Commercial ZrO₂ paints as coatings for SiGe thermoelectric materials

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The use of ZrO_2 paints to coat SiGe materials used in radioisotopic thermoelectric generators was studied. The best results were obtained when the SiGe alloys were double coated with a 200 h anneal at 1000° C after each coating. The thermoelectric properties of these coated samples were about the same as for the SiGe alloys coated by SiO_2 or Si_3N_4. The vapour-supression properties of the best ZrO_2 coatings fell between those of SiO_2 and Si_3N_4. In the SiGe doped with GaP alloys, the interface between the oxide coating and alloy is enriched with Ga_2O_3.

1. Introduction
Silicon–germanium alloys which are used as thermo-electric materials for radioisotopic thermoelectric generators are exposed to high temperatures (up to 1050° C) to maximize their efficiently. Furthermore, these radioisotopic generators must last for a minimum of seven years. Silicon, germanium and the dopants are slowly lost due to sublimation at elevated temperatures [1–5]. In order to suppress sublimation of the silicon–germanium alloys, coatings of Si_3N_4 or SiO_2 are used [6, 7]. Unfortunately these coatings must be applied at temperatures higher than that permitted during the fabrication of the multicouple components of the generator.

In the present study, commercial oxide paints (mainly ZrO_2) were examined as possible vapour-suppression coatings for SiGe alloys. In addition to establishing the conditions for applying these materials, their effectiveness at 1080° C in vacuum was studied. Metallographic, X-ray diffraction (XRD) and electron probe microanalyser (EPMA) studies were used to understand the oxide adherence to the alloy. To determine if the coatings had a detrimental effect on the thermoelectric properties, Seebeck coefficient and resistivity measurements were made on the sample before and after the vaporization studies.

2. Experimental procedures
The n-type SiGe (GaP) and p-type SiGe alloys were prepared by hot-pressing powders of the starting materials of the appropriate concentrations at the Advanced Energy Programs Division of General Electric Company. The composition of the alloys is shown in Table I. The samples for sublimation, and Seebeck coefficient and resistivity measurements were cut to dimensions of 4.5 mm × 8.4 mm × 0.8 mm and 7.7 to 8.4 mm × 20.1 mm × 0.8 mm, respectively, and then were ultrasonically cleaned in acetone and rinsed with methyl alcohol. Prior to coating, the samples were oxidized for 1 h in air at 1000° C.

The commercial oxide paint "Z-prime" [8] was applied to the sample surface by a brush (B) or a spray gun (S) for the samples used in the sublimation studies. Because the coated samples, which were initially heat-treated for 500 h in air at 500° C, showed high mass loss rates by sublimation during heat treating at 1080° C, the subsequent samples for the sublimation studies were heated in air at 1100° C for 100 or 200 h after applying the "Z-prime" coating. Four samples received a single coat of "Z-prime", while a second coat was applied on the remaining four samples after the initial heat treatment followed again by heating in air in 1100° C for 100 h or 200 h. The samples were then heated in a vacuum furnace at 1080° C and taken out periodically to be weighed. The surfaces of the coated samples, which were heated in air at 1100° C for 30, 200 and 400 h, were examined by XRD.

The samples for Seebeck coefficient and resistivity measurements were coated by spraying the "Z-prime" oxide paint on to the alloy surface. The coated samples were intially heated in air at 1100° C for 200 h, and then a second coat was applied on the samples followed by a second heating in air at 1100° C for 200 h. The samples were then heated in a vacuum furnace at 1080° C for 1000 h. After the heat treatment, Seebeck coefficient and resistivity measurements of the alloys were carried out. These data were compared with the Seebeck coefficient and resistivity of uncoated samples

TABLE I Chemical composition of the SiGe alloys

Alloy	Composition (at %)				
	Si	Ge	Ga	P	B
n-type SiGe (GaP)	76.41	19.10	1.96	2.53	–
p-type SiGe	79.79	19.96	–	–	0.25

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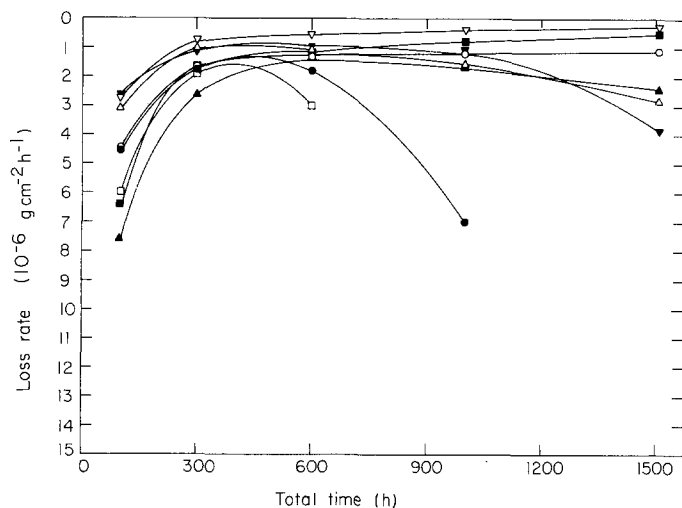
without heat treatment. After sublimation, Seebeck coefficient and resistivity measurements, the samples were examined metallographically and the oxides on the surface were identified by XRD. The cross-section of the coated samples was analysed by EPMA.

3. Results and discussion

Fig. 1 shows the loss rate by sublimation of the coated n-type SiGe (GaP) samples. Low loss rates were observed for samples B-38, S-42 and B-36 which were given two coats of "Z-prime". Samples B-38 and S-42 were heat-treated in air for 200 h after each coating was applied, while sample B-36 was heat-treated in air for 100 h after the application of each coat. High loss rates were observed for samples S-39 and B-35 which

have only one coat of "Z-prime" and had been heat-treated in air for 100 h after coating. The loss rates of samples S-40, S-37 and S-41 were found to lie between the low loss rate and the high loss rate samples mentioned above. The sublimation rate of the three intermediate loss rate samples as well as the two high loss rate samples increased with increasing time after 600 h at 1080°C.

Fig. 2 shows the coated surface of samples B-37, S-41, B-38 and S-42 after 1506 h in vacuum at 1080°C. The grey-coloured oxides for samples B-37 and S-41 were observed in the central area of the samples; these samples have only one coat and had been heat-treated in air for 200 h. Some cracks were detected in the grey-coloured oxide area. This suggests that the
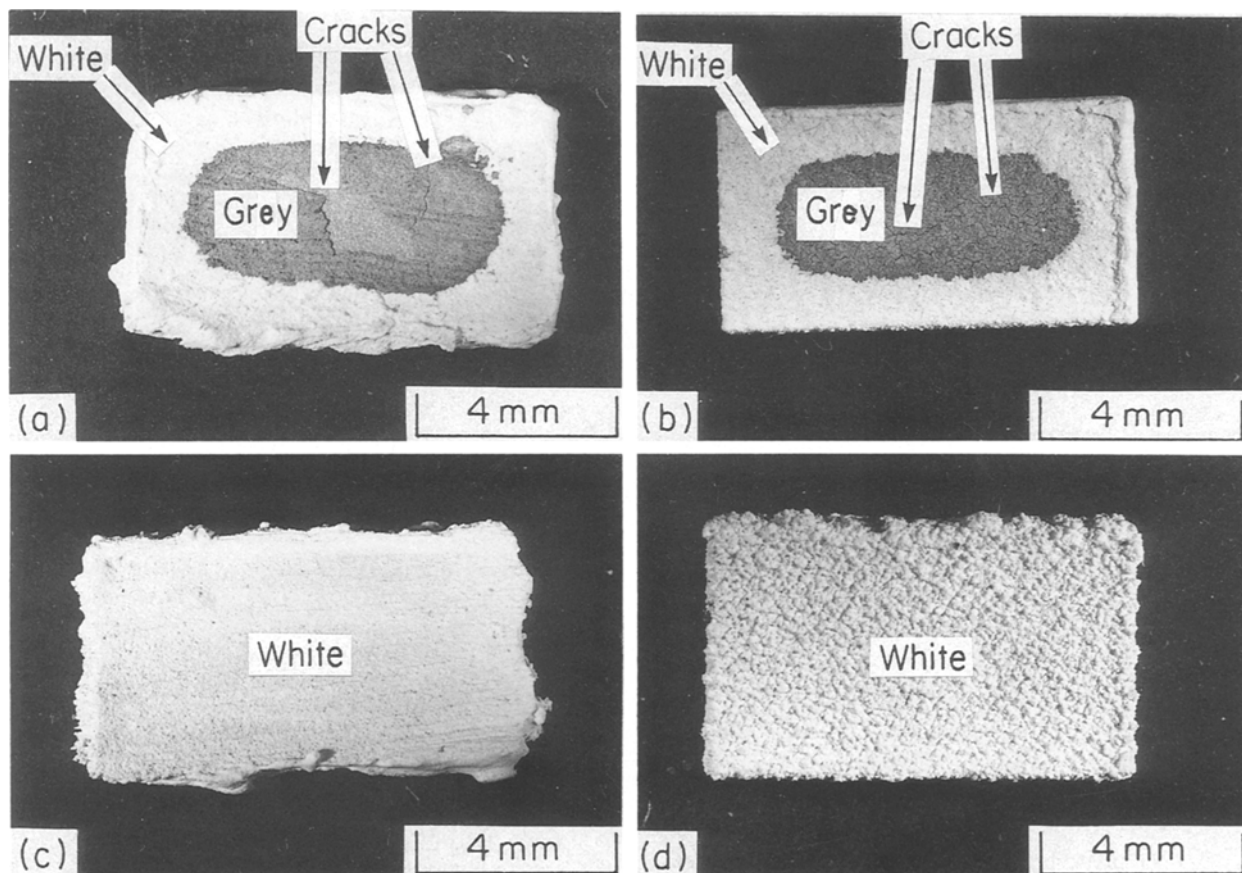

Figure 2 The coated surfaces of the samples B-37, S-41, B-38 and S-42 after 1506 h in vacuum at 1080°C. (a) B-37 (brush, one coat, 200 h), (b) S-41 (spray, one coat, 200 h), (c) B-38 (brush, two coats, 200 h + 200 h), (d) S-42 (spray, two coats, 200 h + 200 h).
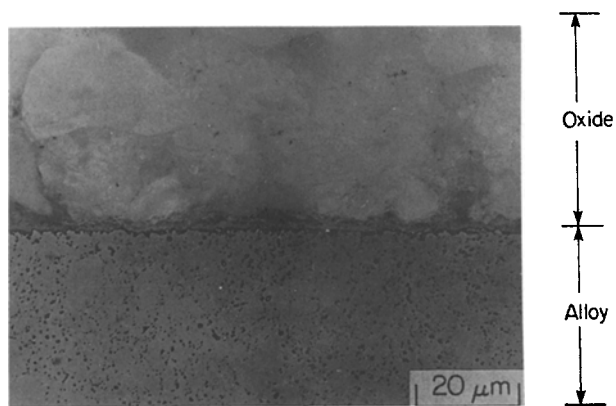
Figure 3 Microstructure of the cross-section of the n-type SiGe (GaP) alloy heated for 30 h at 1100°C in air after "Z-prime" coating.
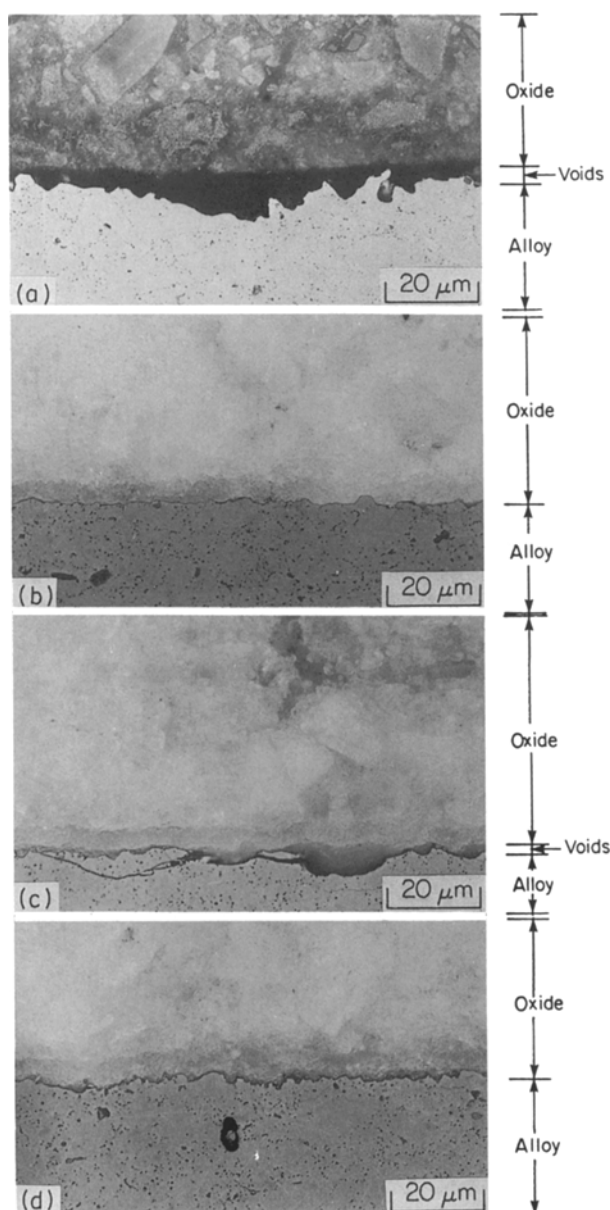

Figure 4 Microstructures of the cross-section of the n-type SiGe (GaP) alloys coated with "Z-prime" heated at 1080°C for 1506 h in vacuum. (a) B-37 (200 h), (b) B-38 (200 h + 200 h), (c) S-41 (200 h), (d) S-42 (200 h + 200 h).

TABLE II Summary of X-ray diffraction analysis of oxides present on n-type SiGe (GaP) alloys heat-treated in air at 1100°C.

Time (h)	Oxides	
30	ZrO_2 (s)	$ZrSiO_4$ (vw)
200	ZrO_2 (s)	$ZrSiO_4$ (w)
400	ZrO_2 (s)	$ZrSiO_4$ (m)

s, strong; m, medium; w, weak; vw, very weak.

spalling of the oxides occurs near cracks. The grey-coloured oxides might be formed by sublimation of n-type SiGe (GaP) alloys. On the other hand, white-coloured oxides were observed over the entire surface for samples B-38 and S-42. In addition, no cracks were found in the surface for these samples.

Fig. 3 shows a microstructure of the cross-section of an n-type SiGe (GaP) alloy, which had been coated with "Z-prime", after heating for 30 h at 1100°C in air. The oxide–alloy interface was smooth and the surface oxides showed good adherence. Fig. 4 shows microstructures of the cross-section of the "Z-prime"-coated n-type SiGe (GaP) alloys (B-37, B-38, S-41, S-42) after heating at 1080°C for 1506 h in vacuum. The oxide adherence of the samples (B-38, S-42), which showed low loss rate, was good. On the other hand, voids were observed at oxide/alloy interfaces of high loss rate samples (B-37, S-41). This is consistent with the results noted above, concerning the formation of cracks in the grey-coloured oxides and subsequent spallation. Void formation might occur by sublimation of the substrate.

Table II lists the phases identified by XRD of the coatings on n-type SiGe (GaP) alloys heat-treated in air at 1100°C. ZrO_2 and $ZrSiO_4$ were detected for all of the samples. The intensities of the Bragg peaks of $ZrSiO_4$ increased with increasing time.

Table III shows the phases identified by XRD of the coatings on n-type SiGe (GaP) alloys heat-treated in vacuum at 1080°C. ZrO_2 and $ZrSiO_4$ were detected for all the samples after heat treatment in vacuum. The intensities of the Bragg peaks of $ZrSiO_4$ were greater for the low loss rate samples (B-36, B-38, S-42) than for the high loss rate samples (B-35, B-37, S-40, S-41). We believe that the low loss rates are due to the improved oxide adherence by the presence of $ZrSiO_4$ in the coating. This in part may be due to the similarities of the coefficient of thermal expansion of n-type SiGe (GaP), $4.2 \times 10^{-6}\,°C^{-1}$ between 500

TABLE III Summary of X-ray diffraction analysis of oxides present on n-type SiGe (GaP) alloys heat-treated in vacuum at 1080°C.

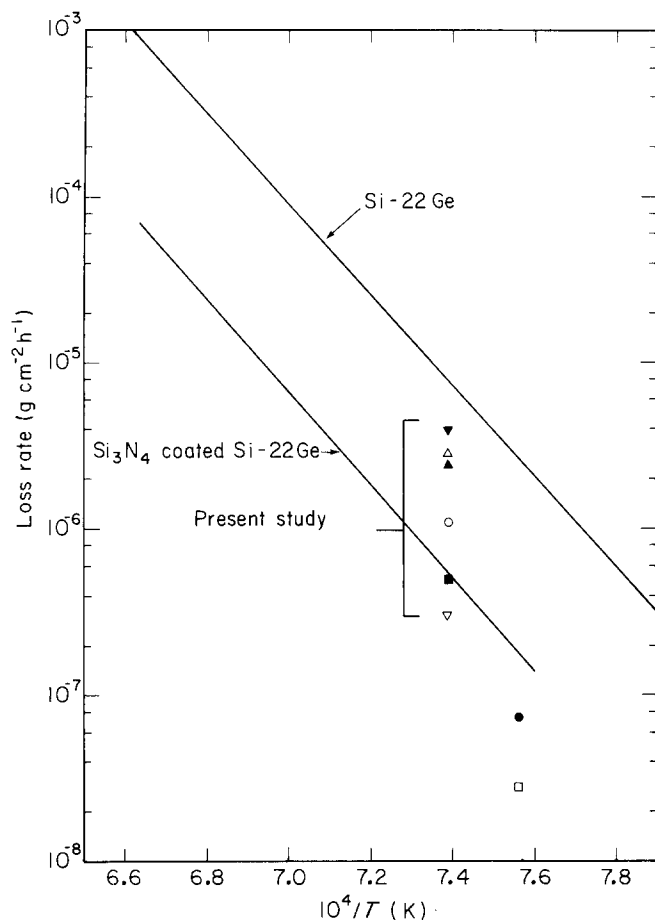| Sample no.	Time (h)	Oxides	
B-35	1006	ZrO_2 (s)	$ZrSiO_4$ (w)
B-36	1006	ZrO_2 (s)	$ZrSiO_4$ (m)
B-36	1506	ZrO_2 (s)	$ZrSiO_4$ (m)
B-37	1506	ZrO_2 (s)	$ZrSiO_4$ (w)
B-38	1506	ZrO_2 (s)	$ZrSiO_4$ (s)
S-40	1506	ZrO_2 (s)	$ZrSiO_4$ (w)
S-41	1506	ZrO_2 (s)	$ZrSiO_4$ (w)
S-42	1506	ZrO_2 (s)	$ZrSiO_4$ (m)

s, strong; m, medium; w, weak.

Figure 5 Loss rate for "Z-prime"-coated silicon–germanium samples compared to the published loss rate for uncoated and Si_2N_3-coated $Si_{78}Ge_{22}$ alloy (after Shields and Noon [7]). (●) SiO_2-coated p-type Si-2O$_2$Ge (GaP), (□) SiO_2-coated n-type Si-2O Ge (GaP). Present study: (○) B-36, (△) B-37, (▽) B-38, (▲) S-40, (▼) S-41, (■) S-42.

and 1000° C [9], and that of $ZrSiO_4$, 3.5×10^{-6} °C^{-1} between 20 and 1200° C [10].

Fig. 5 shows various loss rates for ceramic-coated silicon–germanium alloys. Our data on the loss rates in Fig. 5 shows values obtained for 1506 h in vacuum at 1080° C. The loss rates for samples S-42 and B-38 were found to lie between Si_3N_4-coated SiGe and SiO_2-coated SiGe (GaP) alloys, while the other coatings (B-36, B-37, S-40, S-41) lie between the Si_3N_4-coated SiGe and uncoated SiGe.

To determine if the coatings had a detrimental effect on the thermoelectric properties, measurements of Seebeck coefficient and resistivity of coated n-type SiGe (GaP) and p-type SiGe alloys were carried out after 1000 h in vacuum at 1080° C, and the results are shown in Figs 6 to 9. The oxide adherence of the

alloys, shown in these four figures, was good after heat treatment. Both Seebeck coefficient and electrical resistivity of the "Z-prime"-coated n-type SiGe (GaP) sample showed lower values compared with the uncoated sample. On the other hand, both Seebeck coefficient and electrical resistivity of "Z-prime"-coated p-type SiGe sample were larger than those of the uncoated sample. The increase in Seebeck coefficient and resistivity for the p-type SiGe is what would be expected from the published data [2] for a p-type SiGe alloy held at 1080° C for 1000 h. The effects of long-term heat treatments of n-type SiGe (GaP) alloys have not been published. Results for standard n-type SiGe held at 1000° C show a decrease in the resistivity and Seebeck coefficient with time [2]. The reported decrease is not as great as we have
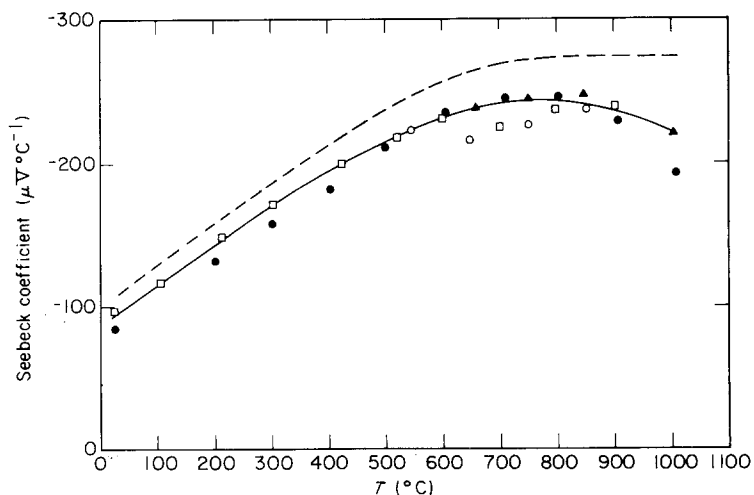

Figure 6 Seebeck coefficient of "Z-prime"-coated n-type SiGe (GaP) alloy, after 1000 h at 1080° C in vacuum. (●) First heating, (○) first cooling, (▲) second heating, (□) second cooling. (— — —) Uncoated p-type SiGe (GaP).
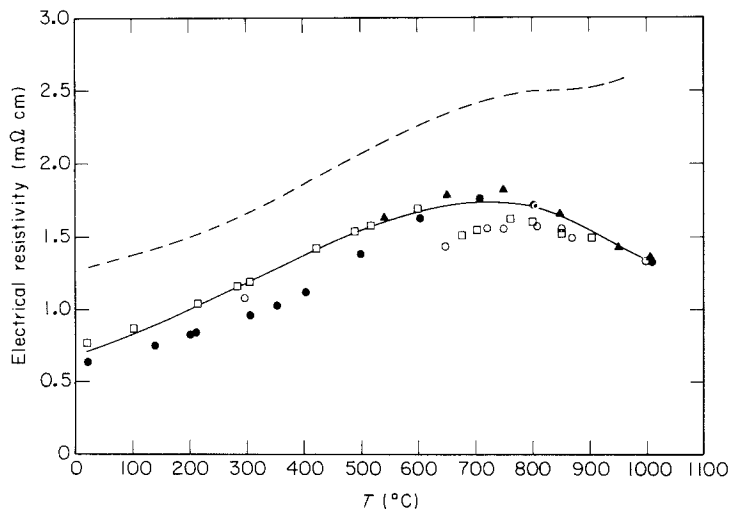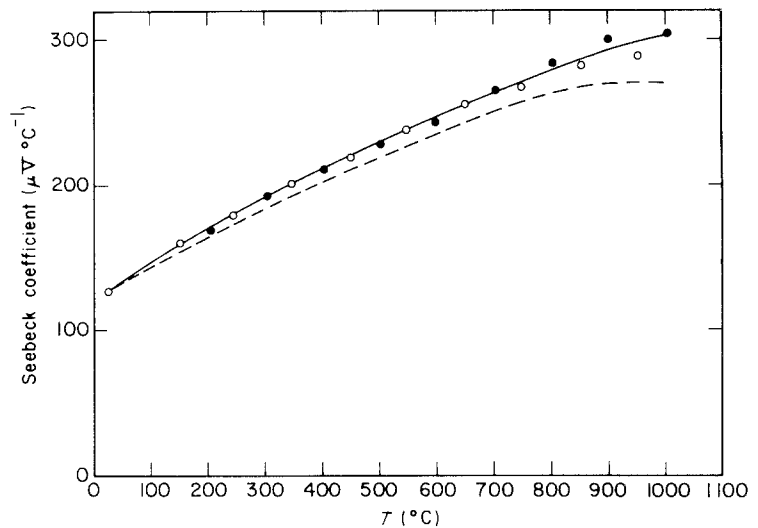
Figure 7 Electrical resistivity of "Z-prime"-coated n-type SiGe (GaP) alloy, after 1000 h at 1080° C in vacuum. (●) First heating, (O) first cooling, (▲) second heating, (□) second cooling. (— — —) Uncoated n-type SiGe (GaP).

Figure 8 Seebeck coefficient of "Z-prime"-coated p-type SiGe (GaP) alloy, after 1000 h at 1080° C in vacuum. (●) First heating, (O) first cooling. (— — —) Uncoated p-type SiGe.

observed for the n-type SiGe (GaP) material. It is interesting to note that the power factor S^2/ϱ is actually 20% higher at 900° C for the heat-treated n-type material than for the as-received alloy.

Studies on the compositional distribution of cross-sections of "Z-prime"-coated n-type SiGe (GaP) alloys after various heat treatments were carried out using a Cambridge Stereoscan 200 with Tracor X-ray spectrometer. Fig. 10 shows a schematic cross-section of n-type SiGe (GaP) alloys coated with "Z-prime". The symbol "A" indicates the point analysed by EPMA in

each sample. A gallium-enriched area was observed after heat treatment. Table IV shows the results of the electron probe microanalysis on the gallium-enriched area of "Z-prime"-coated n-type SiGe (GaP) alloys. The amounts of gallium, silicon and germanium in the area are nearly the same after 30 and 200 h in air at 1100° C. The amounts of gallium and germanium in this area of the alloys S-41 and S-42 are also nearly the same after 1506 h in vacuum at 1080° C. The increased concentration of gallium at the interface is due to the formation of a gallium oxide, probably Ga_2O_3. We
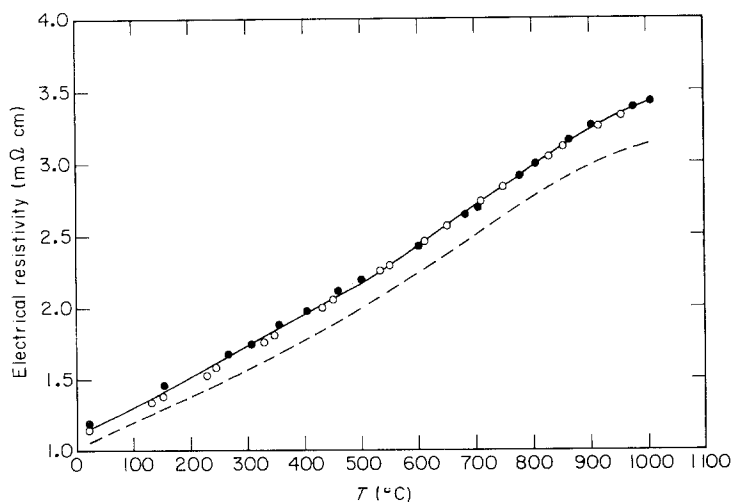

Figure 9 Electrical resistivity of "Z-prime"-coated p-type SiGe alloy, after 1000 h at 1080° C in vacuum. (●) First heating, (O) first cooling. (— — —) Uncoated p-type SiGe.
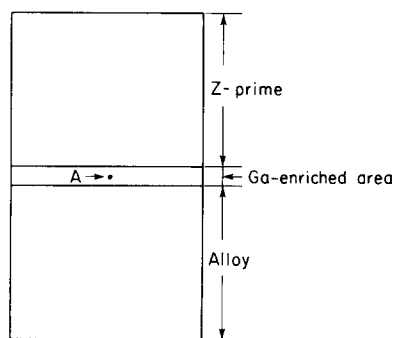
Figure 10 A schematic cross-section of n-type SiGe (GaP) alloys coated with "Z-prime". The symbol "A" indicates the point analysed by EPMA.

believe the oxidation of gallium involved the presence of SiO which is a gaseous species at this temperature and is less stable than Ga_2O_3. The crystal chemistry of Ga_2O_3 and ZrO_2 are such that these two phases do not react with one another, and so the Ga_2O_3 remains between the two layers. As the gallium in the SiGe alloy oxidizes at the interface, the gallium in the alloy is depleted and the chemical potential drives the gallium from the interior of the alloy to the interface vicinity where the process continues, thus building up the Ga (Ga_2O_3) content in the interface layer A.

The hope that these commercial oxide paints could be applied at low temperatures has not been realized. Good adherence and vapour suppression has been achieved, but the high-temperature pretreatment used

in this study on the SiGe samples limits the potential of those coatings because the multicouple construction requires a low-temperature method.

Acknowledgements

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TABLE IV Electron probe microanalysis of gallium enriched area* of "Z-prime"-coated n-type SiGe (GaP) alloys

Heat treatment	Analysed composition (at %)
1100° C, 30 h in air	76 Ga, 18 Si, 5 Ge, 1 Zr
1100° C, 200 h in air	82 Ga, 12 Si, 5 Ge, 1 Zr
1080° C, 1506 h in vacuum[†]	98 Ga, 2 Ge
1080° C, 1506 h in vacuum[‡]	93 Ga, 3 Ca, 2 Ge, 1 Si, 1 Zr

*See Fig. 10. Note: this region also contained an appreciable amount of oxygen (see text).
[†]S-41, the sample exhibited a high vaporization rate.
[‡]S-42, the sample exhibited a low vaporization rate.