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Thick film compositions based on titanium silicides for surge resistors

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Abstract

Thick film compositions based on three titanium silicides: $TiSi_2$, TiSi, and Ti_5Si_3 were prepared and investigated. Resistivities and temperature coefficients of resistance of the layers fired at 850 °C were measured in the temperature range −40 to +160 °C. The resistivities were 0.3–20 Ω per square for the layers containing Pd–Ag addition, fired in air and 20–300 Ω per square for those based exclusively on silicides, fired in nitrogen. Studies of the surge performance of Ti–Si resistors were carried out. The chosen compositions fired in air showed resistivity adequate to print resistors in the rectangular shape, more advantageous for surge resistors than the meander one, low TCR values and small changes in resistivity after high voltage pulsing.

Keywords: Thick films; Titanium silicides; Surge resistors

1. Introduction

Protection against disturbances and damages caused by surges is a serious problem in present complex and sensitive electronic devices. Most often induction of overvoltage takes place due to atmospheric discharges near working devices or switching of high power circuits. Sometimes, especially in the case of telecommunication lines there occur direct lightning strikes. These phenomena are accompanied by pulses of very high voltage (thousands of volts), flow of high currents, generation of great amounts of energy in short periods of time.

The lack of a proper surge protection may be the reason of irreversible damage of some elements in electronic devices resulting in the necessity of their replacement. Recently much attention has been paid to development of surge resistors which can withstand great instantaneous current, efficiently dissipate heat and remain stable in overvoltage conditions with a minimal shift in resistance. The role of these resistors as components in circuits protecting against surges is important especially in the case of telecommunication lines because even small changes in resistance increase the noise level during their operation. Surge resistors are widely applied also in computers, data transmission lines, automobile electronics, measuring devices, etc.

Thick film technology, which utilizes screen printing to deposit the layers with thickness of 1–100 μm, has been widely used for several years in production of conductors, resistors, capacitors, inductors, sensors, etc. The main advantages of this technique are: simplicity, a relatively low cost, flexibility of production, good miniaturization and reliability of elements.

Some producers of thick film pastes, like Ferro, Du Pont, Remex, have recently offered special pastes destined for surge resistors. Ferro company has developed FX-85 series [1–3] of Ag–Pd pastes with sheet resistivities: 0.07, 0.11, 0.2, 0.5, 1.0, and 10 Ω per square and temperature coefficients of resistance (TCRs) not exceeding ± 100 ppm/°C in the temperature range from −55 to +125 °C. The great increase in palladium prices which has taken place in recent few years incline to reduce contribution of this precious metal in resistor materials. Ferro company offers a new low-cost RE 88-series resistors with a significant reduction in the content of Pd, characterized by resistivity of 0.05–0.6 Ω per square, good surge protection capability and long-term reliability [4]. However, TCRs of the new series resistors are much higher (<400 ppm/°C) than those of standard 85-series resistors.

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Du Pont 7400 series of Pd–Ag pastes is also destined for surge resistors [5]. It consists of five pastes of the following resistivities: 0.1, 0.2, 0.5, 1.0, and 3 Ω per square The values of TCR of these compositions are lower than 50 ppm/°C.

Titanium silicides are useful in integrated circuits as Schottky barriers, ohmic contacts and low resistivity metallization for gates and interconnections [6–8]. These materials due to their proper resistivity and high temperature stability are also interesting candidate materials for surge resistors. The melting points of $TiSi_2$ and Ti_5Si_3 are 1540 and 2130 °C, respectively [9]. Resistivities of $TiSi_2$ and Ti_5Si_3 reported by Kuo [9] are $6.2 \times 10^{-4}\ \Omega$ cm and $3.5 \times 10^{-4}\ \Omega$ cm, respectively. Murarka and coworkers [6,7] listed the resistivities of $TiSi_2$ films formed by reacting a thin metal film with polycrystalline silicon or by cosputtering and sintering a mixture of metal and silicon are $1.3 \times 10^{-5}\ \Omega$ cm to $2.5 \times 10^{-5}\ \Omega$ cm. Crystal structure of $TiSi_2$ is orthorombic and that of Ti_5Si_3 is hexagonal [9].

Kuo [9] has developed a series of resistive pastes for surge protection being a combination of titanium silicides $TiSi_2$ and Ti_5Si_3, Ni–Cr and various glasses. The resistivity range was: 0.5–10 Ω per square for $TiSi_2$ pastes, 5 Ω per square–1 kΩ per square for NiCr/Ti_5Si_3, 1 and 10 kΩ per square for Ti_5Si_3/$TiSi_2$. The result of blending of these pastes with compositions based on SnO_2 was the series of resistors with eight orders of resistivity, compatible with copper conductive layers. The TCR values of these resistors were lower than ±100 ppm/°C.

In this work, three silicides—$TiSi_2$, Ti_5Si_3, and TiSi were utilized to prepare thick film compositions. Owing to their resistivities higher than those of the Pd–Ag system a possibility was created to use rectangular patterns, more advantageous for surge protection than serpentine ones. Using rectangular shape patterns one can fully utilize the small available space on a substrate to dissipate the heat generated as a result of high power surges. There will be also no danger of current crowding at corners, which can happen in the case of resistors of meander shape and consequently less failures will take place.

2. Experimental

Three titanium silicides: $TiSi_2$, Ti_5Si_3, and TiSi were used, obtained by the SHS method (Self-Propagating High Temperature Synthesis) [10]. The average grain sizes of all titanium silicides were below 2 μm.

Thick film pastes were prepared by mixing a chosen titanium silicide ($TiSi_2$, Ti_5Si_3, or TiSi), Pd–Ag, B_2O_3–Al_2O_3–CaO–ZrO_2 glass and organic vehicle. The Pd–Ag ratio 3:2 was applied, corresponding to the minimum in temperature coefficient of resistivity and the maximum in resistivity in the Pd–Ag system [5].

Ethyl cellulose solution in terpineol was used as the organic vehicle for the pastes destined for firing in air. For those destined for firing in nitrogen organic composition based on acrylic resin (produced by ITME-Warsaw) was added. This resin undergoes decomposition during thermal treatment of thick films.

The non-organic part of the pastes prepared for firing in air contained 20–55 wt.% (32–67 vol.%) of titanium silicide, 35–70 wt.% (15–42 vol.%) of Pd–Ag, and 10 wt.% (6–25 vol.%) of glass. The pastes destined for firing in nitrogen were based on pure silicides, only with glass addition.

Rectangular resistors consisting of 1–10 squares were screen printed on 96% alumina substrates, dried and fired at 850 °C for 10 min in a BTU VI-zone belt furnace. The width of resistors was 3–4 mm. The Ag–Pd paste produced by ITME-Warsaw fired in air was applied for terminations.

Resistivities and TCRs of resistors were measured in the temperature range from −40 to +160 °C. Phase and chemical compositions as well as the microstructure of the resistive layers were studied using X-ray diffraction analysis, scanning electron microscopy and microprobe analysis.

Investigations of the surge performance of Ti–Si resistors with resistance 20–80 Ω were carried out using a specially constructed, programmable impulse generator. This generator made possible to control:

- maximum voltage in the range 300–2000 V
- maximum current up to 200 A
- impulse width in the range 10 μs–10 ms
- interval between pulses in the range 10 ms–100 s
- number of repeated pulses during testing of one sample in the range 2–100

Software of the generator ensures measurement of current intensity and voltage during the pulse, visual control of pulsing and registration of data.

The lightning strike is usually simulated by 10/700, 10/1000, 0.5/700, and 2/10 μs waveforms. In this work, 10/700 μs pulse shape (rise time 10 μs, decay time to 50% of the initial value −700 μs), delivered by the generator, was applied to test surge performance of Ti–Si resistors. The parameters of the measurement were the following: peak voltage −600 to 1500 V, the pulse intervals −2 to 30 s, number of pulses −1 to 50. Resistors were tested until the failure point.

3. Results and discussion

The layers fired in air made of the pastes based on titanium silicides with the addition of Pd–Ag, showed stable resistivities of 0.3–20 Ω per square. The layers have composite structure consisting of highly conductive metallic particles of Pd–Ag alloy, titanium silicide grains of medium electrical conductivity and glass phase, being electrical insulator. During firing in air grains of titanium silicides were probably oxidized on their surface forming SiO_2 or TiO_2 films. The silicide $TiSi_2$ is known as very stable during oxidation [6]. Murarka [6] reported that for $TiSi_2$ layers formed by reacting a thin titanium film with polycrystalline silicon both

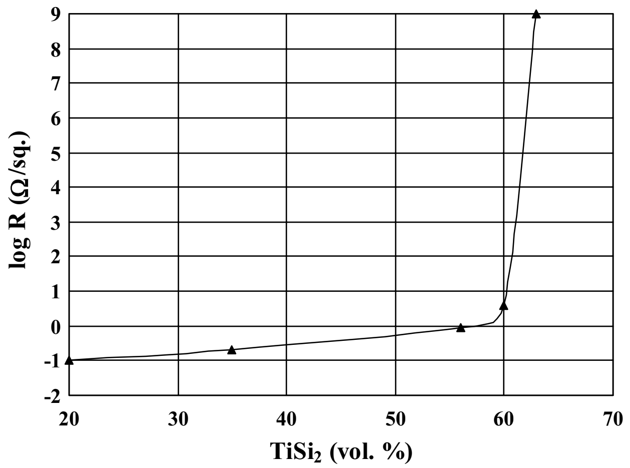

Fig. 1. Relationship between sheet resistivity of a $TiSi_2$–Pd–Ag thick film and the content of titanium silicide.

Ti and Si oxidize due to small differences between the heat of formation of metal oxide and that of SiO_2. X-ray analysis did not exhibit the presence of any crystalline SiO_2 or TiO_2 in the fired layers. However, it can be supposed that small amounts of amorphous oxidation products were dissolved in glass matrix.

It was found that to ensure good conductivity of these layers the limiting silicide content of 50–55 wt.% (60–67 vol.%), corresponding to 15–20 vol.% of Pd–Ag, should not be exceeded. Fig. 1 illustrates a violent increase in resistivity observed for higher contents of $TiSi_2$. This effect indicates that the conduction mechanism of these layers is mainly connected with the contact of metal particles (Pd–Ag). A too high content (above 60 vol.%) of silicide phase with the resistivity lowered by oxidation on grain surfaces is supposed to result in an abrupt increase in resistivity of the whole composite layer Ti–Si–Pd–Ag.

Tables 1–3 present the sheet resistivities and TCRs of the thick films fired in air, based on $TiSi_2$, TiSi, and Ti_5Si_3. Among the films fired in air with similar amounts of various silicides, the lowest resistivity was shown by those based on $TiSi_2$ and the highest by those containing Ti_5Si_3. Medium values of resistivity were characteristic of TiSi layers. These results indicate that among the examined silicides $TiSi_2$ is the most resistant to oxidation one during the thermal treatment in air. The observed differences among the oxidation behavior of three titanium silicides can obviously be ascribed to differences of their crystalline structures. It is worth mentioning that the ionic crystal radii of Ti^{2+}, Ti^{3+}, and Ti^{4+} are known to differ appreciably—a circumstance which could entail differences in the relevant silicide structures.

In Figs. 2–4, the temperature coefficients of resistance for the layers based on $TiSi_2$, Ti_5Si_3, and TiSi, fired in air, are presented. The values of TCR for thick films fired in air were rather low and decreased with increasing temperature. The mean TCR values in the temperature range from −40 to 20 °C were 50–90, 110–120, and 110–130 ppm/°C for $TiSi_2$, TiSi, and Ti_5Si_3 based compositions, respectively. In the temperature range 20–160 °C the mean TCRs were much lower: 2–30, 15–20, and 20–60 ppm/°C for $TiSi_2$, TiSi, and Ti_5Si_3 based layers, respectively. The TCR values for $TiSi_2$ thick films were positive up to 80–140 °C, then they became negative, whereas for TiSi and Ti_5Si_3 based compositions these values remained positive in the temperature range between −40 °C and 120–140 °C. The TCRs for Ti–Si–Pd–Ag thick films are a resultant effect of compensation of negative coefficients of pure silicides by positive ones of Pd–Ag alloy.

Table 1
Properties of $TiSi_2$–Pd–Ag layers fired in air at 850 °C

Composition (wt.%)	$TiSi_2$ (vol.%)	Sheet resistivity (Ω per square)	Mean TCR (ppm/°C)	
			−40 to +20 °C	20–160 °C
$TiSi_2$ 20, Pd–Ag 70, Glass 10	35	0.3	95	30
$TiSi_2$ 30, Pd–Ag 60, Glass 10	45	0.5	85	30
$TiSi_2$ 40, Pd–Ag 50, Glass 10	55	1.3	75	15
$TiSi_2$ 45, Pd–Ag 45, Glass 10	59	3.5	75	15
$TiSi_2$ 50, Pd–Ag 40, Glass 10	63	4.5	75	10
$TiSi_2$ 55, Pd–Ag 35, Glass 10	67	20	50	2
$TiSi_2$ 60, Pd–Ag 30, Glass 10	70	$>10^9$		

Table 2
Properties of Ti–Si–Pd–Ag layers fired in air at 850 °C

Composition (wt.%)	Sheet resistivity (Ω per square)	Mean TCR (ppm/°C)	
		−40 to +20 °C	20–160 °C
TiSi 20, Pd–Ag 70, Glass 10	0.3	110	15
TiSi 40, Pd–Ag 60, Glass 10	1.5	110	15
TiSi 50, Pd–Ag 40, Glass 10	7	110	15
TiSi 55, Pd–Ag 35, Glass 10	700	120	20

Table 3
Properties of Ti_5Si_3–Pd–Ag layers fired in air at 850 °C

Composition (wt.%)	Ti_5Si_3 (vol.%)	Sheet resistivity (Ω per square)	Mean TCR (ppm/°C)	
			−40 to +20 °C	20–160 °C
Ti_5Si_3 20, Pd–Ag 70, Glass 10	32	0.3	110	20
Ti_5Si_3 30, Pd–Ag 60, Glass 10	50	0.6	120	30
Ti_5Si_3 45, Pd–Ag 45, Glass 10	57	6	120	40
Ti_5Si_3 50, Pd–Ag 40, Glass 10	61	10	130	60
Ti_5Si_3 55, Pd–Ag 35, Glass 10	65	>10^9		

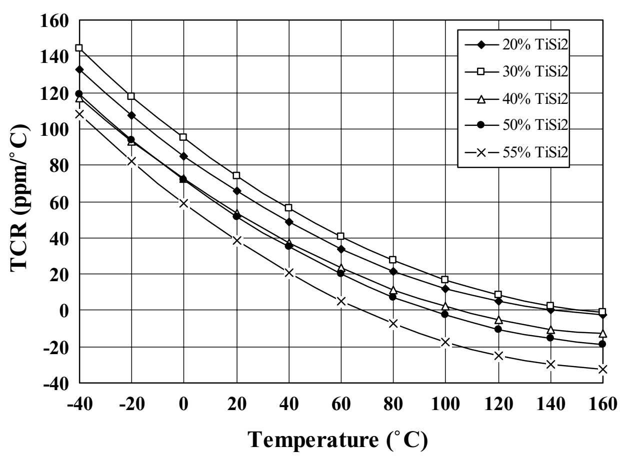

Fig. 2. Temperature coefficient of resistivity in the temperature range −40 to +160 °C for $TiSi_2$–Pd–Ag thick films fired in air.

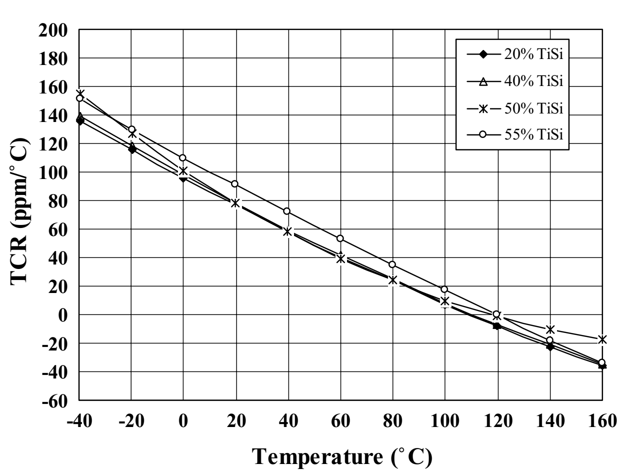

Fig. 3. Temperature coefficient of resistivity in the temperature range −40 to +160 °C for TiSi–Pd–Ag thick films fired in air.

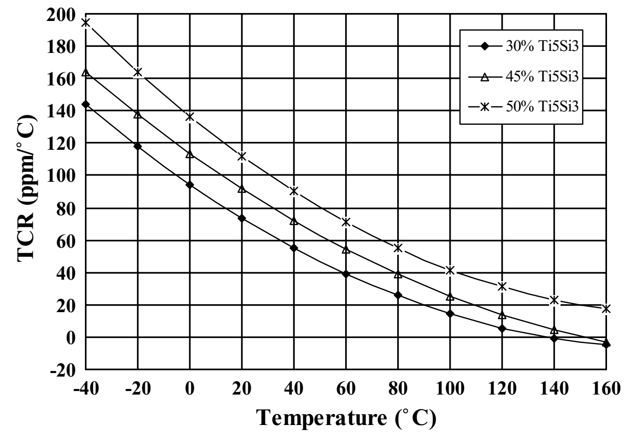

Fig. 4. Temperature coefficient of resistivity in the temperature range −40 to +160 °C for Ti_5Si_3–Pd–Ag thick films fired in air.

Table 4
Properties of Ti–Si layers fired in nitrogen at 850 °C

Composition (wt.%)	Sheet resistivity (Ω per square)	Mean TCR (ppm/°C)	
		−40 to +20 °C	20–160 °C
$TiSi_2$ 90, Glass 10	300	−1200	−1100
Ti_5Si_3 90, Glass 10	20	−3100	−2200
TiSi 90, Glass 10	150	−4200	−2500

In Table 4 there are given for comparison the parameters of the layers fired in nitrogen, based on pure silicides, only with glass addition and without Pd–Ag. Resistivities of these layers were 300, 150, and 20 Ω per square for $TiSi_2$, TiSi, and Ti_5Si_3 based compositions, respectively. Ti_5Si_3 films showed the lowest resistivity and $TiSi_2$—the highest one. This tendency in the dependence of resistivity on silicide

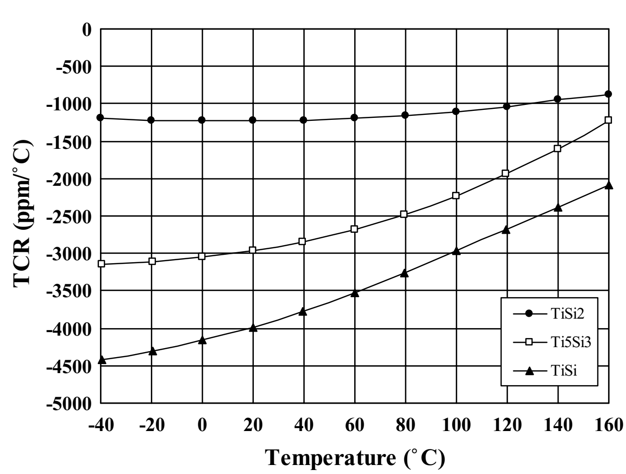

Fig. 5. Temperature coefficient of resistivity in the temperature range −40 to +160 °C for thick films based on $TiSi_2$, TiSi, and Ti_5Si_3 fired in nitrogen.

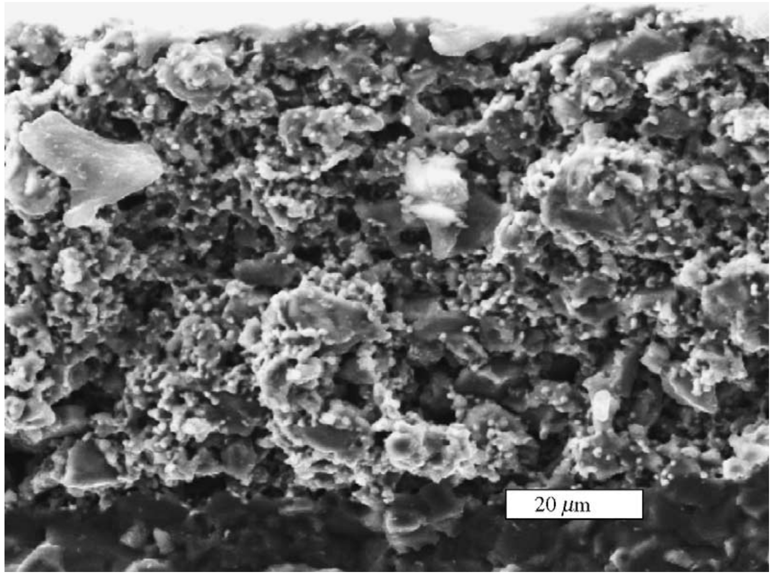

Fig. 6. SEM of fractured cross section of a Ti_5Si_3 based thick film resistor fired at 850 °C in air.

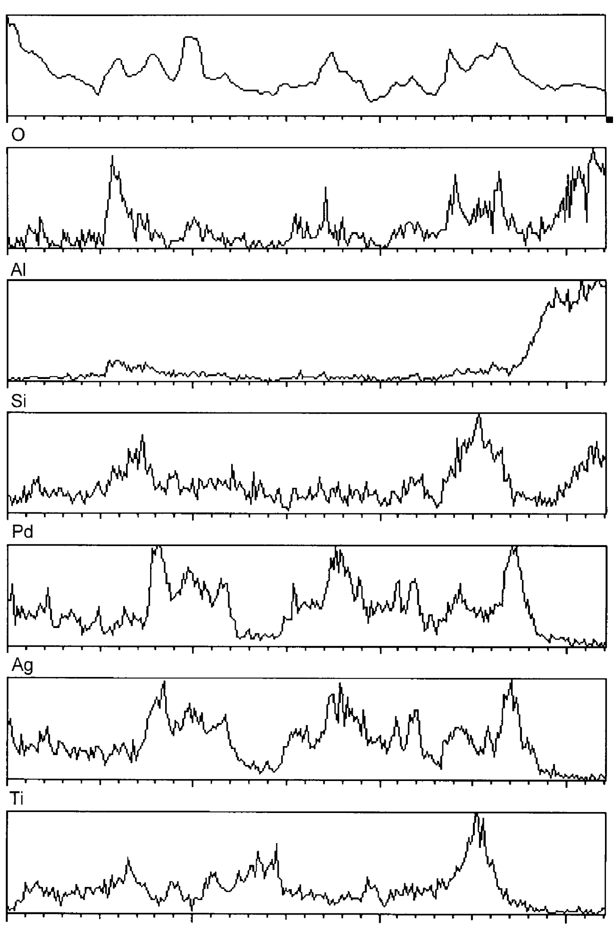

Fig. 7. Microprobe analysis across the $TiSi_2$–Pd–Ag resistor.

composition is contrary to that observed in the case of the layers fired in air.

In Fig. 5 the temperature coefficients of resistance for the layers based on $TiSi_2$, Ti_5Si_3, and TiSi, fired in nitrogen, are presented. The layers composed of pure silicides fired in nitrogen showed high negative mean values of TCR ranging from −1100 to −4200 ppm/°C. This feature has precluded the possibility of using these thick films fired in nitrogen as surge resistors.

Fig. 6 shows a typical scanning electron micrograph of the fracture of a thick film based on Ti_5Si_3 fired in air at 850 °C. The microstructure of the layer is fine-grained and rather dense. The adhesion to the alumina substrate is very good. The grain size of titanium silicide was 1–5 μm. Small spherical particles of metal (about 1 μm in diameter) are visible. The thickness of the resistive thick film was about 20 μm and 30–35 μm for a single and a double layer, respectively. In Fig. 7 the result of the line microprobe analysis across a $TiSi_2$ resistor is presented. It can be stated that the main elements present in the layer, i.e. Pd and Ag (originating from Pd–Ag alloy) as well as Si and Ti (originating from titanium silicide) are distributed uniformly across the thick film. Slight enrichment in oxygen is observed near the surface of the sample caused probably by oxidation of the silicide. The content of Al is at a low level across the thick film (small amounts of Al are introduced with glass), then abruptly grows, indicating the boundary between the resistive layer and the Al_2O_3 substrate.

Fig. 8 shows SEM of the fracture of a thick film based on Ti_5Si_3 fired in nitrogen at 850 °C, screen printed on alumina substrate. This layer is more porous and the average grain size is greater than in the case of thick film fired in air.

The Ti–Si–Pd–Ag thick films fired in air showed good surge performance. In Table 5 the results of pulse testing of the layers based on $TiSi_2$, Ti_5Si_3, and TiSi are presented.

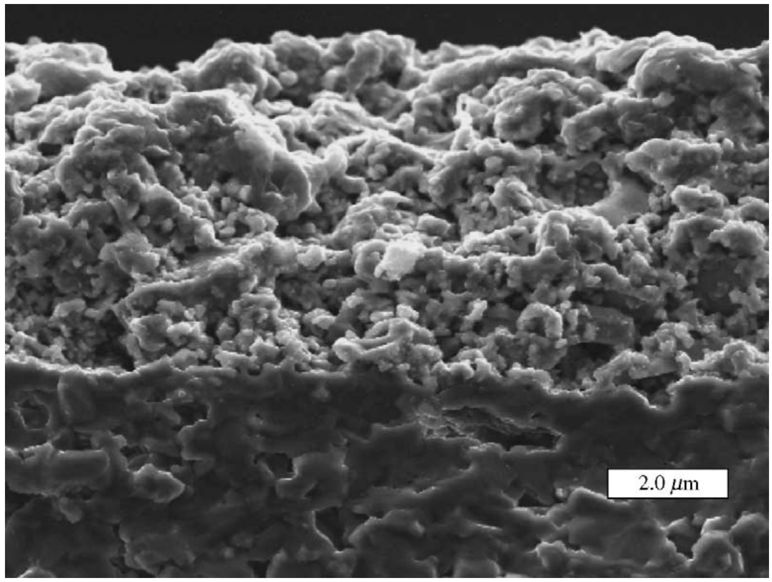

Fig. 8. SEM of fractured cross section of a Ti_5Si_3 based thick film resistor fired at 850 °C in nitrogen.

All examined resistors withstood 50 pulses at 1000 V. The resistance changes after application of pulses of 600 and 1000 V were 0–2.4% and 0–4.5%, respectively, depending on the number of pulses, the kind of silicide and the layer thickness. A few pulses caused a small resistance change of 0–0.5%, greater changes (2–4.4%) occurred after numerous pulses. The resistors made of the pastes containing 50 wt.% of TiSi exhibited the best surge characteristics. Their resistance shift after multiple pulsing at 1000 V did not exceed 0.6%. Layers with a higher density and thickness had better surge performance.

In Fig. 9 courses of voltage and current during testing of a Ti–Si–Pd–Ag resistor by the pulses of maximum voltage of 1500 V are presented. Fig. 9a and b illustrate the course of current and voltage as a function of time during the first pulse, which did not cause any change in resistance. The waveform is presented, characterized by a short rise time (10 μs) and a slow decay time (700 μs). The maximum

Table 5
Surge performance of the resistors based on titanium silicides under pulses of 10/700 μs waveform

Composition (wt.%)	Voltage at failure point	Resistance change after 1000 V pulses (%)				
		Number of pulses				
		1	5	10	20	50
$TiSi_2$ 45 Pd–Ag 45 Glass 10	1200	0	0	0	0.2	1.1
$TiSi_2$ 50 Pd–Ag 40 Glass 10	1300	0	0	0.6	2.2	4.5
$TiSi_2$ 55 Pd–Ag 35 Glass 10	1200	0	0.5	1.1	2	4.2
Ti_5Si_3 50 Pd–Ag 40 Glass 10	1200	0	0.5	1	1.3	2.5
TiSi 40 Pd–Ag 50 Glass 10	1300	0	0	0.6	0.6	1.3
TiSi 50 Pd–Ag 40 Glass 10	1500	0	0	0	0	0.6

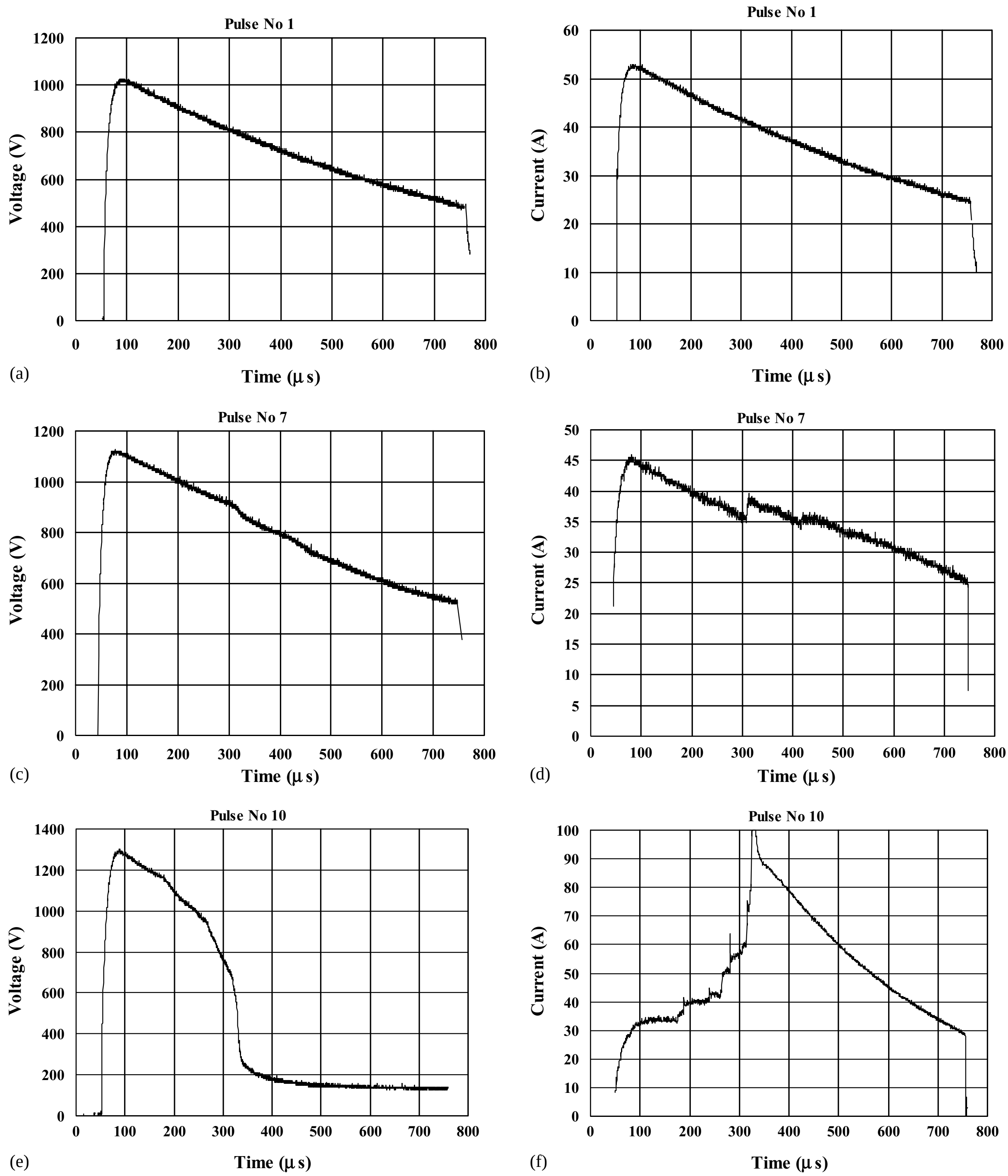

Fig. 9. Courses of current and voltage as a function of time during high voltage pulsing of surge resistors based on TiSi. (a and b) Pulse no. 1—no change in resistance; (c and d) pulse no. 7—a significant change in resistance; (e and f) pulse no. 10—failure of the resistor.

current was about 50 A. During next five pulses, the changes in shape of the observed curves were very small. Fig. 9c and d show a significant change in voltage and current course during the seventh pulse, accompanied by a significant increase in resistance. The courses became then irregular. Step changes of resistance took place, caused probably by the formation of local, small electrical arcs in microregions of the layer, still not visible by eye. Fig. 9e and f present the dependencies of voltage and current on time for the tenth pulse, which was the reason of the failure of the resistor. During this pulse melting of the “paths” across the resistive layer took place. On the plots violent jumps of current can be seen, related to the creation of electrical arcs in the destroyed regions.

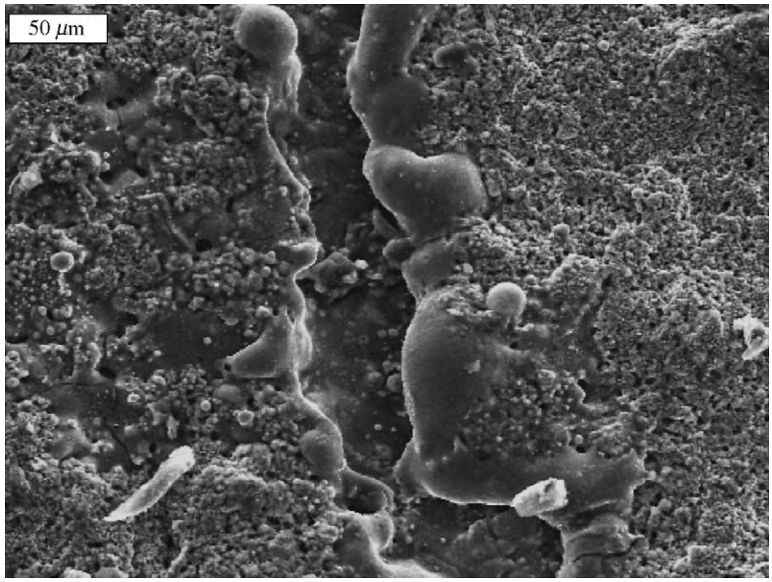

Fig. 10. SEM of the surface of $TiSi_2$ based thick film resistor destroyed by 1500 V pulses, with visible melted "paths" across the layer.

The impulse voltage which caused the catastrophic failure of the examined resistors based on titanium silicides was 1200–1500 V. The view of the resistive layer damaged by a surge is illustrated in Fig. 10.

Fabrication of a typical surge resistor with resistance 50–100 Ω using Pd–Ag pastes requires applying long serpentine patterns. Because of the higher resistivity of the developed pastes based on titanium silicides as compared with Pd–Ag compositions it was possible to manufacture surge resistors of rectangular shape. The advantages of this solution are: better utilization of the substrate surface, more effective dissipation of generated heat and lack of sharp corners where electric charge can be accumulated and a damage of the path under overvoltage is easier. The reasons of the good surge performance of Ti–Si–Pd–Ag resistors fired in air are also: the stable and dense structure of the layers, the high melting temperature and good thermal conductivity of titanium silicides.

4. Conclusions

Thick film resistors fired in air made of the pastes composed of titanium silicides—$TiSi_2$, Ti_5Si_3, and TiSi, Pd–Ag powder and B_2O_3–Al_2O_3–CaO–ZrO_2 glass are characterized by a good surge performance due to high melting temperature and good thermal conductivity of Ti–Si compositions as well as advantageous rectangular shape of patterns. The best results were obtained for the pastes fired in air containing 45–55 wt.% of silicide $TiSi_2$, 35–45 wt.% of Pd–Ag (3:2), and 10 wt.% of B_2O_3–Al_2O_3–CaO–ZrO_2 glass. These compositions showed resistivity of 3–20 Ω per square, low TCR values of 2–75 ppm/°C, and a small shift in resistance after high voltage testing.

The substitution of a significant part of precious metals by much cheaper titanium silicides leads also to lower price of these pastes as compared with conventional Pd–Ag compositions.

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