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The heat capacities of titanium silicides Ti₅Si₃, TiSi and TiSi₂

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Abstract

Titanium silicides Ti_5Si_3 , TiSi and $TiSi_2$ have been prepared and characterized by X-ray powder diffraction and optical metallography. The heat capacities of the silicides have been measured by means of differential scanning calorimetry (DSC) in the temperature range of 230 to 600 K. The heat capacities of Ti_5Si_3 , TiSi and $TiSi_2$ at 298 K have been found to be 181 ± 3 , 47.2 ± 0.6 and 66.6 ± 0.9 J mol⁻¹ K, respectively. The obtained results are compared with literature heat capacity data. © 2001 Published by Elsevier Science B.V.

Keywords: Heat capacity; Differential scanning calorimetry; Titanium silicides

1. Introduction

Titanium disilicide is used for Si interconnects because of its low electrical resistivity and thermal stability [1]. As integrated circuit and electronic package requirements increase, greater efficiency in fabrication processes such as chemical vapor deposition (CVD) will be required. Reliable thermodynamic data on titanium silicides are essential to the continued development and optimization of these advanced thin-film fabrication techniques [2].

Previous reports [3–9] of the thermal properties of Ti silicides revealed some large disparities between values of heat capacities, particularly in the temperature range between 300 and 600 K. Golutvin [3] previously reported heat capacities for Ti_5Si_3 , TiSi and $TiSi_2$ at temperatures between 300 and 1400 K calculated from enthalpy increment measurements performed by means of drop calorimetry. Sylla et al. [4] published heat capacity values for $TiSi_2$ between 350 and 500 K, obtained by differential scanning calorimetry. Sychev et al. [8] reported heat capacity values for Ti_5Si_3 in the temperature range of 15 to 300 K obtained by means of adiabatic calorimetry. Archer et al. [5–7] reported heat capacity values for all three of these silicides between 4.2 and 350 K calculated from enthalpy increments of the titanium silicides mea-

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sured by means of adiabatic calorimetry. For TiSi, Archer evaluated his measurements of enthalpy increments, along with those reported by others [3,9] at temperatures between 298.15 and 1473 K, in order to present values of heat capacities between 4.2 and 1500 K. In this investigation the heat capacities of Ti_5Si_3 , TiSi, and $TiSi_2$ have been measured in the temperature range of 230–600 K by means of differential scanning calorimetry. The goal of the present investigation is to provide direct measurements of the heat capacities of these Ti silicides in this temperature range to compare them with previous measurements in an effort to clarify the thermal functions for titanium silicides.

2. Experimental details

Titanium silicide samples were prepared by arc melting stoichiometric mixtures of elemental titanium (less than 0.01% metal impurities) and silicon (less than 0.005% metal impurities) on a water-cooled copper hearth under a purified argon atmosphere. To remove traces of oxygen and water from argon inside the arc melting chamber, a titanium slug, used as a getter, was arc melted for about 1 min just before a Ti–Si sample. The resulting titanium silicide ingots were turned on their side and remelted at least once. X-ray powder diffraction patterns indicated that the arc melted Ti₅Si₃ and TiSi₂ samples were single phase. In the TiSi samples, however, a significant amount of foreign phases was detected. The arc melted TiSi samples

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were annealed in vacuum (10^{-6} Torr) at 1150°C for 18 h. After annealing of the TiSi samples, X-ray diffraction analysis showed that they were single phase. Lattice parameters of Ti₅Si₃, TiSi and TiSi₂, calculated from X-ray powder diffraction data, are given in Table 1. These values are in good agreement (within 0.5%) with previously reported measurements [4,8,10–12].

Polished cross-sections of the Ti–Si samples were examined by means of optical metallography. The metallographic images revealed that there were some foreign phases present in the samples. The amount of impurity was estimated by measuring the relative area of the phases observed on the metallographic images. The TiSi sample contained less than 1 at.% of foreign phases. The impurity in the TiSi₂ sample was less than 0.1 at.%, and the Ti₅Si₃ sample was contaminated by less than 1 at.%.

The heat capacities of the Ti_5Si_3 , TiSi and $TiSi_2$ samples in the temperature range of approximately 250– 600 K were measured by differential scanning calorimetry (DSC) [13,14]. The equipment used was a Perkin-Elmer DSC2 interfaced to a microcomputer for data acquisition. Sapphire and copper (both obtained from National Institute of Standards and Technology [NIST]) were used as heat capacity standards. The Ti–Si samples were ground into fine a powder, while the sapphire and copper standard samples were used in the form of disks weighing approximately 18 and 50 mg, respectively. The Ti_5Si_3 , TiSi and $TiSi_2$ samples were all approximately 30 mg each. All the samples were encapsulated in commercially available aluminum pans. Variation in the masses of the pans chosen for different samples was less than 0.05 mg.

Temperature calibration of the Perkin-Elmer DSC2 in the temperature range of 230–700 K was performed using high-purity Hg, In, Pb and Zn metals and cyclohexane (the cyclohexane sample was obtained from NIST) as reference materials. Based on the differences between observed and actual melting points of the references, corrections were made to compensate for the discrepancy between actual temperature and the programmed temperature of the instrument.

Heat capacity measurements were performed by the scanning method with temperature intervals of 75 K and scan rates of 0.333 K s⁻¹. The samples were examined in the following sequence: empty Al pan, Cu reference, Ti_5Si_3 , TiSi and $TiSi_2$ samples, sapphire reference. Data were compiled during an initial 180 s isothermal anneal at the lowest temperature, followed by the heating of the sample during 338 s, and finally by a 360 s isothermal

Table 1 Lattice parameters for Ti₅Si₃, TiSi and TiSi₂

1 55 57 2						
	<i>a</i> , Å	b, Å	<i>c</i> , Å			
Ti ₅ Si ₃	7.454 ± 0.001		5.150 ± 0.001			
TiSi	6.522 ± 0.006	3.640 ± 0.003	5.022 ± 0.005			
TiSi ₂	8.274 ± 0.005	4.795 ± 0.002	8.544±0.005			

anneal at the highest temperature of a specific interval. This completed anneal cycle was repeated three times for each sample during 1 day. The third data set was used for data analysis. Sapphire was used as a primary standard for calibrating the measurements of heat flow, while copper was utilized to check the accuracy of the measurements.

The analysis of the differential scanning calorimetry data to determine heat capacities has been previously described in detail [13–15]. First, the DSC signals for both the Ti–Si and for the reference samples were obtained by subtracting the data due to the empty Al pan from the total DSC signal of an encapsulated sample. For each set of runs, the ratio between the known heat capacity values for sapphire [16] and the observed signal for a sapphire reference sample was then used to calculate a calibration factor as a function of temperature within a specific temperature range. The heat capacities for Ti_5Si_3 , TiSi and $TiSi_2$ samples were calculated by multiplying the observed signal for the samples by the calibration factor. Variations in the calibration factor from run to run or from day to day were typically within 1%.

3. Results and discussion

Figs. 1–3 show heat capacities of Ti_5Si_3 , TiSi and $TiSi_2$, respectively, in the temperature region of approximately 250–600 K. Solid lines on the plots represent polynomial fits to the data in the form

$$C_{\rm p} = A + BT + CT^2 + DT^{-2} \tag{1}$$

Coefficients of the polynomial fits along with heat capacities for the three titanium silicides at 298 K are summarized in Table 2. The majority of the data are within



Fig. 1. Heat capacity vs. temperature for Ti_5Si_3 as measured by means of DSC. (\blacktriangle) – data points; (——) – polynomial fit to all of the data.



Fig. 2. Heat capacity vs. temperature for TiSi as measured by means of DSC. (\blacktriangle) – data points; (——) – polynomial fit to all of the data.



Fig. 3. Heat capacity vs. temperature for TiSi_2 as measured by means of DSC. (\blacktriangle) – data points; (——) – polynomial fit to all of the data.

1% of the fitted values, while some of the data points agree to within 2-3%.

Fig. 4 shows the percent deviation of the heat capacity values for Ti_5Si_3 obtained in this study from the previously published data of Archer et al. [5], Sychev et al. [8], and Golutvin [3]. Agreement with the data of Archer et al. and Sychev et al. is within 1 to 2%, while the disagreement



Fig. 4. Percent deviations of the data from this study for Ti_5Si_3 from previously reported experimental data: (\Box) – Archer et al. [5]; (\bullet) – Sychev et al. [8]; (\bullet) – Golutvin [3].

with Golutvin's data at temperatures between 300 and 450 K is significant, reaching approximately 30% at 300 K. In a similar fashion, Fig. 5 compares the data for TiSi₂ from this study with the data of Archer et al. [7], Sylla et al. [4], and Golutvin [2]. The data for TiSi₂ from this study agree with those of Archer et al. [7] and Sylla et al. [4] within 1



Fig. 5. Percent deviations of the data from this study for TiSi_2 from previously reported experimental data: (\Box) – Archer et al. [7]; (\bullet) – Sylla et al. [4]; (\blacktriangle) – Golutvin [3].

Table 2

Heat capacities at 298 K and heat capacity parameters^a for Ti₅Si₃, TiSi and TiSi₂ in the temperature range of 250-600 K as measured by DSC

	Α	В	С	D	$C_{\rm p}$ at 298 K, J mol ⁻¹ K
Ti ₅ Si ₃	236	-0.101	1.38×10^{-4}	-3.07×10^{6}	181±3
TiSi	49.8	0.0177	-1.18×10^{-5}	-5.98×10^{5}	47.2 ± 0.6
TiSi ₂	68.9	0.0249	-1.38×10^{-5}	-7.56×10^{5}	66.6±0.9

^a $C_{p} = A + BT + CT^{2} + DT^{-2}$.



Fig. 6. Percent deviations of the data from this study for TiSi from previously reported experimental data: (\Box) – Archer et al. [6]; (\blacktriangle) – Golutvin [3].

to 2%, but disagree considerably with the values given by Golutvin [3]. Fig. 6 displays percent deviation of the heat capacity values for TiSi obtained in this study from the data of Archer et al. [6] and Golutvin [3]. Also included in Fig. 6 are data gleaned by Archer [5] from analysis of others' (primarily Golutvin's) enthalpy increment data. The data from this study for TiSi and those of Archer disagree by between 4 and 8%. Nevertheless, it can be seen in Fig. 6 that the agreement with the data of Archer is much better than with those of Golutvin, where deviations of up to 50% are observed.

General agreement of the data obtained in this study with the calculated heat capacity values of Archer would tend to validate to his thermal functions. Agreement of 1 or 2%, or the accepted capability of the differential scanning calorimeter, was generally observed. In the case of TiSi, it can be speculated that the 4-8% deviation between the data from this study and those of Archer is due to differences in compositions of the TiSi samples used in the two investigations. Of the three Ti-Si phases of interest, the single phase TiSi samples were found to be the most difficult to prepare. High temperature annealing and room temperature grinding were required for the TiSi samples to limit the amount of secondary phases. Contamination by foreign phases during these preparation procedures may have caused the observed difference in the reported heat capacity values.

In the temperature region of interest, approximately 230–600 K, reasonably good agreement with the data of Golutvin was observed only near 600 K. However, good agreement with the data of the other investigators is found

over comparable temperature ranges. Archer's values of heat capacity for TiSi for temperatures above 350 K are based primarily on reanalysis of Golutvin's enthalpy increments. The improved agreement between our direct measurements of heat capacity and Archer's calculations for heat capacity in the temperature range of 250–600 K would lend credence to Archer's fitting procedure [6].

To summarize, in the temperature range of 250-350 K, the measured heat capacity values for the three titanium silicides are more consistent with the data reported by Archer et al. [5–7] and others [4,8], then with the values of Golutvin [3]. Archer's reanalysis [6] of Golutvin's data would indicate that while Golutvin's enthalpy increment data are of reasonable accuracy, his heat capacity functions fail at the lower temperatures of his data ranges. A suitable combination of Archer's thermal functions [5–7], the data from this study, and, for temperatures above 600 K, Golutvin's heat capacity functions would be recommended for use in the thermal functions for the titanium silicides.

Acknowledgements

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