

Application of Anti-sulfurized Resistors

§0 . Abstract

Generally speaking, anti-sulfurized resistors often refer to thick film resistors. Ordinary chip resistors also have a certain degree of resistance to sulfuration. However, as certain electronic products or devices are used in an environment of high concentration of sulfurized substances, it is necessary to use chip resistors that have stronger resistance to sulfur. At present, the solution of thick film resistors' anti-sulfurization often adopts the following two schemes: one is to adjust the composition of the electrode paste, add some precious metal to the silver electrode paste, and enhance the bonding power of silver to improve the anti-sulfuration performance; the other is to adjust the structure of the resistor or increase the protective layer of the electrode to achieve the purpose of anti-sulfurization.

§1. Sulfuration mechanism

When there are corrosive substances such as S, Cl or Br in external atmosphere, S may enter the gap and react with the silver layer, resulting in partial non-conductivity or poor conductivity of the silver layer. In serious cases, the silver layer will be disconnected, resulting in OPEN resistance value. Figure 1 shows the phenomenon of an electrode being sulfurized (corroded), the silver layer below the plating layer at the junction of the top electrode being corroded, and Figure 2 shows the normal condition of an electrode.



Figure 1 Left top terminal is corroded

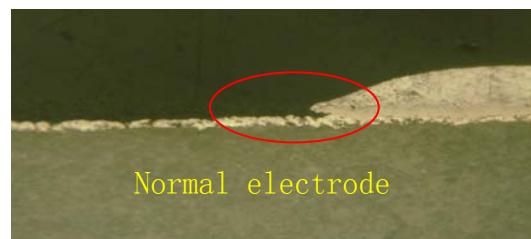


Figure 2 Right top terminal is normal

Measure top electrode junction as shown in Figure 3

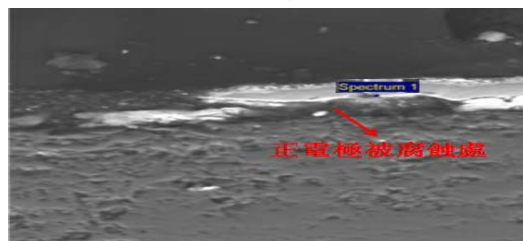


Figure 3 Top electrode junction

The corroded substance in the silver layer below the plating layer at the disconnection of the top electrode has been measured with SEM, and the sulfur content in the corroded area is measured. The specific components are shown in Figure 4.

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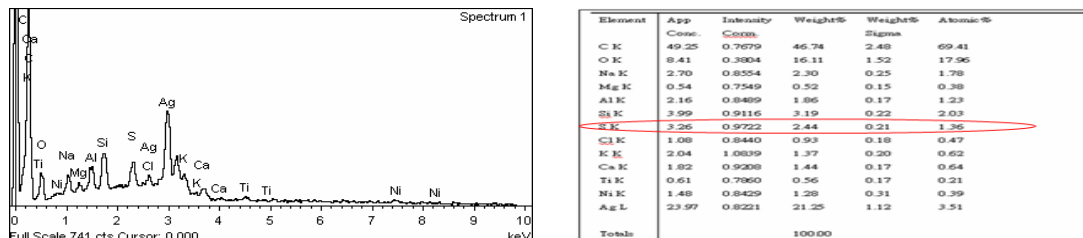


Figure 4 Specific composition list

A schematic diagram of the structure of a common resistor before use is shown in Figure 5. G1 and G2 are both protective layers of the resistor, and these two layers together act as an insulating layer to prevent harmful substances outside from directly immersing into the R surface.

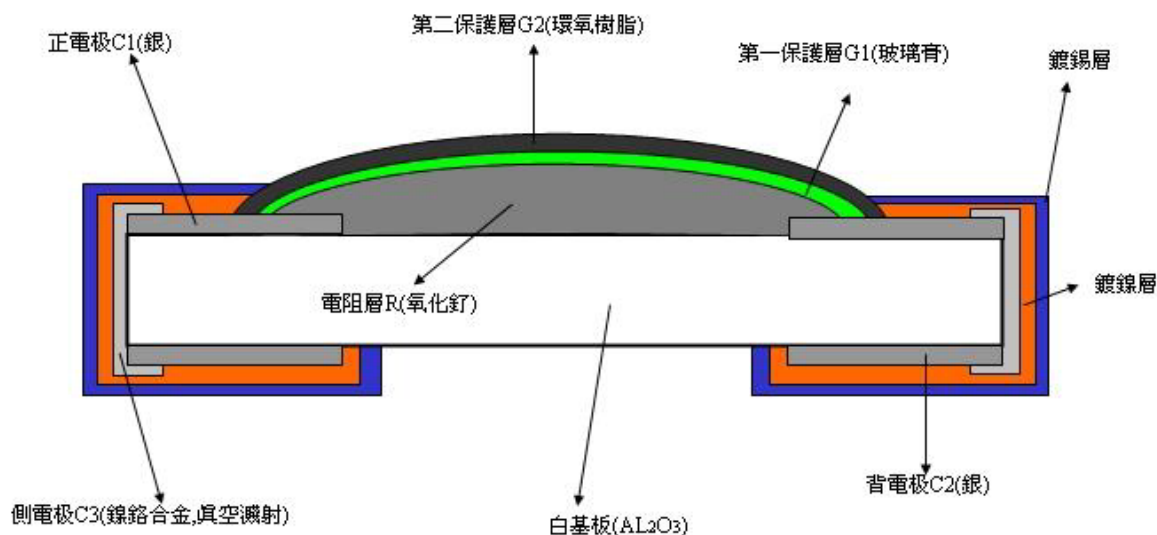


Figure 5 Structure of a common resistor before use

However, after several welding or thermal shocks, the resistor's G2 protective layer and the tin layer and nickel layer will have small gaps (because the nickel layer and G2 protective layer are the junction surface of metal and non-metal, and the thermal expansion and contraction coefficients are different). As shown in Figure 6.

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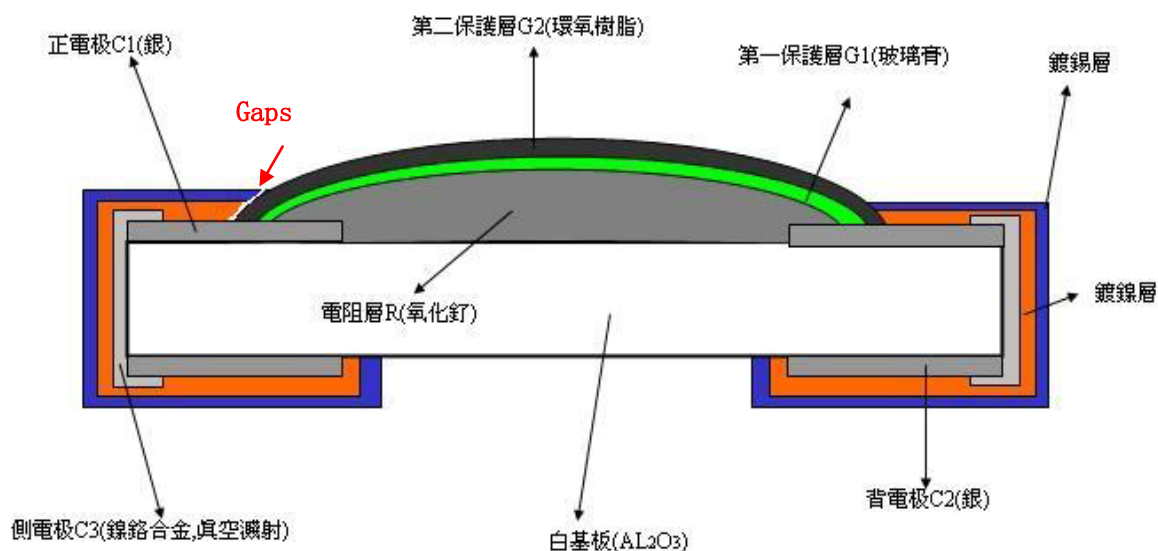


Figure 6 Structure of a common resistor after use

External substances such as water, S, Br and Cl will invade the silver surface through cracks, as shown in Figure 7

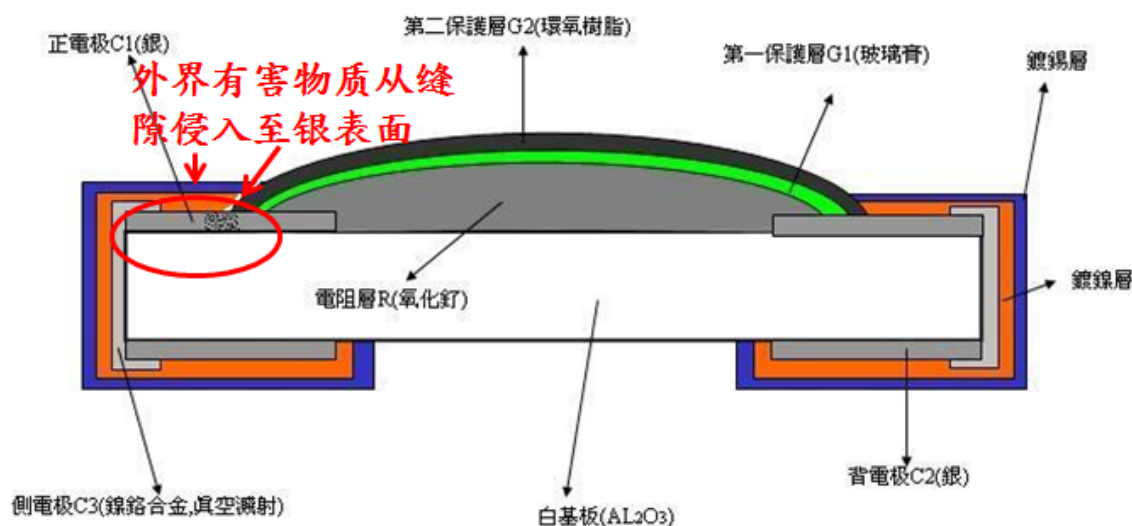


Figure 7 Structure of harmful substances after use

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The invaded sulfur and silver will have sulfuration reaction, which will produce silver sulfide, resulting in partial non-conductivity or poor conductivity of the silver layer. In serious cases, the electrode will be disconnected, resulting in OPEN resistance value. The Chemical equation of the reaction is: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\uparrow$, $\text{S}^{2-} + 2\text{Ag}^+ \rightarrow \text{Ag}_2\text{S} + 2\text{e}^-$, chemical reaction mechanism is shown in Figure 8 , 9.

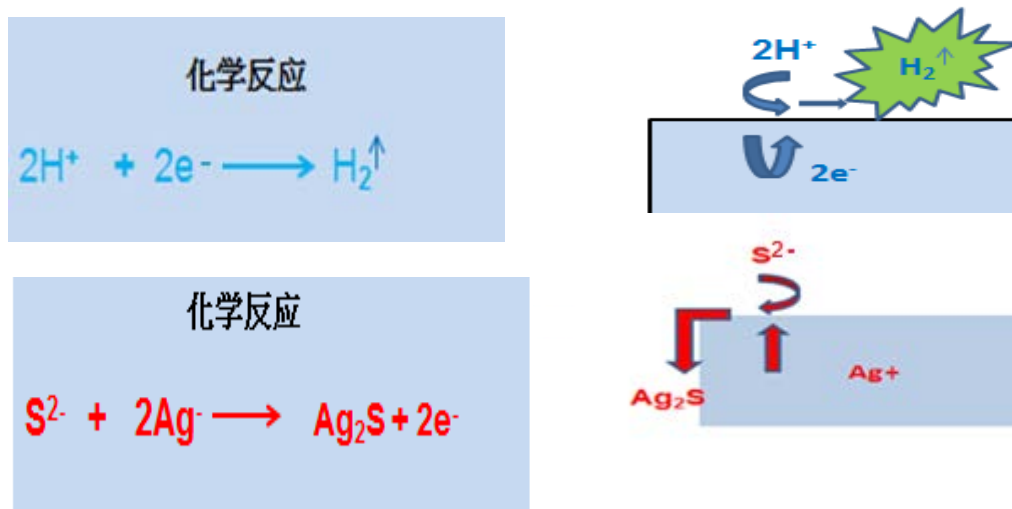


Figure 8 Chemical reaction mechanisms

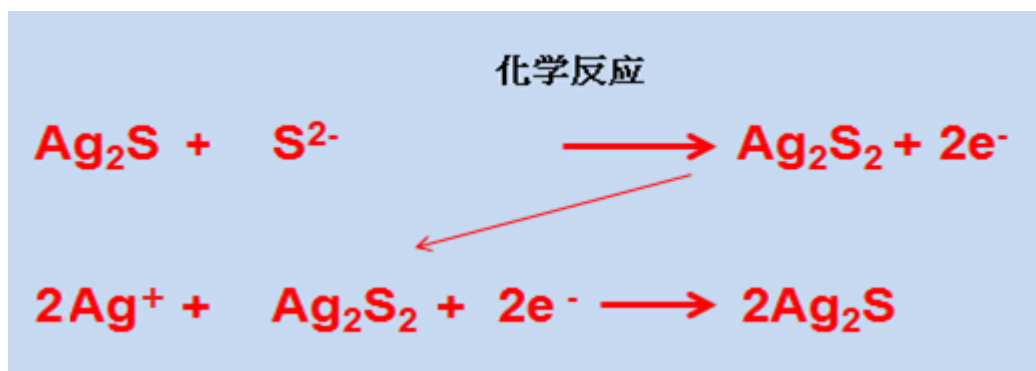


Figure 9 Chemical reaction equation of sulfurized silver

Sulfurized silver further develops into needle-like crystals (monoclinic sulfur), and the reaction formation is shown in Figure 10.

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§2 . Silver migration mechanism

After ordinary resistors are used in the voltage sharing feedback circuits for a period of time, tiny cracks may form between the G2 protective layers and the nickel layers(for ordinary products, cracks cannot be avoided after use). As the nickel layer and the G2 protective layer (epoxy resin) are the junction surface of metal and non-metal, due to the thermal expansion is different, cracks will form after a long time of application. When corrosive substance such as CL or Br enter from the gap, silver migration occurs under DC voltage, and the migrated silver is connected in parallel with the resistance layer, resulting in defect of low resistance.

Ionization of metallic silver occurs due to the potential difference between silver electrodes and the presence of water adsorbed from the surrounding environment on the surface: $\text{Ag} \rightarrow \text{Ag}^+$, $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$; Ag^+ and OH^- generate AgOH precipitation at the anode end : $\text{Ag}^+ + \text{OH}^- \rightarrow \text{AgOH}$; AgOH decomposes and forms Ag_2O at the anode, which is dispersed in a colloidal form. The Ag_2O generated by $2\text{AgOH} \rightleftharpoons \text{Ag}_2\text{O} + \text{H}_2\text{O}$ reacts with water, causing the silver ions to move towards the cathode and precipitate, forming a dendritic structure (as shown in Figure 11): $\text{Ag}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{Ag}^+ + 2\text{OH}^-$.

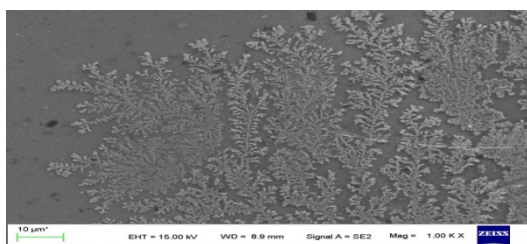


Figure 10 Dendritic structure

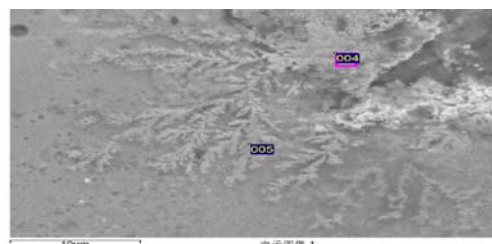


Figure 11 Sampling and testing

Two points in Figure 11 were taken for elemental analysis under EDS, and both sampling points contained Ag.

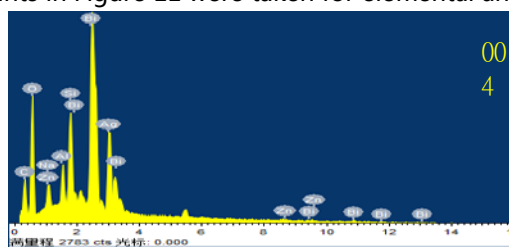


Figure 12 Point 004 contains Ag

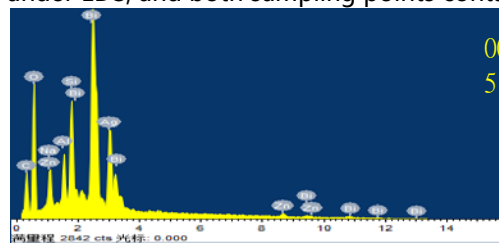


Figure 13 Point 005 contains Ag

Processing option: All elements analyzed (normalized), all results displayed by weight percentage.

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谱图	在状态	C	O	Na	Al	Si	Zn	Ag	Bi	总的
004	是	0.82	24.65	1.25	2.04	4.86	1.33	18.67	46.38	100.00
005	是	0.97	25.17	1.51	2.55	5.28	2.52	17.69	44.31	100.00
平均		0.90	24.91	1.38	2.29	5.07	1.93	18.18	45.35	100.00
标准偏差		0.11	0.37	0.19	0.36	0.30	0.84	0.70	1.47	
最大		0.97	25.17	1.51	2.55	5.28	2.52	18.67	46.38	
最小		0.82	24.65	1.25	2.04	4.86	1.33	17.69	44.31	

Figure 14 Element proportion result table

§3 . Series voltage sharing feedback circuit and its characteristics

The complete machine cannot be free from AC power. Generally, to stabilize the output voltage, a voltage sharing feedback circuit is designed at the output end. The purpose is to ensure that the actual voltage can be divided onto resistors according to the resistance values. When the output voltage fluctuates, the voltage sharing on the resistors will also change. This change will be reflected in former section and adjusted by the circuit to ensure stable output voltage. However, if the series resistance value used changes, error signals will feedback, causing the entire machine to shut down. The series voltage sharing feedback circuit is shown in Figure 15.

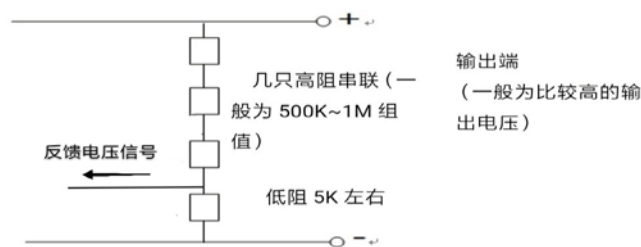


Figure 15 Series voltage sharing feedback circuit

- Resistor operates under DC voltage;
- The load rate of the resistor is relatively high;
- The product has some problems after being used by the customer for a period of time
- This circuit is sensitive to resistance values, and changes in resistance values can change the magnitude of the voltage sharing.

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§4 . Introduction of Anti-sulfurized Resistors

In response to the migration and sulfuration issues of resistor silver layer, UR has specially developed anti-sulfurized resistors, which can effectively prevent resistor silver migration and sulfuration. As shown in Figure 16.

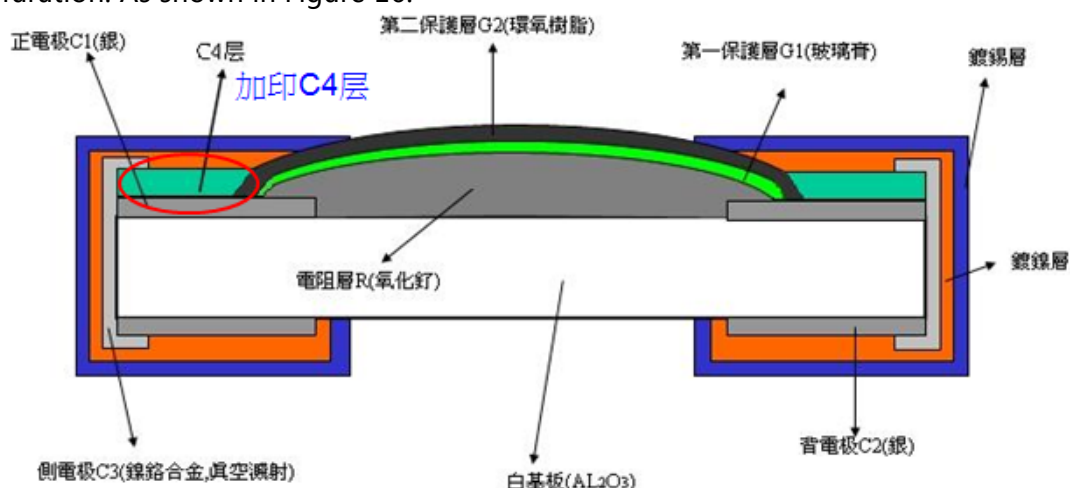


Figure 16 Structure diagram of anti-sulfurized resistor

The C1 electrodes of UR anti-sulfurized resistors contain palladium. Gaps will easily form between the G2 protective layers and the nickel layers and tin layers of ordinary products. Anti-sulfurized products have added a C4 layer, thus no cracks will form between the C4 layer and G2 layer (combination of the same substance), which can effectively prevent external substances from entering. Therefore, C4 can prevent silver migration and sulfuration.

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§5 . Comparison between ordinary resistors and anti-sulfurized resistors

序号	产品类型	额定功率	主要特性	产品特性指标
1	0603	1/10W	1. 普通的设计结构 2. 70℃额定负载寿命	/
2	NQ03	1/10W	1. 特殊的抗硫化设计结构 2. 抗硫化性能指标 工业用油含硫磺成份3.5%，105℃±3℃ 500H， $\Delta R \leq \pm 5\%$ 3. 70℃额定负载寿命	/
3	NS03	1/5W	1. 特殊的抗硫化设计结构 2. 抗硫化性能指标 工业用油含硫磺成份3.5%，105℃±3℃ 500H， $\Delta R \leq \pm 5\%$ 3. 脉冲能力 4. 70℃额定负载寿命	/
比较		NS03功率高	1. 硫化指标：0603<NQ03=NS03	降功率曲线，精度，阻段，TCR电压指标相当

§6 . Application of Anti-Sulfurized Resistors

Based on current understanding, electronic products can also be sulfurized and corroded in the following environments. Anti-sulfurized products are mainly applied to electronic products such as automobiles, industrial power supplies, high-end computers, outdoor billboards and other outdoor products, laptops, and automation applications. Automotive resistors, communication base stations and resistors used in chemical plants, mining and thermal power plants also have the risk of being sulfurized.

In addition, resistors used in the places where volcanic gas is emitted, electronic equipment of thermal power station, hot spring areas and areas where electronic products come into contact with sulfurized rubber during processing also have the risk of being sulfurized..



Automobile



Industrial power supply



High-end computers



Outdoor billboard



Chemical plant



Volcanic gas emission area

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§7. Summary

When silver migration occurs, the following points should be noted. The surface of the resistance layer is affected by moisture, adsorbing water and ionizing, resulting in silver ions moving towards the cathode and precipitating into dendritic structures. Waterproof and moisture-proof measures need to be taken. Due to the structure of resistors and different thermal expansion and contraction coefficients, after repeated welding or thermal shocks, cracks will form on the metal and non-metal junction surface of nickel layers and G2 protective layers. Measures such as waterproofing and cleaning need to be taken to prevent external substances such as water, S, Br and Cl from invading the silver surface from cracks. The anti-sulfurized thick film chip resistor is a product specifically designed to resist sulfuration, so its anti-sulfuration test results are superior to other products.