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$SrTiO_3$ film fabrication and powder synthesis from a non-polymerized precursor system of a stable Ti(IV) complex and Sr(II) salt of edta

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Fabrication of $SrTiO_3$ thin films on quartz glass and Si(100) single crystal substrates was achieved by firing an adhered precursor at 600 °C in air. The precursor ethanolic solution was prepared by mixing ethanol solutions of a Ti(IV) complex and of an Sr(II) salt of edta in the presence of dibutylamine. The solution of the Ti(IV) complex was prepared by reaction of neutral $[Ti(H_2O)(edta)]$ with dibutylamine and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) in ethanol. The solution containing Sr(II) was obtained by reaction of $Sr(H_2edta)\cdot 3H_2O$ with dibutylamine in ethanol. It was elucidated by XRD that perovskite-type $SrTiO_3$ film formation was attainable by employing the mixed precursor derived from the stable Ti(IV) metal complex and Sr(II) salt, with no evidence for polymerization. A facile preparation for the precursor ethanolic solution and the properties of the precursor powder elucidated by evaporation of the precursor solution are also reported, along with the optical properties of a thin film on quartz glass.

1 Introduction

Strontium titanate is a well known perovskite structured material, which has a cubic paraelectric phase above 105 K. It has a high dielectric constant which is nearly temperature independent and therefore can achieve a reasonable charge storage density for high density memory applications.[1] Moreover, thin films of strontium titanate are chemically and compositionally very stable and have excellent optical transparency. The deposition of $SrTiO_3$ thin films has, therefore, been studied recently by sputtering,[2,3] laser ablation,[4] reactive coevaporation,[5] *etc.* On the other hand, there is limited information on the preparation of $SrTiO_3$ thin films by sol–gel procedures,[6–11] though thin films formed by this method are very attractive candidates for a variety of new applications in microelectronics and integrated optics.

In our recent work, we reported Co_3O_4 thin film formation on a glass substrate by a flow-coating method of an ethanol solution of a monomeric tetrabutylammonium Co(III)–edta complex salt (H_4edta = ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid).[12] Furthermore, we found that reaction of neutral $[Ti(H_2O)(edta)]$ with dipropylamine in ethanol affords an excellent precursor solution for anatase thin film deposition on soda lime glass by firing the adhered film consisting of a Ti(IV)–edta complex salt.[13] The lack of moisture sensitivity of the precursor solution was notably different from those conventionally used in the sol–gel method, though the optical properties of the resultant thin films are comparable. It is significant that film formation can be attained by combination of anionic species involving metal ions in the presence of an alkylammonium cation, without any polymerization process. Prompted by these results, we have developed this novel wet process for film fabrication of mixed metal oxides *via* the corresponding mixed metal complex system, which involves both edta as a ligand and alkylamines to generate counter cations. We report here the preparation of an Sr(II)–edta salt and a precursor solution suitable for film deposition of strontium titanate $SrTiO_3$. The first application of the wet process *via* a non-polymerized precursor to form a mixed metal oxide is also reported.

2 Experimental

Materials

Ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid, a solution of titanium(III) chloride (20 mass%), and strontium(II) acetate hemihydrate of the purest commercially available grade were purchased from Kanto Chemicals Co., Inc. Ethanol used was purchased from Amakasu Chemical Industries Co., Ltd, and was of GR grade (99.5%) and was dried on 4Å molecular sieves (Wako Pure Chemicals Co., Ltd.), before use. Other materials were used without further purification.

Preparation of $[Ti(H_2O)(edta)]$ and the precursor solution of titanium dioxide

The starting aqua complex, $[Ti(H_2O)(edta)]$, and a 15 mass% (0.295 mmol g^{-1}) ethanol solution, obtained from the reaction of the aqua complex with dibutylamine and 4-(*N*,*N*-dimethylamino)pyridine (DMAP), was prepared by a similar method as reported previously,[13] with slight modification. $[Ti(H_2O)(edta)]$ (10.62 g, 29.99 mmol) was suspended in 86.47 g of dried ethanol and 4.27 g (33.04 mmol) of dibutylamine and 0.37 g (3.03 mmol) of DMAP were added, and the mixed solution heated at reflux for 1 h. The resultant pale-yellow transparent solution A was used to prepare the precursor solution of the mixed metal oxides.

Preparation of $Sr(H_2edta)\cdot 3H_2O$

To an aqueous solution (1000 ml) of 12.87 g (59.94 mmol) of strontium(II) acetate hemihydrate, 17.59 g (60.19 mmol) of the edta was added in several portions with stirring at 80 °C, in an open-air beaker. The resultant clear solution was continuously stirred and heated at 80 °C for 30 min. After cooling to room temperature, the solution was evaporated to *ca.* 60 ml under reduced pressure and was kept at ambient temperature overnight. The white crystals formed were filtered off and washed twice with a small amount of ethanol, diethyl ether, and air-dried. Yield; 23.2 g (89%). Elemental analysis indicated a high degree of purity (calc. for $SrC_{10}H_{14}N_2O_8{\cdot}3H_2O$: C, 27.88, H, 4.72, N, 6.30. Found C, 27.81, H, 4.67, N, 6.49%).

Preparation of the precursor solution for $SrTiO_3$ film formation

A 10 mass% ethanol solution (0.137 mmol g^{-1}) was prepared by reaction of the edta salt of Sr(II) obtained above with dibutylamine in ethanol. 3.78 g (8.75 mmol) of $Sr^{II}(H_2edta){\cdot}3H_2O$ was suspended in 57.28 g of dried ethanol. 2.61 g (20.19 mmol) of dibutylamine was then added slowly to the suspended solution in a flask, and the mixed solution was refluxed for 4 h. A transparent colorless solution B was obtained which was refluxed for a further 1 h. The precursor solution C containing the edta complex of titanium and the strontium salt of edta was prepared as follows: 1.00 g of the 15 mass% titania precursor solution A was added to 2.14 g of the 10 mass% Sr–edta–dibutylamine solution B to give a molar ratio Ti : Sr of 1 : 1. The resultant transparent pale yellow solution C was used for adherence of the precursor on a quartz glass and on an Si(100) single crystal. Transparent precursor films were formed on both substrates. A conventional flow-coating procedure was employed for the coating of the precursor solution onto the substrates in order to prepare the samples for firing. A spin-coating method could also be applied. The precursor films formed on the substrates were dried at 80 °C for 30 min, and then fired for 30 min at 500, 600, 700, 800 or 900 °C. For the measurement of the trasmittance spectra of the oxide films, a thin film of *ca.* 0.5 μm thickness was prepared on a quartz glass, by coating and firing at 600 °C for 30 min after each coating. This procedure was repeated five times.

Preparation of the mixed oxide precursor powder

Mixed oxide precursor powders were prepared from the hygroscopic yellow–brown product obtained by the removal of the solvent from precursor solution C under reduced pressure, followed by heating at 180 °C for 30 min.

Measurements

IR spectra were measured on a Shimadzu FT-IR 1600 spectrophotometer for KBr disks. ^1H and ^{13}C NMR spectra were measured on a JEOL JNM-270 (270 MHz) spectrometer in D_2O with tetramethylsilane (TMS = 0.0 ppm) as an external reference. Thermogravimetry (TG) and differential thermal analysis (DTA) were performed by use of an MAC Science TG-DTA 2000S. The crystal structure of the oxide films was determined by XRD at room temperature, using a Rigaku Rint-2500V Model (50 kV, 180 mA) diffractometer with graphite-monochromated Cu-Kα radiation. A parallel beam optic system (incident angle; 2.0°) was used for the thin films. Transmittance spectra were measured with a Shimadzu UV-1200 spectrophotometer. The film thickness was measured using a Dektak 3030 stylus profilometer.

3 Results and discussion

Preparation of the edta salt of Sr(II)

Reaction of strontium acetate with H_4edta in hot water led on cooling to white crystals of $Sr(H_2edta){\cdot}3H_2O$ in high yield.

Structure of $Sr(H_2edta){\cdot}3H_2O$

The ^1H NMR spectrum of $Sr(H_2edta){\cdot}3H_2O$ shows only two singlets at 3.01 and 3.26 ppm, which can be assigned to ethylene protons NCH_2CH_2N and to the four methylene protons NCH_2CO_2 of the glycinate residues in edta, respectively. When glycinate groups coordinate to metal ions, a characteristic AB quartet pattern derived from the protons of glycinate chelate rings should be observed but no such AB pattern was observed here. Also, in the ^{13}C NMR spectrum, only three peaks at 51.8, 58.3, and 171.0 ppm were observed and can be assigned to the carbon atoms of ethylene, methylene and carboxylate groups, respectively. These NMR spectra in D_2O indicate that the obtained compound is a simple salt of Sr^{2+} aqua ion with H_2edta^{2-}. In the IR spectra, a band shift for $\nu_{asym}(COO)$ from 1698 cm^{-1} for free H_4edta to 1632 cm^{-1} in the salt is observed (Fig. 1). A similar shift is also observed for Na_2H_2edta,[14] indicating a simple salt both in aqueous solution and in the solid state.

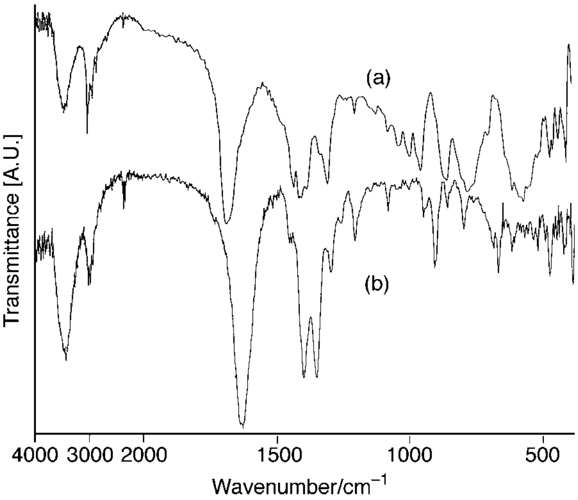

Fig. 1 (a) The IR spectrum of $Sr(H_2edta){\cdot}3H_2O$, as compared with that of free H_4edta (b).

Preparation of the mixed precursor solution C

Since $Sr(H_2edta){\cdot}3H_2O$ does not dissolve in ethanol its reaction with dibutylamine in ethanol was examined in an attempt to dissolve it and use of 2 mol equivalents of the amine led to a transparent solution B. Solution B containing the dibutylammonium salt of strontium and edta ions was then mixed with titania precursor solution A ensuring a Ti : Sr mol ratio of 1 : 1. The precursor titania solution A was prepared by a method reported previously,[13] with slight modification. Addition of a small amount of DMAP to a suspension of $[Ti(H_2O)(edta)]$ and an equimolar amount of dibutylamine was extremely effective in dissolving the complex. The high nucleophilicity of DMAP 10 000 × that of pyridine[15] may lead to deprotonation of the coordinated aqua group in the $[Ti(H_2O)(edta)]$, which may aid dissolution of the insoluble complex in ethanol.

Thermal properties of the mixed oxide precursor powder

TG and DTA curves of the mixed oxide precursor powder are shown in Fig. 2. In the DTA curve, several exothermic peaks at 349, 373, 392, 497 °C are observed, and can be attributed to combustion of the ligand and the amine. Since no exothermic peak appeared above 500 °C, it was concluded that combustion of the organic component was complete by 500 °C, *i.e.* slightly lower than that for the $[Ti(H_2O)(edta)]$.[13]

Thin film formation

The coatability of the mixed oxide precursor solution was examined on a quartz glass and a silicone wafer. On both substrates, transparent precursor thin films could be formed by a flow-coating method. The adhering films were then fired in air at several temperatures. In all cases transparent thin crack free films were obtained and the film thicknesses measured with a profilometer were *ca.* 100 nm.

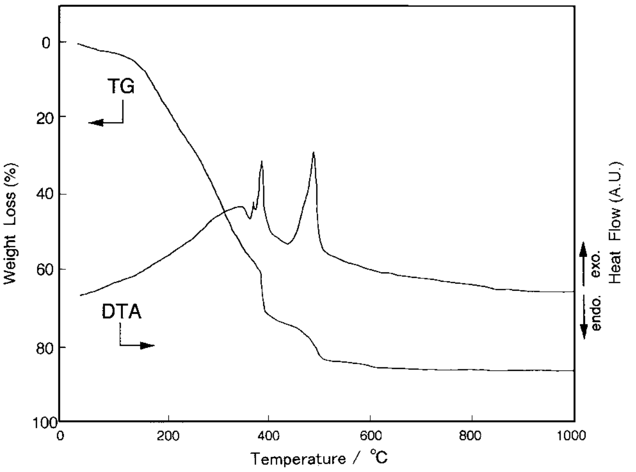

Fig. 2 TG–DTA curves of the precursor gel obtained by the evaporation of the $SrTiO_3$ precursor solution.

Crystal structure of the thin films

In order to identify the transparent films, their XRD patterns were examined. XRD patterns of the films on a quartz glass are shown in Fig. 3(a)–(e). Firing below 500 °C leads to amorphous films, since no peaks due to a crystalline compound were observed. By contrast, characteristic peaks of cubic strontium titanate were observed in the spectra of the samples obtained above 600 °C. Peaks at 2θ 32.4, 39.9, 46.4, 57.8 and 67.7° can be assigned to the (110), (111), (200), (211) and (220) reflections, respectively, of cubic strontium titanate.[15] The lattice constant, $a(=b=c)$, estimated from the d value of the (110) reflection, is 3.909 Å and is comparable with the reported value of 3.905 Å. No peaks due to other compounds were observed. XRD patterns of the thin films formed on an Si(100) crystal are shown in Fig. 4(a)–(e). In Fig. 4(b)–(e), a weak peak at 22.7°, which can be assigned to the (100) reflection of cubic strontium titanate,[16] was observed, in addition to the reflections found in the spectra of the thin films on quartz glass. The lattice constant estimated from the d value of the (100) reflection is 3.897 Å, which is almost identical with the lattice constant obtained above. Thus, it is confirmed that the crystallization behaviour is independent of the substrates. The absence of the (100) reflection in the case of quartz glass is a consequence of a broad band in the 2θ range 15–35° for this substrate.

Optical property of the thin films

The transmittance spectrum of a thin film fired at 600 °C on a quartz glass with a film thickness of *ca.* 0.5 μm is shown in Fig. 5. It is seen that the film has a very high transparency. The band gap for the film fired at 600 °C was *ca.* 3.4 eV, close to the reported single crystal value.[17] The spectrum also confirms formation of a strontium titanate thin film.

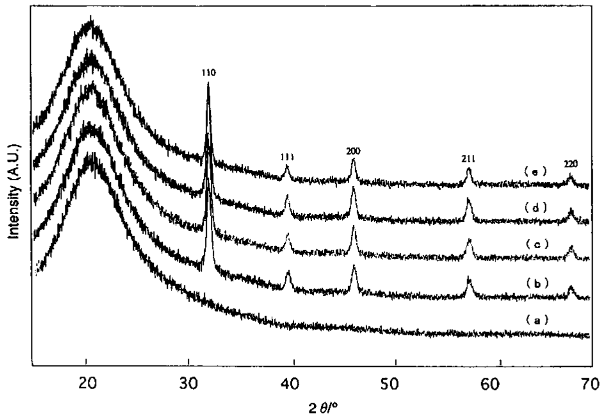

Fig. 3 The XRD patterns of the thin films formed on the quartz glasses at various temperatures: (a) 500, (b) 600, (c) 700, (d) 800 and (e) 900 °C.

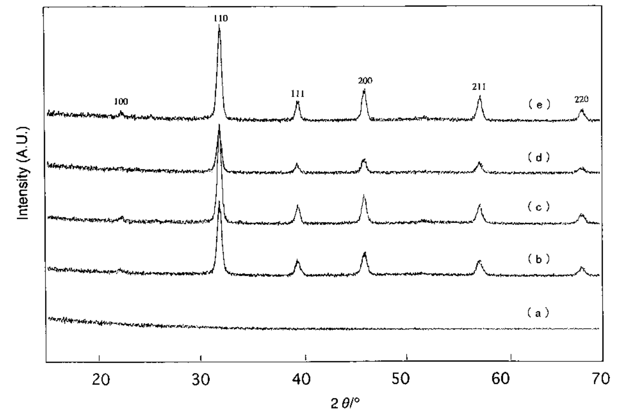

Fig. 4 The XRD patterns of the thin films formed on the Si(100) single crystals at various temperatures: (a) 500, (b) 600, (c) 700, (d) 800 and (e) 900 °C.

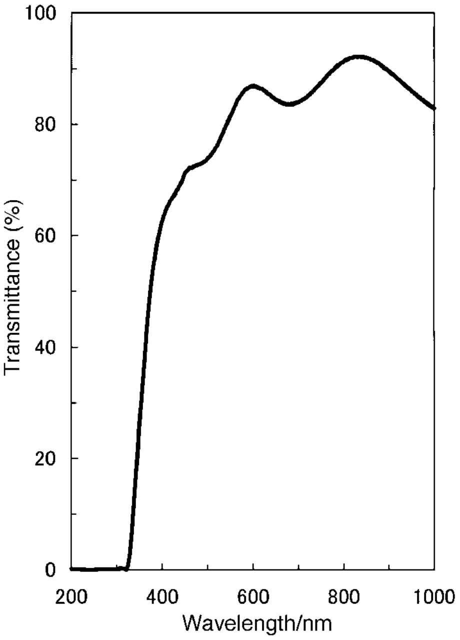

Fig. 5 The optical transmittance spectrum of a polycrystalline $SrTiO_3$ thin film of thickness *ca.* 0.5 μm, on quartz glass fired at 600 °C.

4 Conclusion

A schematic representation of the novel procedure for the preparation of perovskite $SrTiO_3$ thin films is shown in Fig. 6. It is clear that the mixed solution A of the non moisture-sensitive titania precursor solution previously developed and the ethanol solution B obtained from reaction of $Sr(H_2edta)$ with dialkylamine in ethanol leads to a suitable readily handled precursor solution C for the preparation of perovskite strontium titanate thin films. Use of $Sr(H_2edta)$ alone was not feasible owing to its low solubility in a variety of solvents. This facile method employing the solubilization in alcohols of metal salts or complexes containing edta ligands by the use of their reaction with alkylamines may be applicable to film fabrication of many mixed metal oxides, especially for titanium systems.

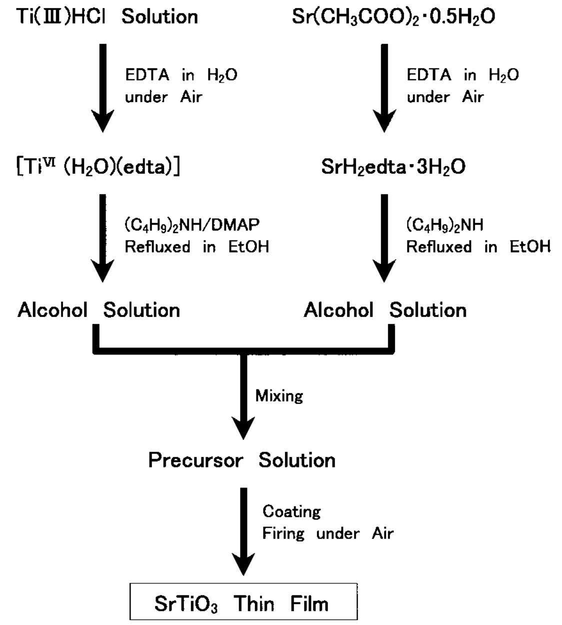

Fig. 6 Schematic representation of $SrTiO_3$ thin film fabrication by the non-polymerized precursor system.

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