



Improvement of reliability for high-ohmic Cr–Si thin film resistors in a heat and humid environment: Removing moisture source by electrocatalytic decomposition of water

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ABSTRACT

The reliability of high-ohmic Cr–Si thin film resistors in a heat and humid (HH) environment is often guaranteed by packaging materials as protection layers. Our previous study shows that Cr–Si–Ni film has a better performance in HH resistance than Cr–Si film in the same experimental conditions, and the proposed hypothesis that the electrocatalytic activity of Ni in the resistive film leads to water decomposition is considered as the reason behind it. In addition, NiMo alloy film is reported to have a better electrocatalytic activity on water decomposition than Ni film. So an issue arises: will the Cr–Si film co-doped by both Ni and Mo have a better performance in HH resistance than Cr–Si film only doped by Ni? In our current full paper, Cr–Si–Ni–Mo and Cr–Si–Ni films with low temperature coefficient of resistance (TCR) were prepared and compared in the same conditions to study their performance in a HH environment, which may address the raised issue from experimental data and further verify the proposed hypothesis. Possible reasons for the experimental results were discussed. If the proposed hypothesis is true, another way may be opened up to improve the reliability of high-ohmic Cr–Si resistors in a HH environment.

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1. Introduction

Resistor is one of the commonly used electronic components. Its reliability is critically important to the stability of circuit response over long hours of operation, which can be learned from the series failure model proposed by Weibull [1]. Whether a resistor can operate steadily is not only closely related to resistive film but also greatly influenced by its operating environments, especially those aggressive ones. High-ohmic Cr–Si thin film resistors are preferred in application due to high resistivity of Si-rich resistive films that may help to the miniaturization of resistors, which is the requirements of high-density ICs. However, when this kind of resistors works in a heat and humid (HH) environment, they often show instability and even fail due to resistance change ratio ($\Delta R/R$) out of the specified resistance tolerance (RT), which limits the wide application of Cr–Si thin film resistors. We have attempted to solve the issue from the packaging materials that are used for resistor protection [2,3]. Although some progress is made for high-ohmic Cr–Si thin film resistors with resistance value less than 300 k Ω ($\Delta R/R \leq 0.1\%$ after heat and humid experiments), higher-ohmic Cr–Si resistors such as 2.2 M Ω show a poor performance ($\Delta R/R$ is often more than 0.4% after experiments) regardless of epoxy (EP) or phenolic (PF) resin based paints, or PF/EP composite paints. The function of protection

layers seems limited for higher-ohmic Cr–Si resistors. In our previous research [4] it has been found that metal Ni can improve the ability of Cr–Si film to resist heat and humidity to an extent. The reasons behind it were discussed, which may be attributed to the electrocatalytic activity of Ni in Cr–Si–Ni film via the decomposition of water. If so, another way may be opened up to improve the reliability of high-ohmic Cr–Si resistors in a HH environment.

It has been reported that Ni alloy films with other metals such as Mo and W have a better electrocatalytic activity on water than pure Ni film [5–11]. If the electrocatalytic activity of metal Ni is considered to be responsible for the performance improvement of Cr–Si–Ni film in HH resistance, will the ability of Cr–Si–Ni film to resist heat and humidity be further improved when metal Mo is introduced? With the above raised issue, we prepared Cr–Si–Ni–Mo resistive films and studied their comprehensive properties [12]. Preliminary experiments show that 2.2 M Ω Cr–Si–Ni–Mo film resistors have a good performance in a HH environment with a $\Delta R/R$ less than 0.4%. However, the above study cannot very surely answer the raised issue due to the difference in film properties caused by film deposition methods between Cr–Si–Ni [4] and Cr–Si–Ni–Mo [12] film resistors.

In this study Cr–Si–Ni–Mo and Cr–Si–Ni film resistors were prepared and compared in the same conditions to study their performance in a HH environment, which may answer the raised issue from experimental data. Meanwhile, the chemical reaction mechanism determining the fate of resistive films working in a humid environment is discussed from

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the perspective of electron transfer based on experimental results and the electron structure characteristics of *d* orbits of transitional metals Cr, Ni and Mo, which may be the key to understand the raised question.

2. Experimental

2.1. The preparation of Cr–Si–Ni and Cr–Si–Ni–Mo film

Studies in [12] have shown that resistive films with micro-defects and rough surface are sensitive to water and easy to fail in a HH environment due to $\Delta R/R$ out of RT. In addition, resistors with a big temperature coefficient of resistance (TCR) more than ± 50 ppm/°C show strong temperature dependence and are easy to fail due to $\Delta R/R$ out of RT. In order to reduce the interference of these factors to HH experiments, Cr–Si–Ni and Cr–Si–Ni–Mo films were deposited at a low current of 150 mA using a TRC2020 magnetron sputtering vacuum coating machine in this study based on our previous study [12]. Resistive films using this deposition method have a better quality (less micro-defects and smoother surface) and a smaller TCR (less than ± 10 ppm/°C). The detailed preparation conditions of Cr–Si–Ni and Cr–Si–Ni–Mo films in the paper are summarized in Table 1.

2.2. HH experiments and resistance change

In this study accelerated experimental method in [4] was used, in which boiling–electrifying step was alternatively performed for coated resistors. After boiling operation of coated resistors in a boiling autoclave, water may gradually permeate through the protective layer of a resistor and expose the resistive film of the resistor to a moisture environment due to the degradation of the coating. In the next electrifying operation, the water permeating through protective layer and appearing on the surface of resistive film in the previous operation will take place chemical reactions with metals in Cr–Si–based alloy film under the function of electric field. As a result, a resistor will fail due to an increase of resistance value caused by the electrochemical corrosion (ECC) of resistive film. Herein, the presence of adsorbed water on the surface of resistive film is the root cause of failure for a working resistor. The boiling–electrifying step can be repeated many times according to the requirements of HH experiments, and finishing a boiling–electrifying operation is considered a cycle of HH experiments.

2.3. Characterization of Cr–Si–Ni and Cr–Si–Ni–Mo deposition films

The surface morphology of the annealed Cr–Si–Ni and Cr–Si–Ni–Mo films was examined by a JEOL/JSM-6700F scanning electron microscopy (SEM) to observe micro-defects. The two resistive films were also analyzed on a Rigaku D/MAX-2500 X-ray diffractometer (XRD) with Cu-K α radiation, the data of which may help to analyze the change behavior of resistance value in HH experiments.

Table 1

Preparation conditions of Cr–Si–Ni and Cr–Si–Ni–Mo thin films.

Preparation conditions	
Alloy target	Cr–Si–Ni [4]* Cr–Si–Ni–Mo [12]*
Columnar alumina substrate	$\Phi 1.0$ mm \times 5.0 mm
Base pressure (Pa)	3×10^{-3}
Work pressure (Pa)	6×10^{-2}
Work voltage (V)	300–500
Work current (mA)	150
Argon flow rate (sccm)	15–20
Deposition time (h)	2.5
Film annealing	550°C/2 h/N $_2$

* Cr–Si–Ni–Mo target (40 wt% Cr, 55 wt% Si, 3 wt% Ni and 2 wt% Mo) was designed and prepared based on Cr–Si–Ni target (40 wt% Cr, 55 wt% Si, 5 wt% Ni), and the two alloy targets with size about $380 \times 127 \times 14$ mm 3 were prepared by the powder metallurgy technology.

3. Results and discussion

3.1. Properties of annealed Cr–Si–Ni and Cr–Si–Ni–Mo films

The film thickness (*t*) and TCR of Cr–Si–Ni and Cr–Si–Ni–Mo films were tested after annealing treatment, as shown in Fig. 1. The *t* of the two kinds of resistive films is basically the same, ranging from 410 to 560 nm due to the same deposition conditions at a low current of 150 mA. Furthermore, these two kinds of resistive films deposited by small current sputtering method have a low TCR at the same annealing conditions, ranging from +2 to –10 ppm/°C (Fig. 1), which can eliminate the interference of temperature to HH experiments.

SEM images of Cr–Si–Ni and Cr–Si–Ni–Mo films in Fig. 2 show that they have smooth surface and no significant micro-defects. Therefore, such two kinds of resistive films are insensitive to water according to study results in [12], which can reduce the interference of film micro-structure to HH experiments to a maximum extent. The main characteristics of the XRD patterns for Cr–Si–Ni–Mo and Cr–Si–Ni films are basically same because only a small content of Mo in the former target (40 wt% Cr, 55 wt% Si, 3 wt% Ni and 2 wt% Mo) [12] is used to replace Ni in the latter target (40 wt% Cr, 55 wt% Si and 5 wt% Ni) [4]. The crystal grains in Cr–Si–Ni and Cr–Si–Ni–Mo films deposited by low-current sputtering method are nanoscale, and the mean grain size of each phase in the two resistive films can be estimated by Scherrer's equation from XRD spectra in Fig. 3, ranging from 5 to 30 nm. In the study of Cr–Si–Ni–W film (40 wt% Cr, 55 wt% Si, 3 wt% Ni and 2 wt% W) deposited by ion beam sputtering method [13], the XRD peak of each phase is very strong even if the resistive film is not treated by annealing, and AFM experiments show that the deposition film mainly consists of micron-level big particles with observable grain boundaries and particle gaps. Furthermore, a comparison shows that the surface of the Cr–Si–Ni–W film in [13] is not as smooth as Cr–Si–Ni–Mo film in this study due to more defects (e.g., protuberance, dent, hole) in the former, as can be clearly seen from their SEM images. As a result, it can be inferred that the smooth Cr–Si–Ni and Cr–Si–Ni–Mo films deposited by low-current sputtering method is mainly composed of fine small particles due to their closely spaced arrangement in the process of film formation. XRD experiments in [13] reveal that each big particle in Cr–Si–Ni–W film is mainly composed of CrSi $_2$ and a small amount of Ni and W dopants. Similarly, each fine small particle forming Cr–Si–Ni and Cr–Si–Ni–Mo films should be mainly composed of CrSi $_2$ and a small amount of Ni and Mo dopants, as can be identified from their XRD patterns in Fig. 3. In addition, CrSi $_2$ is a kind of low-energy-gap semiconductor material with a band gap of 0.35 eV [14,15], which makes it possible for Ni and Mo as shallow level impurities in Cr–Si–Ni–Mo films to share their *d* electrons. It may help to understand the electrocatalytic synergistic effect happening on Cr–Si film that is co-doped by Ni and Mo for water decomposition

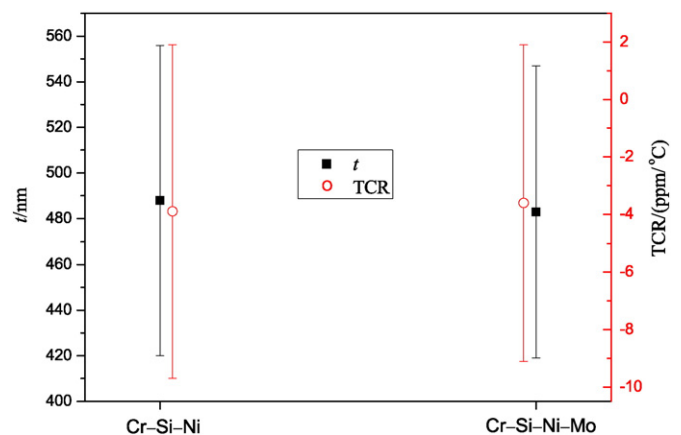


Fig. 1. Film thickness (*t*) and TCR of annealed Cr–Si–Ni and Cr–Si–Ni–Mo films. *t*: mean values from five pieces of resistors; TCR: mean values from 10 pieces of resistors.

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