Piranha 改性玻璃基板液相沉积制备 $SrTiO_3$ 功能陶瓷薄膜

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摘要：以 Piranha 溶液处理玻璃基板,采用液相沉积技术,制备了钛酸锶晶态薄膜。改性基板的亲水性测定与偏光显微镜测试表明,Piranha 溶液能够有效改善玻璃基板的亲水性,并且基板表面的硅烷醇对钛酸锶薄膜的沉积具有积极指导作用;X 射线衍射(XRD)与扫描电镜(SEM)表征显示,制备成功的钛酸锶薄膜纯度高,结晶良好,样品表面均匀,在垂直基板表面方向上呈纤维花簇状生长。文章同时对基板表面硅烷醇形成过程进行了研究。

关键词：Piranha；液相沉积；钛酸锶
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Preparation of $SrTiO_3$ Functional Ceramic Thin Film on Glass Wafers Treated by Piranha Solution with Liquid Phase Deposition Method

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Abstract: $SrTiO_3$ thin film was prepared on glass wafers treated by piranha solution (a mixture of sulfuric acid and hydrogen peroxide) with Liquid Phase Deposition method. Contact angle measurement of glass wafers and photographs of polarizing microscope indicate that hydrophilic characteristic of the substrate is improved by piranha solution, and an induction of deposition $SrTiO_3$ thin film by Si-OH groups. XRD and SEM results show that the pure and homogeneous $SrTiO_3$ thin film is a well-crystalline one. The prepared $SrTiO_3$ thin film is grown vertically on the glass substrate. The formation mechanism of Si-OH groups is also discussed.

Key words: piranha; liquid Phase deposition; $SrTiO_3$

Perovskite-type $SrTiO_3$ (STO) is an attractive material for its excellent capability, such as high dielectric constant, low dielectric loss, chemical and thermal stability, and good insulating properties. So many excellent capabilities make STO widely used in ceramic capacitor, piezoelectricity materials, thermal sense organ, microwave organ, insulated semiconductor and memory materials, such as capacitor dielectric in dynamic random access memory (DRAM)[1], a substrate for high-T_c superconducting devices[2], and the next-generation complementary metal oxide semiconductor (CMOS) device[3].

At present, $SrTiO_3$ thin film have been synthesized by several processes such as electron-cyclotron-resonance (ECR) plasma sputtering[4], molecular beam deposition[5], chemical-vapour-deposition (CVD)[6], chemical solution deposition (CSD)[7], atomic layer deposition (ALD)[8], hydrothermalelectrochemical method[9], Self-Assembled Monolayers technique[10], etc. But all these techniques require special equipment, complicated techniques, vacuum, high temperature, higher energy etc.

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Liquid Phase Deposition (LPD) is one of the most simple, energy-efficient, environment-friendly, and cost-effective processes for preparing two-component oxide thin films, such as TiO_2[11], SiO_2[12], SnO_2[13], WO_3[14], etc. But it is rarely used for multi-component thin films. Here we report pure and high crystalline $SrTiO_3$ thin film on glass wafers treated by piranha solution with LPD method.

1 Experimental

1.1 Preparation of substrate

Glass wafers employed for the substrates were cleaned ultrasonically in acetone, ethanol and deionized water. After drying in air, the cleaned and dried substrate was immersed into an anhydrous piranha solution containing 70% volume of concentrated H_2SO_4 and 30% volume of H_2O_2 for 5~50 min, which modified the surface of the glass wafer and resulted in the change of the original hydrophobic groups. Water-drop contact angle measurement (Contact Angle Meter, JC2000D, Zhongchen Tech. (Shanghai) Inc., Ltd. Shanghai) was conducted to check the formation of functional groups by piranha.

1.2 Deposition of $SrTiO_3$ thin film

Boric acid (H_3BO_3 (BA), AR, Yongda Chemical Reagent Co., Tianjin), ammonium hexafluorotitanate ($(NH_4)_2TiF_6$ (AHFT), CP, Sanaisi Chemical Co., Shanghai) and strontium nitrate ($Sr(NO_3)_2$ (SN), AR, Guangfu Chemical Institute, Tianjin) were employed as the starting materials. They were dissolved in water separately and then mixed to form a homogeneous solution containing 25 mmol·L^{-1} AHFT, 25 mmol·L^{-1} SN, and 75 mmol·L^{-1} BA (n_{AHFT}:n_{SN}:n_{BA}=1:1:3). The pH value of the solution was 3.0. The deposition was conducted by immersing the substrate treated by piranha solution at 60 ℃ for 4~8 h. Then the substrate with a deposit was rinsed carefully in distilled water before air-drying. Finally, the as-deposited film was calcined at 600 ℃ for 2 h.

1.3 Measurement and Characterization

Contact angle (Contact Angle Meter, JC2000D, Zhongchen Tech. (Shanghai) Inc., Ltd. Shanghai) was used to characterize the surface of the glass wafers treated by piranha solution. The structure and phase composition were characterized by X-ray diffraction (XRD, D/max-2500PC, RIGAKU, Japan, Cu target, working voltage 40 kV, working current 100 mA, λ = 0.154 18 nm, Ni filter, scanning step length 0.02°, scanning speed 10°·min^{-1}, scanning angle from 5° to 90°). The morphology of the final products was observed by Field emission SEM (FE-SEM, S-4800, HITACHI, Japan, at an accelerating voltage of 5.0 kV) and Polarizing Microscope (XPL-2, Nanjing Jiangnan Novel Optics Co. Ltd, Nanjing).

2 Results and discussion

2.1 Characteristics of substrate treated by piranha solution

Appearance for water contact angle of 37.96° could be found in Fig.1(a). When soaking time is over 5 min, the decreasing trend of contact angle becomes slow, reaching 12.88° at 20 min. The drip lays low on the substrate. Appearance for water contact angle of 12.88° could be found in Fig.1(b).

Relationship between soaking time and contact angle can be seen in Table 1 and Fig.2. Along with

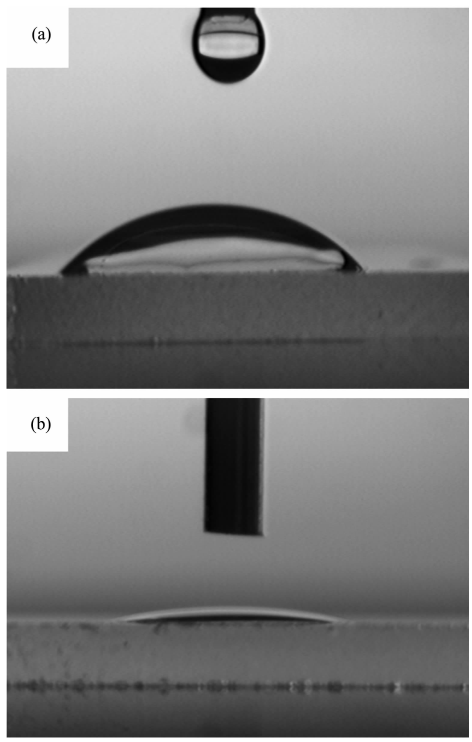

Fig.1 Contact angle photographs of glass wafers: before treated (a) and treated for 20 min (b)

Table 1　Contact angle measurement of glass wafers treated by piranha solution

Soaking time / min	0	5	10	15	20	25	30	35	40	45	50
Contact angle / (°)	37.96	27.25	22.20	19.25	12.88	17.27	17.89	16.58	20.50	16.73	18.50

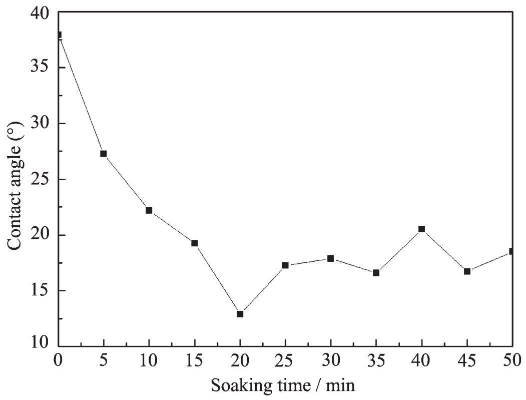

Fig.2　Relationship of contact angle with substrate soaking time

extending the soaking time, the substrate contact angle decreases gradually, especially in the first 5 min, contact angle is decreased from 37.96° to 29.25°. The result caused by piranha solution could be analyzed as follows: under the effect of piranha solution, Na^+ and Ca^{2+} presented on the surface of glass wafer are replaced by H^+[15]. The reaction forms polar functional silanol (Si-OH) groups on the surface of substrate.

The process of the replacement can be seen in Fig. 3. The functional Si-OH groups possess strongly hydrophilic characteristic, so water can spread out on the surface of substrate.

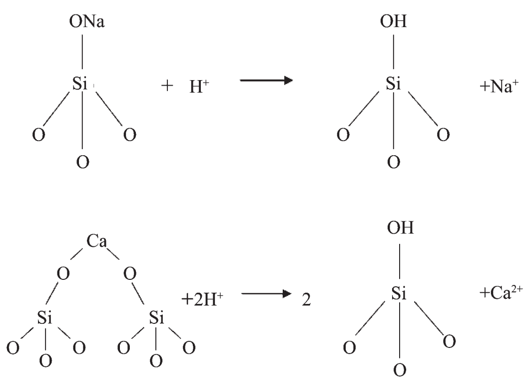

Fig.3　Scheme for Si-OH groups formation processes on glass wafer

2.2　Photographs of polarizing microscope

The substrate treated by piranha solution possesses strong hydrophilic characteristics, so the solution with ceramic precursors can spread out on its surface. This functionalized surface should be reactive to a variety of chemical coupling reactions, such as chemical adsorption of ceramic precursors from a solution.

Photographs of polarizing microscope as shown in Fig.4 were used for observing the differences between STO thin film deposited on normal glass wafer and the glass wafer treated by piranha solution. The thin film deposited on functional Si-OH groups (Fig.4b) has uniform surface without any obvious disfigurement, whereas many black shadows and blank areas could be observed in Fig.4a. The inhomogeneous surface of normal substrate results in the STO thin film growing up uniformly and unconventionally. Si-OH groups on the surface of substrate propitious to the adsorption of ceramic precursors show direct effect on STO thin film deposition.

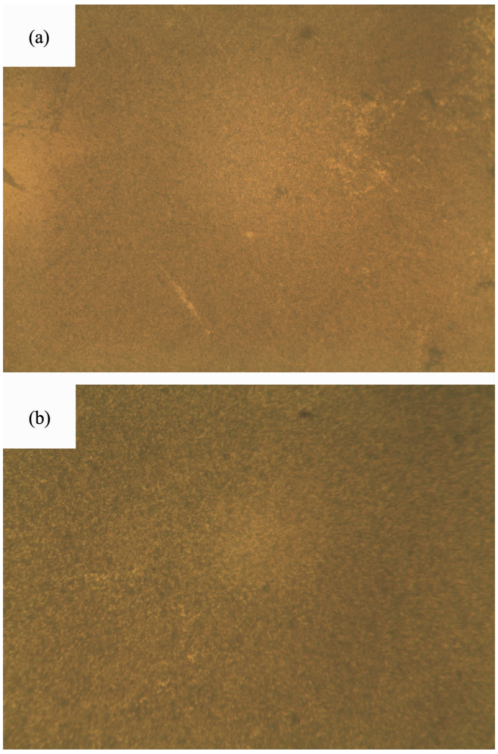

Fig.4　Polarizing microscope photographs of $SrTiO_3$ thin film deposited on normal glass wafer (a) and on Si-OH groups (b)

2.3 Characteristics of XRD

Fig.5 shows the XRD patterns of STO sample after annealing at 600 ℃ for 2 h in air. It can be seen that all the peaks can be indexed to cubic phase STO. The pure STO product is obtained without any impurities. The diffraction peaks of (110) and (200) are strong, and the full-width at half-maximum is small, suggesting the high crystallinity of the product. The as-deposited STO precursor solid is crystallized into STO after annealing at 600 ℃.

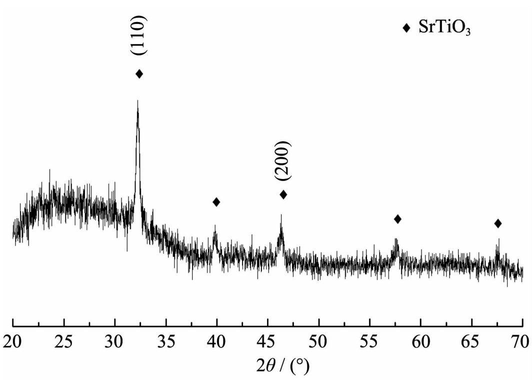

Fig.5 XRD pattern of $SrTiO_3$ thin film deposited on Si-OH groups

2.4 Photographs of FE-SEM

Fig.6a suggests that the substrate deposited for 6 h

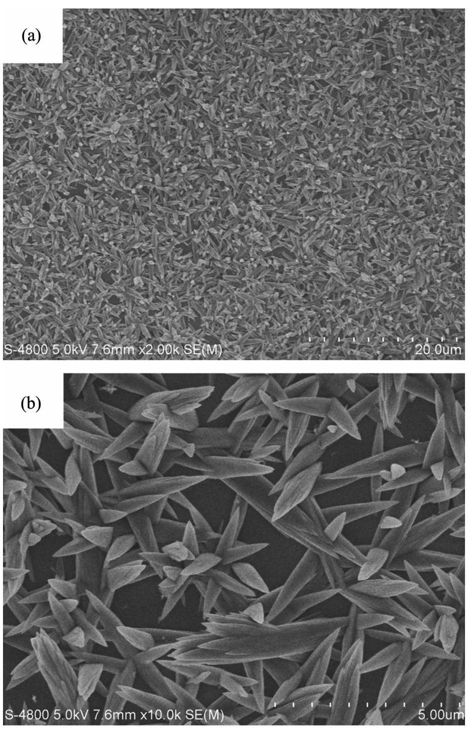

Fig.6 SEM photographs of $SrTiO_3$ thin film deposited on Si-OH groups

is covered with STO thin film completely, and the surface of STO thin film is homogeneous without any obvious disfigurements. Fig.6b shows that STO thin film with flower-like morphology is grown vertically on the glass substrate. In order to reduce the energy of the prepared solution, the electronegative Si-OH groups obtained by immersing the substrate into piranha solution would adsorb Sr^{2+}, then Sr^{2+} adsorbs the hydrolysate of $[TiF_{6-n}(OH)_n]^{2-}$. Finally the growth of STO thin film is achieved by continuous adsorption of Sr^{2+} and $[TiF_{6-n}(OH)_n]^{2-}$.

3 Conclusions

In summary, $SrTiO_3$ thin film was prepared on Si-OH groups with Liquid Phase Deposition method. Measurement of contact angle shows that the hydrophilic capability of the substrate is improved by immersing glass wafers into piranha solution. Photographs of Polarizing Microscope suggest that Si-OH groups have positive effect on the deposition of $SrTiO_3$ thin film. XRD and SEM results indicate that the thin film is of pure cubic phase $SrTiO_3$ and composed of flower-like morphology.

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