all the films obtained were consistent with cubic perovskite phase (not shown here) . Fig.8 shows the effect of RTA temperature on dielectric constant and loss tangent of the 600°C , 10% OMR BST films deposited . The figure reveals that the dielectric constant is increased when annealing temperature is increased from 500°C to 700°C . According to XRD patterns in Figs.6 and 7 , the BST (110) peak is stronger for the films annealed at higher temperature . Therefore , the dielectric constant of the high temperature annealed films should be higher due to the better crystallinity . The dependence of the leakage current density measured at 100 kV/cm with a delay time of 5 sec on the RTA temperature in O_2 and N_2O ambient is shown in Figs.9 and 10 . When the RTA annealing temperature was increased to 600°C in O_2 or N_2O ambient , both the dielectric constant and the leakage current are increased . It also shows further increase in the leakage current for the BST films annealed at 700°C , as shown in Fig.11 .

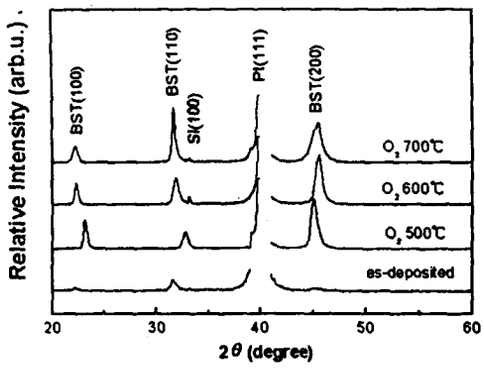

Fig.6 XRD patterns of BST thin films deposited at 600℃ with 10% OMR. The measurements were carried out at various RTA temperatures in O_2 ambient.

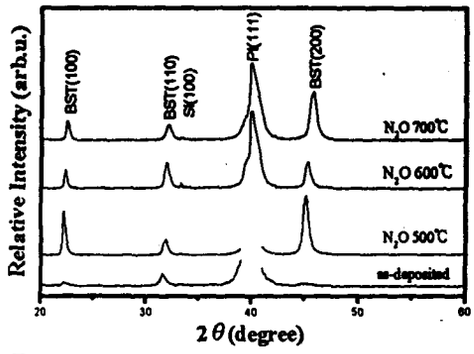

Fig.7 XRD patterns of BST thin films deposited at 600℃ with 10% OMR. The measurements were carried out at various RTA temperatures in N_2O ambient.

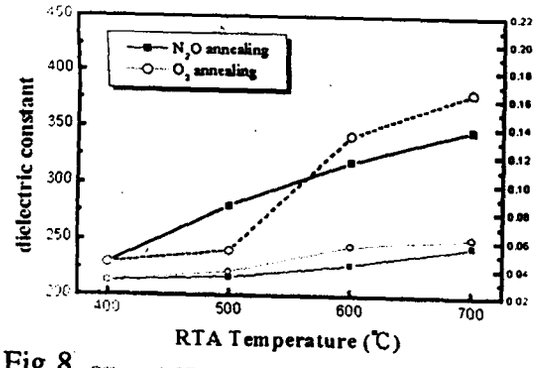

Fig.8 Effect of RTA temperature on dielectric constant and loss tangent of the BST films deposited at 600℃ with 10% OMR.

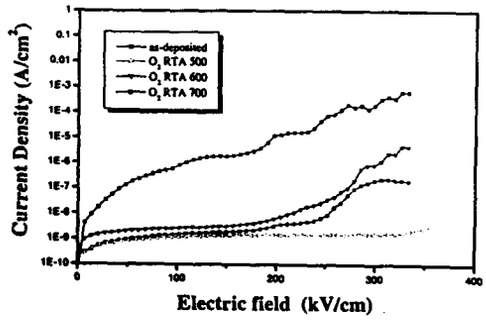

Fig.9 Leakage current density versus applied voltage for the BST thin film deposited at 600℃ with 10% OMR. The measurements were carried out at various RTA temperatures in O_2 ambient.

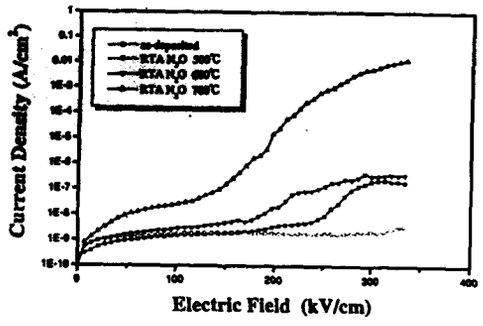

Fig.10 Leakage current density versus applied voltage for the BST thin film deposited at 600℃ with 10% OMR. The measurements were carried out at various RTA temperatures in N_2O ambient.

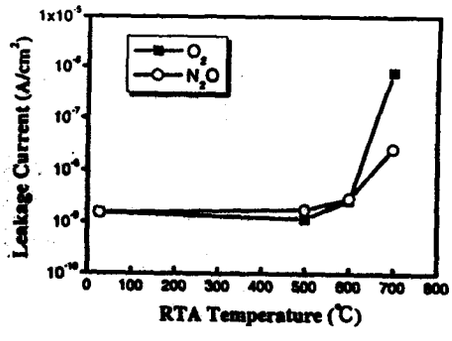

Fig.11 Effect of RTA temperature on leakage current of 10% OMR BST films deposited at 600℃.