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Synthesis of RuO_2 and $SrRuO_3$ powders by means of aqueous solution gel chemistry

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Abstract

Phase pure RuO_2 and $SrRuO_3$ powders were obtained by a water-based solution-gel route. By reacting ruthenium(III)acetylacetonate with H_2O_2 in a citric acid solution, a stable aqueous Ru-precursor solution could be prepared. An aqueous Sr-precursor is synthesized by dissolving Sr acetate in a citric acid solution. After mixing the Ru-precursor with the Sr-precursor solution in stoichiometric quantities, a clear aqueous solution for the preparation of $SrRuO_3$ could be obtained. Gelation resulted in amorphous precursors that were homogeneous down to nanoscale as was confirmed by means of transmission electron microscopy. With the appropriate thermal treatment phase pure RuO_2 and $SrRuO_3$ powders were synthesised as verified by X-ray diffraction.

Keywords: Electron microscopy; Perovskites; Sol-gel processes; Transition metal oxides; X-ray methods

1. Introduction

In recent years, there has been a considerable interest in ferroelectric materials like lead zirconate titanate (PZT) and strontium bismuth tantalate (SBT), due to their application in non-volatile ferroelectric random access memories (NV-FeRAM).[1] Generally Pt bottom electrodes are used in these devices, but in the case of PZT a number of problems such as leakage current and fatigue are observed.[2,3] Several authors state that conductive oxides can overcome these problems and it has already been reported that RuO_2 and $SrRuO_3$ are very good alternatives for electrode application.[4–6]

Both RuO_2 and $SrRuO_3$ are highly conductive oxides with a strong resistance against chemical corrosion and a good thermal stability.[7,8] RuO_2 is a rutile structured transition oxide and has a bulk resistivity of 35 μΩ. cm.[7] The perovskite oxide $SrRuO_3$ has a resistivity value of 280 μΩ. cm. The crystal structure as well as the lattice constants of $SrRuO_3$ are in very good agreement with ferroelectric perovskite titanates,[5,8] making $SrRuO_3$ an excellent candidate material for bottom electrode in micro-electronic devices. Up to now, very few reports are known about solution synthesis of RuO_2 and $SrRuO_3$.[9,10] In most cases these electrodes are produced successfully by techniques like pulsed laser deposition,[11] reactive sputtering[6,12,13] and MOCVD (metal organic chemical vapour deposition).[14,15] Although good results are obtained with these techniques a disadvantage is the expensive equipment required.

Here, an aqueous solution-gel route is presented to prepare RuO_2 and $SrRuO_3$. In our research group several electroceramic oxides, such as ZnO,[16,17] and ferroelectric materials as PZT,[18] PZN[19] (lead zincate niobate), SBT,[20] SBN[21,22] (strontium bismuth niobate) and BLT[23] (lanthanum substituted bismuth titanate) are synthesized in this way. This "wet chemistry" method has various advantages in comparison with conventional "dry synthesis" routes. The fact that the metal ions are initially dissolved implies that they are mixed at a molecular level, which results in better homogeneity and lower processing temperatures.[16–23] A significant advantage of chemical solution deposition (CSD) is that the stoichiometry of the intended material can easily be varied. The use of water as a solvent certainly adds environmental as well as economical benefits. In addition dip- and spin-coating are reliable techniques to

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prepare the large area thin films that are necessary in these NV-FeRAMs. In this way instrumental complexity is avoided. This results in a cost-effective and ecologically friendly synthesis route.

However, the choice of a suitable start product for the synthesis of an aqueous Ru-precursor is not obvious. Most of the water soluble Ru-compounds contain chloride ions which deteriorate the electrical properties of the finally produced conductor materials. Once these chloride ions are introduced in the solution it is not evident to remove them. Furthermore the use of water soluble nitrosyl containing Ru-compounds is not advisable due to the possible release of NO which may damage DNA if taken up in large concentrations.[24] Although ruthenium(III)acetylacetonate is not soluble in water, it was possible, through reaction with H_2O_2 and citric acid in water, to use it here as start product for the preparation of a stable homogeneous aqueous solution.

2. Experimental

2.1. Materials and reagents

The following materials and reagents were used: citric acid [Aldrich 99%, $C(OH)(COOH)(CH_2COOH)_2$], ammonia (Aldrich 5.07 N solution in water, NH_3) ruthenium(III)acetylacetonate ($Ru(acac)_3$) [Strem Chemicals 99% $Ru(C_5H_7O_2)_3$], hydrogen peroxide (Acros Organics 35 wt.% H_2O_2 solution in water, stabilized), and strontium acetate [Aldrich 99.995% $Sr(CH_3COO)_2$].

2.2. Methods and apparatus

Metal ion concentrations in solution were determined by means of ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) on a Perkin-Elmer Optima 3000 DV. In order to confirm that no segregation occurred TEM (transmission electron microscopy) studies were performed on a Philips CM 12. A free standing thin film of a certain precursor solution was prepared by bringing a tiny droplet of the solution on a Au 700 mesh grid and heating this grid in an oven at 60 °C for 1 h. The decomposition of the precursor gels and the phase formation of the oxides occurred in a TGA furnace (thermogravimetric analysis) (TA Instruments TGA 951-2000) in 100 ml/min synthetic dry air (mixture of 20% O_2/ 80% N_2). The amorphicity of the precursor gels and the phase formation of the oxides were evaluated on a Siemens D 5000 diffractometer with Cu K_α radiation.

2.3. Preparation of the precursor gels

$Ru(acac)_3$, as such not soluble in water, was mixed with an aqueous solution of citric acid (Cit) (molar ratio Cit: $Ru(acac)_3$ 3:1). This suspension was heated to 40 °C and subsequently hydrogen peroxide was added. Only small portions of H_2O_2 were added at a time because it causes a highly exothermic reaction. Upon the addition of 120 equivalents H_2O_2 to ruthenium a clear dark red solution was obtained with a pH of 1.9. Refluxing this solution at 90 °C for 3 h gave rise to a pH decrease to 1.5 and a change of colour from dark red to dark green, which may point to a change of the coordination sphere of ruthenium. Final concentration of the precursor was 0.040 M. When this solution was poured into a Petri vessel and the water was evaporated in an air-flushed furnace at 60 °C a brown gel was formed (Fig. 1).

A 0.2 M Sr-precursor solution was obtained by dissolving Sr acetate in an aqueous solution of citric acid. Stability of this precursor was checked for a variety of pH values obtained by adding different amounts of ammonia and for various Cit:Sr molar ratios. Table 1 shows which of the solutions remain clear for at least 1 week.

The Sr-precursor with Cit:Sr 4:1 at pH = 2.3 (without addition of NH_3) was used to prepare a $SrRuO_3$ precursor solution.

After checking the metal ion concentrations of the individual solutions, the Ru- and Sr-precursors were mixed in the right stoichiometric ratio. The bimetallic precursor was gelated in the same way as the Ru-precursor, resulting in a green transparent gel (Fig. 1).

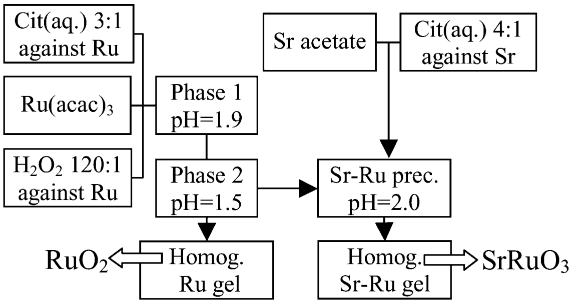

Fig. 1. Flowchart RuO_2 and $SrRuO_3$ preparation.

Table 1
Overview of the observations after 1 week of aqueous Sr precursors prepared at different pH and with different amounts of citric acid[a]

Cit:Sr	No NH_3	pH = 5.0	pH = 6.0	pH = 7.5	pH = 9.0
1/1, 2/1, 3/1	P	P	P	P	P
4/1	S	P	P	P	P
6/1	S	P	S	S	S

[a] P, precipitation within 1 week; S, clear, stable solution for at least 1 week

3. Results and discussion

3.1. Synthesis of RuO_2

A great asset of this solution-gel route is that chemical homogeneity is maintained throughout the whole synthesis process. During gelation of the precursor solution the coordinating ligands form an organic network in which the metal ions are homogeneously distributed.[19,25] The TEM study revealed that no phase segregation had occurred in the prepared ruthenium gel film down to the nanometer level. Only diffuse diffraction rings were observed in the TEM-diffraction pattern indicating the amorphicity of the gel, which was additionally confirmed by means of X-ray diffraction.

When the gel powder was heated in a TGA furnace at 10 °C/min the organic matter was combusted until, at a temperature of approximately 200 °C, an exothermic reaction took place during which the Ru ions were reduced to the metallic state (Fig. 2a). The presence of metallic Ru was verified by means of an XRD measurement. Durán et al.[26] and Nelis et al.[21] also observed an analogue phenomenon for Bi, another element that is easily reduced. A possible explanation for this sudden reduction is that the organic matrix is incompletely oxidized during heating, resulting in the formation of carbon monoxide instead of CO_2. Subsequently this CO may reduce ruthenium to the metallic state. In order to avoid such runaway reaction the thermal treatment of the gel powder was adjusted. Lowering the heating rate to 5 °C/min however did not change the decomposition profile. In order to allow the organic matrix to burn out gradually, isothermal periods were introduced beneath the temperature where the exothermic combustion took place. Upon optimization of the temperature and duration of these isothermal periods the reduction of ruthenium to the metallic state could be prevented. The heating profile that resulted in RuO_2 is shown in Fig. 2b. X-ray diffraction confirmed that after the adjusted thermal treatment phase pure RuO_2 was formed (Fig. 3).

3.2. Synthesis of $SrRuO_3$

The chemical stability of the precursor solution is a key element in avoiding phase segregation in further stages of the multimetal oxide formation. Therefore it is necessary to fine-tune the different monometallic precursor solutions to each other.

Since the Ru-precursor is stable at low pH values, it was obvious that the Cit: Sr 4:1 solution without addition of NH_3 is the preferred precursor (Table 1). In this manner the organic matter was minimized and the use of NH_3 was avoided, and hereby also the release of nitrous gasses and formation of amides which decompose at elevated temperatures.[16] As expected, by adding this Sr-precursor to the Ru-precursor a clear aqueous Sr–Ru precursor solution was obtained (Fig. 1). TEM demonstrated that no phase segregation arose down to nanometer level during gelation. In the dark field image of the diffuse diffraction ring the whole gel lights up, which indicates its entire amorphicity (Fig. 4). This was also confirmed by the absence of diffraction peaks in XRD. Combusting the gel powder in a TGA furnace at 5 °C/min to 750 °C resulted in phase pure $SrRuO_3$ as was indicated by XRD (Fig. 5).

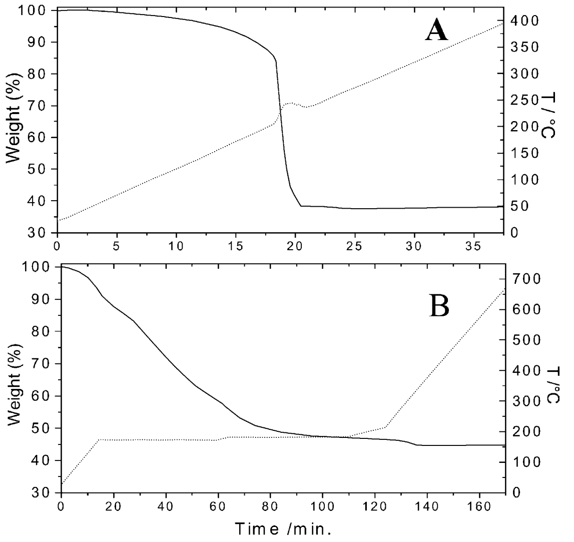

Fig. 2. TGA of Ru precursor gel, ⋯⋯ temperature °C, ——weight (%); (A) resulting in metallic Ru, (B) resulting in RuO_2.

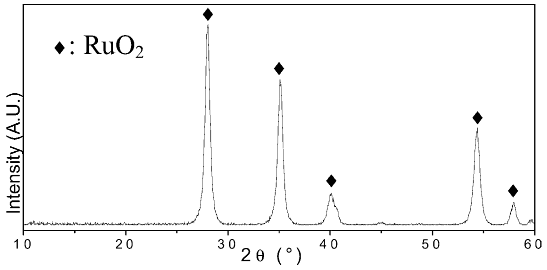

Fig. 3. XRD spectrum of RuO_2 (Siemens D 5000 Cu K_α).

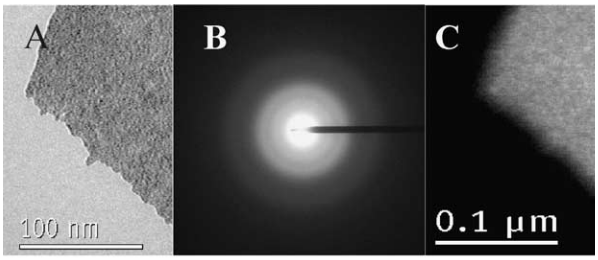

Fig. 4. TEM studie on Sr-Ru gel. (A) right field image (B) diffuse rings in diffraction pattern (C) dark field image.

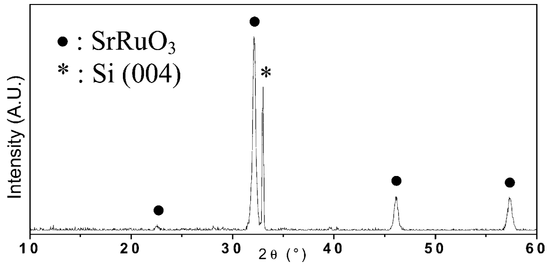

Fig. 5. XRD spectrum of $SrRuO_3$ (Siemens D 5000 Cu K_α).

Since thin films of several electroceramic oxides were already successfully prepared at our laboratory,[17,18,22] it is expected that this aqueous precursor system can be applied for CSD of thin films of RuO_2 and $SrRuO_3$.

4. Conclusions

A new aqueous solution gel route was developed for the preparation of powders of electrode materials RuO_2 and $SrRuO_3$. Both the materials were synthesized from precursor gels that are homogeneous to nanoscale as was seen in TEM. Phase purity of the conductive oxides was confirmed by means of XRD. Future experiments will include spin coating of the Ru and mixed Sr–Ru precursors for the preparation of thin films.

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