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Thin film resistive materials: past, present and future

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Abstract. This paper explores the key developments in thin film resistive materials for use in the fabrication of discrete precision resistors. Firstly an introduction to the preparation of thin films and their fundamental properties is given with respect to well established systems such as NiCr, TaN and CrSiO. The effect of doping these systems in both solid and gaseous forms to further refine their structural and electrical properties is then discussed before the performance of more recent materials systems such as CuAlMo and Mn_3AgCuN are reviewed. In addition to performance of the materials themselves, the effect of varying processing parameters such as deposition pressure and temperature and subsequent annealing environment, as well as laser trimming energy and geometry are also studied. It is shown how these parameters can be systematically controlled to produce films of the required properties for varying applications such as high precision, long term stability and high power pulse performance.

1. Introduction

Thin film resistive materials possessing moderate resistivity and low temperature coefficient of resistance (TCR) properties are of great importance to the microelectronics industry for the production of precision thin film resistors (TFR) [1]. When used in the manufacture of discrete resistors, thin film materials can offer enhance performance and reliability and reductions in size when compared to alternative thick film and wirewound technologies. TFR's are typically employed when high stability, high accuracy or low noise are required in applications such as electronic measuring devices, strain gauges, pressure sensors and accelerometers [2].

As well as possessing a suitable resistivity and TCR, TFR's must be sufficiently stable so that any changes in resistance during their operating life can be reliably expected not to exceed a pre-specified value. Moreover the TFR must be able to be manufactured to this specification at a realistic cost.

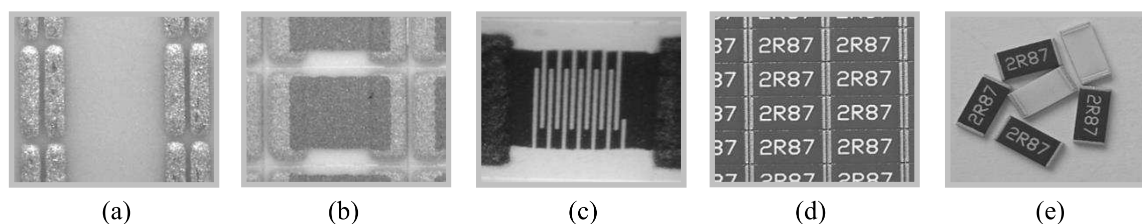

Figure 1. Typical SMD TFR process flow

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Figure 1 shows a typical manufacturing process flow for a surface mount device (SMD) TFR. A ceramic substrate is patterned with high conductivity electrodes (Fig 1a) before being deposited with a sub-micron (µm) layer of resistive material (Fig 1b). The resistive film is then heat treated to obtain the required TCR and pre-value resistance [3] which is then subsequently adjusted to target value by removing sections of the film to increase its overall effective length, usually by a laser trimming machine [4] (Fig 1c). The substrate is then encapsulated in a protective coating (Fig 1d) before being snapped into individual components to allow application of external wraparound terminations to permit subsequent soldering during PCB manufacture (Fig 1e).

Perhaps the two most important stages of the TFR manufacturing process are the deposition and heat treatment of the thin resistive film. Both the chemical composition and structure of the film are functions of the deposition environment and essentially provide the base electrical characteristics of the TFR. These key properties can then be modified by subsequent heat treatment of the film to fine tune its performance to the required specification.

This paper discusses the key electrical properties and characteristics of a number of currently well established and potential future thin film resistive materials and the effects of varying deposition and heat treatment process parameters on their performance and long term reliability.

2. Key electrical properties

Some of the most important fundamental electrical properties of the resistive material are its sheet resistance, TCR and resistance stability.

2.1. Sheet resistance (Rs)

As the measured resistance, *R*, of the thin film material is directly proportional to its resistivity, ρ, and inversely proportional to its thickness, *d*, it is usual to use the sheet resistance of the film, *Rs*, which is defined as ρ/d, to describe thin film resistors [5]:

resistance, $$R = \frac{\rho l}{dw} \quad (1)$$

however, $$\frac{l}{w} = \square \quad \text{(no. of squares in film pattern)} \quad (2)$$

hence, $$R_s = \frac{R}{\square} = \frac{\rho}{d} \quad (3)$$

2.2. Temperature co-efficient of resistance (TCR)

A parameter equally as important as sheet resistance is the temperature co-efficient of resistance (TCR) of the film. TCR describes the change in resistance of the film with change in its temperature *dR(T)/dT*. However, as *dR(T)/dT* is nearly constant for most metal films it is common practice to use an average TCR parameter [6]:

$$TCR_{Av} = \frac{1}{R_{Tref}}\frac{\Delta R}{\Delta T} \times 10^6 \; ppm/^{\circ}C \quad (4)$$

Where R_{Tref} is the initial reference resistance at 20˚C and ΔR is the change in measured resistance with a change in temperature ΔT from 20 to 70˚C.

2.3. Resistance stability, (ΔR/R)

Resistance stability or reliability is basically a measure of the change in resistance of the film against a certain specification over a period of time. There are a number of conditions under which the reliability of the component can be tested such as DC load, dry heat or humidity.

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The severity of the effects of a test condition on the resistor depends greatly upon film thickness. For thicker films the resistance value is inherently lower and hence the dc load voltage that can be applied will also be lower. Moreover, humidity is also likely to have less effect on a more robust thicker film.

Perhaps the most convenient and universal test condition is that of dry heat (temperature) as the test can be performed by simply storing the film in an oven. Dry heat stability tests generally entail measuring the change in the resistance value of the film, ΔR, following storage at the upper category temperature, usually 155ºC for axial leaded resistors and 125ºC for surface mount resistors, for a period of 1000hrs [7]:

$$\frac{\Delta R}{R} = \frac{R_e - R_i}{R_i} \times 100\% \tag{5}$$

Where R_i is the initial resistance and R_e is the end resistance following storage.

3. Thin film resistive materials

Materials used in the manufacture of thin film resistors typically require resistivities in the range 100-2,000 μΩ-cm and a TCR of ±50ppm/ºC. However, owing to their mechanical structure, bulk metals and alloys cannot have resistivities much in excess of the lower limit of this range and TCR is usually large and positive, see Table 1. Conversely, bulk semiconductors can readily satisfy these resistivity requirements, but this is usually at the cost of a very negative TCR.

Table 1. Electrical properties of some bulk metals and alloys [8].

Metal or alloy	Resistivity (μΩcm)	TCR (ppm/ºC)
Aluminium	2.7	4200
Chromium	12.9	4500
Copper	1.7	4300
Molybdenum	5.7	4600
Nickel	7.3	6500
Tantalum	13.5	3800
Ni 80% / Cr20%	100	170

Fortunately when deposited in thin film form most metals produce resistivity values which are much greater than that when in bulk form and frequently without acquiring a large positive TCR. There are a number of mechanisms which can produce this phenomenon as illustrated in Table 2.

Table 2. Mechanisms causing metal films to have resistivities greater than the bulk [9].

Description	Mechanism for resistivity increase	effect on TCR
Ultra thin film	Conduction electron scattering	$\rightarrow 0$
Insulating phase	Inter grain barriers	$\rightarrow -\infty$
Porous film	Construction resistance	$\rightarrow -\infty$
Trapped gas	Impurity scattering	$\rightarrow 0$
Discontinuous	Particle separation	$\rightarrow 0$
Double layer	TCRs cancel	$\rightarrow 0$
New structure	Fewer carriers	$\rightarrow 0$

The thin film material systems available for resistor manufacture can therefore largely be divided into

three main groups, depending upon the conduction mechanism present:

1. Metal alloys
2. Single metal systems
3. Cermets (metal-insulator)

3.1. Metal alloys

Metals are known to have a periodic crystal structure at low temperatures which provides a regular field for mobile electrons to flow [8]. Any distortions in this periodic nature of the lattice will distort the flow of electrons and thus increase its resistivity. This distortion can be caused by a number of defect types; lattice dislocations, contamination due to foreign atoms or atoms interstitially located within the lattice or non-stoichiometric ratio of constituents. Resistance can also be increased on a temporary basis due to lattice distortions caused by vibration increases with temperature; hence the reason TCR is generally positive for all metals. By alloying metals, the lattice distortions are dissolved in one another thus increasing the resistivity of the solution. In general the resistivity rises with increasing impurity concentration, reaching a maximum for an alloy concentration of approximately 50% impurity [10].

By far the most successful of the metal alloy systems used in the manufacture of bulk material resistors is nickel chromium, or Nichrome, with a composition of NiCr 80:20 wt.%. Over the years there have been a number studies undertaken on the properties of Nichrome thin film resistors [11-17]. Work has focused on the effects of varying substrate materials and process parameters on the electrical performance and structural properties of the fixed composition NiCr 80:20 binary alloys.

Among all the different substrates experimented, it was found that alumina substrates were the most suitable for the fabrication of thin film resistors due to their superior power handling capabilities [12]. By varying deposition parameters such as pressure, power and substrate temperature [17] films with sheet resistances of 10 to 1000 Ω/□, and TCR in the range +50 to +250 ppm/ºC could be achieved. Subsequent annealing of these films led to typical long term stability figures of better than 0.5% [16]. Optimum annealing conditions were found to be in the range 200 to 600ºC for 1.5 to 6 hours in air ambient [11-13]. Even to this day thin films of NiCr 80:20 still receive a substantial amount of interest in both resistor and strain gauge applications due to its high resistivity, low TCR and widespread commercial availability [14, 15]. To supply the increasing demand of high performance TFR`s in mid-1970`s, it was soon discovered that the TCR of the film could be reduced by increasing the chromium content in the film [18-24].

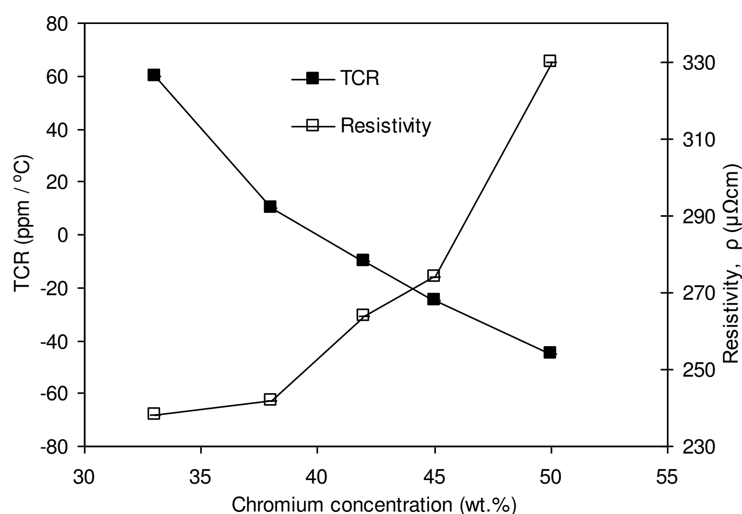

Figure 2. Variation of TCR and resistivity in NiCr films as a function of chromium concentration [23].

A plot of TCR and resistivity against chromium content for NiCr films deposited on oxidized silicon wafers is shown in figure 2. As can be seen the TCR steadily decreases while resistivity rises, with increase in chromium content in the film, passing the zero TCR line at approximately 40 wt.% having a value of around 250 μΩcm. These marked changes against the properties of 80:20 alloy are due mainly to two reasons; firstly the decrease in grain size of the film as the Cr content increased leading to a more amorphous structure having higher resistivity [22] and secondly the higher quantity of chromium oxide (Cr_2O_3) formation with negative TCR in the film [21]. The occurrence of amorphous and crystalline metastable phases are related to characteristics such as a large immiscibility gap between the two solid solutions (nickel fcc and chromium fcc solid solution), the existence of a relatively deep eutectic point and the presence of complex tetrahedral close-packed structures [19].

As chromium has a higher chemical affinity with oxygen than does nickel, then as its ratio in the film increases so does the amount of chromium oxide formed with residual oxygen in the deposition chamber [25]. Partial pressures in the range 2-6% reactive oxygen in the inert argon atmosphere were reported to give further increases in the content of chromium oxide in the film and hence a lower TCR [26]. There are a number of studies which report a near zero TCR for films with chromium content in the range 30 to 60 wt.%, both sputtered in argon and mixed argon/oxygen environments. It seems that in addition to film composition, accurate TCR control can be also be achieved through varying the deposition temperature and annealing treatment used. For films with negative as grown TCR, annealing in the temperature range 300 to 350ºC appears to be essential if a near zero TCR is to be achieved [21, 26]. Heat treatment methods rely on the mechanisms such as grain growth and reduction of impurities to reduce resistivity and in turn increase TCR. In addition to the desirable change in the TCR properties of the film, increasing the chromium concentration of the film and sputtering in an oxygen partial pressure can also improve the long term resistance stability of the film. Some research shows that stability figures as low as 0.3% change following 1000 hrs at 155ºC are not untypical for films sputtered in an oxygen partial pressure of $3x10^{-5}$ Torr [27]. Again the reason for this improved performance is attributed to the increase in chromium oxide formation at the surface of the film. As the chromium oxide grows it forms a protective passivation layer, similar to aluminium oxide, which protects the film from further attack [28].

Once it was realised that the addition of a third element, oxygen, into the film could give improvements in resistance stability, a number of investigations were carried on doping or modifying the NiCr alloy with a third element incorporated into the sputtering target itself. Probably the most widely documented of these elements is aluminium [29-32]. Additions of aluminium were proven to stabilise the film and reduce the TCR to values around zero [31]. Three regions have been found in the NiCrAl composition which result in highly stable resistive films with a very low TCR; one with less than 3at.% Al, one with 28-32 at.% Al and one with 45-60at.% Al. The role of aluminium is reported to be to stabilise the amorphous structure and state of ordering of the atoms in the deposited nickel chromium film. This can lead to stability figures of better than 0.08% following 1000 hrs storage in air at 155ºC [30]. Moreover the addition of aluminium allows thin film resistors with lower sheet resistances in the range below 10 Ω/□ to be produced [33]. Of the other elements which have been proven to improve the performance of NiCr films, Silicon is perhaps the most widely documented [34-36]. Additions of around 5 to 10 wt. % Si can produce films with TCRs of ±20 ppm/ºC and long term resistance stability of better than 0.05%. It is assumed that the improved thermal stability of the NiCrSi film is due to the diffusion limiting effect of silicon [35]. Not satisfied with the performance of ternary film compositions, there have also been several studies investigating the effect of adding two extra elements to the NiCr alloy to form quaternary composition films. Thin film resistors based on the Evanohm, Ni-Cr-Cu-Al alloy are the most popular and have been reported to possess very low TCRs of ±10ppm/ºC [37, 38].

Apart from NiCr the most popular metal alloy system used in the production of thin film resistors is probably copper nickel. Cu-45 wt.% Ni alloy, known as "constantan" is a typical material of low resistivity around 50 to 60 μΩ-cm and with a low TCR value of less than +50 ppm/ºC [39-41]. Films were deposited having resistivities below 50μΩ-cm making it suitable for low ohmic applications. However the lower limit for the sheet resistivity of the sputtered CuNi films was 1 Ω/□ [33]. In order to

produce thicker films of CuNi with even lower resistivities, electroless deposition is required. Films of up 10μm in thickness are achievable producing CuNi films possessing resistivities of around 40 μΩ-cm. Following post deposition stabilisation the TCR of the films shifted to near zero. However the electroless deposition rate of the alloy was reported to be remarkably slow [40].

An alternative low resistivity material to CuNi is copper aluminium molybdenum (CuAlMo). This recently developed material has been proven to produce films with sheet resistances of < 1 Ω/□ and low TCR of ±15 ppm/ºC. These properties when combined with its excellent long term stability make it ideal in precision current sense applications [42].

3.2. Single metal systems

As is evident for the nickel chromium films discussed above, the resistivity of the thin film is usually dominated by the background gases which are incorporated into the film during the deposition process, rather than the resistivity of the source material itself. With this realisation the focus of many researchers turned to the use of single metal systems as problems such as alloy composition control and fractionation could be automatically eradicated.

By far the most widely documented of the single metal systems is tantalum, reactively deposited in nitrogen to produce tantalum nitride (TaN) [43-55]. The as-deposited resistivity of pure tantalum is close to that of bulk tantalum (13 μΩ-cm). However when reactively sputtered in a nitrogen atmosphere the tantalum and nitrogen atoms combine to form a nitride which is trapped in the growing film. As shown in figure 3, this nitride produces an increase in resistivity and subsequent decrease in TCR [47].

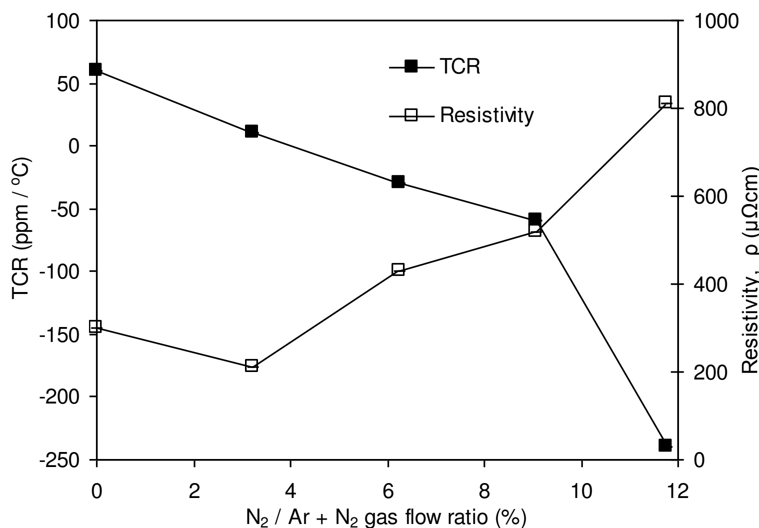

Figure 3. Variation of TCR and resistivity in TaN films as a function of nitrogen flow rate [47].

As can be seen TaN possesses similar electrical properties to that of NiCr and is generally used in the same mid-range area of resistor manufacture. However the intrinsic properties of linear TCR and physio-chemical inertness made TaN thin film material superior to the more popular NiCr for thin film resistors [43] and the mass production of TaN thin film resistors by magnetron sputtering with sheet resistivity of 50-100 Ω/□ and TCR of about -80 ppm/ºC was announced in the early 1980's [44]. Recent investigations have suggested properties similar to NiCr, with films sputtered to thicknesses of between 300-1000 nm possessing resistivities of 100-450 μΩ-cm and giving sheet resistances of around 10 to 100 0Ω/□ and TCR values of around -50 to -100 ppm/°C. Again post deposition stabilisation at around 200 to 400°C in both air and N_2 atmospheres was reported to produce films with TCR's of -5 to +5 ppm/°C and a resistance stability of better than 0.1% [45-47]. As with NiCr, to further develop the

properties of TaN, third element was introduced to produce a ternary system. There were two main issues with TaN; its negative as deposited TCR and the need to further improve its stability for precision resistor applications.

The first issue was tackled with the addition of copper [56, 57]. By varying the Cu concentration in a TaNCu sputtering target, as-deposited films of 150μΩ-cm with near zero TCR were produced. To further improve resistance stability, as with NiCr the incorporation of aluminium was used [58-61]. Reports showed that additions of 35-60 wt.% of Al to TaN could produce films of sheet resistance 50-600 Ω/□ with long term resistance stabilities of better than 0.05% [58]. Investigations were also conducted for binary systems of TaAl, with sheet resistance of around 150-300 μΩ-cm resulting. However the elimination of nitrogen from the film appeared to result in inferior stabilities of around 0.3% [59, 60].

3.3. Cermets

Electron conduction is greatly impeded by a potential barrier in the path of the flow and although the energy of the electron may be less than the barrier height there is a finite probability that the electron will pass the barrier. This form of conduction is called tunnelling and is an extremely useful mechanism for the production of high resistivity materials [5]. In the case of a cermet, a heterogeneous mixture of ceramic insulator and conductive metal material is formed producing the potential barrier, hence the name cermet. As the inclusion of ceramic, an insulator, has the effect of increasing resistance, cermet films usually find application at the higher sheet resistance values >1 kΩ/□.

The most successful cermet to date has been the chromium-silicon monoxide (CrSiO) system [62, 63]. Its main use in thin film resistor manufacture is in the 1k to 10 kΩ/□ range where standard alloy films such as NiCr and TaN are too thin. However, although CrSiO produces a thicker, more robust film at these higher ohmic ranges, its resistance stability and TCR are far inferior to that of the alloy and single metal systems [62].

3.4. Future candidates for Thin Film Resistors:

As discussed above, alloying different metals in suitable proportions (NiCr) or depositing metals in a reactive environment (TaN) is seen to bring resistivity and TCR in a suitable range for thin film resistor fabrication. But recent interest in a hybrid structure of Manganese alloy deposited in reactive nitrogen environment has revealed some unique properties [64]. This structure is called Manganese based Antiperovskite structure (AP) and is represented as Mn_3AX: where A represents a transition metal, present on the cubic corners and X represents an interstitial element like N or C, present at the body centred position [65], see figure 4.

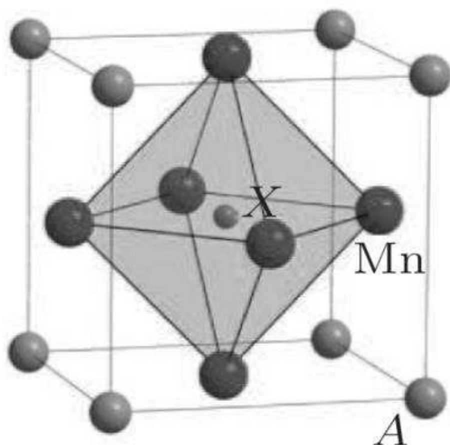

Figure 4. Mn based antiperovskite structure with a transition metal at the cubic corner and an interstitial atom at the body centre position [65].

Mn was always considered a suitable material for thin film resistor application because of its high resistivity and low TCR values [66]. Alloys based on Mn like Manganin and Zeranin have found widespread use in the production of shunt resistors [67], but because of a lack of proper research into the deposition of Mn based alloys, they have not been utilised in the manufacture of thin film resistors as extensively as NiCr or TaN.

Experiments have been conducted to study the AP structure with various transition metals like Ni [68, 69], Cu [70-72], Ag [73], Zn [74, 75], Ga [76], and depending upon the transition metals at the cell corners, this structure exhibits various interesting properties. Mn_3CuN is reported to show large magnetostriction [77], Mn_3ZnN shows negative thermal expansion [75], giant magnetoresistance in Mn_3GaC [76], superconductivity in Ni_3MgC [78], and lattice contraction in $Mn_3Zn(Ge)N$ [72]. Low TCR behaviour is so far shown to be exhibited by the Mn_3AN structure with Ni, Ag and Cu at the cubic corners [68], and electrical properties exhibited by these materials were better than the currently established thin film resistor materials with bulk resistivities in the range of 250 to 400 μΩ-cm [79], see figure 5a.

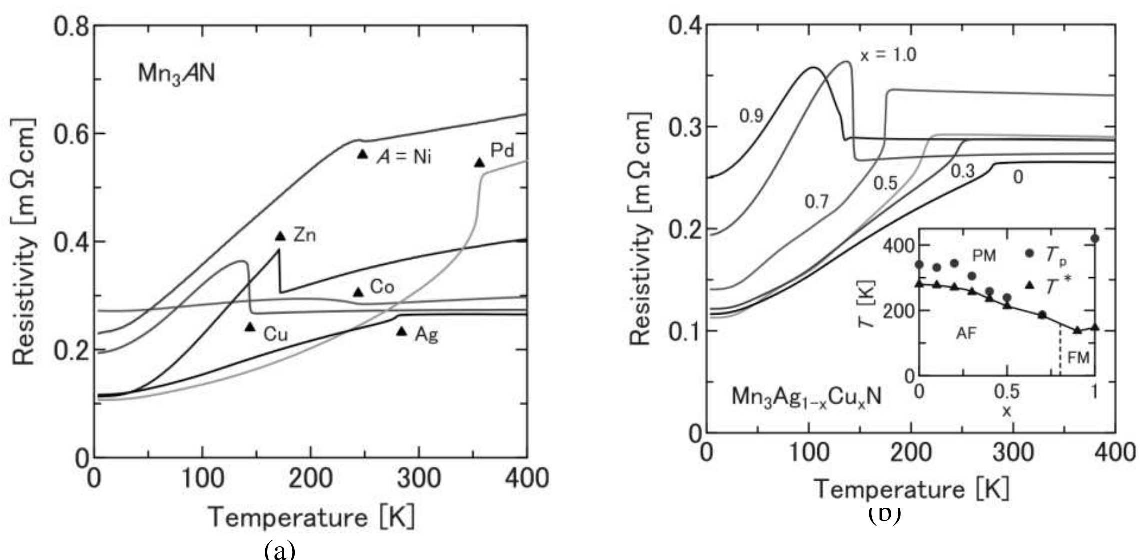

Figure 5. (a) Temperature dependence of resistivity for different transition metals at the cubic corner of the AP structure, (b) Temperature dependence of resistivity for different concentrations of Cu in the AP structure [79].

Partial substitution of the transition metal by a third metal is seen to provide better control to fine tune these properties. For example, partial substitution of Cu by Ge in Mn_3CuN was observed to introduce negative thermal expansion and better control over the magnetic transition temperature of the structure [80]. Similarly, a better control over TCR was gained by partially substituting Ag by Cu in Mn_3AgN, resulting in an average TCR <1 ppm/˚C between 294 to 304˚K, see figure 5b [79].

However, most of these studies have conducted electrical analysis of this structure on bulk samples prepared by solid state sintering of individual metal constituents [64, 68, 73, 79, 81, and 82]. And the few studies done on thin film did not prioritise electrical characteristics; hence sheet resistance values are not readily available. But films are reportedly deposited in thickness ranging from 100 to 400 nm [69-72], so it could be expected for them to have sheet resistances in the range of 10 to 1000 Ω/□. Moreover, sintered bulk samples have been observed to have an extremely low drift rate of 9.1 μΩ/Ω/year (0.001%), which is one order of magnitude lower than the current industry standards [81]. It has also been shown that the direction of this resistance drift can be shifted from negative to positive by annealing the antiperovskite structure for 30 min in air at 500˚C [82].

A sharp transition in physical and electrical properties is observed at magnetic transition temperature, above which magnetic orders re-arrange, and it supports the argument that re-arrangement of magnetic orders changes the band structure and is responsible for low TCR observed in these materials [79]. A low resistivity slope ($d\rho(T)/T$) in combination with a large resistivity (ρ_0) is considered to be the reason for the low TCR of Mn_3CuN, whereas in Mn_3NiN, a subtle balance between carrier mobility and carrier density, (which are both temperature dependent) at the transition temperature is held accountable for its low TCR [65]. In Mn_3AgCuN, it was proposed that quasi particle states break down due to strong magnetic scattering, and the short range orders generated exhibit negative TCR which counteract the positive TCR from phonon scattering, resulting in a net near zero TCR [79]. But still a unified reason for low TCR behaviour of the manganese based AP nitride (Mn_3AN) structure is not yet present [65].

4. Conclusions

The previous review has shown that there are primarily four material systems currently used in the manufacture of thin film resistors and there are potential novel materials under research with promising properties for future development. A summary of the basic electrical properties of these films is presented in Table 3

Table 3 Electrical properties of sputtered thin film resistor material systems.

Film type	ρ (μΩcm)	Rs (Ω/□)	d (nm)	TCR (ppm/°C)	ΔΩ/Ω (%)	Stabilisation	
						temp (°C)	time (hrs)
NiCr NiCrO NiCrSi NiCrAl NiCrCuAl	100-500	10-1000	10-500	<5	0.1 0.01 0.08	200-400	2-5
CuNi CuAlMo	50 80	1-50 0.1-10	500-5000	<15	0.15 0.1	100-500	1-5
Ta TaN TaNAl	100-450	10-1000	300-1000	<10	0.3 0.1 0.05	200-400	2-5
CrSiO		1-10k		<25		200-600	2-5
Mn_3AgCuN	250-400	10-1000	100-400	<5	0.001	500	0.5

Alloys of nickel and chromium either in binary form or with small additions of doping elements such as aluminium or silicon are used in the mid-range of sheet resistance from approximately 10 to 1000 Ω/□ and possess excellent TCR and long term stability properties. Alloys of copper and nickel and copper, aluminium and molybdenum find use in the lower sheet resistance range of around 0.1 to 50 Ω/□ and have similar stability properties to that of NiCr.

Single metal systems of tantalum, reactively sputtered in nitrogen are also used in the same mid-range sheet resistance area as nickel chromium, but possess slightly worse TCR and stability properties. The main advantage of TaN is in its corrosion resistance under humid conditions, meaning it usually finds use in the high reliability military and aerospace applications.

Ceramic metallic systems of chromium silicon monoxide are used when higher sheet resistances in the kilo-ohm range are required. TCR and stability are poor in comparison to the alloy

and single metal systems; however the inherent high resistivity properties of the cermet systems mean they continue to find widespread application.

Because of their suitable resistivity in the range 200 to 400 μΩ-cm and better TCR (<5 ppm/˚C) than NiCr and TaN, hybrid structures like Mn based antiperovskite have the potential to be used to manufacture future thin film resistor of mid-range sheet resistance value. But researches concerning these materials are still in the initial stages and a clear understanding of the reasons behind their unique behaviour needs to be fully understood. It is very much necessary to conduct further studies on these structure and is hoped that this will help to overcome the challenges related to successful deposition of thin films of this structure.

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