A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 53 2008 Issue 3

K. SZOSTEK*, W. GRUDZIEL*, Z. WOKULSKI*

GROWTH AND MICROSTRUCTURE OF SELF-ORGANIZED $CoSi_2$-Si *IN SITU* EUTECTIC COMPOSITE

WZROST I MIKROSTRUKTURA SAMOORGANIZUJĄCEGO SIĘ KOMPOZYTU EUTEKTYCZNEGO $CoSi_2Si$

The aim of the study was to determine the type of the $CoSi_2$-Si eutectic *in situ* composite microstructure in function of the growth rate value. All growth processes were carried out using a directional crystallization technique with the Bridgman method at the constant value of the temperature gradient equals 170K/cm. The influence of the growth rate on eutectic microstructure was examined. The range of applied growth rates was (20 500)μm/min. The prepared samples were investigated using light microscopy (OPTON interference microscope, Nikon alphaphot 2) and scanning electron microscopy (SEM). Phase composition analysis was carried out using PHILIPS PW 1130 diffractometer. It was ascertained that an application of growth rates of 100 μm/min or lower allows to receive the continuous lamellar character of the $CoSi_2$-Si *in situ* composite microstructure. For growth rates from the range of (100 500)μm/min microstructure of the $CoSi_2$-Si *in situ* composite takes broken-lamellar form in parallel sections and at the 500μm/min value of growth rate the transition of oriented microstructure type into irregular is observed.

Keywords: eutrctic *in situ* composite, Bridgman technique, growth rate, crystallization front temperature gradient

Celem badań była charakterystyka mikrostruktury kompozytu eutektycznego $CoSi_2$-Si *in situ* w funkcji prędkości wzrostu. Wszystkie procesy wzrostu przeprowadzone zostały przy użyciu techniki kierunkowej krystalizacji z wykorzystaniem metody Bridgmana przy stałej wartości gradientu temperatury, wynoszącej 170K/cm. Badano wpływ prędkości wzrostu na mikrostrukturę otrzymywanej eutektyki. Zakres stosowanych prędkości wzrostu mieścił się w przedziale (20-500)μm/min. Przygotowane próbki badano przy użyciu mikroskopii świetlnej (mikroskop interferencyjny OPTON, Nikon Alphaphot 2) i elektronowej mikroskopii skaningowej (SEM). Analiza składu fazowego została przeprowadzona przy pomocy dyfraktometru polikrystalicznego PHILIPS PW 1130. Wykazano, iż zastosowanie prędkości wzrostu równych 100μm/min, bądź niższych, pozwala otrzymać mikrostrukturę kompozytu $CoSi_2$-Si o charakterze płytkowym. Dla prędkości wzrostu z przedziału (100 500)μm/min mikrostruktura sprzężonych faz $CoSi_2$/Si na przekroju wzdłużnym wykazuje liczne nieciągłości, natomiast przy prędkości 500 μm/min obserwuje się przejście zorientowanej mikrostruktury w nieregularną.

1. Introduction

The metal-semiconductor eutectic *in situ* composites obtained using directional crystallization techniques are interesting and excellent materials in respect of many special physical properties. That kind of materials possesses many advantages as simple processing technique, high thermodynamic stability of constituent phases, regular phases distribution, high microstructure controllability or strong anisotropic performance [1]. The one of the first commercial applications of the oriented eutectic *in situ* composite in microelectronic have been the InSb-NiSb field plates [2]. In this case the high conductivity NiSb metallic fibres increase the magnetic field influence on the resistance of the InSb semiconducting matrix that are embedded into.

Since few last years the intensive studies concerning the $MeSi_2$-Si eutectic *in situ* composites (Me = Ti, Cr, Co, Ta, W) have been conducting. The $TaSi_2$-Si composite obtained using Czochralski as well as electron beam floating zone technique is a favorable field emission material due to relatively low work function, good electron conductivity, and three dimensional array of Schottky junctions grown in the composite spontaneously [3, 4]. So it is an ideal candidate for field emission array cathode in the newest FED (Field Emission Display) technology.

* DEPARTMENT OF CRYSTALIOGRAPHY, INSTITUTE OF MATERIALS SCIENCE, UNIVERSITY OF SILESIA, 12, BANKOWA STR. 40-007 KATOWICE, POLAND

However there is not much data in a literature concerning the $CoSi_2$-Si eutectic *in situ* composite that also belongs to aforesaid type. The cobalt disilicide ($CoSi_2$) thin films have already found wide application in advanced silicon technology of very large scale integration systems (VLSI and ULSI) [5]. In this case a key parameter that determines the ability of the silicide to be grown epitaxially on silicon is the lattice mismatch of the silicide to the single crystal silicon substrate, η, which is defined as:

$$\eta = (a_{silicide} - a_{Si})/a_{Si},$$

where $a_{silicide}$ is the lattice parameter of the crystalline plane of the silicide that is lattice matched to silicon and a_{Si} is the lattice parameter of silicon. For good quality epitaxial films, the lattice mismatch between the silicide and the silicon substrate is typically less then 3% [6]. Among other things the relatively low value of the $CoSi_2$/Si lattice mismatch coefficient (η = 1,2%) makes the $CoSi_2$ promising candidate for metallic phase in the metal semiconductor eutectic *in situ* composite.

The eutectic microstructure can exhibit many geometrical forms. It can be regular-lammelar, regular-rod-like, irregular, complex regular, quasi-regular, broken-lamellar, spiral and globular. In respect of the specific mass transport ahead of a solid/liquid interface of growing phases this type of materials is known as self-organized microstructure eutectics [7]. The first theoretical description of the coupled lamellar growth of eutectics has been proposed by Jackson and Hunt (J-H theory) [8]. The J-H theory being originally not precise in many respects has been repeatedly revised by many authors [9, 10, 11]. The one of the latest modification of the J-H theory proposed by Wołczyński [12] consists in introduction of a new model for the formation of a concentration field ahead of growing regular lamellaes with respect to the solid/liquid interface shape.

During directional solidification process of the eutectic *in situ* composites except the materials parameters two basic technological parameters as growth rate, v and temperature gradient, G have fundamental influence on eutectic preparation. In case of regular eutectic growth both parameters decide on interlamellar spacing, λ [13]. In order to obtain a specified microstructure type of such composites it is necessary to determine values of mentioned variables. Because of strong influence of both variables on the eutectic microstructure it is necessary to establish one of these parameters as constant.

Therefore the aim of the study was to determine the type of the $CoSi_2$-Si eutectic *in situ* composite microstructure in function of the growth rate value.

2. Experimental

The preparation of the $CoSi_2$-Si eutectic ingots was carried out in a vertical quartz reactor in a helium protective atmosphere (99.999%) at the pressure of 1 atm [14, 15]. As a starting materials Si (99.999%) and Co (99.8%) were used. In order to melt the charge an induction generator was used. The starting materials were melted in conical point bottom alumina crucible with circular section. After homogenization process that was carring out at the temperature of 1500°C and the time of 2 hours the crucible with the melt was pulling down to lower temperature zone. An optical pyrometer was used to measure the temperature of the melt. Tab. 1 presents listing of the selected samples discussed in this paper.

TABLE 1

Listing of the selected samples obtained using Bridgman technique

Sample No.	Chemical composition [at.%]		Components masses [g]		Charge mass [g]	Growth rate [μm/min]	Temperature gradient [K/cm]
	Co	Si	Co	Si			
1	22.5	77.5	7,7	12,57	20,27	20	170
2			7,55	12,33	19,88	50	
3			7,65	12,56	20,217	100	
4			7,55	12,33	19,88	500	
5			7,65	12,56	20,21	100/500	

First of all the obtained ingots were cut using a spark-erosion SMD SERVOMET machine. Then the samples were mechanically polished on vibration polishing machine in an Al_2O_3 slurry and chemically etched in deionized water 30% KOH solution at the temperature of 80°C and time of 5 sec in order to remove

the Si phase and reveal a microstructure of the $CoSi_2$ matrix. Prepared in this way specimens were submitted to metallographic observations conducted using Nikon Alphaphot-2 light microscope. Phases in the prepared specimens were identified by X-ray diffraction using PHILIPS PW 1130 X-ray diffractometer with radiation CuK_α and wavelength λ=1,54056Å. Besides, the chemical microanalysis studies also were performed. In order to this the scanning electron microscope of Jeol JMS-6480 equipped with an EDXS spectrometer was used.

3. Results and discussion

The metallographic observations of prepared surfaces showed that the growth rate has a significant influence on morphology of the $CoSi_2$-Si eutectic *in situ* composite. A series of the $CoSi_2$-Si *in situ* composite growth processes conducted at the constant value of temperature gradient (170K/cm) allows to characterize the microstructure in function of the growth rate value from the range of (20-500)μm/min. An application of growth rates of 100μm/min or lower allows to receive the continuous lamellar character of microstructure (Fig. 1). In this case the structure of received composite takes the form of the silicon channels embedded into the $CoSi_2$ matrix. Microphotographs parallel to the growth direction (Fig. 1 a, c) shows a continuous character of both coupled phases regularly arranged in the entire ingot volume. However the cross-section microstructure (Fig. 1. b, d) exhibits an undetermined shapes of the silicon channels.

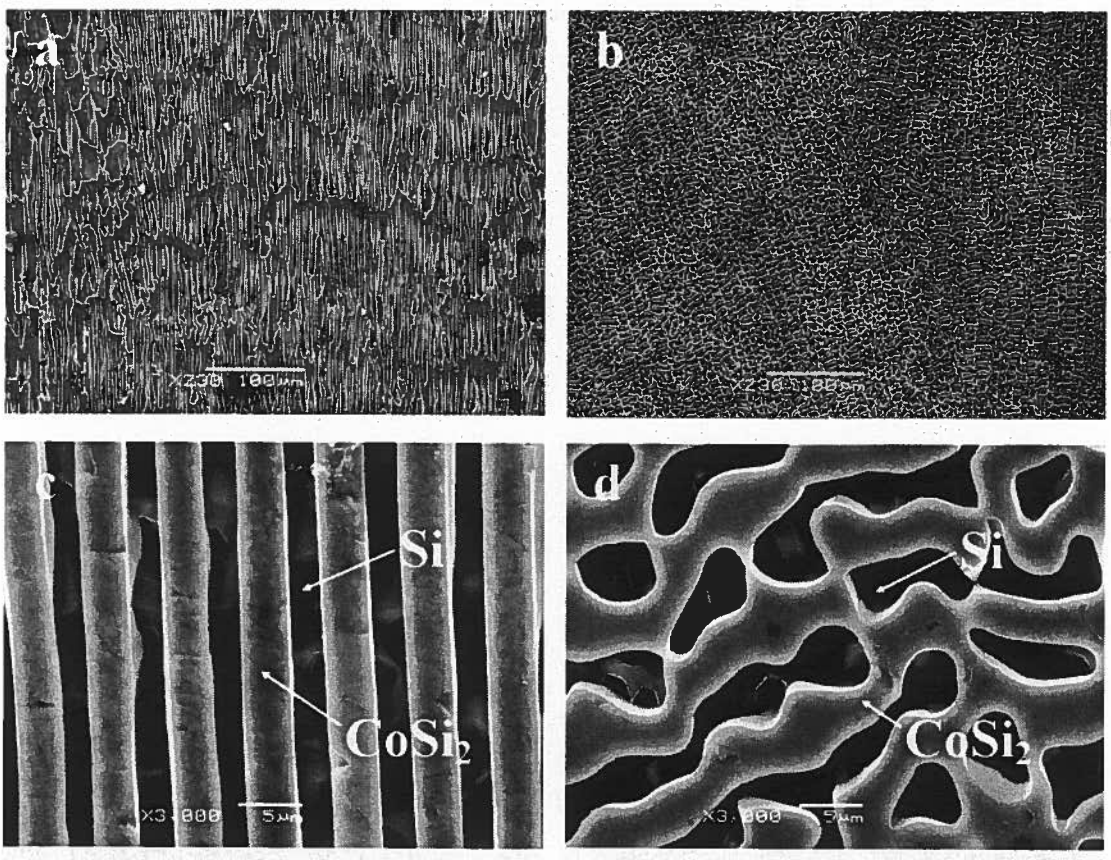

Fig. 1. SEM images of the $CoSi_2$-Si eutectic *in situ* composite microstructure parallel (a, c) and transverse (b, d) to the growth direction (Sample No. 2)

The samples received using growth rates of 100μm/min and lower, exhibiting the regular continuous lamellar character of microstructure were the subject of the average interlamellar spacing λ measurement. Because of the undetermined shapes of the silicon channels of cross sections the measurement had a statistical character dependent on the parallel sections lamellaes arrange. It was ascertained that the interlamellar spacing λ is proportional to the applied growth rate (Fig. 2) but the character of this dependence is nonlinear.

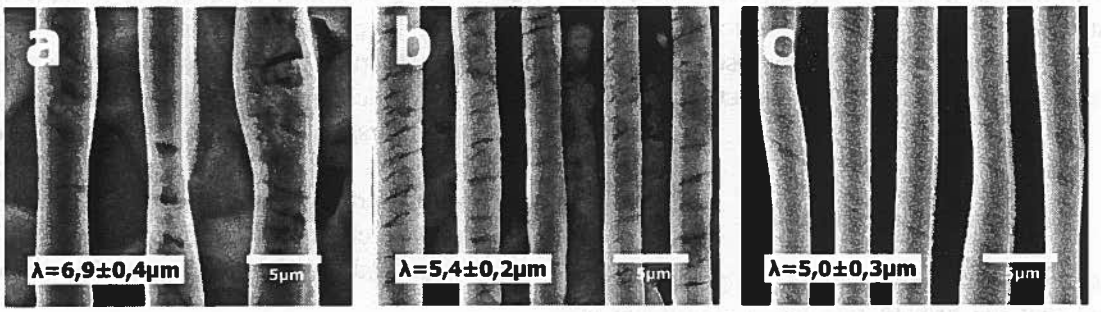

Fig. 2. Comparison of the average $CoSi_2$-Si eutectic lamellar spacing λ in function of the growth rate according to values: (a) 100μm/min (Sample No. 3), (b) 50μm/min (Sample No. 2), (c) 20μm/min (Sample No. 1);

An application of growth rates not much higher than 100μm/min causes interruptions in lamellar growth in the parallel section. The microstructure in this case takes the form of broken lamellaes. The result of the further growth rate increase is the floating decrease of the longitudinal dimension of broken lamellaes. At the 500μm/min value of growth rate the transition of oriented microstructure type into irregular is observed (Fig. 3).

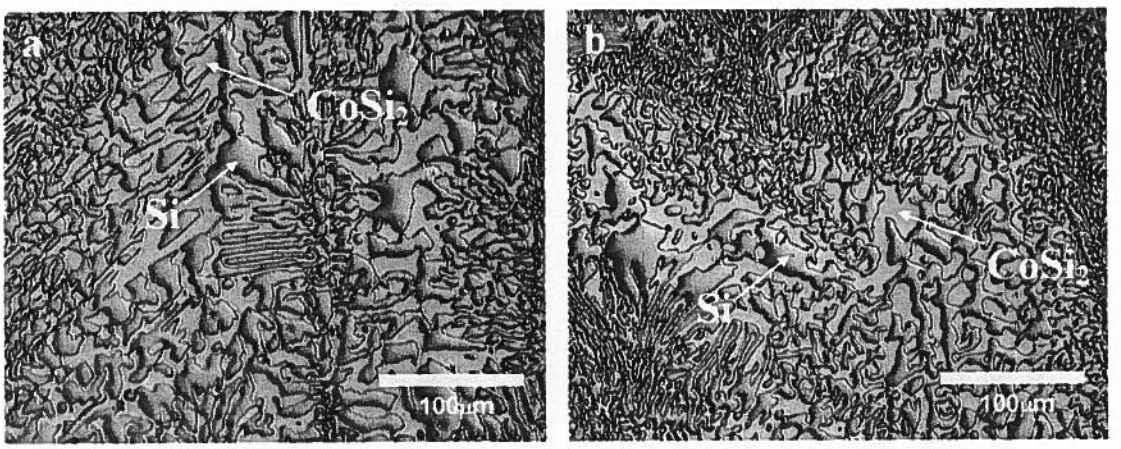

Fig. 3. Microstructure of the $CoSi_2$-Si eutectic *in situ* composite parallel (a) and transverse (b) to the growth direction (Sample No. 4)

In order to test the influence of a spontaneous growth rate change during the solidification process on microstructure a growth process with application of two considerably different growth rates values have been conducted. The solidification process in this case was begun with growth rate of 100μm/min and terminated with growth rate of 500μm/min. Fig. 1 shows a microstructure in function of the growth rate. The growth rate change boundary is marked on the microphotograph by a white dashed line. The change of the growth rate caused the direct transition of oriented continuous lamellar microstructure into irregular and undetermined type (Fig. 4).

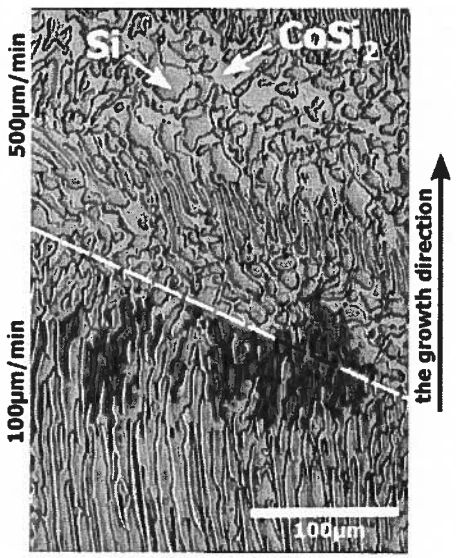

Fig. 4. Microstructure of the $CoSi_2$-Si eutectic *in situ* composite in function of the growth rate, parallel to the growth direction (Sample No. 5)

From the point of view of most microelectronic applications a more interesting microstructures would be the regular shapes ones first of all in respect of repeatability of the obtained structures. The regular shapes seem to be well-suited i.e. for the photonic crystal application [7]. The lamellar shape would be more appropriate for one-dimensional crystals and the rod-like shape for two-dimensional crystals. So it would be favourably to acquire the regular shapes of the silicon channels cross-sections in the $CoSi_2$-Si eutectic composite. In order to do this it would be necessary to conduct the series of growth processes at the constant value of the growth rate to determine the microstructure in function of the temperature gradient. It would be also favourable in respect of the temperature gradient influence on interlamellar spacing examination.

However the irregular or complex-regular shapes as kind of percolated structures may have potential in the field of metamaterials, for example, in creating materials with giant dielectric constant [16].

4. Conclusions

The $CoSi_2$-Si eutectic in situ composite using the directional crystallization technique with the Bridgman method was obtained. It was ascertained that an application of growth rates of 100μm/min or lower at the constant value of the temperature gradient equals 170K/cm allows to receive the continuous lamellar character of the $CoSi_2$-Si *in situ* composite microstructure. The cross-sections morphology of the silicon channels embedded into $CoSi_2$-Si matrix in this case exhibits an undetermined shapes. The average interlamellar spacing λ is proportional to the applied growth rate but the character of this dependence is nonlinear.

For growth rates from the range of (100-500)μm/min microstructure of the $CoSi_2$-Si *in situ* composite takes broken-lamellar form in parallel sections and at the 500μm/min value of growth rate the transition of oriented microstructure type into irregular is observed.

REFERENCES

[1] W. Kurz, P. R. Sahm, Gerichtet erstarrte eutektische Werkstoffe; Springer; (1975).
[2] H. Weiss, Met. Trans. **2**, 1513 (1971).
[3] J. Zhang, C. Cui, M. Han, J. Chen, N. Xu, L. Liu, H. Fu, J. Crystal Growth **276**, 92 (2005).
[4] C. Cui, J. Zhang, Z. Jia, H. Su, L. Liu, H. Fu, J. Crystal Growth **310**, 71 (2008).
[5] S. P. Murarka, Intermetallics **3**, 173 (1995).
[6] L. A. Clevenger, R. W. Mann, Properties of Metal Silicides; INSPEC, the Institution of Electrical Engineers, 61 (1995).
[7] K. Kołodziejak, S. Turczyński, R. Diduszko, L. Klimek, D. A. Pawlak, Opto-Electronics Review **14(3)**, 205 (2006).
[8] K. A. Jackson, J. D. Hunt, Trans. AIME **236**, 1129 (1966).
[9] L. L. Zheng, D. J. Larson Jr., H. Zhang, J. Crystal Growth **209**, 110 (2000).
[10] A. V. Catalina, S. Sen, D. M. Stefanescu, Metall. Mater. Trans. **34A**, 383 (2003).
[11] S. Akamatsu, M. Plapp, G. Faivre, A. Karma, Metall. Mater. Trans. **35A**, 1815 (2004).
[12] W. Wołczyński, Defect Diffus. Forum **272**, 123 (2007).
[13] W. Wołczyński, B. Billia, Mat. Science Forum **215-216**, 313 (1996).
[14] W. Gurdziel, Z. Wokulski, K. Szostek, J. Krawczyk, P. Stępniewski, Solid State Phenom. **130**, 85 (2007).

[15] Z. Wokulski, W. Gurdziel, J. Krawczyk, K. Szostek, Solid State Phenom. **130**, 233 (2007).
[16] C. Pecharroman, F. Esteban-Betegon, J. F. Bartolome, S. Lopez-Esteban, J. S. Moya, Adv. Mater. **13**, 1541 (2001).

Received: 20 June 2008.