Data a

Comparison Data of the Withstanding Surge Current Test

Each n＝5

Product number	Current product A（glass frit for lead-based electrode ）	Comparative product（glass frit for non lead-based electrode）
Test values（rated value）	1000A×1time	
V1mA rate of change	positive direction 0.20% negative direction -1.20%	positive direction 0.80% negative direction -8.50%
Withstanding surge current	1500A	1000A

In case of using an electrode with non lead-based glass frit, there is no balance threshold value relative to the rated value as the withstanding surge current deteriorates.

Data b

Comparison Data of the High Temperature Load Life Test

Test 1 each n=5

Product number	Current product B (glass frit for lead-based electrode)		Comparative product (glass frit for non lead-based electrode)	
Test conditions	85℃, Current application rate DC90%, 1200 hours			
V1mA rate of change	positive direction	2.40%	positive direction	1.30%
	negative direction	0.60%	negative direction	0.00%
Withstanding surge current	1500A		1000A	

A significant difference was not found in the 85℃ high temperature load test.

Test 2 each n=5

Product number	Current product B (glass frit for lead-based electrode)		Comparative product (glass frit for non lead-based electrode)	
Test conditions	125℃, Current application rate DC10%, 1150 hours			
V1mA rate of change	positive direction	4.80%	positive direction	3.60%
	negative direction	-1.50%	negative direction	-9.20%
Withstanding surge current	1500A		1000A	

The non lead-based product shows a fluctuation range close to ±10% of the decision criterion of V1mA rate of change when the period of high-temperature load test exceeds 1000 hours.

Data c

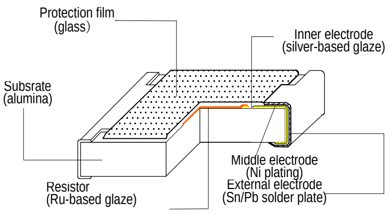
Substance / Usage

Type of substance	Usage	Reduction difficulty level
Glass frit contained in a thick film material forming electronic device	Resistors, capacitors, chip coils, chip inductors, resistance networks, capacitor networks, hybrid ICs	**Substitution by 2008 is not assured**

Reason for usage

Portion of usage (Sketch)	Reason for usage
Ex) Chip resistance	Material and characteristics of glass frits for thick film technology

Ex) Chip resistance



Material and characteristics of glass frits for thick film technology

	Pb glass	Zn glass	P-Sn glass	Na-Al-P-B
Compatibility of component	○	△	△	○
Low softening temperature	○	△	○	○
Thermal expandability coefficient	○	○	○	△
Climatic conditions	○	○	△	△

The lead-based glass is composed to have the flexibility to satisfy the characteristics required for thick film materials and it is inexpensive. Therefore, it is used for many glass frit compositions.

Substitution difficulty

Though we have examined many alternative glass frit compositions in the past, they do not satisfy the requirement for glass frit mentioned above. For example, P_2O_5-SnO-based glass and Na_2O-Al_2O_3-P_2O_5-B_2O_3-based glass have been developed, though they are not practical in application as they are inferior to lead-based glass in Climatic conditions.

There are many glass frit compositions containing lead in the world. A long period of time will be required to develop lead-free glass frit to replace them.

Explanation of Technical terms

Technical terms	Explanation

・Thick film technology	・Form the pattern out of functional material such as conductors, resistors, and dielectric bodies on substrates using screen printing technology. The material is processed in paste form and calcinated at around 800℃.
・Glass frit	・Glass finely ground into powder form

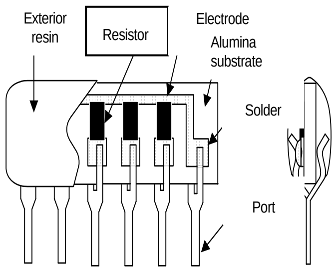
Data d

Substance / Usage

Type of Substance	Related Usage	Reduction difficulty level
Lead in thick film resistors as the resistance component of various resistance parts	RC networks , potentiometers, hybrid ICs, chip resistance , chip resistance networks, chip RC networks , chip capacitor networks , chip resistance arrays, trimmer potentiometers, etc.	A (Substitution by 2008 is impossible)

Reason for usage

Portion of usage (Sketch)	Reason for usage
(Example) Resistance network	Thick film resistors are used by printing a resistive paste of thick film on the alumina substrate and calcinating it. Thick film resistors cannot be produced without lead. Table1 shows the ingredient example of typical resistive paste.



Name of material		e (wt%)
Conductive materia	Pb2Ru2O7	15～20
Glass frit	Pb-Si-B-O	20～45
Vehicle	resin, solvent	30～45
Metal oxide	MnO,CuO etc	0.1～5

Table 1

Lead (Pb) is found in lead ruthenium oxide ($Pb_2Ru_2O_7$) of conductive materials and glass frit.
The range of resistance value of lead (Pb) is as wide as 10^{-3} Ω・cm～10^{4}Ω・cm.
It is the key material for resistors with TCR characteristics of -55□～150□ and ±100ppm～±250ppm.
Lead ruthenium oxide has a wide range of resistance value and the fine grain and coarse grain are well balanced, which enhances the current withstand and contains the contact resistance. See Figure 1.

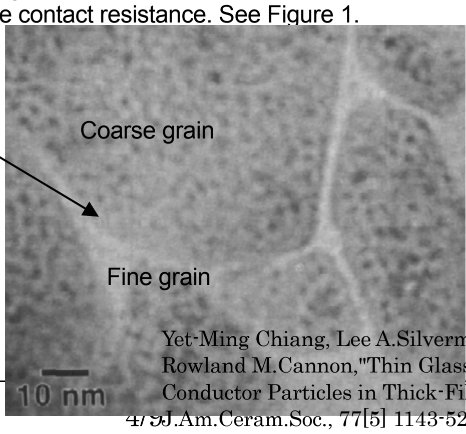


Figure 1

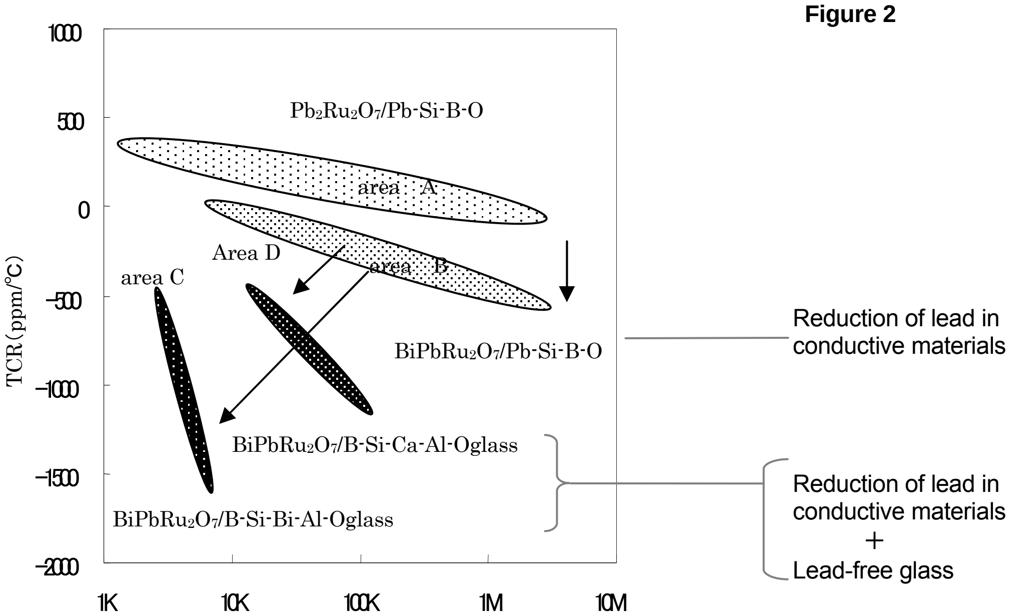
Yet-Ming Chiang, Lee A.Silverman, Roger H.French and Rowland M.Cannon,"Thin Glass Film between Ultrafine Conductor Particles in Thick-FilmResistors", 479J.Am.Ceram.Soc., 77[5] 1143-52 (1994)

	Lead-containing glass has a wide range of softening point and wettability with conductive particles, forming a thin glass layer between the particles easily, which is deeply connected with the good TCR properties.

Substitution Difficulties

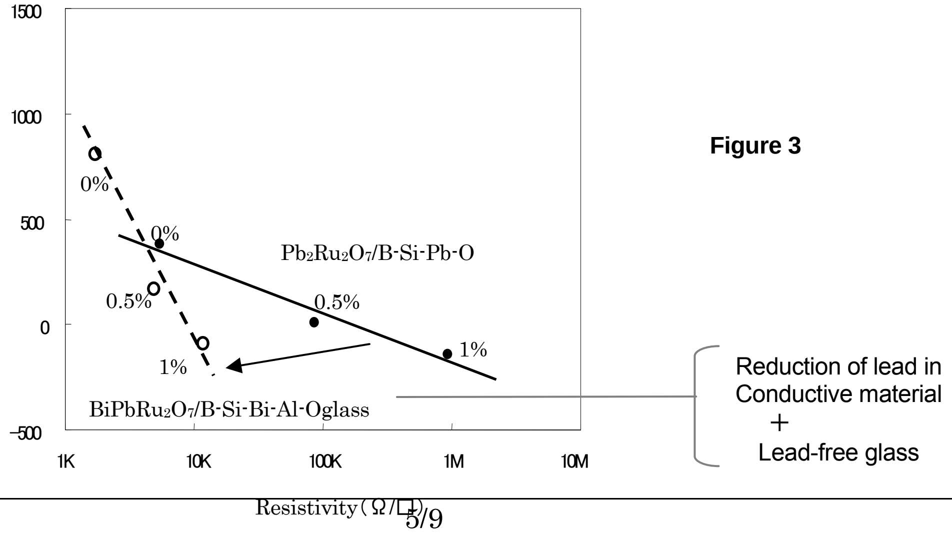
When we substitute a part of lead of lead ruthenium oxide with Bi, the area A changes into Area B as shown in Figure 2 and the range of resistance values shrinks, deteriorating TCR properties. Moreover, when we substitute the material of this glass with Ca-Al or Bi-Al, it changes into Area C or Area D and the resistance values and TCR properties deviate from the range of use.

Figure 2



Metal oxide UMnO or CuO) is used as an additive to adjust TCR to be closer to a particular required area.
As shown in Figure 3, the non lead-based conductive material and glass material violates such properties of metal oxide（MnO or CuO）.

Figure 3



Alternative non lead-based substances used in the above evaluation are the most feasible option.

Explanation of technical terms

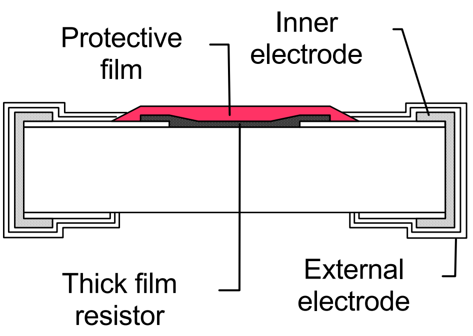
Technical terms	Explanation
Paste	Liquid in which large amount of fine solid particle is scattered.
TCR	Coefficient to indicate the fluctuation of resistance values when the ambient air temperature rises by 1℃. Resistance temperature coefficient。
Contact resistance	Electrical resistance present between the contact surfaces of two substances
Softening point	Temperature at which the substance softens
Wettability	Penetration and blending of glass into the gap of conductive particles

Data e

Item / object

Item	Object	Reduction difficulty level
Lead contained in glass which is a thick film insulator	Fixed metal glaze flat chip resistors, Chip-shaped R networks , multiple chip-fixed resistors Chip-shaped RC networks , chip–shaped C networks etc	Substitution by 2008 is not assured

Reason for usage

Parts of usage	Reason for usage
Fig. 1 shows the structure of a square chip resistor used in glass as thick film insulator. The protective film contains a lead compound as material and the protective film is made of two layers of pre-coated glass and protection-coated glass.  **Fig.1 Structure of a square chip resistor**	**Pre-coated glass** 1. Low fusing point When correcting resistance values of thick film resistors by trimming, the pre-coated glass must be able to be cut with the heat of laser trimming. Therefore, the pre-coated glass formed on the thick film resistor needs to be sintered at a relatively low temperature (600°C). 2. Moisture & Acidity resistance Pre-coated glass is required to control the fluctuation of resistance values due to moisture and acid etc. Due to these reasons, lead-based glass is used. **Protection coating** Use of non lead-based alternative product is possible.

Reason of difficulty of substitution

Pre-coated glass

Due to the absence of materials superior to lead-based substances in moisture resistance and acidity resistance.

Characteristics of substitute glass ○:Excellent △:Slightly poor ×:Poor

Material	Trimming properties	Acid resistance	Moisture resistance	Heat resistance
Lead glass	○	○	○	○
Bi Glass	○	×	△	○
P glass	○	×	△	○

Explanation of technical terms

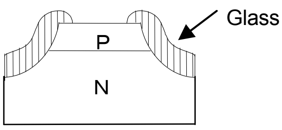
Technical terms	Explanation
Pre-coated glass	Material used to control the fluctuation of resistance values in post-processes etc.
Coated glass	Material used to protect resistors
Laser trimming	Method to correct the resistance values to obtain the given resistance values

Data f

Substance／usage

Type of substance	Related products	Reduction difficulty level
Lead-based glass (Pb glass) :Used for the protection of surfaces of semiconductor chips	Bridge rectifying devices, power diodes , power thyristors, power transistors etc	A Impossible to substitute

Reason for usage

Portion of usage (Sketch)	Reason for usage
 Cross section of a power diode	Widely used as the passivation film on the surface of P・N junction of power semiconductor devices. The glass material to be used for this purpose needs to satisfy all the following conditions. ①High electrical stability ②Thermal expandability similar to that of silicon ③Calcination temperature is at 1000℃ or below ④High chemical resistance Pb glass is equipped with all the properties from ① to ④ above.

Difficulty for substitution

The main ingredient of Pb glass is PbO and Pb glass also includes Al_2O_3 and SiO_2 etc as well.
This glass does not contain the material to reduce the chemical resistance and it is extremely stable towards various chemicals used in semiconductor processing.
Moreover, the thermal expandability coefficient relatively similar to silicon can be obtained as the thermal expandability coefficient can be adjusted with the composition of Pb O and SiO_2. The calcination temperature for this is low at 1000℃ or below and does not affect the property of P-N junction.
In terms of reliability, since it can be made into a thick film, it is highly resistant to moisture and its characteristics are stable under high voltage in the range from several hundred V upto 1000 V.

On the other hand non lead-based glass materials include Zn glass, quartz glass and borosilicate glass, etc.
Table 1 shows the comparison of characteristics of these glasses and Pb glass.

1

Type of glass	Electric stability	Thermal expansion coefficient	Calcination temperature	Chemical resistance
Pb glass	○	○	○	○
Zn glass	○	○	○	×
Quartz glass	○	×	×	○
Silicate glass	×	○	×	○

Table 1

Zn, which is the main ingredient of Zn glass has low resistance for etching and the chemical resistance is very low. Figure 1 shows the result of acid treatment of Pb glass and Zn glass. Zn glass is extensively damaged by this treatment though Pb glass is not. Therefore, Zn glass cannot be used.

The thermal expandability coefficient of quartz glass is too small and the calcination temperature is too high to use.

The borosilicate glass cannot be used because the calcination temperature is too high and the alkali ingredient in glass deteriorates the electric characteristic too much.

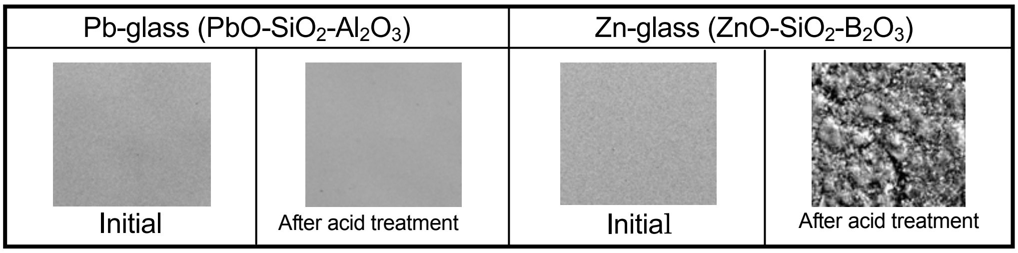


Fig.1 Photo of scanning electron microscope x150
Conditions for acid treatment: Nitric acid (HNO_3) Boiling 3 min.

Due to these reasons, it is impossible to use Pb-free glass as substitution for Pb glass.

Explanation of Technical terms

Technical terms	Explanation
Passivation	Stabilization layer on the surface of semiconductors
Bridge rectifying device Power diode Power thyristor Power transistor	Type of electric semiconductor element
P-N junction	Basic structure of semiconductor elements
Calcination temperature	Temperature to form glass film
Zn glass	Glass mainly composed of ZnO
Quartz glass	Glass mainly composed of SiO_2
Borosilicate glass	Glass mainly composed of SiO_2, B_2O_3 and Na_2O