METAL FILM PRECISION RESISTORS: RESISTIVE METAL FILMS AND A NEW RESISTOR CONCEPT

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Abstract

Metal-films for precision resistors combine a very low temperature dependence of the electrical resistance with a tolerance of the resistance of only 0.1%. Corrosion resistance and adhesion to the substrate are of major importance. There are different classes of materials being utilised. For low ohmic applications, we use Cu–Ni alloys with a composition of about 65 at.% (atomic percent) of Cu. For this special alloy, the low temperature coefficient of the resistance (TCR) is a stable, intrinsic property. For most alloys, however, annealing is essential to approach the state of zero TCR. This is the case for the NiCrAl alloys, used for the mid-range of resistances and for SiCrN for high ohmic applications. In high ohmic films, metals are often combined with non-metallic substances like oxides or nitrides. Variation of alloy composition, sputtering conditions and annealing procedures are important for obtaining optimum thin-film properties. Important tools for thin-film characterisation are electron microscopy and related techniques together with high-temperature resistance measurement.

Keywords: resistor; sheet resistance; temperature coefficient of the resistance (TCR); metal films; sputtering; trimming; SiCrN, SiCrO, NiCrAl, CuNi.

1. Introduction

The metal-film precision chip resistor MPC01 is characterised by $|TCR| < 25$ ppm/K, and by a tolerance of the resistance after trimming of only 0.1%; it is a surface mounted device (SMD), size 1206. The TCR is defined by:

$$ TCR = \frac{1}{R} \frac{dR}{dT} $$

(1)
Design of MPC

Fig. 1. The metallic precision chip resistor MPC01.

where $R$ is the total resistance or alternatively, the sheet resistance $R_s$. The sheet resistance is defined by:

$$R_s = \frac{\rho}{d}$$

(2)

where $d$ is the film thickness; this is an important parameter in thin-film resistor practice.

The heart of a thin-film resistor (see Fig. 1) consists of a metal film sputter deposited onto sintered $Al_2O_3$ substrates to thicknesses between 0.01 and 0.5 $\mu m$. Research into metal films for (MPC) is focused on finding, understanding and improving materials with very low TCR and of sufficient stability.

The classical resistive film used within Philips consists of an alloy of Ni, Cr and Al with a resistivity of 150–300 $\mu\Omega cm$. Using different resistor patterns and film thicknesses, the range of 10 $\Omega$ to 100 $k\Omega$ is covered. For values beyond this range, alloys of CuNi (50 $\mu\Omega cm$) and SiCrN (2500 $\mu\Omega cm$) have been developed. This development implies the finding of the proper combination of film composition, sputtering conditions, annealing temperature and annealing ambient. In this context, theory is of very limited use. Even for simple single-phase materials, quantitative theories predicting electrical properties are lacking. Therefore, the development often has an trial and error character and there is much room for materials research in the field.

The central topic in this paper is the temperature coefficient of the resistance. In Sec. 2, some principles are given for realising zero TCR; Sec. 3 deals with the practice of sputtering, sputter target fabrication and the measurement of $R$ and TCR during heat treatment of the sputtered films.

The most important alloys are reviewed in Sec. 4. In the classical type of resistor, variations in thin-film composition and heat treatment are limiting factors in the TCR accuracy. In Sec. 5, it is shown how, in a new type of resistor, the TCR can be trimmed to zero, eliminating materials problems to a large extent.
2. The realisation of near zero TCR

Most pure metals have a positive TCR of several thousand ppm/K. By alloying, the TCR can be reduced but it generally remains positive. This is not the case for metastable (amorphous) states. Negative TCR occurs in several amorphous metals and in other metastable states like the so-called quasicrystalline materials [1].

Stable alloys with near zero TCR (<25 ppm/K) are rare. A few compositions of CuNi and AgPd have zero TCR. This is brought about by special magnetic and electronic effects [2] and for these alloys zero TCR is an equilibrium property. On the other hand, there are many more non-equilibrium states in which TCR equals zero. As mentioned before, various amorphous alloys show negative TCR; upon crystallisation, the TCR will become positive, because the majority of all crystalline alloys have positive TCR. Partial crystallisation therefore forms an interesting means for producing materials with a new zero TCR. This is illustrated in Fig. 2. Upon annealing at temperature $T_0$ for a given period of time, a mixture of amorphous and crystalline constituents results, with a total TCR of zero. Upon further heating, the amorphous remainders will crystallise progressively, accompanied by an increase in TCR above zero.

The TCR in such mixtures of amorphous and crystalline constituents depends not only on the individual TCRs but also on the spatial distribution of the phases (the microstructure of the film) and on their resistivities [1].

![Fig. 2. Variation of TCR during crystallisation. The sputtered film is in an amorphous state with negative TCR; upon heating, crystals with positive TCR are formed. At $T_0$, zero TCR is reached.](image-url)
The state in which $TCR = 0$ is called metastable; at room temperature nothing changes. Upon heating above $T_0$, however, further crystallisation will occur, spoiling the zero TCR. Heating above $T_0$ should therefore be avoided during the course of production and use.

The TCR accuracy depends on the precision in both annealing treatment and film composition. Also the degree of amorphism may depend on sputter conditions and thereby influence the final TCR. An improved accuracy is aimed at in the concept of the trimmable TCR resistor, the TICR. In the TICR, one-half of the resistor has positive TCR, the other half negative TCR. Laser trimming of both halves permits the simultaneous adjustment of both TCR and resistance of the resistor as a whole.

3. Experimental

The testing of new materials includes the following steps:

- Fabrication of sputter targets of the alloy compositions of interest. This is done by arc melting and casting or by powder technological procedures like sintering or hot pressing.
- Sputtering of thin films, sometimes with reactive components added to the sputtering gas. An important point is the transferability of results from laboratory sputtering units to industrial practice.
- Characterisation of the films: are they amorphous/crystalline, what is the microstructure, thickness, chemical composition? What are the electrical properties and how are these affected by annealing of the film? Annealing may be done in various atmospheres, sometimes resulting in completely different properties.

The results are used to improve alloy composition, sputter conditions and annealing procedures until the films are fit for use.

3.1. Sputtering and target preparation

Alloy targets for laboratory use are usually arc melted and cast. For materials like SiCrO, the powder metallurgical route has to be followed to produce sputter targets. An alternative for producing films of materials like SiCrO and SiCrN is reactive sputtering. A cast SiCr target is used, and the O or N is added to the sputter gas, from which it is built into the growing film [2].
3.2. Measuring R and TCR during heat treatment

When a pure, crystalline metal is heated, its resistance increases as a rule. This is caused by the increased scattering of the conduction electrons by lattice vibrations. Upon cooling, the initial value of the resistance is resumed; the behaviour is reversible. An exception occurs when heating and cooling have caused lasting changes. Such irreversible changes can be the crystallisation of parts of an amorphous film, the formation of oxides, changes in grain size or dislocation density, the formation of cracks and so on. Reversible as well as irreversible changes can be traced by resistance measurement as a function of temperature. A suitable temperature profile to follow processes like crystallisation is shown in Fig. 3a.

Isothermal annealing at 200 and 300°C is interrupted by cooling below 100°C. The sample is then heated to a higher annealing temperature \( T_a \). The resistance is measured during these steps. The results for a \( Si_{70}Cr_{30} \) film are shown in Fig. 3b where \( R_0 \) is given as a function of temperature (time increases along the curves as indicated by the numbers).

The TCR at any point of the curves is given by the slope, \( dR_0/dT \) over \( R_0 \). During the first heating (see line 1–2 in Fig. 3b), the TCR has a value of about \(-800 \) ppm/K. Upon cooling (see line 2–3 in Fig. 3b), this value is raised to \(-200 \) ppm/K. This proves that irreversible changes have taken place, in spite of the fact that electron microscopy and diffraction do not show the least signs of crystallisation at this stage. The irreversible changes are tentatively attributed to configurational changes of the atoms in the amorphous phase. Crystallisation of the \( Si_2Cr \) phase sets in at 275°C; it is accompanied by a steep rise in resistance, see e.g. line 4–5 in Fig. 3b. After cooling from 300°C to 75°C (point 6), the slope \( dR_0/dT \) is positive and so is TCR. At room temperature the value of the TCR is even more positive due to the curvature of line 5–6. The ageing temperature \( T_o \), required to obtain zero TCR (at room temperature), is found to be 280°C, which is too low for practical application. The \( T_o \) values, as obtained from these experiments, should be confirmed by isothermal annealing at \( T_o \). The influence of ageing time, heating rate, etc., can then also be studied.

Apart from the low value of \( T_o \), the serious curvature of lines like 5–6 in Fig. 3b is another disadvantage of these \( Si_{70}Cr_{30} \) films. This curvature is connected to the properties of the \( Si_2Cr \) phase [3]. The curvature is defined by:

\[
C = \frac{d(TCR)}{dT}
\]  

(5)

For precision resistor, \( C \) must not exceed \( 0.1 \) ppm/°C. In Fig. 3b it is seen that \( C \) becomes far too high as soon as the formation of \( Si_2Cr \) sets in.
4. Results and discussion

4.1. Introduction

We confine ourselves to three materials, SiCr, NiCrAl and CuNi, suitable for high-, mid- and low-ohmic resistors. SiCr has a high resistivity (2000 $\mu\Omega \text{cm}$) which, moreover, can be raised by the usual addition of oxygen or nitrogen [2]. These Si–Cr–O/N alloys are used for high-ohmic resistors (>100 k$\Omega$). For the thinnest layers, which are only 10 nm, we have

$$R_s = \frac{\rho}{d} = 2k\Omega$$ (4)

and for a resistor of 500 squares, we find a total resistance of 1 M$\Omega$.

NiCrAl is the classical Philips alloy for the range 10 $\Omega$ to 100 k$\Omega$. The resistivity varies between 150 and 300 $\mu\Omega \text{cm}$, depending on composition. NiCrAl is the only material used in precision resistors at the moment. For low-ohmic thin-film resistors, CuNi can be used. Among the low TCR alloys, CuNi has one of the lowest resistivities, 40–45 $\mu\Omega \text{cm}$, so that sheet resistances below 1 $\Omega$ are attainable.

4.2. SiCr for high ohmic applications

Silicon and chromium form several compounds as shown in the phase diagram in Fig. 4. At room temperature, the resistivity increases
monotonically from Cr to Si. For sputtered thin films, this relationship is shown in Fig. 5.

The TCR is positive for all phases except Si and for the amorphous phase which can be formed by the sputtering of SiCr with 70–80 at.% Si. These amorphous films crystallise below 300°C (see Sec. 3.2) which is too low to
Fig. 4. Equilibrium phase diagram for Si–Cr alloys. Sputtered Si$_{70}$Cr$_{30}$ films are amorphous; upon heating they decompose into the equilibrium phases Si$_2$Cr and Si.

be practical. The addition of nitrogen (and some other elements, see [2]) raises the crystallisation temperature to acceptable values.

Nitrogen, supplied to the sputter gas, is trapped in the growing film. It contributes to the resistivity and diminishes the curvature, provided that the proper sputter conditions are used. The effect of nitrogen on $T_0$ (the temperature required for obtaining zero TCR) is shown in Fig. 6, together with the $R_o$ obtained after annealing at $T_0$.

The ageing ambient temperature has some influence as well. An example of resistance measurement during heat treatment is given in Fig. 7. A 20 nm film is sputtered using 7 vol.% N$_2$ in Ar and an Si$_{70}$Cr$_{30}$ sputter target. The change of $R_o$ during heat treatment in air is shown in Fig. 7. A horizontal slope is found after cooling from 450°C down to 25°C. In this state, the curvature has the acceptable value of 0.2 ppm/°C$^2$. In other words, the problems existing for Si$_{70}$Cr$_{30}$, outlined in Sec. 3.2, are overcome by the addition of
Fig. 5. Resistivity versus composition of sputtered Si–Cr films.

nitrogen. An important point is that the formation of Si$_2$Cr which started around 300°C for films without nitrogen (see Fig. 3b) is now postponed to 600°C. When this temperature is reached, Si$_2$Cr is formed, resulting again in considerable curvature (see Fig. 7). Of course, this is of no consequence since zero TCR has already been reached at lower $T_a$.

4.3. NiCrAl

Alloys of nickel, chromium and aluminium were patented by Mooy and
Franssen in 1972 [4]; it still is the material most frequently used in metal film resistors. Films with zero TCR can be produced along the lines described in Sec. 2. Sputtered films of NiCrAl alloys generally have a negative TCR. Depending on composition and deposition conditions, they are in the amorphous state or in metastable crystalline states. The stable states are given by the phase diagram (see Fig. 8) which is crowded with single phase areas (dark in Fig. 8) and with equilibria between two or three phases (white triangles). This dense filling of the phase diagram implies that small changes
in alloy composition cause considerable shifts in the phase equilibria. Although the zero TCR films are only halfway to equilibrium (see Fig. 2), the phase diagram is useful in predicting the phases that may appear during heat treatment. The annealing temperature $T_0$ required to obtain zero TCR varies strongly with composition (see Fig. 9). The fact that there is no obvious correlation between the $T_0$ mapping in Fig. 9 and the phase diagram (see Fig. 8)
shows the limitations of the latter. On the way towards equilibrium, several unexpected situations may occur. Figure 10 shows the results of heating an Al-rich alloy in the electron microscope. The crystallisation of one of the equilibrium phases (NiAl) starts at 450°C; the formation of the $Al_8Cr_5$ phase is retarded until 500°C. Such events, of course, do influence the electrical properties obtained after cooling to room temperature and thereby affect $T_0$ as well.
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In general, the electrical properties of a multiphase film depend not only on the electrical properties of the individual phases but also on their amount and spatial distribution [1]. Besides, all types of defects, ranging from atomic displacements to cracks and voids, may affect the electrical properties and thereby $T_0$. Another important factor is whether the sputtered film is completely amorphous or already contains traces of crystalline phases. The influence of the impurity content in the sputtering gas is illustrated in Fig. 11; the differences in the degree of crystallinity are clear.

The NiCrAl alloys have a thin but very protective oxide layer, which is responsible for their excellent corrosion resistance [5,6]. For the full development of this property, the NiCrAl films are heated in air at 350°C. This is why

Fig. 10. Crystallisation sequence in an amorphous NiCrAl film.
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Fig. 11. Crystallinity and texture of NiCrAl films as a function of the sputtering base pressure (TEM).

$T_0$ should not be lower than 350°C, otherwise the TCR would turn positive during the oxidising anneal.

4.4. Cu–Ni alloys

In the Cu–Ni alloy system, there are two compositions with zero TCR [7] (see Fig. 12.). The resistivities are below 50 $\mu\Omega$cm, making CuNi suitable for low-ohmic applications. The lower limit for the sheet resistivity of sputtered CuNi is about 1 $\Omega/\square$. It is bounded by the maximum thickness of sputtered layers, which is about 0.5 $\mu$m.

Recently, we have shown that much thicker layers with comparably good properties can be produced by electrodeposition, expanding the range of sheet resistivities considerably.

It has been speculated that the special electrical properties, in particular the (below) zero TCR of CuNi alloys, are related to tiny clusters of Ni atoms [1]. Direct evidence is lacking because Cu and Ni atoms can hardly be distinguished by electron microscopy and related techniques.
We also attempted to dilute CuNi by SiO₂, using hot pressed sputter targets containing broadly equal volumes of CuNi and SiO₂. We succeeded in producing CuNi films which, in the aged condition, combined the low TCR of CuNi with huge sheet resistances. The reproducibility, however, is poor.

By electron microscopy, it could be confirmed that upon ageing, percolating paths of CuNi particles are present throughout the film. The fact that only a small fraction of these CuNi strings extends from one end of the film to the other explains the ultra-high sheet resistivities.
5. TTCR

Variations in materials composition and heat treatment are limiting factors for the accuracy. In a new resistor concept [8], these problems are overcome (see Fig. 13a). Resistor halves with positive and negative TCR are combined to form a single resistor with a trimmable temperature coefficient of the resistance, the TTCR. Conventional laser trimming, applied to both halves,
permits the setting of the total resistance as well as the TCR. Very low temperature dependencies have been realised in this way.

**Principle**

The total resistance is given by:

\[ R_t = R^+ + R^- \]  \hspace{1cm} (5)

the total TCR by:

\[ TCR_t = \frac{\frac{1}{R_i} \cdot \frac{dR_t}{dT}}{R^+ + R^-} = \frac{R^+ \cdot TCR^+ + R^- \cdot TCR^-}{R^+ + R^-} \]  \hspace{1cm} (6)

Denoting the ratio of \( R^+ \) and \( R^- \) by \( Y \), equation (6) can be rewritten as:

\[ TCR_t = \frac{TCR^- + Y \cdot TCR^+}{1 + Y} \]  \hspace{1cm} (7)

Thus the TCR, is determined by materials constants (TCR\(^+\) and TCR\(^-\)) and by the ratio \( Y = R^+/R^- \). This ratio can be adjusted by trimming one of the resistor halves until the TCR equals zero. This occurs for \( Y_0 = -TCR^-/TCR^+ \) [see equation (7)].

The resistance can then be raised to the desired value by increasing both \( R^+ \) and \( R^- \). Zero TCR is maintained as long the ratio of \( R^+/R^- \) remains as \( Y_0 \), therefore \( R^+ \) and \( R^- \) should increase proportionally in this exercise. In practice, the trims of \( R^+ \) and \( R^- \) to arrive at a given combination of \( R_t \) and TCR\(_t\) can be calculated straightforwardly from TCR\(^+\), TCR\(^-\), and the initial values of \( R^+ \) and \( R^- \). These last four quantities can be measured using the mid-contact of the TTTCR (see Fig. 13a).

Results of a laboratory experiment with CuNi films are given in Fig. 13b. The part with a positive TCR consists of Cu\(_{70}\)Ni\(_{30}\) (TCR = 50 ppm/°C), the other part is made of Cu\(_{64}\)Ni\(_{36}\) with TCR = -30 ppm/°C. Figure 13b shows the variation of the resistance (standardised) as a function of temperature. The lines \( R^+ \) and \( R^- \) represent the Cu\(_{70}\)Ni\(_{30}\) and Cu\(_{64}\)Ni\(_{36}\) parts. The line \( R_{\text{total}} \) gives the resistance of the entire resistor before trimming; the TCR, which is then 10 ppm/°C, is reduced to 1 ppm/°C by the final trimming (see the line \( R_{\text{trimmed}} \)).

6. **Summary and conclusions**

The quality of precision resistors is governed by the temperature dependence of the resistance. For applications in the fields of electronic data
processing and measuring equipment, $R$ should change less than 0.25% over 100°C i.e. $TCR < 25$ ppm/°C. This conflicts strongly with usual metal behaviour.

In order to find alloys suitable for resistor practice, the following routine has been developed.

(1) The production of sputtering targets of promising alloy compositions (by casting or powder metallurgy).
(2) Sputtering of thin films in various ways.
(3) Characterisation of the sputtered films:
   (a) The electrical properties as a function of temperature are measured as routine (heat treatment is often vital to the quality of the production).
   (b) The composition, uniformity, microstructure etc., are characterised when appropriate. The results are used for feedback and cycle 1–3 is repeated until the goals are reached.

This way, various materials for use in the metal-film precision chip resistor (MPC) (a product of Component Roermond) have been developed and/or improved. Examples are CuNi for the low-ohmic end of the resistor range and SiCrN for the high end. Variations in materials composition and heat treatment are limiting factors for the accuracy.

In a new type of resistor, these problems are overcome. Two resistor halves with positive and negative temperature dependence are combined to form a single resistor with trimmable temperature coefficient of the resistance (TTCR). Applying conventional laser trimming to both halves permits the setting of both the total resistance and the temperature dependence. Very low temperature dependencies have been realised this way.

REFERENCES
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Authors’ biographies

Jan van den Broek, metallurgist, has been active in various projects in the fields of physical and chemical metallurgy since he entered Philips Research in 1967. His current work is on metal films for precision resistors, comprising alloy design, the realisation of sputtering targets by casting or by powder metallurgy, sputtering of the alloy films, heat treatment in order to adjust physical properties, characterisation of the films: electrical properties, microstructure, etc.


Richard A.F. van der Rijt studied physics at the HBO, Eindhoven; after graduation he joined the Philips Research Laboratories Eindhoven (1993–). He is currently involved in the research and development of precision thin-film resistors (SMD components).

Janssen T.M. Jos graduated in Chemical Process Technology at the University of Technology, Delft, in 1982. He was engaged by Philips Electronic to work on the development of optical components for Compact Disc Players and Projection television sets. In 1989 he joined the Fixed Resistors Business Unit where he is currently in charge of process and product development for high-end applications.