Fabrication of $La_{0.78}Sr_{0.22}CuO_{2.5-d}$ Nanodots on Silicon Surface by RF-Sputtering Using Nanoporous Anodic Alumina as Template

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Abstract: It have been investigated that the tetragonal perovskite $La_{1-x}Sr_xCuO_{2.5-\delta}$ (LSCu) was presented in a narrow range of $0.2 \le x \le 0.25$. The structure stability of LSCu was greatly dependent on the strontium concentration. However, in this study, the trinary perovskite oxide, $La_{0.78}Sr_{0.22}CuO_{2.5-\delta}$, nanodots on the silicon surface have been produced by RF-sputtering using a template-assisted approach. Due to the step coverage limitation of RF-sputtering, the template should be from with the straight and through pores. The nanoporous anodic alumina templates were fabricated by two-step anodization process after aluminum thin film was deposited on the silicon substrate by E-beam evaporation. The pores of the template made by this approach were straight and through with 50 nm in diameter and 30 nm in length. By RF-sputtering using nanoporous anodic alumina as template, the $La_{0.78}Sr_{0.22}CuO_{2.5-\delta}$ nanodots on silicon surface were produced with a 50 nm in diameter.

Key-Words: LSCu, nanodot, RF-sputtering, mixed conductor, alumina, template

1 Introduction

In Recent years, it have been investigated that the tetragonal perovskite Sr-doped lanthanum cuprate with composition of $La_{1-x}Sr_xCuO_{2.5-\delta}$ (LSCu) was only presented when strontium addition in a narrow range from 20% to 25% ($0.2 \le x \le 0.25$). The structural stability of LSCu is greatly affected by the amount of strontium addition. When the lanthanum lattice sites are occupied by the doped strontium ions, the defects with negative effective charge, Sr_{La}', are formed. Based on the electroneutrality, the defects with positive effective charge including of the electron holes, $h^{\bullet}$, and the doubly charged oxygen vacancies, $V_o^{\bullet\bullet}$, are created [1,2]. These oxides may have high electrical conductivities (≈1000 S/cm at room temperature), and high oxygen diffusivities depending on strontium content (x). Therefore, LSCu may have potential applications as superconductor, catalyst, gas sensor, and electrode materials [2,3].

In this study, the LSCu was deposited on the silicon surface without using PAA template by the RF-sputtering to find the deposition parameters, and the syntheses temperature. For the fabrication of the LSCu nanodots on the silicon substrates, the porous anodic alumina (PAA) was used as masks. Due to the controllable pore characteristics and simplicity to produce, PAA is now one of the most popular materials for the fabrication of nano-sized structure [4-6]. One dimensional nanostructure could be obtained by depositing materials into the PAA through many methods including of chemical deposition, physical vapor deposition, electrodepostion, electroless deposition, and sol-gel deposition [7-10]. For of the syntheses of the trinary perovskite LSCu, the structural stability is highly dependent on the chemical composition. Therefore, the RF-sputtering is one of the most powerful tools for the fabrication of LSCu nanodots. In this study, the LSCu was deposited on (100) silicon substrate by RF-sputtering using PAA as template. The structural characterizations and morphologies of the deposited LSCu was analyzed by X-ray diffraction (XRD), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and field-emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectrometry (EDS).

2 Experimental

2.1 RF-sputtering

The LSCu film and nanodots were grown by RF-sputtering from a $La_{0.725}Sr_{0.275}CuO_{2.5-\delta}$ target with a 2 in. diameter. After the calcined LSCu

powder was cold-isostatically pressed at 200 MPa, the target was sintered at 950°C for 20 hours. The LSCu powder was calcined from an appropriate amount of La_2O_3, $SrCO_3$, and CuO powder mixture which was mixed and ball-milled in ethanol solution for 24 hours. The LSCu deposition was carried out in the pressure range of 5 mTorr after pre-sputtering for 10 minutes. The Ar and O_2 flow rates were set at 10 sccm and 30 sccm, respectively. The RF power was 65 W and the distance between the substrate and the target was 60 mm. After RF-sputtered, the specimens were heat treated at 650°C~850°C in air for 2 hours.

2.2 PAA template fabrication

The PAA template was fabricated by two-step anodization [11-13]. After the aluminum film was deposited on the (100) silicon substrate by E-beam evaporation, the deposited aluminum film was first anodized at 40 V (producing 50 nm diameter pores) in a bath of 0.3 M oxalic acid solution in the cooling circulation bath of 13°C. The anodized alumina formed in the first anodization step was removed by the mixture of 12 wt% H_3PO_4 and 6 wt% $H_2Cr_2O_4$. The remaining aluminum was oxidized (40 V) again till it was all converted into alumina. Finally, the barrier layer at the alumina/Si interface was removed by immersing the specimen into a 5 wt% H_3PO_4 solution for 60 minutes.

2.3 Characterization

The crystal structure of the samples were analyzed by X-ray thin film diffractometer (Rigaku ATX-E) at room temperature with monochromated Cu $K_{\alpha 1}$. The XRD traces were obtained at a scanning rate of 2?/min covering a 2θ range from 20° to 80°. The chemical composition of LSCu was analyzed by ICP-AES. The morphologies of the porous alumina and LSCu nanostructure were observed by FESEM (Hitachi S4200) and the chemical component was examined by EDS.

3. Results and discussion

3.1 Structure characterization

In order to find the RF-sputtering deposition parameters, and the heat treatment temperature, the LSCu was deposited on the (110) silicon wafer. The XRD patterns for deposited LSCu thin film before and after heat treated at 650°C, 750°C and 850°C for 2 hours are presented in Fig.1. Without heat treatment, the as-deposited LSCu thin film was formed in amorphous structure on the silicon substrate. When the specimen was heat treated at 650°C, the mixture of perovskite LSCu and La_2CuO_4 phases were observed (Fig.1(b)). However, when the heating temperature was increased to 750 °C, the single tetragonal perovskite LSCu phase was obtained (as shown in Fig 1(c)). As the specimen was heated treated at 850°C, as shown in Fig.1(d), the perovskite phase was disappeared. On the contrary, the mixture of $Sr_4(Si_4O_{12})$ and La_2CuO_4 phases were formed. The decomposition of perovskite LSCu may due to the reaction between LSCu and silicon substrate. As LSCu reacted against silicon, the traction product of $Sr_4(Si_4O_{12})$ was formed, therefore the strontium concentration in the LSCu was decreased. As a result, the structural stability of perovskite LSCu was destroyed, and the LSCu phase was phase transferred to La_2CuO_4. The heat treatment of the deposed LSCu was controlled at 750°C for 2 hours. The chemical composition of deposited LSCu was examined by ICP. The cation atomic ratio of La:Sr:Cu is about 78:22:100. Hence, the stoichiometry of LSCu was determined as $La_{0.78}Sr_{0.22}CuO_{2.5-\delta}$.

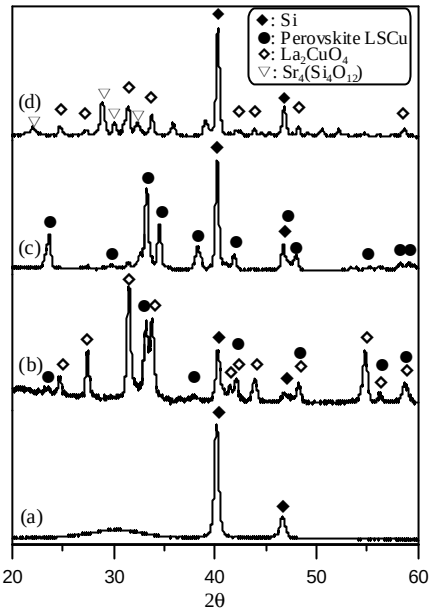

Fig.1 XRD patterns of (a) as-deposited, (b) 650°C heat treated, (c) 750°C heat treated, and (d) 850°C heat treated LSCu thin film

3.2 Deposition of LSCu nanodots on silicon substrate

Due to the step coverage limitation of the RF-sputtering, a template with an appropriate aspect

ratio and straight through holes is necessary. Therefore, the two-step anodization process for the PAA template fabrication is adopted. First, the aluminum membrane, whose thinness is 1.2 μm, was deposited on silicon substrate. And then the nanoporous anodic alumina template was fabricated by two-step anodization process. For the first anodization step, partial aluminum membrane (900 nm in thickness) was anodized. After removing the anodized alumina, the remaining aluminum film with a thinness of 300 nm was oxidized again till it was all converted to alumina. The cross-section and top-view SEM micrographs of the PAA template on silicon surface are shown in Fig.2. Using the two-step anodization technique, a through-hole alumina template with good ordering over micro size area is obtained. The thickness of PAA template membrane is about 300 nm and the pore size is about 50 nm in diameter.

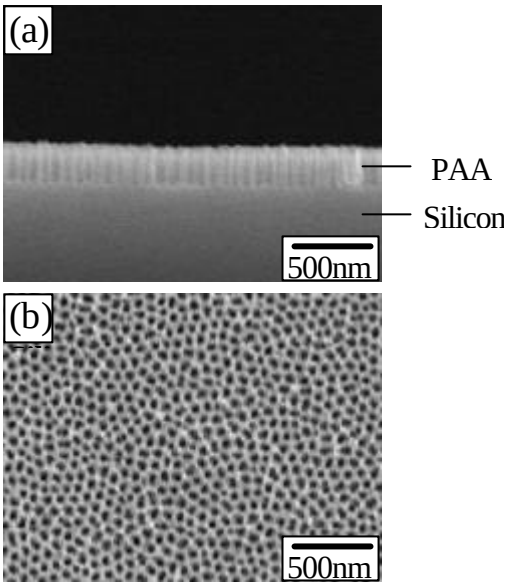

Fig.2 The (a) cross-section and (b) top-view SEM micrographics of the PAA fabricated by two-step anodization process

To obtain the LSCu nanodots on the silicon substrate, the PAA covered silicon substrate was deposited by RF-sputtering. Fig.3 shows the cross-section of the PAA/Si template before (Fig.3(a)) and after (Fig.3(b)) deposited. As shown in Fig.3(b), the LSCu was deposited on both silicon substrate and the top of PAA template. Before LSCu deposition, the nanoholes of PAA were observed in straight and through into the silicon surface. After LSCu was deposited on PAA/silicon substrate by RF-sputtering, both of the silicon surface and the top of PAA template covered with LSCu. To produce the

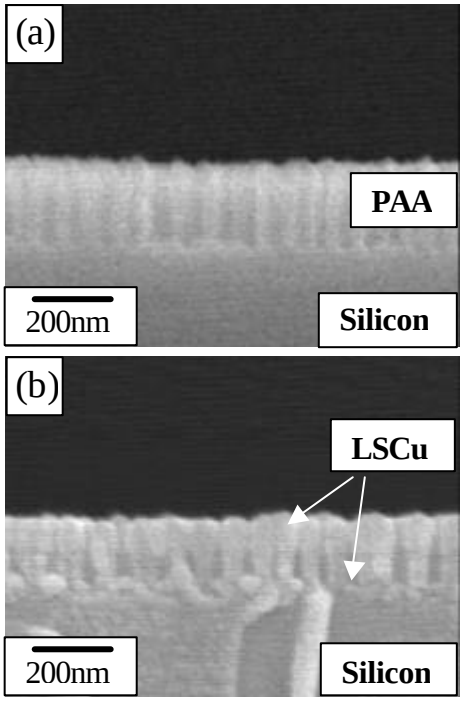

Fig.3 The cross-section SEM micrographics of (a) PAA/silicon template before LSCu deposited and (b) as-deposited PAA/silcon substrate

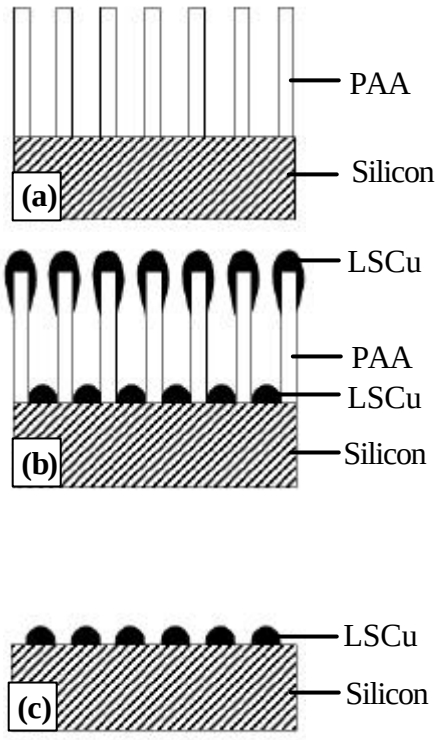

Fig.4 Schematic of the LSCu nanodots fabrication on silicon surface: (a) shows the PAA template on silicon surface, (b) as-deposited PAA/silicon template (c) LSCu nanodots on silicon surface.

LSCu nanodots, the PAA template and the deposited LSCu on top of the PAA template should be removed. As the specimen was immersed into a H_3PO_4 solution after LSCu deposition, the PAA template and the LSCu deposited on the top of PAA surface was removed. This technique for the LSCu nanodots fabrication was schematically shown in Fig.4. When the PAA/silicon substrate was deposited an appropriate amount of LSCu, the LSCu nanodots on the silicon surface may be formed after PAA removing.

The SEM micrographic of the specimen before and after PAA removed was shown in Fig.5. As shown in Fig.5 (a), the pore sized of the PAA was decreased to about 35 nm. This may due to the deposition of the LSCu on the wall of the PAA pole (which was schematically shown as Fig.4(b)). Fig. 5(b) shows the top-view of the specimen after removing the PAA, the LSCu nanodots with about 50nm in diameter were produced. The resulting LSCu nanodots had dimensions the same as the pores in the two-step anodized PAA template.

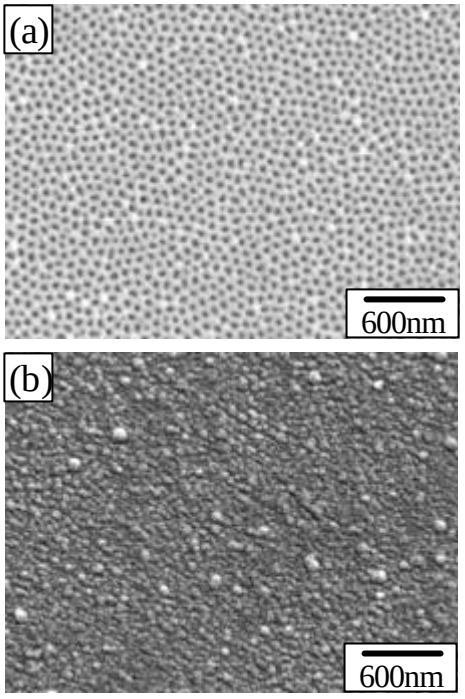

Fig.5 Top-view SEM micrographs of as-deposited PAA/silicon template (a) before and (b) after PAA was removed.

4 Conclusion

We have employed an alumina template-based method to fabricate LSCu nanodots on silicon substrate by RF-sputtering. Due to step coverage limitation of RF-sputtering, the PAA template with straight through pores is necessary. The PAA template was anodized by two-step anodization process. The pore size of the template was about 50 nm in diameter, and 300 nm in length. After LSCu deposition and PAA removing, the LSCu nanodots, whose diameter are about 50 nm, were produced. The size of the LSCu nanodots are the same as the pore size of the PAA template. Our results indicate that the trinary perovskite oxide, $La_{1-x}Sr_xCuO_{2.5-\delta}$, nanodots on silicon surface can be produced by this approach.

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