Investigation of the interface layer phase composition obtained by hot pressing of Cr and Si

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The possibility of synthesizing layers of the medium-temperature thermoelectric $CrSi_2$ by hot pressing of the initial components (Cr and Si) has been investigated. The phase composition of samples obtained by hot pressing of Cr and Si before and after annealing in the region of their contact boundary has been investigated by X-ray analysis. It is shown that, under certain conditions, low-temperature synthesis of a $CrSi_2$ layer with a thickness of 50 to $300\,\mu$m is possible at the interface between Cr and Si. The synthesis occurs at a temperature significantly lower than that given in the phase diagram, which opens up new technological possibilities for obtaining the $CrSi_2$ compound.

Keywords: thermoelectrics, chromium disilicide, phase interface, X-ray phase analysis.

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1. Introduction

Thermoelectric materials based on transition metal silicides are of interest for the production of thermoelectric generators and sensor devices due to their chemical and mechanical resistance in an oxidizing environment at high temperatures, their compatibility with silicon technology, and the possibility of production of *n*- and *p*-type materials.

Chromium disilicide is a promising medium-temperature *p*-type thermoelectric with a bandgap of 0.35 eV and a record-high power factor $\sigma \cdot S^2$ (S is the thermoelectric coefficient and σ is the electric conductivity) with its maximum of $45\,\mu W/(K^2 \cdot cm)$ at $T = 600\,K$ [1]. According to the phase diagram, four compounds exist in the Cr−Si system [2–4]. Their composition and crystallographic parameters are listed in Table 1.

The only chromium silicide with semiconductor properties is $CrSi_2$. Cr_3Si, CrSi, and Cr_5Si_3 are semimetals. The stability of thermoelectric properties of $CrSi_2$ single crystals was examined in [8,9], where their potential for industrial application was demonstrated.

Since $CrSi_2$ has a wide homogeneity range, the method of its production exerts a strong influence on its thermoelectric properties, structure, and microstructure [10,11]. As was demonstrated in [2,9], the power factor of $CrSi_2$ samples produced by directional crystallization depends on the crystallization rate. The power factor increases considerably in the case of protracted crystallization and reaches a value of $45\,\mu W/(K^2 \cdot cm)$. It was found that the power factor of $CrSi_2$ decreases, e.g., to $20\,\mu W/(K^2 \cdot cm)$ at $T = 600\,K$ [8] if single crystals are annealed at 1573 K for 170 h. This effect of reduction of the power factor after long-term high-temperature annealing was observed in studies of pressed $CrSi_2$ microcrystals grown from solution in molten tin [9].

While $CrSi_2$ features high values of thermoelectric coefficient S, conductivity σ, and the power factor, its thermoelectric figure of merit ($Z = \sigma \cdot S^2/\kappa$) is low. The latter fact is attributable to its high thermal conductivity κ [12].

Nanostructuring is one of the ways toward reducing the lattice thermal conductivity. The scattering of carriers off nanoinhomogeneities reduces the thermal conductivity and electric conductivity and may result in enhancement of the thermal emf. This enhancement may be associated with selective scattering of carriers off the boundaries of nanocrystallites.

Nanocrystalline $CrSi_2$ may be produced by thermal annealing of the amorphous phase. The method of magnetron sputtering of presynthesized $CrSi_2$ onto a cold substrate is used to produce the amorphous phase. A film obtained this way is amorphous in structure and crystallizes with the formation of $CrSi_2$ nanocrystallites 10−20 nm in size [13]. The thermoelectric properties of films prior to crystallization are close to the properties of amorphous metals. The crystallization of $CrSi_2$ films commences at a temperature of 600 K. If the temperature and/or duration of annealing increase further, the ratio between amorphous and nanocrystalline phases changes. The thermoelectric

Table 1. Chromium silicide compounds

Phase	Spatial group	Cell parameters, Å			Ref.
		A	*b*	*c*	
Cr_3Si	$PM\bar{3}n$	4.555	4.555	4.555	[5]
$CrSi_2$	$P6_222$	4.422	4.422	6.351	[5]
CrSi	$P2_13$	4.62	4.62	4.62	[5]
Cr_5Si_3	$I4/mcm$	9.17	9.17	4.636	[6]
$CrSi_2$	$P6_422$	4.4283	4.4283	6.368	[7]

Table 2. Phase composition of samples in the Cr–Si interface region after pressing and annealing

Sample number	Initial materials	Pressing	XPA before annealing	Annealing and material state after annealing	XPA after annealing
1	Si (crystal plate), Cr (metal plate)	$T = 300$ K, $P = 40$ t/cm^2	Adhesion without chemical interaction	$T = 1263$ K, $\tau = 160$ h mechanically stable	$Cr_{9.1}Si_{0.9}$
2	Si (crystal plate), Cr (metal plate)	$T = 1213$ K, $P = 1$ t/cm^2	$Cr_{9.1}Si_{0.9}$ α-Cr	$T = 1263$ K, $\tau = 160$ h mechanically stable	$Cr_{9.1}Si_{0.9}$ $CrSi_2$
3	Si (powder), Cr (powder) filling in layers	$T = 1213$ K, $P = 1$ t/cm^2	$Cr_{9.1}Si_{0.9}$ α-Cr (70%) $CrSi_2$ (30%)	$T = 1263$ K, $\tau = 160$ h mechanical breakdown	$Cr_{9.1}Si_{0.9}$; $CrSi_2$; traces of Cr_3Si
4	Si (single crystal), Cr (powder), Si at the center of Cr powder volume	$T = 1213$ K, $P = 1$ t/cm^2		$T = 1263$ K, $\tau = 160$ h mechanically stable	$CrSi_2$ $Cr_{9.1}Si_{0.9}$

properties of thin $CrSi_2$ films were detailed in [14,15]. The power factor of an amorphous film is significantly lower than the one of a nanocrystalline film (due to low thermal emf values). Long-term annealing at a temperature of 1000 K results in a transition from the nanocrystalline state to the microcrystalline one. The electric conductivity increases in the process, while the thermal emf values decrease. The power factor of a film in the nanocrystalline state is higher than the corresponding factor of the same film in the microcrystalline state [15].

The results of examined studies demonstrate that the thermoelectric properties of a material depend strongly on technological factors. It was noted in these studies that morphological, phase, and structural transformations affecting the thermoelectric properties of $CrSi_2$ occur in the vicinity of the critical temperature of 600 K.

2. Experimental procedure

The possibility of low-temperature synthesis of $CrSi_2$ at the interface between layers of chromium and silicon taken in excess amounts, which do not correspond to the stoichiometric composition, was examined in the present study. In view of the possible fluctuation of the semiconductor composition within the homogeneity range [2] and the probable emergence of secondary phases in the process of annealing, the phase composition of the Cr–Si interface needed to be examined.

In order to obtain a clear interface between Cr and Si, samples were prepared by hot pressing with subsequent annealing in air.

X-ray phase analysis (XPA) of samples was performed using a DRON-3 (CuK_α-radiation) diffractometer. The region of sample irradiation (interface between the initial materials) was set by adjusting the width of the slit in front of the sample (1 mm and/or 0.1 mm; the slit height was 8 mm) and aligning the X-ray beam axis with the center of the interface. The XPA results are presented in Table 2.

3. Experimental results and discussion

It can be seen from Table 2 that the interaction of chromium with silicon at the initial stage of formation of the boundary layer results in the production of a metastable $Cr_{9.1}Si_{0.9}$ phase (isostructural α-Cr phase). This is indicative of the possibility of low-temperature diffusion-cumulative phase formation in the boundary layer. This compound is neglected in phase diagrams taken from literature, but it features in X-ray data from the international ASTM catalogue.

Figure 1 (2, 3) shows the X-ray spectra of sample 3 prepared by hot pressing and annealing of the initial

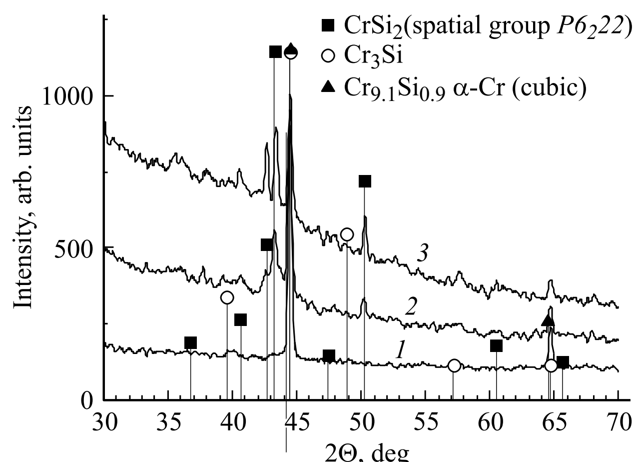

Figure 1. X-ray diffraction pattern of samples 1, 3; symbols denote different phases in accordance with the ASTM catalogue. *1* — sample 1, Cr and Si plates after cold pressing and annealing; *2* — sample 3 after annealing; *3* — sample 3 before annealing.

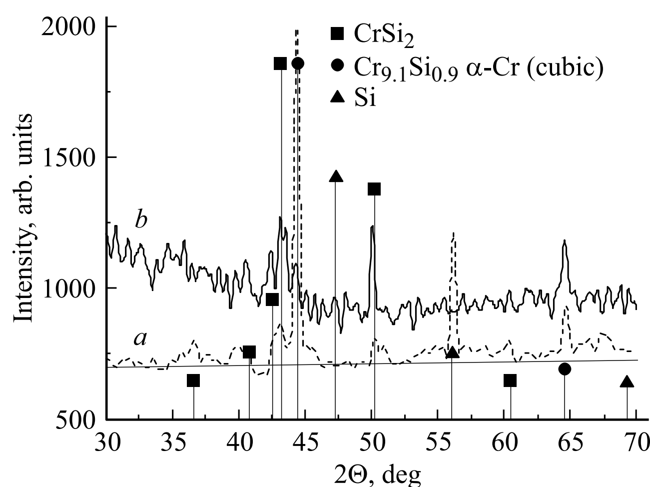

Figure 2. X-ray diffraction pattern of sample 4. *a*) dashed curve — the slit in front of the sample is 1 mm; *b*) solid curve — the slit in front of the sample is 0.1 mm. Symbols denote different phases in accordance with the ASTM catalogue.

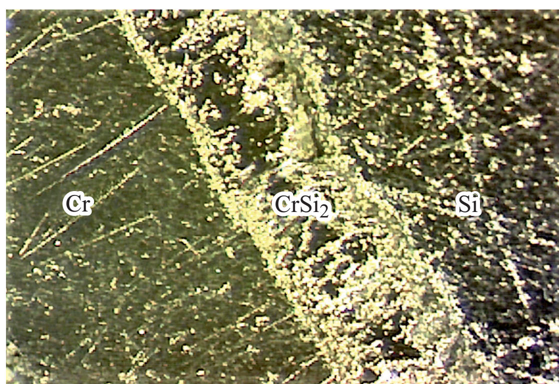

Figure 3. $CrSi_2$ layer at the interface between single-crystalline silicon and chromium powder after hot pressing and annealing (sample 4).

components in powdered form (with the pressing chamber filled in layers). The material is mechanically unstable and breaks down after annealing.

In the case of complete pressing-in of single-crystalline silicon within the bulk of Cr powder (sample 4), hexagonal chromium disilicide (spatial group $P6_222$) forms at the interface between the initial components (Fig. 2). The results of optical microscopy reveal that the layer thickness is $50-300\,\mu$m (Fig. 3).

According to the Cr–Si phase diagrams, $CrSi_2$ is synthesized at $T = 1748-1843$ K [2–4]. These temperatures are significantly higher than the one at which crystalline silicon was pressed in chromium powder in the present study (1213 K). The obtained data hint at the possibility of low-temperature diffusion-cumulative phase formation in the boundary layer.

4. Conclusion

The results of X-ray phase analysis of samples revealed that a layer with a thickness of $50–300\,\mu$m corresponding to hexagonal chromium disilicide with spatial group $P6_222$ forms at the interface between components in the case of complete pressing-in of single-crystalline silicon within the bulk of electrolytic chromium powder at an excess (any) ratio of the amounts of initial components. This synthesis occurs at a temperature that is considerably lower than the one given in the phase diagram (at any ratio of the initial components).

Conflict of interest

The authors declare that they have no conflict of interest.

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