An investigation into the surface topology and thickness profile of functional ceramic spinel manganate sputtered, evaporated and screen-printed layers


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Abstract

In this paper an atomic force microscopy and scanning electron microscopy analysis of the surface grain structure of negative temperature coefficient of resistance (NTCR) thermistor nickel manganate layers produced by radio frequency (RF) magnetron sputtering, electron-beam evaporation and screen-printing is presented. Thin sputtered and evaporated films exhibited a dense low porosity surface with evidence for grain alignment in a brick layer fashion, whereas thick screen-printed layers displayed perceptible surface porosity. The layer thicknesses and the thickness distributions were analysed by surface profileometry. The three different deposition techniques used for film production are compared and described in detail, including the paste production for screen-printing, deposition conditions and post-deposition annealing and sintering processes for all three techniques. The effects of the differences in the film production processes on the film microstructure are discussed. This is important, because differences in microstructure can result in variations in the resistivity versus temperature characteristics.

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1. Introduction

Thermistor materials based on spinel manganate NiMn2O4 exhibit a uniform exponential decrease of resistance with increasing temperature up to ~300 °C, i.e. a negative temperature coefficient of resistance (NTCR), which makes the compound well suited for use as a thermistor material in specific temperature sensors and attenuators [1,2]. Because the charge transport activation energies are reasonably below the infrared spectrum, spinel manganates can also be used for infrared radiation detection devices [3]. Recent applications of these materials in microwave or low temperature co-firing ceramic (LTCC) microelectronics make thick-film production interesting [4,5], whereas thin films are needed for infrared detection, or can be used in relevant thermistor applications. Considerable effort has been made in the past to study the preparation and characteristics of films using various deposition techniques, including electron-beam evaporation [6,7], RF magnetron sputtering [8–10], screen-printing [11–13] and electrophoretic deposition [14].

One of the most important features of film type sensors is their surface topology, and in the case of polycrystalline films for thermistor applications their dense grain packing. In general, a dense film exhibiting low porosity is desired, in order to maximise mechanical stability of the device and to minimise effects of the surrounding ambient such as changes in humidity or oxygen partial pressure, which can affect the sensor’s performance by altering the electrical resistivity of the layer.
Porous materials commonly exhibit an electrical resistivity sensitive to such ambient conditions [15].

In this study, the effect of different film production techniques on the surface micro-topology is presented for NiMn2O4 based thermistor films. The electrical transport properties have been presented in detail in previous publications: electron-beam evaporated films on soda-lime glass [7] and Al2O3 substrates [16], screen-printed films on Al2O3 [17] and sputtered films on Si[1 0 0] [9]. It was found that a power law dependency for polaron variable-range hopping (VRH) or a simple thermally activated nearest neighbour hopping (NNH) model can describe the charge transport properties. Both cases are accounted for in the following generalised expression, describing NNH ($\rho = \alpha = 1$) or VRH ($0.25 < \rho = \alpha/2 < 0.5$) resistivity versus temperature ($\rho$–$T$) behaviour [17]:

$$\rho(T) = C T^\alpha \exp \left( \frac{T_0}{T} \right)^{\rho}$$  \hspace{1cm} (1)

where $C$ is the temperature independent contribution to the resistivity, $\alpha$ describes the pre-exponential temperature dependence, $T_0$ a characteristic temperature and $\rho$ describes the exponential power law dependence. In previous publications it was shown that $\alpha$, $\rho$ and $T_0$ in Eq. (1) vary in films depending on the production process [7,9,16,17]. These differences in the $\rho$–$T$ behaviour have been described in detail and have been associated with differences in the film microstructure. This, in turn, was suggested to be a result of the differences in the film production processes [7,9,16,17], but the microstructure–production process relationships have not been analysed in detail so far. This paper is an attempt to relate the origin of the variations in film microstructure to differences in: (i) the source production: paste production for screen-printing target shaping for Electron Beam Evaporation and RF magnetron sputtering; (ii) the mechanisms of the deposition processes: electron-beam evaporation (EBE) in vacuum, RF magnetron sputtering in an argon–oxygen gas enriched environment and screen-printing (SP) at ambient conditions; (iii) the post-deposition annealing processes: variations in annealing temperature and time.

The experimental details of the film deposition processes and the post-deposition annealing/sintering techniques have been described briefly already [7,18–20], but all are described in detail here in order to achieve completeness and to enable comparison. This work contains a full scanning electron microscopy (SEM) and atomic force microscopy (AFM) analysis of the surface structure of all types of films directly after deposition/printing and after an additional annealing/sintering treatment. In previous publications [18–20], only AFM/SEM images of films after post-deposition annealing/sintering processes had been presented, in the case of sputtered films only for two different substrate temperatures during deposition, and in the case of screen-printed films for only one sintering time. Here, AFM images of sputtered films deposited at four different substrate temperatures are presented in the as-deposited and post-deposition annealed state. The formation of a polycrystalline phase by annealing from a poor crystalline phase in the as-deposited state is demonstrated. For electron-beam evaporated films the formation of a polycrystalline phase by annealing is shown as well, on the SEM images presented. SEM images of SP films in the as-deposited and sintered state for different sintering times are shown. A clear grain growth mechanism and an increasing film surface porosity with increasing sintering time are demonstrated. For films containing a glass frit, the opposite effect was observed, i.e. a contraction of the grains by capillary action of the glass frit during liquid phase sintering.

Furthermore, an in-depth analysis of the predictability of the thickness of screen-printed films is given. For electron-beam evaporated films a method is proposed to estimate the sticking coefficient of the electron-beam vapour on the substrate from the film thickness distribution and the amount of evaporated material.

2. RF magnetron sputtering

Standard radio frequency (RF) argon ion magnetron sputtering procedures [21–24] have been established to deposit Ni0.87Mn2.13O4+ films. Sputtering targets were prepared by pressing Ni0.87Mn2.13O4+ powder into pellets using an Apex 10 t hydraulic press, followed by an optimised sintering densification process at 1200 °C to ensure high mechanical stability of the target during argon ion bombardment and low material porosity to limit charge carrier leakage paths [24,19]. Source powder was obtained by traditional ceramic precursor oxide processing using NiO and Mn3O4. After sintering, the pellets were annealed in air at 800 °C for up to 60 h to restore phase purity [25,26]. Si[1 0 0] substrates were cleaned by immersion in commercial grade hydrofluoric acid for 10 min followed by rinsing in de-ionised water. The substrates were placed horizontally above the target cathode in an on-axis configuration (see Fig. 1). The deposition chamber was evacuated using a rotary backed turbo-molecular pump to a base pressure of ~8–10–5 Pa, before admitting a constant oxygen/argon gas flow of variable ratio, which lead to a pressure of ~5 Pa. Before admission to the deposition chamber, the individual argon and oxygen gas flows were adjusted using custom built mass flow controllers. After mixing the two flows together in a tube containing glass balls, the oxygen content of the mixture was measured using an Anacon Model 78 oxygen sensor. The well controlled gas mixture was then admitted to the deposition chamber.

The oxygen content of the deposition ambient affected the absolute value of the electrical resistivity $\rho$ and the characteristic temperature $T_0$ of as-deposited films, because oxygen reacts with sputtered material (reactive sputtering) and influences the oxygen stoichiometry in the films [9]. $T_0$ and $\rho$ also change upon annealing in air as this alters the oxygen stoichiometry, too [9]. A 13.56 MHz ac voltage of ~1 kV amplitude giving a target power density of 3 W cm–2 was applied for different oxygen/argon ratios and the substrates were heated to 35 °C, 100 °C, 200 °C or 250 °C. Uniform layers of 560–830 nm thickness were grown at a deposition rate of 5–10 nm min–1, which decreased with increasing substrate temperature during deposition. This
may be understood by assuming an increased desorption rate of sputtered particles, which are initially adsorbed on the substrate but gain sufficient thermal energy for desorption, provided by the heated substrate [19,26].

The thickness of each film was measured at three different positions on the as-deposited film by locally removing the film from the substrate. The height of the substrate–film step in the surface profile was then measured using a stylus profileometer Tencor Alphastep 200 system. The thickness distribution was found to be approximately uniform, which may be a result of the relatively small substrate size compared to the target area exposed to the argon plasma.

In the as-deposited state, films showed no sign of distinct ceramic grain formation (Fig. 2), which correlates with previous findings of a poor degree of crystallinity of films in the as-deposited state [19]. It can be seen from Fig. 3 that well defined ceramic grains formed on the film surface upon post-deposition annealing in air at 800°C for 1 h for substrate temperatures of at least 200°C or 250°C during deposition. This is in agreement with the report of an optimum crystallinity of films deposited on substrates heated to at least 200°C or 250°C and annealed at 800°C for 1 h [19]. Reference [19] contains a combined X-ray diffraction and AFM study, showing that films grown at a substrate temperature of 200°C displayed the highest degree of crystalline order after annealing. It was further reported that in the as-deposited state the films showed a slightly improved degree of crystallinity with increasing substrate temperature during deposition, which may be a result of the increased thermal energy available. This may be the equivalent mechanism responsible for improved crystallinity by post-deposition annealing, and could be regarded as an instant annealing effect. This instant annealing effect has the drawback that the deposition rate is reduced due to the increased thermal energy as mentioned above. It may be concluded that an instant annealing effect during deposition is required to ensure a certain initial degree of crystallinity, in

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**Fig. 1.** Experimental set-up for on-axis RF magnetron sputtering.

**Fig. 2.** AFM images (1200 nm × 1200 nm) of as-deposited films, sputter deposited at different substrate temperatures.

**Fig. 3.** AFM images (1200 nm × 1200 nm) of films annealed in air at 800°C for 1 h, sputter deposited at different substrate temperatures (200°C and 250°C; images reprinted from [19] with permission from Elsevier).
order to obtain a fully crystallized film surface by post-deposition annealing, displaying a distinct grain structure.

Fig. 3 shows that a dense polycrystalline surface with negligible or no porosity was achieved for substrate temperatures of 200 °C/250 °C during deposition, and RF magnetron sputtering deposition may be regarded as suitable for the production of thin film thermistor and radiation detection devices.

3. Electron-beam evaporation

Electron-beam evaporation of NiMn$_2$O$_4$+ powder was carried out by accelerating a 20 mA beam current emitted from a tungsten filament through a 5 kV potential drop onto the source material contained in a carbon crucible on a water cooled holder (pedestal), to cause sublimation (see Fig. 4), and the vapour condensed on a heated substrate. In the proximity of the active source area the density of emitted vapour particles is high and transport is diffusive. Away from the source a transition to straight molecular/ionic flow occurs [27,28]. The diffusive contributions can often be neglected if the source–substrate distance is large compared to the diffusive area. For conventional evaporator designs this occurs if the deposition rate is below conventional evaporator designs this occurs if the deposition rate is below 0.8 nm s$^{-1}$ (low deposition rate EBE) [28], in which case the thickness distribution of films can be modelled using the Hertz–Knudsen equation and the cosine law of emission. For high rate EBE more complex models have to be employed [29]. In this study, the beam current and high voltage were operated at the upper limit of the EBE kit in order to achieve a maximum deposition rate, which was $\sim$0.8 nm s$^{-1}$. This classifies the process as low deposition rate EBE and the film thickness $d$ was adequately described by [30]:

$$d = \frac{\kappa M_e}{2\pi \rho v s^2} \left(1 - \frac{1}{\sqrt{1 + (4h^2s^2)/(h^2 - s^2 + l^2)}} \right)$$

(2)

We have introduced the sticking coefficient $\kappa$ here to describe the fraction of evaporated particles which stick on the substrate and are not desorbed or specularly reflected. $M_e$ is the total mass of evaporated material, $\rho$ is the specific weight of the material, $s$ is the radius of the (ideally) circular active source area, all other parameters are defined in Fig. 4. This relationship was applied for a film evaporated on 1 mm thick soda-lime glass substrates, which had been cleaned with common liquid detergent, followed by an ultrasonic water bath containing dissolved decontamination agent (Decon 90) and finally by applying a refluxing procedure in hot isopropyl alcohol for 4 h (all substrates for EBE were cleaned in this way). During deposition, substrates were heated to 100 °C and the deposition chamber evacuated to a base pressure of $\sim$10$^{-3}$ Pa using a rotary backed oil diffusion pump. The optimised deposition parameters were: distance source–substrate $h = 85$ mm, source–film distance $= 25$ mm, filament diameter = 15 mm, and the radius $s$ of the electron spot on the source surface, i.e. defining the active source area, was 1.5 ± 0.3 mm.

It has been shown previously that the thickness profile agrees well with Eq. (2) at the inner area of the film [7], but a sharp drop in thickness occurred at the outer areas due to the shielding effect of the electron focusing cage (Fig. 4 shows the limiting source–cage–film trajectories). In the central regular film area the thickness variations was below 0.2 $\mu$m over a distance of $\sim$1.25 cm at a maximum film thickness of 1.7 $\mu$m. For the macroscopic film surface dimensions here, thickness variations may be assumed to be insignificant and the technique regarded suitable for the production of films for devices. To further reduce the thickness variations, a high evaporation rate set-up may be used, wherein an increased area of diffusive type transport particles possesses only a net vertical velocity component. The sticking coefficient was estimated from the total mass of evaporated material using Eq. (2) to be $\sim$0.8 ± 0.015.

For a film deposited on an Al$_2$O$_3$ substrate, it was demonstrated that the surface crystallinity was poor in the as-deposited state, but improved significantly with annealing in air at 800 °C for 30 min by forming a distinct ceramic grain structure with negligible or no porosity (Fig. 5). This behaviour is equivalent to sputtered films, and both methods may be considered to belong to the same class of deposition technique.

![Fig. 4. Experimental set-up for low rate electron-beam evaporation.](image-url)
Screen-printing is a fundamentally different technique, as described in the next section.

4. Screen-printing

Screen-printing is a direct printing technique, which can circumvent common problems in evaporation deposition processes such as compositional deviations of the films compared to the target. Powdered source material, tailored to produce the desired properties, is mixed and dispersed in chemically non-interacting carrier material, and the resulting paste is printed directly onto the substrate. The production of sub-micron grain sized NiMn$_2$O$_4$ powder via wet chemical processing of precursor oxalates has been described previously [20]. Preparation and control of the carrier (vehicle) and powder composition is the main technological challenge in this technique. The printing process, illustrated in Fig. 6, requires a pseudoplastic rheological behaviour of the paste with a slightly time dependent thixotropic effect. Initially, a sufficiently high paste viscosity is required to avoid premature flow of the paste through the open screen mesh, which must then reduce when a shear rate is applied to the paste by means of the blade stroke, in order to flow smoothly through the screen. After printing, the paste regains its original viscosity with a short time delay (thixotropy) to allow it to “flow” together, thus forming an even surface, but without disfiguring the printing pattern in the long term (Fig. 6) [31]. As a screen material polyester was selected over other common materials such as nylon or stainless steel [32]. Al$_2$O$_3$ thick-film substrates (CeramTec AG, Marktredwitz, Germany) containing 4 wt.% glass were cleaned by immersion in tartaric acid solution in an ultrasonic bath and rinsed with de-ionised water prior to screen-printing. The source powder was dispersed in a commercial vehicle (ESL Europe, type 403), which is composed basically of a solvent and an organic binder. It offered well controlled thixotropic behaviour if mixed with the source powder in the appropriate optimised ratio. In a second batch of samples an organic dispersing agent was added also to the paste to support deagglomeration of inorganic particles during mixing and homogenisation on a three-roller mill. Additionally, a glass frit was added for the second batch of samples to ensure strong bonding of the film to the glass containing substrate and to enable liquid phase sintering of the films. At sintering temperatures above ~600 °C standard glass frits exhibit a sufficiently low viscosity to allow essential rearrangement of grains and their compaction by capillary action [33]. This use of a glass frit for the design of functional thermistor...
A sintering densification process of the film is necessary, because the drying process and the thermal decomposition of the organic components result in porous films. The upper three images in Fig. 7 demonstrate this densification for films prepared with glass frit and dispersing agent containing pastes, as-deposited and sintered for 10 min and 30 min. For sintering times longer than 30 min no significant improvement in surface density occurred. Conversely, films without a frit showed an increase in pore size with sintering time up to 12 h due to grain growth (Fig. 8). Films without glass, deposited on a substrate, densify by constrained sintering, which means that film shrinkage occurs in the z out-of-plane direction (i.e. thickness reduction), but not in the x-y in-plane directions. In the case of pastes with a glass frit, liquid phase sintering leads to grain rearrangement which improves the grain packing and minimises porosity in x-y and z directions. A stronger shrinkage in z direction occurs compared to films without glass, where, in the absence of a liquid phase and grain rearrangement, the merger of grains during grain growth results in porous films. Grain growth in the glass containing samples on the other hand is minimised (see the lower three images in Fig. 7), because a glass
film covers the grains such that contraction by capillary action leads to a densification without grain merger.

The expected final reduced film thickness was calculated from the dimensions of the meshes used and from the volume fractions of the powder, vehicle, dispersing agent and glass frit in the printed paste.

The initial wet-layer thickness directly after printing is given by [35]:

$$d_{in} = \left( \frac{w}{w + u} \right)^2 \cdot D$$

(3)

where $w$ is the mesh opening, $u$ the screen wire diameter and $D$ is the mesh thickness governed by the wire diameter and the weaving technique. The wet-layer thickness (in our study 51 μm) reduces after printing during: (i) the evaporation of the solvent, (ii) the thermal decomposition of the organic additives including the vehicle and (iii) the sintering densification process. The reduced film thickness was calculated, assuming that the films, in a porous state after the evaporation of the carrier material, completely densified due to the following sintering process. In the case of films without the glass frit, the reduced film thickness after 30 min sintering was measured using laser profilemetry to be 30 μm, which was higher than the calculated 26 μm value. Therefore, it may be concluded that densification was incomplete, which is in agreement with the SEM images presented in Fig. 8. Films with glass frit were 25 μm thick and matched the calculated reduced film thickness of 25 μm, which confirms the desired densification mechanism of the glass frit.

Another technological task in SP is the optimisation of the “snap off” distance (Fig. 6). If the screen–substrate separation is too small, screen snap off from the substrate is delayed (screen sticking), which reduces film uniformity. A large separation causes the paste to ‘rip’ within the mesh resulting in an incomplete release of paste on the substrate. Attempts have been made to express both snap off conditions as functions of paste viscosity, initial screen stress, speed of the blade stroke, mesh size and blade–frame distance [35], but here an empirical adjustment was found to be more effective.

5. Discussion and conclusions

EBE and sputtered films show a dense surface due to a random shape of grains, which form a brick layer pattern exhibiting an intimate inter-granular contact with negligible porosity. These grains are formed during annealing from a poor crystalline amorphous-like phase. Conversely, in SP films the grain structure is inherited from the source powder and annealing leads to a grain growth and increased porosity, unless this is prevented by adding a glass frit which contracts the grains by capillary action resulting in a dense grain packing. It has been suggested previously that these fundamentally different film microstructures lead to different levels of crystal strain and disorder in the material [16], which can explain the differences in the charge transport behaviour reported.

The three film deposition processes discussed here have been used to produce films of different thicknesses. The deposition rate for RF magnetron sputtering was 5–10 nm min⁻¹ and the films deposited were ~700–800 nm thick, low rate electron-beam evaporation deposition was carried out at a rate of ~50 nm min⁻¹ resulting in films of 1–2 μm, and the screen-printed films were printed with a screen designed for 25 μm thickness, which was matched rather well for films including a glass frit. The deposition rates (sputtering and electron-beam evaporation) and expected film thickness (screen-printing) are in a typical range for the respective method applied. The resulting film thicknesses depended on the deposition time (sputtering and electron-beam evaporation) and the degree of film densification achieved (screen-printing).

The three processes show clear advantages as well as disadvantages over the others. EBE is probably the simplest technique, because the source powder can be of any average grain size and grain size distribution and needs no further developing, the deposition process does not require a specific gas atmosphere, and the deposition rate can be varied easily by adjusting the beam current. The surface properties are satisfactory, the films are polycrystalline and show negligible or no porosity after annealing. A major drawback is the lack of control of the film stoichiometry. In the deposition of ternary compounds such as NiMn₂O₄⁺, the cation (Ni: Mn) ratio in the films can vary significantly from the target composition [7, 36]. This problem is less severe in sputtering procedures, where the Ni: Mn ratio was shown to stay approximately constant [25]. The surface properties were as satisfactory as in EBE, but the technique may be technologically more challenging, because an argon plasma has to be formed in an environment of a balanced argon/oxygen gas ratio, which needs to be maintained by steady argon and oxygen gas flows and simultaneous evacuation, and monitored by gas flow meters and sensors.

The low deposition rate for sputtering and EBE makes the production of thicker films time consuming, which can be a problem due to the high sheet resistances found in the thin films presented here up to 10⁶ Ω at room temperature. For commercial application where low cost mass production is required SP may be more suitable. The technique is well established and has been industrially exploited extensively for making printed circuit boards, and more recently its use for production of various thick film sensors has been reported [37–40]. SP compromises on the surface quality though, as the porosity is comparatively high. Still, the authors believe that further paste development focusing on the powder/glass/vehicle composition should further reduce porosity, and SP is the strongest candidate to be commercially utilised for thermistor device fabrication.

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