Thin Solid Films 518 (2010) 4675–4679

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Depositions of $SrRuO_3$ thin films on oxide substrates with liquid-delivery spin MOCVD

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ARTICLE INFO

Available online 16 December 2009

Keywords:
Liquid-delivery MOCVD
Thin films
$SrRuO_3$
Perovskite substrates
Structural properties

ABSTRACT

Systematic variations of the deposition conditions for thin epitaxial $SrRuO_3$ films with a liquid-delivery spin MOCVD were performed in order to get a detailed understanding of the physical and chemical issues in the growth process. We have observed that at very low as well as at high growth rates the structural ordering of the films and the lattice strain is low, while for optimized conditions (~0.14–0.2 nm/min) films can be grown under high compressive strain on $SrTiO_3$ and under tensile strain on $DyScO_3$, showing an electrical resistivity of ~250 μΩcm. Films on $NdGaO_3$ are nearly totally plastically relaxed. In contrast to PLD, step-flow growth could not be detected due to significantly higher carbon incorporation.

1. Introduction

Epitaxial heterostructures based on oxides with perovskite structure have attracted a great interest for future electronic device applications. Depending on chemical composition, nature of the cations, and crystal structure these materials exhibit a large variety of functional properties like ferroelectricity, piezoelectricity, electro-optical activity, superconductivity, and ferromagnetism (e.g. [1] and references therein). In the last years the itinerant metallic ferromagnetic $SrRuO_3$ has attracted great interest both from fundamental and technological point of view due to its chemical stability, better fatigue tolerance, structural similarity to most perovskite substrates, possibility of coherent growth on vicinal substrates, and excellent electrical conductivity [2,3]. Therefore it has been found to be very useful for application as electrode of ferro-/piezoelectric devices. Furthermore, $SrRuO_3$ has been investigated as a model system to study the initial stages of epitaxial growth of thin oxide films [4,5]. Growth mechanism of films depends critically on the surface morphology, termination of the surface layer, crystal structure, and lattice mismatch with the substrate [6,7]. On the other hand also growth conditions like supersaturation, gas phase composition, and incorporation of impurities determine the growth mode of thin films (e.g. [8–12]).

$SrRuO_3$ thin films with low electrical resistivity have been deposited by different deposition methods such as PLD [13,14], rf sputtering [15,16], and MOCVD [17,18]. Persistent step-flow growth mode on vicinal substrates has been published by several authors [4–6,12,19] for the case of PLD, but to our knowledge there is only a single work on MOCVD step-flow growth of thin $SrRuO_3$ films on $SrTiO_3$ [20].

The primary goal of this study was to systematically investigate the influence of growth parameters and of different perovskite substrates on the structural properties and growth mode of thin $SrRuO_3$ films.

2. Experimental

The strontium-ruthenate films with a thickness between 15 and 30 nm were deposited with a liquid-delivery spin MOCVD. Two peristaltic pumps are used for the transport of the liquid precursor solutions to a flash evaporator with $T_{FE} = 240$ °C. $Ru(tmhd)_3$ and $Sr(tmhd)_2$-tetraglyme, dissolved in toluene with a concentration between 0.001 M and 0.1 M, were used as sources for Ru and Sr, respectively. Argon, employed as carrier gas for the transport of the vaporized precursors and as dilution gas, the reaction gases, and oxygen were introduced through a showerhead into the vertical growth chamber at $2.6 \cdot 10^3$ Pa. The strontium-ruthenate films were deposited on $SrTiO_3(001)$, $NdGaO_3(110)$, and $DyScO_3(110)$ substrates with a regular step-and-terrace surface structure, generated by a chemical and/or thermal treatment. The substrates were rotated with 500 rpm to improve homogeneity and growth rate. The deposition temperature was varied between 670 and 760 °C and the Ru to Sr ratio in the precursor solutions was altered between 0.08 and 0.5.

The film thicknesses were determined by spectroscopic ellipsometry. $\theta/2\theta$ high-resolution X-ray diffraction (HR-XRD) scans were used to identify structural phases while strain state $\Delta d/d$ of the films was calculated from the (002) reflexes of film (pseudocubic notation) and substrate material. Surface morphology and roughness were analyzed by atomic force microscopy (AFM). The carbon content in the films was estimated by GDOES (glow discharge optical emission

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doi:10.1016/j.tsf.2009.12.057

spectroscopy). Resistivity measurements were performed at RT by the van der Pauw method.

3. Results and discussion

Ru(tmhd)$_3$ and Sr(tmhd)$_2$-tetraglyme were chosen as precursors due to an overlapping temperature window for T_{FE}. Since both precursors are very sensitive to ambient conditions (light and moisture sensitive in case of Ru(tmhd)$_3$ and Sr(tmhd)$_2$-tetraglyme, respectively), reproducible stoichiometric films are only provided by high-quality MO precursors. At $T_{FE} = 240$ °C stoichiometric, highly strained $SrRuO_3$ films without any foreign phase were obtained at a Ru to Sr ratio of 0.08–0.13 in the precursor source solutions. The optimal ratio is significantly lower than 1 owing to the different evaporation efficiencies of the Ru and Sr precursor in the flash evaporator. For a lower Sr supply the films on $SrTiO_3$ (i) contain foreign phases like RuO_2 or Ru and (ii) are less ordered and exhibit reduced compressive strain (Fig. 1). Besides the improvement of the structural ordering we also observed an increase of the growth rate with decreasing Ru/Sr (i.e. increasing Sr flux at constant Ru supply): with increasing Sr supersaturation at the surface a higher amount of Ru, which is always offered in excess, can be incorporated at the film surface to form stoichiometric $SrRuO_3$ film. This results in a higher growth rate. Otherwise, excess Ru is evaporated as RuO_4 [18,20] or in minor amount incorporated as extra phase (RuO_2 or Ru).

Fig. 2 shows the incorporated lattice strain in the films due to the lattice mismatch between substrate ($SrTiO_3$) and film ($SrRuO_3$) in dependence of the growth rate. Two different regions can clearly be determined: For higher growth rates (>0.14–0.2 nm/min) the structural ordering and consequently the lattice strain of the films decreases with increasing growth rate. Excessive supersaturation on the surface prevents the growth of well-ordered films and leads to small grain sizes. However, at growth rates below ~0.14 nm/min the compressive strain in the films decreases, presumably because of the enhanced incorporation of carbon (or carbon derivatives) into the films. The growth rate can be decreased by a lower supersaturation on the surface or higher re-evaporation of Sr and Ru, but the supply of carbon will remain constant, since toluene as solvent of the precursors is always supplied at the same rate. Therefore the incorporation of carbon will stay more or less at the same level even if the growth rate is changed, so that the growth of well-ordered films is more unlikely for very low growth rates. The carbon incorporation during an MOCVD process up to several atom percent is well known from literature and leads to strong reduction of the surface diffusion [10,21–25]. Indeed we also detected a carbon concentration of about 5% in the films.

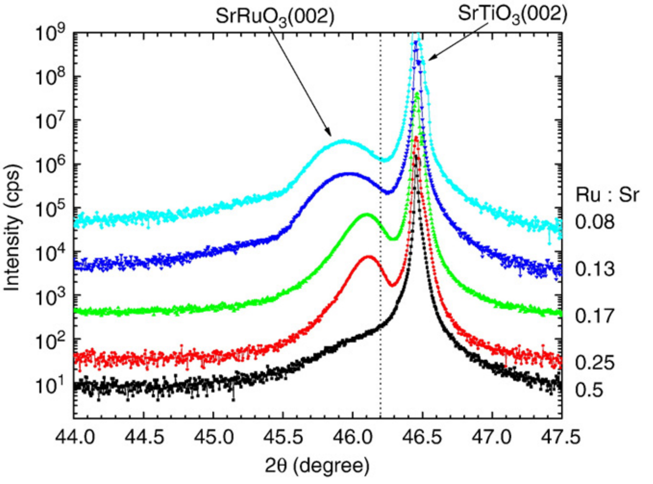

Fig. 1. $\theta/2\theta$ HR-XRD scans of thin $SrRuO_3$ films on 0.1° off-oriented $SrTiO_3$(001) substrates for different Ru to Sr ratios in the precursor solutions. The dotted line shows the position of the $SrRuO_3$(002) reflex of an unstrained film (pseudocubic notation).

The dependence of the growth rate on the concentration of the precursors in the source solutions at a fixed Ru/Sr value shows a linear behavior (Fig. 3a). According to the arguments described above, we observed that the strain increases by decreasing the concentration as long as the growth rate is not too low (<0.1 nm/min). For the substrate temperature we observed an obvious dependence of the growth rate with a maximum rate at 700 °C (Fig. 3b). Since the growth rates for this temperature series were at or below the aforementioned limit of ~0.14–0.2 nm/min the films at 700 °C showed the highest strain. At lower temperatures the growth rate is reaction-rate limited and films are less ordered because of low surface diffusion. If the substrate temperature lays over 700 °C, the growth rate decreased again, because desorption from the surface is enhanced.

The structure and composition of the $SrRuO_3$ thin films further critically depend on the ratio of the argon to oxygen gas flux during the three phases of deposition (heating, film growth, cooling):

(i) For conservation of the steps on the bare $SrTiO_3$ surface during heating up of the substrates before the growth process starts, it is necessary to add a small amount of oxygen (2%) to the Ar atmosphere. The SrO diffusion from the bulk to the surface is enhanced at excess of the oxygen partial pressure due to the higher chemical potential of O_2 above the surface, leading to the formation of Ruddlesden–Popper (R–P) $SrO\cdot(SrTiO_3)_n$ phases [26]. Otherwise an annealing in vacuum or pure Ar atmosphere can cause damage in the step-and-terrace structure by decomposition of the surface, similar to observations of the $SrRuO_3$ surfaces in Ref. [27]. Small amounts of hydrocarbon contaminants, for instance from air exposure before the substrates are introduced into the reactor, may induce local reduction of the surface and lead to the formation of pits, presumably associated to the loss of small amounts of SrO, Ti or TiO_2, CO_2, and O_2.

(ii) If the O_2 partial pressure during deposition process was below a certain limit (<30% for $T_{FE} = 240$ °C) deposition of well-ordered $SrRuO_3$ was not possible and only a metallic Ru phase was observed. However, a high oxygen partial pressure simultaneously supplied with a high Ru excess in the reactor leads to the formation of an extra RuO_2 phase.

(iii) The HR-XRD scans in Fig. 4 show that the composition of the gas phase during the cooling procedure from growth temperature to room temperature can have a crucial effect on films composition and structure. For cooling in a pure Ar atmosphere a broad film peak at 43.7° emerges, which is attributed to the R–P phase $Sr_3Ru_2O_7$. This observation is explained according to Refs. [27,28], who found that $SrRuO_3$ can be converted into metallic Ru and SrO or more likely a Sr rich R–P structure Sr_2RuO_4 and $Sr_3Ru_2O_7$ under reducing conditions. On the other hand using a high oxygen partial pressure (here: pure oxygen) a decomposition of $SrRuO_3$ to SrO and RuO_4, which is volatile, can reduce lattice strain caused by a degraded structural ordering which results in a shift of the $SrRuO_3$(002) peak to the bulk value. However, if the cooling is performed in an atmosphere with small oxygen addition (2%) the well-ordered $SrRuO_3$ film structure could be preserved, which agrees well with the observations of Lee et al. [29].

A series of AFM observations on samples of different thickness (Fig. 5) showed that in the early stages of the growth process small islands were already formed on the terraces of the stepped surfaces. With increasing thickness the island density increased while the step-and-terrace structure of the bare surface disappeared. When the density was high enough, coalescence of the islands was observed. From our observations and literature data [17,18] we conclude that in