# CRYSTAL GROWTH, CHARACTERIZATION AND RESISTIVITY MEASUREMENTS OF TiSi<sub>2</sub> SINGLE CRYSTALS

#### O. THOMAS, R. MADAR and J. P. SENATEUR

INPG, ENSPG, Unité associée au CNRS 1109, Domaine Universitaire, B.P. 46, 38402 Saint Martin d'Hères (France)

### O. LABORDE

CRTBT, SNCI, Centre National de la Recherche Scientifique, Avenue des Martyrs 166 X, 38042 Grenoble Cédex (France)

(Received May 2, 1987)

### Summary

Bulk single crystals of titanium disilicide  $\text{TiSi}_2$  have been grown from a levitated melt with a modified cold crucible Czochralski method. The as-grown crystals were characterized by X-ray diffraction, density measurements and resistivity along the three main directions of the orthorhombic structure.  $\text{TiSi}_2$  follows the classical behaviour of a metallic compound with a resistivity at room temperature near 10  $\mu\Omega$  cm and a residual resistance ratio in the range 50 - 90. The values obtained indicate an anisotropic behaviour for the conductivity at high temperature smaller then 20%.

### 1. Introduction

The refractory metal disilicides are of current interest to the microelectronics industry as new gate electrodes and interconnect materials [1-3]. Among the four compounds which can be used for these applications,  $WSi_2$ ,  $TaSi_2$ ,  $MoSi_2$  and  $TiSi_2$ ,  $TiSi_2$  is the most widely used because of its low resistivity at room temperature (about 15  $\mu\Omega$  cm).

Despite its technological importance, little is known about its fundamental electronic band structure and transport properties. Data are scarce and mostly questionable when obtained on sintered materials or polycrystalline thin films since it is difficult to estimate the effect of the microstructure on the transport properties.

This communication (part of a wider research project on bulk monocrystalline refractory metal silicides) reports the growth and characterization of large  $TiSi_2$  single crystals. There is an acknowledged need for experimental studies on bulk materials and, in particular, single crystals in order to determine the ultimate limits to the obtainable properties.

# 2. Materials preparation and crystal growth

The phase diagram of the Ti-Si system has been studied in detail [4] and five binary compounds (Ti<sub>3</sub>Si, Ti<sub>5</sub>Si<sub>3</sub>, Ti<sub>5</sub>Si<sub>4</sub>, TiSi and TiSi<sub>2</sub>) have been reported. TiSi<sub>2</sub> crystallizes in a face centred orthorhombic structure [5] represented in Fig. 1 (type C54, space group *Fddd*) with parameters a = 8.266(4) Å, b = 4.798(7) Å and c = 8.550(3) Å and melts congruently at a temperature between 1500 and 1540 °C [6].

Various attempts have already been made to grow single crystals of this silicide and they are summarized in Table 1 [7, 8]. Surprisingly, despite its congruent melting point, the previous attempt to grow single crystals from the melt using the Czochralski method [9] led to the synthesis of poor quality crystals characterized by a considerable deficiency of silicon with respect to the stoichiometric composition  $(\text{TiSi}_{1.8} - \text{TiSi}_{1.93})$ . Since we could find no data on a possible homogeneity range for TiSi<sub>2</sub>, we began by determining this range, which is of crucial importance for both the crystal growth process and the understanding of the transport properties. For this purpose, we prepared bulk samples with Ti:Si atomic ratios equal to 0.56 and 0.16 corresponding to the compositions of the eutectics TiSi-TiSi<sub>2</sub> and TiSi<sub>2</sub>-Si. In this way, we can obtain both limits of the homogeneity range of TiSi<sub>2</sub> for a given annealing temperature.



Fig. 1. TiSi<sub>2</sub>:orthorhombic crystal structure.

#### TABLE 1

Crystal g	growth	of	TiSi <sub>2</sub>	single	crystals
-----------	--------	----	-------------------	--------	----------

Technique	Composition	Shape and size of the crystals	Reference
Czochralski	TiSi <sub>1.80</sub> - TiSi <sub>1.93</sub>	rods mm <sup>3</sup>	[9]
Salt electrolysis	TiSi <sub>2</sub>	1 mm	[10]
CVD	TiSi2	0.1 - 0.2 mm	[11, 12]
Solution growth in zinc solvent	TiSi <sub>2</sub>	0.1 - 0.2 mm	[13]
CVT(Br <sub>2</sub> )	TiSi <sub>2</sub>	$1 \text{ mm}^3$	[14]
$CVT(Cl_2, Br_2, I_2)$	TISi <sub>1.92</sub> - TiSi <sub>1.98</sub>	1 - 10 mm	[8]

The corresponding amounts of titanium (purity, 99.99%) and silicon (purity, 99.9999%) were melted together in a conical-shaped cold copper crucible under pure argon. The crystalline structure of these alloys was checked after annealing at 900 °C for 48 h by X-ray powder diffraction in a Seeman-Bohlin-type focusing camera using Cr K $\alpha_1$  radiation, with silicon as internal calibration standard. The measured lattice parameters were a = 8.269 Å, b = 4.800 Å and c = 8.550 Å for TiSi<sub>2</sub> in equilibrium with TiSi and a = 8.270 Å, b = 4.799 Å and c = 8.552 Å for TiSi<sub>2</sub> in equilibrium with silicon.

Taking into account the experimental uncertainties, we may consider that both sets of values are almost identical and in agreement with those previously reported. This is a good indication that if there is any homogeneity range for  $TiSi_2$ , it must be extremely narrow, in contradiction with the results reported by other workers [8, 9].

After the homogeneity range has been established, the only problem left for the crystal growth of  $\text{TiSi}_2$  is the choice of a crucible. Indeed, no suitable crucible materials are available to contain liquid  $\text{TiSi}_2$  ( $T_m \approx 1540$  °C) without contaminating it. The previous attempt to grow  $\text{TiSi}_2$  single crystals from the melt was performed using quartz crucibles which react with the molten alloy. This may explain the poor results that were obtained in this experiment [9].

As for  $MoSi_2$  [15], we used a cold copper crucible in which the melt is r.f. levitated. Crystals were grown by the Czochralski technique from a levitated drop in a modified Hukin-type crucible. In this technique, the coupling is highly dependent on the molten volume. This implies a continuous variation in the power supply during the growth process. To avoid this undesirable effect, a solid bar of alloy with the same composition as the crystal, is pushed into the melt at a speed which compensates for the solidified mass already pulled out. Synthesis of the solid bar of TiSi<sub>2</sub> is first achieved in the same crucible by direct melting of high purity titanium rods (purity, 99.99%) and silicon lumps (purity, 99.9999%). The growth chamber is filled with 1.5 bar of pure argon. In a first step oriented [100] seeds were cut from a polycrystalline ingot obtained by pulling with a tungsten needle. Large oriented single crystals (9 mm in diameter and 30 mm in length) were grown with these seeds at a pulling rate of approximately 5 cm h<sup>-1</sup>.

The single-crystal rod was then mounted with wax on a goniometer and oriented by the Laue X-ray diffraction technique. Hence a direction was determined and slices were cut by mechanical grinding along the three main crystallographic directions.

Density was measured on a single crystal by the Archimedes method using  $CCl_4$  as the immersion liquid. We obtained  $d_m = 4.08$  g cm<sup>-3</sup>. The lattice parameters measured by X-ray powder diffraction on the same monocrystalline rod were a = 8.267(2) Å, b = 4.799(9) Å and c = 8.553(5) Å.

With eight formula units per unit cell and assuming the composition  $TiSi_2$ , this leads to a calculated density  $d\alpha = 4.07$  g cm<sup>-3</sup> in very good agreement with the measured density. Thus, not only is the homogeneity range

of  $TiSi_2$  extremely narrow but it is also almost centred on the stoichiometric composition.

## 3. Resistivity measurements: results and discussion

Samples were cut from the single-crystal rods. Their typical dimensions were  $1 \text{ mm} \times 1 \text{ mm} \times 5 \text{ mm}$ . The larger dimension was taken parallel to one of the main crystallographic directions; the [100], [010] and [001] axes.

Unlike the other disilicides studied,  $TiSi_2$  is very brittle. Under machining, small chips can break off, and the final shape of the sample can be slightly different from the desired parallelepiped. This leads to a poor accuracy of the form factor and as a result, poor accuracy of the absolute value of the resistivity which is known only with an accuracy of 5% in the best case. The density of each sample investigated was remeasured, in order to test for the presence of voids. Results did not differ by more than 1% from the calculated value. Such an effect is undetectable and in any way does not affect the absolute value of  $\rho$ .

The resistivity was measured from 4.2 K to room temperature by a four-probe a.c. method. Details of the apparatus and the techniques can be found elsewhere [15, 16]. The results are summarized in Tables 2 and 3. Samples are referred to by the corresponding crystallographic axis along which the current flows. The residual resistance ratio (RRR) which characterizes the amount of defects in the material, ranges from about 50 - 90. This is a fairly high value for a metallic compound and is a test of the good quality of our crystals. The RRR varies from sample to sample and can also change from one part to another part of the same sample, depending on the position of the potential leads. We have thus a very sensitive means of characterization of the material. The absence of any resistivity minima at lower temperatures, which is sometimes observed in titanium compounds [17] because of the presence of magnetic impurities, can also be noted. The resistivity at room temperature is near 10  $\mu\Omega$  cm in good agreement with previous reports on single crystals [9] and on thin films [18, 19] (when the residual resistivity is subtracted).

 $TiSi_2$  follows the classical behaviour of a metallic compound, with a temperature independent residual resistivity and an intrinsic resistivity which

# TABLE 2

Samples	[100]	[010]	[001]
$\rho$ (293 K) ( $\mu\Omega$ cm)	$10.9 \pm 1$	$10.1 \pm 0.5$	$11.5 \pm 1$
$\rho(293 \text{ K})/\rho(4.2 \text{ K})$	62	51	87
$\rho_0 \ (\mu \Omega \ \mathrm{cm})$	0.174	0.200	0.131
$A (\mu \Omega \text{ cm})$	92.57	87.55	96.08
$\theta_{\mathbf{D}}(\mathbf{K})$	535	543	524

Results of the resistivity measurements

**TABLE 3** 

T <sub>K</sub>	$\rho_{i}$				
	[100]	[010]	[001]		
40	0.47	0.43	0.40		
50	1.14	1.09	1.04		
60	2.31	2.25	2.22		
70	4.06	3.97	3.96		
80	6.44	6.30	6.39		
110	12.90	12.67	13.06		
120	21.16	20.82	21.66		
150	35.43	35.00	36.37		
200	61.18	61.05	62.04		
250	87.62	87.71	88.05		
273	100	100	100		
300	114.11	114.26	114.33		

 $\rho_i$  values normalized at 273 K

is a function of temperature. If the residual resistivity  $\rho_0$  at low temperatures results from the scattering by defects and impurities, the thermal variation in  $\rho$ , usually referred to as the ideal part of the resistivity is ascribed to the scattering of conduction electrons by phonon excitations. Some experimental values of the ideal resistivity  $\rho_i$  normalized at 273 K are given in Table 3 for the three samples at different temperatures.  $\rho_i$  is defined as follows.

$$\rho_{\rm i} = 100 \times \frac{R(T) - R(273 \, \text{K})}{R(4.2 \, \text{K}) - R(273 \, \text{K})}$$

At lower temperatures  $(T < 50 \text{ K}) \rho_i$  varies as  $T^n$ , with *n* close to 5. This justifies a fit for the measured resistivity, based on the Bloch-Grüneisen formula.

$$\rho(T) = \rho_0 + A\left(\frac{T}{\theta}\right)^5 J_5\left(\frac{\theta}{T}\right)$$

With

$$J_5(x) = \int_0^x \frac{z^5 dz}{(e^z - 1)(1 - e^{-z})}$$

This expression usually gives a reasonably good description of the electron-phonon contribution to the resistivity of simple metals. The three independent parameters  $\rho$ , A and  $\theta_D$  calculated in this way are quoted in Table 2 for each sample. Experimental data and calculated Bloch-Grüneisen resistivity are shown in Fig. 2 for a TiSi<sub>2</sub> sample measured along the [010] direction.  $\rho_{meas} - \rho_{calc}$  is also plotted with a magnified scale in the lower part of the figure. The fit is rather good; however, small deviations from the



Fig. 2. Ideal resistivity for TiSi<sub>2</sub> with I/[010] against T: upper part, experimental data (\*) and  $\rho$  calculated with the Bloch-Grüneisen formula (----), also shown are  $\rho_{cal} + 1 n\Omega \text{ cm} (- \cdot - \cdot)$  and  $\rho_{cal} - 1 n\Omega \text{ cm} (- \cdot - \cdot)$ ; lower part,  $\rho_{meas} - \rho_{calc}$  against T.

 $T^{5}$  law occur at low temperature. They are quite common and can be attributed to interband transitions or electron-electron interactions.

The Debye temperatures  $\theta_D$  determined are about 500 - 550 K larger than the usual values for transition metals [20]. This probably reflects the different nature of bonding in silicides and pure metals, with an increasing importance of covalent bonds, M—Si, in the former. The same effect has previously been reported in MoSi<sub>2</sub> with an even larger Debye temperature. However, the difference in mass alone, between titanium and molybdenum, cannot explain the large difference in  $\theta_D$  between the two silicides.

The values given in Tables 2 and 3 seem to indicate an anisotropic behaviour for the conductivity at high temperature which is not larger than the estimated uncertainty and is certainly smaller than 20%. We also notice that the  $\rho_i(T)$  values are not the same for the three crystallographic directions. This could also provide evidence for an anisotropic behaviour of TiSi<sub>2</sub> or may result from deviations from Matthiessen's rule. Indeed, such deviations occur in MoSi<sub>2</sub> with  $\rho_0$  similar to the residual resistivities measured here for TiSi<sub>2</sub>. They could induce spurious curvatures in the curves  $\rho$  vs. T which could be reflected in the fitted parameters. This hypothesis is supported by the continuous variation observed for A and  $\theta$  against  $\rho_0$ , independent of the crystallographic orientation. This is shown in Fig. 3 where A and  $\theta_D$  are plotted vs.  $\rho(4.2 \text{ K})/\rho(273 \text{ K})$  for the three samples studied previously and also for a fourth experiment performed along [010]. Further investigations and data are needed, however, to reach an unambiguous conclusion on this point.



Fig. 3. Fitted parameters A and  $\theta_D$  (see text) vs. R(4.2 K)/R(273 K).

We have previously shown that the resistivities at room temperature of  $TaSi_2$  [21] and  $MoSi_2$  [16] single crystals are anisotropic For the latter silicide we have related this behaviour to the anisotropy of the electronic structure. Such an anisotropic resistivity was not found in  $WSi_2$  [21] and the result reported here for  $TiSi_2$  leads to an anisotropy smaller than 20% for this alloy. However, we note that a small anisotropy of the magnetic susceptibility was observed on single crystals of this compound [9].

The ideal resistivity of  $MoSi_2$  is also significantly different from  $TiSi_2$ . They differ by their initial T variations at low temperatures; only a slight deviation from the expected  $T^5$  law occurs for  $TiSi_2$ , whereas a strong departure from this law was observed for  $MoSi_2$  [16]. They also differ by the calculated value of  $\theta_D$  as noted above. This can probably be explained by their electronic structures. The occurrence of two bands at the Fermi level was proved for  $MoSi_2$  by magnetoresistivity [16], and de Haas van Alphen [22] measurements and by electronic structure calculations [23]. These data are not presently available for  $TiSi_2$ , but it is likely that a lone electronic band could account for the observed behaviour of this compound. Investigation is in progress on this point.

#### References

- 1 S. P. Murarka, J. Vac. Sci. Technol., 17 (1980) 775.
- 2 M. A. Nicolet and S. S. Lau, in N. G. Einspruch and G. B. Larrabee (eds.), VLSI Electronics: Microstructure Science, Vol. 6, Academic Press, New York, 1983, p. 329.
- 3 F. M. d'Heurle, in C. J. Dell'oca and W. Bullis (eds.), VLSI Science and Technology, Electrochemical Society, Pennington, New Jersey, 1982, p. 194.
- 4 V. N. Svechnikov, Yu. A. Kocherzhinskii, L. M. Yupko, D. G. Gulik and E. A. Shishkin, Dokl. Akad. Nauk SSSR, 193 (1970) 393.

- 5 F. Dietrich, T. Smith and C. R. Houska, J. Am. Ceram. Soc., 61 (1978) 276.
- 6 M. Hansen, H. D. Kessler and D. J. McPherson, Trans. Am. Soc. Met. Preprint no. 4 (1951).
- 7 K. N. Mason, Prog. Cryst. Growth. Charact., 2 (1979) 269.
- 8 P. Peshev and M. Khristov, J. Less-Common Met., 117 (1986) 361.
- 9 J. Beaudouin, C.R. Acad. Sci. Paris, Ser. C, 263 (1966) 1065.
- 10 R. V. Chernov, A. P. Nizov and Yu. K. Delimarskii, Ukr. Khim. Zh., 37 (1971) 422.
- 11 K. Th. Wilke, Z. Phys. Chem. (Leipzig)., 20 (1962) 137.
- 12 J. J. Nickl and K. K. Schweitzer, Z. Metallkd., 61 (1970) 54.
- 13 V. N. Gurin, Z. Terent'eva, I. R. Kozlova and A. P. Obukhov, *Izv. Akad. Nauk SSSR*, Neorg. Mater., 8 (1972) 1917.
- 14 J. J. Nickl and J. D. Koukoussas, J. Less-Common Met., 23 (1971) 73.
- 15 O. Thomas, J. P. Senateur, R. Madar, O. Laborde and E. Rosencher, Solid State Commun., 55 (1985) 629.
- 16 O. Laborde, O. Thomas, J. P. Senateur and R. Madar, J. Phys. F, 16 (1986) 1745.
- 17 R. K. Williams, P. F. Becher and C. B. Finch, J. Appl. Phys., 56 (1984) 2295.
- 18 V. Malhotra, R. L. Martin and J. E. Mahan, J. Vac. Sci. Technol. B, 2 (1984) 10.
- 19 J. C. Hensel, Mater. Res. Soc. Symp. Proc., 54 (1986) 499.
- 20 G. K. White and S. B. Woods, Philos. Trans. R. Soc. London, Ser. A, 251 (1959) 273.
- 21 O. Thomas, Ph.D. Thesis, Institut National Polytechnique de Grenoble (1986).
- 22 J. M. Van Ruitenbeek, W. Joss, R. Pauthenet, O. Thomas, J. P. Senateur and R. Madar, *Phys. Rev. B*, to be published.
- 23 B. K. Bhattacharyya, D. M. Bylander and L. Kleinman, Phys. Rev. B, 31 (1985) 2049, 5462.