Synthesis of nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films for flexible thermoelectrics

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Synthesis of nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films for flexible thermoelectrics

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Abstract

During energy generation, transportation and usage, large amounts of energy are lost as waste heat. With increasing energy consumption and environmental issues, exploiting this waste heat has drawn extensive attention. Thermoelectric energy conversion is an approach to take advantage of the ability of thermoelectric materials to convert waste heat into electricity.

The thermoelectric effect was initially studied in the early 19th century with the discovery of the Seebeck effect. Thermoelectric materials and devices can directly convert thermal energy (temperature gradients) into electric energy (voltage) and vice versa. Thermoelectric devices have been used in space as energy generators and as coolers in small-scale instruments and devices. However, thermoelectrics remain limited in terms of applications. The traditional state-of-the-art thermoelectric materials, such as Bi_2Te_3 , PbTe , and SnTe , exhibit high thermoelectric properties, but their disadvantages of toxicity, extreme rarity of tellurium, and oxidation when exposed to high temperature air restrict them from widespread use in applications. Compared to traditional thermoelectric materials, misfit-layered $\text{Ca}_3\text{Co}_4\text{O}_9$ not only has the typical advantages of oxides including low cost, being environmentally friendly, and good chemical stability at high temperatures, but also has relatively high thermoelectric properties due to the complex structure which composed of CoO_2 conductive layers and rock-salt type Ca_2CoO_3 insulating layers. Many strategies have been used to enhance the thermoelectric performance of $\text{Ca}_3\text{Co}_4\text{O}_9$. Compared with bulk materials, thermoelectric thin films can exhibit improved thermoelectric properties and new application in flexible devices and miniaturization. Flexibility can be induced in $\text{Ca}_3\text{Co}_4\text{O}_9$ by nanostructural tailoring to act as fully inorganic flexible thermoelectrics.

In order to explore how to produce $\text{Ca}_3\text{Co}_4\text{O}_9$ nanoporous thin film and control the porosity in the films, I have investigated the nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ system. Nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films were synthesized using sequential reactive magnetron sputtering and post annealing to determine the key factors of nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ formation and tailoring of the porosity.

Preface

This licentiate thesis is part of my PhD studies in the Energy Materials unit in the Thin Film Physics Division at the Department of Physics, Chemistry, and Biology (IFM), at Linköping University starting at November 2017.

I would like to acknowledge the financial support from Chinese Scholarship Council (CSC). The research has also been supported by the Knut and Alice Wallenberg Foundation through the Wallenberg Academy Fellows program, the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No. 2009 00971), and the Swedish Energy Agency under project 46519-1.

Populärvetenskaplig sammanfattning

Under produktion, transport och användning av energi förloras stora mängder som spillvärme. Med ökande energiförbrukning och miljöfrågor har utnyttjande av spillvärme fått mer uppmärksamhet de senaste åren. Termoelektrisk omvandling av energi är ett tillvägagångssätt som utnyttjar förmågan hos termoelektriska material att omvandla spillvärme till el.

Den termoelektriska effekten studerades ursprungligen i början av 1800-talet med upptäckten av Seebeck-effekten. Termoelektriska material och enheter kan direkt omvandla termisk energi (temperaturgradienter) till elektrisk energi (spänning) och vice versa. Termoelektriska komponenter har använts i rymden som energikällor och för kylning i småskaliga instrument och anordningar. Emellertid förblir termoelektriska komponenter begränsade när det gäller breda tillämpningar. Traditionella termoelektriska material som Bi_2Te_3 , PbTe och SnTe , har bra termoelektriska egenskaper, men deras nackdelar med toxicitet och oxidation när de utsätts för luft vid hög temperatur begränsar dem från utbredd användning, liksom det faktum att råmaterialet tellur är mycket sällsynt. Jämfört med traditionella termoelektriska material har $\text{Ca}_3\text{Co}_4\text{O}_9$ inte bara de typiska fördelarna med oxider som låg kostnad och kemisk stabilitet vid höga temperaturer utan har också relativt goda termoelektriska egenskaper på grund av den komplexa strukturen som består av ledande CoO_2 -skikt och isolerande Ca_2CoO_3 -skikt. Många strategier har använts för att förbättra dess termoelektriska prestanda. Termoelektriska tunna filmer kan uppvisa förbättrade termoelektriska egenskaper och leda till nya tillämpningar i flexibla enheter och miniatyrisering. Mekanisk flexibilitet kan induceras i $\text{Ca}_3\text{Co}_4\text{O}_9$ genom att styra nanostrukturen.

För att utforska hur man producerar $\text{Ca}_3\text{Co}_4\text{O}_9$ tunna filmer och kontrollerar porositeten i filmerna har jag undersökt det nanoporösa $\text{Ca}_3\text{Co}_4\text{O}_9$ -systemet. Nanoporösa tunna $\text{Ca}_3\text{Co}_4\text{O}_9$ filmer syntetiserades med sputtring för att bestämma de viktiga faktorerna som påverkar bildning och porositet i $\text{Ca}_3\text{Co}_4\text{O}_9$ -filmer.

List of paper

Papers included in this thesis

Paper I

Calcium cobaltate films with tailored nanoporosity from $\text{Ca(OH)}_2/\text{Co}_3\text{O}_4$ multilayers for thermoelectric and mechanical properties

Authors: **Binbin Xin**, Erik Ekström, Jun Lu, Anna Elsukova, Ganpati Ramanath, Arnaud Le Febvrier, Biplab Paul and Per Eklund.

Manuscript in final preparation.

Author's contribution:

I planned and coordinated the experiments. I performed the depositions and the XRD, SEM, Seebeck coefficient, and four-point measurement. I wrote the manuscript.

Paper II

Effects on formation of nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ of component distribution in calcium-hydroxide/cobalt-oxide multilayers

Authors: **Binbin Xin**, Arnaud Le Febvrier Ganpati Ramanath, Biplab Paul, and Per Eklund.

Manuscript in final preparation.

Author's contribution:

I planned and coordinated the experiments. I performed the depositions and the XRD, SEM, Seebeck coefficient, and four-point measurement. I wrote the manuscript.

Papers not included in this thesis

Paper III

Deposition of MAX phase containing thin films from a (Ti,Zr)₂AlC compound target

arXiv preprint arXiv:1909.04097 (2019)

Authors: Clio Azina, Benu Tunca, Andrejs Petruhins, **Binbin Xin**, Melike Yildizhan, Per O. Å. Persson, Jozef Vleugels, Konstantina Lambrinou, Johanna Rosén, Per Eklund

Paper IV

Mechanochemical formation of protein-nanofibril: graphene-nanoplatelet hybrids and their thermoelectric properties

Accepted for publication in ACS Sustainable Chemistry & Engineering

Authors: Lei Wang, **Binbin Xin**, Anna Elsukova, Per Eklund and Niclas Solin

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1. Introduction and motivation

During energy generation, a large amount of the energy is lost as waste heat. For example, the industrial total waste heat in the European Union is estimated to 300 TWh/year [1]. Not only that, more than 60% of the primary energy of fossil fuels, even around 70% in vehicles, is lost as waste heat [2]. It is important to find efficient ways to recycle the world's energy consumption. Researchers are investigating many different solutions to utilize the waste heat. Thermoelectric energy conversion is an approach to take advantage of their ability of converting waste heat into electricity.

Thermoelectric generators [3-13] can directly convert thermal energy (temperature gradients) into electric energy (voltage) and vice versa. The field of thermoelectrics began in the early 19th century with the discovery of the Seebeck effect [14, 15]. It was not until the 1960s that the first application appeared; radioisotope thermoelectric generators (Transit IV-A) were used in space to convert the heat generated by the radioisotope into stable, continuous, and autonomous electricity [16]. However, thermoelectrics remain restricted to small-scale applications due to their relatively low efficiency.

The typical characteristics of an ideal thermoelectric material are a high Seebeck coefficient (S), high electrical conductivity (σ), and low thermal conductivity (κ) at the same time. It is a challenge to enhance all of them because S , σ and κ are strongly coupled through the carrier concentration. Thus, they cannot be improved independently [17]. Classical state-of-the-art thermoelectric materials typically contain bismuth, lead, and tellurium, that are toxic and in the case of tellurium extremely rare [18]. They also oxidize easily when exposed to high temperature air [19]. Compared to traditional thermoelectric materials, oxide thermoelectric materials have advantages of low cost, being environmentally friendly, and good chemical stability at high temperatures [20]. Despite this, they were for a long time not considered as thermoelectric materials due to their low carrier mobility and high thermal conductivity [21]. In the early 1990s,

researchers became interested in oxide thermoelectric materials, such as $\text{In}_2\text{O}_3\text{-SnO}_2$ [22]. The discovery of Na_xCoO_2 as a thermoelectric material has attracted great attention due to the large Seebeck coefficient and relatively low resistivity [23]. The crystal structure of Na_xCoO_2 is layered, consisting of CdI_2 -type CoO_2 layers and Na layers, alternatingly stacked along its c -axis. However, a disadvantage of Na_xCoO_2 is the stability, since Na will react with moisture in the air and cause hydration, if Na_xCoO_2 is exposed to ambient atmosphere for long time. The loss of Na leads to degradation of the compound and its TE performance. Misfit-layered thermoelectric $\text{Ca}_3\text{Co}_4\text{O}_9$ has a similar structure with Na_xCoO_2 , composed of both CoO_2 conductive layers and rock-salt type Ca_2CoO_3 insulating layers. Similar to Na_xCoO_2 , $\text{Ca}_3\text{Co}_4\text{O}_9$ exhibits high thermoelectric performance [24]. However, different from Na_xCoO_2 , $\text{Ca}_3\text{Co}_4\text{O}_9$ shows higher thermal stability from room to high temperature in an oxygen rich environment [25].

Many strategies have been used to enhance the thermoelectric performance of $\text{Ca}_3\text{Co}_4\text{O}_9$ [26-29]. Compared with bulk materials, thermoelectric thin films can exhibit improved thermoelectric properties due to size effect and quantum confinement [7, 10, 30]. Otherwise, thin film materials can extend the field of application to flexible devices and miniaturization due to the light weight and lack of restrictions on shape [31-35]. Flexibility can be induced in $\text{Ca}_3\text{Co}_4\text{O}_9$ by nanostructural tailoring [36-38] or by hybridization with polymers [29]. However, most conductive polymers in the hybrid thermoelectric materials are unstable in air at high temperature, while fully inorganic flexible thermoelectrics can be stable at high temperature.

Motivated by this general background, the research in this thesis is focused on how to produce $\text{Ca}_3\text{Co}_4\text{O}_9$ nanoporous thin film and control the porosity of the films. This is a meaningful way to tailor the mechanical flexibility with retained or enhanced thermoelectric properties, with potential use in mechanically flexible energy-harvesting applications.

2. Thermoelectric materials and devices

2.1 Thermoelectrics

Thermoelectric materials can directly convert heat into electricity, and vice versa. A thermoelectric generator can be considered as a solid-state heat pumping system which can induce motion of charge carriers (holes (p-type) and electrons (n-type)) from the hot side to the cold side. Solid-state thermoelectric devices have the advantages of no moving parts, no noise, no greenhouse-gas emissions, and feasibility for miniaturization and long-term use. The qualities of thermoelectric materials can be represented by the dimensionless figure of merit ZT :

$$ZT = \frac{\sigma S^2}{\kappa} T, \quad (2.1)$$

where σ is the electrical conductivity, S is the Seebeck coefficient, κ is the thermal conductivity and T is the absolute temperature. The term σS^2 is the power factor (PF). A high PF indicates a high power-output of thermoelectric devices.

The Seebeck coefficient (S) is the magnitude of the thermoelectric voltage induced by the temperature gradient across the material. For degenerate semiconductors, it can be expressed as the following relation:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}, \quad (2.2)$$

where k_B is Boltzmann's constant, e is the carrier charge, h is Planck's constant, m^* is the effective mass of the charger carrier and n is the carrier concentration. Thermoelectric materials with higher m^* have larger Seebeck coefficient [12]. Otherwise, lower carrier concentration is desirable for thermoelectric materials to obtain higher Seebeck coefficient. That is, there is a rather narrow range in m^* and carrier concentration that yield optimum Seebeck coefficient and other thermoelectric properties.

Electrical conductivity (σ) is decided by the carrier concentration and carrier mobility, which is defined as:

$$\sigma = ne\mu, \quad (2.3)$$

where n is the carrier concentration, e is the carrier charge, and μ is the mobility. Thermoelectric materials with high electrical conductivity require high carrier concentration; however, low carrier concentrations are desired for high Seebeck coefficient. Therefore, the ideal carrier concentration should typically be in the range from 10^{19} to 10^{21} cm^{-3} [39].

Thermal conductivity (κ) consists of contributions from both electrons and phonons (lattice), defined as the following:

$$\kappa = \kappa_e + \kappa_l = L\sigma T + \kappa_l, \quad (2.4)$$

where κ_e is the electronic thermal conductivity, κ_l is the lattice thermal conductivity and L is the Lorenz factor. For semiconductors, phonons are the majority contribution in total thermal conductivity.

According to these parameters, the Seebeck coefficient, the electrical conductivity and the thermal conductivity are not independent. There is a balance for S , μ and κ to obtain optimized thermoelectric materials, as illustrated in Fig. 2.1. It is challenging to obtain an ideal thermoelectric material which combines of high power-factor and low thermal conductivity.

Figure 2.1. The relation between carrier concentration and ZT , S , σ and κ [12].
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2.2 Flexible thermoelectric thin films

Mechanically flexible energy supplies are being developed for portable and wearable devices [40]. However, flexible energy storage components, including flexible lithium-ion batteries and supercapacitors, have one remaining challenge in their requirement for frequent recharging and replacement. Flexible thermoelectric devices are one possible approach to accommodate the demand for wearable devices that are maintenance-free and with long lifetime. To date, there are mainly three different options for flexible thermoelectrics: organic, hybrid, and inorganic materials.

2.2.1 Conducting polymers

Conducting polymers are potential candidates for flexible thermoelectric materials due to their good mechanical flexibility, low κ and inherent electrical conductivity. Conducting polymers commonly have conductive ordered domains surrounded by poorly conductive disordered domains [41]. The current commonly investigated polymer materials are p-type

including poly-pyrrole (PPy), polyaniline (PANI), poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate) (PEDOT: PSS), and n-type including poly(perinaphthalene) (PPN), poly(Cu-benzenehexathiol) (CuBHT) [42, 43].

2.2.2 Organic-inorganic hybrids

Conducting polymers can be hybridized with inorganic thermoelectric materials to improve thermoelectric properties, exploiting the combination of high electrical conductivity and Seebeck coefficient from inorganic materials and low thermal conductivity and high mechanical flexibility from conducting polymers [44, 45]. The thermoelectric properties can be tuned by the size, morphology, crystalline structure, distribution, and interfaces of inorganic and polymers in the hybrid composites [45, 46]. For instance, polymer/CNTs [47, 48], PEDOT:PSS/Te nanowires[49], PEDOT:PSS/SnSe[50], TiS_2 /organic hybrid superlattices [51] have been reported and shown good thermoelectric properties and flexibility.

2.2.3 Flexible inorganic materials

However, materials based on polymers have been limited in use due to their limited stability at higher temperature. Traditional inorganic thermoelectric materials, such as Bi_2Te_3 , PbTe, can show superior thermoelectric properties from room temperature to relatively high temperature [5]. However, they are restricted for application in flexible thermoelectric devices due to their inherent rigidity. Recently, strategies for flexible thermoelectric devices have been developed by growing or depositing inorganic thermoelectric materials on flexible inorganic substrates or free-standing thin films [32, 40, 52]. Furthermore, classical state-of-the-art thermoelectric materials normally including bismuth, lead, and tellurium, have the disadvantage of toxicity, lack of stability in air ambience at high temperature, and in the case of tellurium also being very rare.

Compared with typical thermoelectrical materials, the layered cobalt oxides have advantages of low cost, being environmentally friendly, and good chemical stability at high temperature, as well as relatively good thermoelectric performance due to their layered crystalline structure.

2.2.4 Layered-cobalt-oxide-based thermoelectric materials

Metal oxides are widely applied in many fields including catalysts, sensors, energy storages and solar cells due to abundant in earth, low cost, nontoxic and environmentally friendly [53-57]. However, metal oxides were for a long time not investigated as thermoelectric materials because of their low carrier mobility and high thermal conductivity [21]. Further, it is difficult to confine the electronic properties and the phonon properties in one simple crystalline material simultaneously.

The concept of “phonon glass electron crystal” (PGEC) was introduced by Slack in 1995 [58]. The basic concept of PGEC is that the crystalline semiconductors allow efficient transmission of charge carriers (like crystals) to ensure electronic properties (S and σ), while blocking heat flow by the lattice (in analogy with a glass) to obtain as low thermal conductivity as possible. PGEC materials, such as skutterudites [59], Zintl phases [60], and clathrates [61], exhibit good thermoelectric performance. Layered cobalt oxides, such as Na_xCoO_2 and $\text{Ca}_3\text{Co}_4\text{O}_9$, with the periodic arrangement of layers with different electron and phonon transport characteristics are one kind of PGEC [20, 62].

Na_xCoO_2

The crystal structure of Na_xCoO_2 is composed by alternating stacks of hexagonal CdI_2 -type CoO_2 layer and Na layer along the c -axis, as shown in Fig. 2.2a. Na_xCoO_2 presents good p-type thermoelectric properties [23], but is impeded by its limited chemical stability. Na will react with moisture in the air and cause hydration, if Na_xCoO_2 is exposed to ambient atmosphere for a long time.

Ca₃Co₄O₉

Compared to Na_xCoO₂, Ca₃Co₄O₉ has a similar layered structure and is another promising candidate p-type thermoelectric material with higher thermal stability, even at 1000 K in air [21]. The crystal structure of Ca₃Co₄O₉ is composed of CdI₂-type CoO₂ layer with edge-sharing CoO₆ octahedra and rock salt-type Ca₂CoO₃ layers alternatingly along the *c*-axis, as seen in Fig. 2.2b. However, each adjacent CoO₂ and Ca₂CoO₃ layer is incommensurate with respect to the other monoclinic *b* lattice parameter. The misfit layered Ca₃Co₄O₉ has different electron and phonon transport characteristics; the CoO₂ layers are electrical transport layers by hopping of holes from Co⁴⁺ to Co³⁺ while the interlayers (Ca₂CoO₃) act as a charge reservoir where the phonons can be scattered at the mismatched interfaces leading to a low thermal conductivity [63, 64]. Layered Ca₃Co₄O₉ typically shows Seebeck coefficient, electrical conductivity and thermal conductivity of 90-130 $\mu\text{V K}^{-1}$, 10-80 S cm^{-1} , and 1.6×10^{-4} -2.5 $\text{W m}^{-1} \text{K}^{-1}$ at room temperature, respectively [28, 65, 66].

Figure 2.2 Schematic illustration of the crystal structure of (a) Na_xCoO₂ and (b) Ca₃Co₄O₉.

2.2.4 Flexible substrates

Thermoelectric materials can be grown or printed onto flexible substrates including polyimide (PI), polydimethylsiloxane (PDMS), glass, mica to fabricate flexible thermoelectric devices. For instance, PEDOT: PSS thin films grown on PDMS show good stretching properties combined with increased thermoelectric power factor [67]. Compared with glass or polymer substrates, muscovite mica can be stable at high temperature. The crystal structure of muscovite mica was first studied in 1927 [68]. Mica is a natural phyllosilicate mineral with layered sheet structure. The

common chemical formula of muscovite mica is $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ (monoclinic, $a = 5.17 \text{ \AA}$, $b = 8.94 \text{ \AA}$, $c = 20.01 \text{ \AA}$, $\beta \sim 96^\circ$, space group $C2/c$). The layered mica structural unit is composed of intervening aluminum octahedral ($\text{AlO}_4(\text{OH})_2$) layer between two silicate tetrahedral sheets (SiO_4) and interlayer cations inserted between these layer stacks, as shown in Fig. 2.3. The bonding between the interlayer cations and these layer stacks is weak, resulting in easy cleavage along the ab-plane and obtain a clean and flat surface. Muscovite mica is widely used because of its flatness and because it shows mechanical flexibility when delaminated.

Figure 2.3 Schematic illustration of the crystal structure of mica.

3. Physical vapor deposition

Physical vapor deposition (PVD) techniques are common methods for thin-film synthesis. PVD processes mean that the deposition species are vaporized from solid sources by thermal heating the source or by bombardment by energetic particles (electrons, atoms, ions, molecules or phonons), transport in a vacuum chamber, and condense on the substrate. PVD includes many different techniques, such as evaporation, pulsed laser deposition (PLD), vacuum-arc-based deposition, and different modes of sputtering deposition. In this thesis, reactive radio frequency (RF) magnetron sputtering is the technique used to grow the films, as shown in the Fig. 3.1. Reactive RF magnetron sputtering is a rather complex method. This presentation will therefore be divided into and introduced by four parts: sputtering, magnetron sputtering, reactive sputtering and radio frequency sputtering.

Figure 3.1 Schematic illustration of a reactive RF magnetron sputtering system (using Ca/Co/O₂ system as an example).

3.1 Sputtering

The basic sputtering process is that the energetic particles knock the cathode target atoms off the surface. Specifically, the gas (typically Ar) is ionized in the vacuum chamber by applied voltage ($e^- + Ar \rightarrow 2e^- + Ar^+$) and more gas atoms are ionized by the cascade collision process. The species are sputtered off the cathode (target) bombarded by the energetic ions driven by the negative applied potential. The charged gas of particles is called as plasma and consists of ions, neutral species and electrons. The plasma is quasineutral, i.e., the ion and electron densities are roughly equal at the macro-scale. Ions are accelerated towards and bombard the cathode driving by the applied voltage. For sputtering the atoms off the target surface, the ions should have the enough energy to overcome the binding energy of the target atoms. The sputtered atoms can condense on the substrate. This type of sputtering technique is called dc diode sputtering. For sputtering, a vacuum is necessary for the vaporization, ignition, and transportation of the species. Ultra-high vacuum (UHV) means a base pressure below 10^{-7} mbar to keep the clean chamber (reducing water vapor and hydrogen) in the sputtering system. In order to obtain UHV in reasonable time, the chamber wall needs to be baked (heating to ~ 150 °C for several hours) to desorb the water absorbed on the wall.

The sputter-process requires suitable low deposition pressure (Ar pressure typically ~ 0.4 Pa) to lower the ignition voltage for the plasma [69]. The collision between the gas and sputtering particles deciding by the pressure affects the energy of the species arriving the substrate. Normally, the targets used in DC sputtering are conducting, not non-conductive dielectric targets. Generally, DC diode sputtering has the disadvantage of low sputter rate and low deposition rate and is rarely used in practice today.

3.2 Magnetron sputtering

Magnetron sputtering can have high plasma density and sputtering rate by adding extra magnetic field to the vicinity of cathode. There are several different cathode geometries, including planar, conical, cylindrical, and hollow, based on closed-loop effect. The most common shape of cathode is planar, with the magnetic field created magnets behind the target (the central magnet and outer circle magnets with opposing poles) . Typically, the outer set of magnets in the magnetron cathode is stronger than the inner one, which is called unbalanced magnetron sputtering cathode. The strength of the inner and outer magnets is roughly equal in the balanced magnetron sputtering configuration. However, an unbalanced magnetic field can not only trap the electrons and form dense plasma in front of the target where the magnetic field focus as same as balanced magnetic field, but can also catch the escaping energetic electrons by the excess magnetic field and produce a dense secondary plasma near the substrate which is an order of magnitude higher than that in balanced magnetic field. A high plasma density can therefore efficiently enhance the sputtering deposition rate.

3.3 Reactive sputtering

Reactive sputtering is a deposition technique to grow thin compound film by adding reactive gas (e.g., O_2 for oxides, N_2 for nitrides, C_2H_2 or CH_4 for carbides) into the sputtering process. Typically, the partial pressure of the reactive gas is lower than that of the inert gas (Ar). The sputtered metal atoms can react with reactive gas (O_2 in this thesis) to form oxides film on the substrates. However, the gas molecules will react with the target surface and top layer of target changes from metallic to compound, which called poisoning of the target, as the reactive gas flow increase. Fig. 3.2 represents the function between sputtering rate and reactive gas flow.

The electrically insulating compound layer on the surface of target dramatically reduces the sputtering rate and deposition rate. There is a challenge in the reactive sputtering process to control the stoichiometry

of the film with retained high deposition rate by changing the reactive gas flow. In addition, electrical breakdown (arcs) will occur on the target surface when electric charge builds up and a voltage drop across the insulating layer during the discharging. Arcs will destabilize the plasma and are not desired in the sputtering process. RF sputtering can effectively avoid the formation of the insulating layer on the metallic target in the reactive gas.

Figure 3.2 Schematic illustration of hysteresis in the sputtering rate as a function of the reactive gas flow.

3.4 RF sputtering

RF sputtering is a deposition technique using the power with an alternating current (AC) at high frequency. By alternating the electrical potential between cathode and anode, the extra ions absorbed on the target surface can be removed and the electric charge cannot build up on the surface with each cycle. On the positive cycle, the electrons are attracted to the target material and the ions are removed from the surface. On the negative portion of the cycle, ion bombardment of the target to be sputtered continues. In the low frequency range (less than 1 MHz), the ions will have enough time to travel to the substrate and chamber wall.

This is unwanted in the sputtering process during the positive cycle. At high frequency (13.56 MHz), the electrons can be accelerated to oscillate between cathode and anode while the ions remain in the vicinity of the target surface to form continuously plasma due to the electrons are much more mobile (lighter) than ions. Because of this mechanism, RF sputtering can reduce the arcing to obtain stable plasma and has the ability to sputter insulating and metallic targets.

4. Measurements and analysis

4.1 Scanning electron microscopy

Scanning electron microscopy (SEM) is versatile analytical tool to study surface topography with both high resolution and high magnification, as shown in Fig. 4.1. The resolution is several orders of magnitude better than in an optical microscope (OM) but cannot compete with that of transmission electron microscopy (TEM). SEM usually requires little effort in terms of specimen preparation. SEM is a very common research apparatus in both research and industrial laboratories. The basic principle of SEM is that the accelerated electron beam is scanned over the surface of the sample and detect the electrons coming from the interaction between surface and the scanning beam. There are several different electron excitation results including Auger electrons, secondary electrons, backscattered electrons, visible light, and characteristic X-rays when the primary electrons with energy (typically 1-20 keV in the SEM) scan the materials. These different electrons and X-rays can be analyzed different detectors giving different results. The most common detectors are secondary electron detectors, including In-Lens detector giving high resolution images, secondary electron detector optimized for topographical imaging, and backscattering electron detector giving element-compositional images (i.e., brighter contrast corresponding to higher atomic weight).

Figure 4.1 Schematic illustration of SEM.

4.2 Transmission electron microscopy

4.2.1 Imaging

Transmission electron microscopy (TEM) is a powerful analytical technique to investigate the microstructure and composition of semiconductor, alloys and biological samples, the basic image mode is shown in Fig. 4.2 a. The basic principle for TEM is similar as optical microscope with the illumination system based on the focused electron beam accelerated by a voltage of around 200 keV, which results in the short wavelength (around 2.5 pm) of electrons and high resolution to atomic scale [70]. Different results are obtained by analyzing the elastic scattering electrons, secondary electrons and X-ray through different detectors. TEM requires the sample to be very thin, less than 100 nm, to be penetrated by the focused electron beam. The preparation of a TEM specimen is relatively time-consuming and destructive. Furthermore, the obtained information may not represent all the sample due to the small volume of the specimen.

Figure 4.2 Schematic imaging system in a conventional TEM including Imaging mode (a) and diffraction mode (b).

There are several interactions including absorption, transmission, scattering and backscattering when the electrons transmit the sample. Different images and spectroscopy techniques can be obtained based on the different interactions. The images will visualize crystal grains in bright field (BF) where the objective aperture located in back focal plane blocks the diffraction beam and the image is constructed by the transmitted beam, the principle is shown in Fig. 4.3 a. In contradistinction, the dark field (DF) mode is achieved by moving the objective aperture located in the back focal plane to block the transmission beam and using diffraction beam to image, as shown in Fig. 4.3 b. The major benefit of DF imaging is the increased contrast of features such as dislocations. High resolution transmission electron microscopy (HRTEM) can reveal the atomic structure by imaging individual lattice spacings information.

Figure 4.3 (a) Bright-field image with diffraction contrast; (b) dark field image.

4.2.2 Selected-area electron diffraction (SAED)

A diffraction pattern from specific area of the sample can be formed at back focal plane when the selected area aperture is inserted in image plane, which called select-area electron diffraction (SAED), as shown in Fig. 4.2 b. The advantage of SAED is that crystallographic information can be obtained from a very small area of interest avoiding the interference of substrate or different crystal grains.

4.2.3 Energy-dispersive X-ray spectroscopy (EDS)

Figure 4.4 Schematic illustration of the principle of EDS.

Energy-dispersive X-ray spectroscopy (EDS) uses the characteristic X-rays emitted from materials excited by incident electrons to extract the chemical information in the researched materials. The principle of EDS is shown in Fig. 4.4. This analytical tool is integrated both in SEM and TEM. In this thesis, EDS is mainly used to determine the element distribution on the cross section of the as-deposited films to study the multilayers. The element distribution on the cross section of the sample is identified by TEM due to the thickness of the sample is too thin.

4.3 X-ray diffraction

X-ray diffraction (XRD) is a powerful, versatile, and non-destructive analytical materials technique for identification and determination of the crystal structure and atomic spacing in solid materials. The technique is based on the interactions between X-rays and atoms (coherent scattering, incoherent scattering, absorption). Constructive interference can occur in coherent scattering when the incident X-rays with a particular wavelength (λ) are scattered by the atomic planes. This occurs only if the path difference is an even number of wavelengths, which determined by Bragg's law:

$$n\lambda = 2d_{hkl} \sin \theta \quad (4.1)$$

Here d_{hkl} is the spacing between diffracting planes with Miller indices hkl , θ is the angle between sample and incident X-rays, n is any integer, and λ is the wavelength of the beam. The principle of Bragg's law is illustrated in Fig. 4.5.

Figure 4.5 The principle of Bragg's law.

In XRD measurements, the θ - 2θ Bragg-Brentano geometry is often used. It is made in a symmetric configuration between incident x-ray beam and ejected x-ray beam. A diffraction peak is obtained when the lattice plane

oriented parallel with the surface and the incident angle (θ) fulfill Bragg's law. But fulfilling Bragg's law is not the only condition to give diffraction peaks; it is also determined by the structure factor which in turn is given by the crystal structure.

5. Electrical properties

5.1 Four-point probe measurement

Figure 5.1 Schematic of a four-point probe setup.

The four-point probe technique is applied to measure the resistivity of thin films. A four-point probe setup is shown in Fig. 5.1. A pair of outer probes introduce current and a pair of inner probes measure the voltage at the same time. For an infinite 2D sheet, the sheet resistance R_{sh} can be calculated by the following relation:

$$R_{sh} = \frac{\pi}{\ln 2} \frac{V}{I} \quad (5.1)$$

For a thin film with the finite thickness t , the resistivity ρ can be defined as:

$$\rho = R_{sh} t F\left(\frac{t}{s}\right) \quad (5.2)$$

In these equations, I is the applied current, V is the measured voltage dropping between the two inner probes, t is the thickness of the film, s is the probe spacing between the two probes and F is the correction factor. If $t \ll s$, the correction factor approaches 1 (assuming infinite in-plane dimensions). The resistivity of the thin film can then be calculated according to

$$\rho = R_{sh} t \quad (5.3)$$

5.2 Seebeck measurement

Figure 5.2 Schematic drawing of Seebeck coefficient measurement setup.

The Seebeck coefficient is measured by a homemade four-probe system, as shown in Fig. 5.2. The heater in both hot and cold side consist of a Peltier device, and a Cu block with cooling system. In this setup, the film is pressed onto the copper block to obtain good connection. When a temperature difference is applied, the sample will give a voltage output. The temperature is measured by two K-type thermocouples and the voltage is measured by a Keithley 2001 Multimeter at the same time. The Seebeck coefficient can be calculated by the following:

$$S = V/\Delta T \quad (5.4)$$

To deduce the error, S is calculated from the slope of the voltage vs temperature gradient plot with 10 different temperature gradients between 0 and +10 K at room temperature (Fig. 5.3).

Figure 5.3 Seebeck coefficient measurement curve of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin film growing on mica for calibration.

5.3 Flexibility measurement

In order to qualitatively evaluate the effect of mechanical flexibility on electrical properties, two-point resistance is measured during bending and unbending process with different bending radius and number of bending cycles. The resistance is denoted as R_0 and R_1 when flat and during bending, respectively. The change ΔR in the measured resistance, $\Delta R = R_1 - R_0$, therefore provides a straightforward of estimating the effect of mechanical flexibility. A constant resistance during bending thus corresponds to $\Delta R/R_0 = 0$ and indicates good mechanical flexibility and that the electrical properties are not affected by bending.

Figure 5.4 Schematic of mechanical flexibility measurement setup.

6. Summary of appended papers

In this thesis, I investigate the formation mechanism and how to tune the porosity in nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films. In **Paper I**, nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films were synthesized by annealing $\text{Ca}(\text{OH})_2/\text{Co}_3\text{O}_4$ multilayers obtained through sequential reactive RF-magnetron sputtering. A set of multilayers with different $\text{Ca}(\text{OH})_2/\text{Co}_3\text{O}_4$ bilayer thicknesses, b_t . The b_t can be controlled by changing the deposition times of CaO and Co_3O_4 while keeping the total nominal multilayer thickness constant. The SEM analysis indicated that the porosity can be controlled by changing the b_t . TEM results revealed that the annealed films consist of a crystalline $\text{Ca}_3\text{Co}_4\text{O}_9$ layer separated from the substrate by an amorphous glass layer. The higher porosity films exhibit not only higher electrical conductivity of $\sim 80 \text{ S cm}^{-1}$ as well as a high Seebeck coefficient of $\sim 135 \mu\text{V K}^{-1}$, leading to a good power factor of $\sim 1.47 \mu\text{W cm}^{-1} \text{ K}^{-2}$ at room temperature. Meanwhile, the nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ films show stable mechanical flexibility.

In **Paper II**, the effects of component composition and distribution in calcium hydroxide and cobalt oxide multilayers on nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ formation were investigated. Different multilayers, including $\text{CaO}/\text{Co}_3\text{O}_4$ and CaO/CoO , were obtained by sequential reactive RF-magnetron sputtering, analogous to **Paper I**. Nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films could be obtained after annealing the $\text{Ca}(\text{OH})_2/\text{Co}_3\text{O}_4$ multilayers.

After annealing the $\text{CaO}/\text{Co}_3\text{O}_4$ or CaO/CoO multilayers film without $\text{Ca}(\text{OH})_2$, the resulting $\text{Ca}_3\text{Co}_4\text{O}_9$ films show very low porosity and small pores. The porosity of the films increased with increasing $\text{Ca}(\text{OH})_2$ fraction in the $\text{Ca}(\text{OH})_2/\text{Co}_3\text{O}_4$ multilayers. My results indicate that the conversion of CaO to $\text{Ca}(\text{OH})_2$ prior to annealing is crucial to the formation of nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$. In particular, water release from $\text{Ca}(\text{OH})_2$ and volume shrinkage during reaction with Co_3O_4 lead to the formation of faceted pores. I thus demonstrate that the distribution of $\text{Ca}(\text{OH})_2$ and Co_3O_4 phases plays a significant role on nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ formation.

Overall, the results in this thesis describe the key factors and tuning the porosity in the nanoporous formation in $\text{Ca}_3\text{Co}_4\text{O}_9$. They therefore provide a contribution and guideline to control the morphology as well as pore size and distribution of calcium cobaltate.

7. Future work

The nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films investigated in this thesis exhibit mechanical flexibility. Flexible thermoelectric generators can utilize heat, such as body heat, but are limited in practical use because of the limited temperature stability of organic materials. Expanding inorganic thermoelectric materials in flexible applications is therefore of interest.

Through investigating the formation mechanism of the nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$, I have found that it is possible to obtain $\text{Ca}_3\text{Co}_4\text{O}_9$ nano-islands with the same crystalline orientation (c axis) by controlling the depositing parameters. This type of nanoporous structure in the $\text{Ca}_3\text{Co}_4\text{O}_9$ thin film constitutes an opportunity to hybridize the material by combining it with a conductive polymer. Considering the advantages of conductive polymers, such as low thermal conductivity and high inherent mechanical flexibility, inorganic/organic hybrids with nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films and conductive polymers is a worthy way to further improve the combination of mechanical flexibility and thermoelectric properties.

One can formulate this idea as forming flexible thermoelectric materials in which the “glass” layers in a “phonon glass electron crystal” are replaced by the conductive polymers with low thermal conductive and high mechanical flexibility.

The future work based on the above suggestions can be beneficial to understand the fabrication and properties of inorganic/organic hybrids in flexible thermoelectric field.

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Papers

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