J Therm Anal Calorim (2011) 103:111–116
DOI 10.1007/s10973-010-1136-7

Reactive diffusion in W–Mo–Si thin films

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Received: 31 May 2010 / Accepted: 26 October 2010 / Published online: 8 December 2010
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Abstract This study reports the phase formation in the ternary thin films system Mo–W–Si. The metallic films were deposited onto Si (100) substrate by sputtering. Two kinds of samples were prepared, either by sequential deposition or by co-deposition. The phase formation was investigated by In situ X-ray diffraction measurements from 300 to 900 °C. The influence of the sample preparation, namely sequential deposition and co-deposition, on the mechanism of phase formation has been evidenced.

Keywords Thin films · Reactive diffusion · Silicides · Molybdenum · Tungsten

Introduction

Refractory silicides have been used in various aspects of very large-scale integrated circuit (VLSI) devices because of their low resistivity and the ability to withstand high temperatures required for integrated circuit processing [1].

$MoSi_2$ and WSi_2 are among the main refractory silicides that were selected by the microelectronic industry [2]. They are also among the first silicides to be used in metal oxide semiconductor devices [3, 4].

Furthermore, the molybdenum silicides are probably the newest class of materials considered as highly promising for structural applications at high temperatures, in aerospace and energy-related industries due to the combination of high melting point, relatively low density and good corrosion resistance [5]. The $MoSi_2$ intermetallic compound has attracted great research interest; however, monolithic $MoSi_2$ shows extreme brittleness and poor impact strength at room temperature and has low strength and creep resistance at elevated temperatures (>1200 °C). By alloying $MoSi_2$ with WSi_2, significant property improvement has been readily obtained [6–8].

For microelectronic applications, the metal silicides are obtained by solid-state thermal reactions between a metallic thin film and the silicon substrate. The investigation of the mechanism of phase formation is of great importance to understand the behavior of the materials and to optimize their properties. This study has already been performed for both W–Si and Mo–Si systems [9–12]. However to our knowledge, the ternary system Mo–W–Si has not been investigated yet. Thus, the aim of this study is to fill in this lack of knowledge and to determine the relationships between the phase formation in Mo–W–Si thin films and the corresponding ternary phase diagram.

The binary and ternary phase diagrams

Tungsten and molybdenum elements show great similarity both in electronic and structural properties. They belong to the same group of the periodic table; they both crystallize

It was presented at JEEP2010 Montpellier, France

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Table 1 Crystallographic data of molybdenum, tungsten, and related silicides

Phase	Structure	Space group	Lattice parameters/nm	
			a	*c*
Mo	Cubic	*Im3m*	0.3147	
W	Cubic	*Im3m*	0.3164	
Mo_3Si	Cubic	*Pm3n*	0.489	
Mo_5Si_3	Tetragonal	*I4/mcm*	0.9648	0.4913
W_5Si_3	Tetragonal	*I4/mcm*	0.9601	0.4972
h-$MoSi_2$	Hexagonal	$P6_222$	0.4596	0.655
t-$MoSi_2$	Tetragonal	*I4/mmm*	0.3204	0.7844
t-WSi_2	Tetragonal	*I4/mmm*	0.3211	0.7829

in the *Im3m* (229) space group and present very close lattice parameters (see Table 1). As a consequence, a total solid solution is found in the Mo–W system [13].

The phase diagram of the W–Si system shows two intermediate phases W_5Si_3 and WSi_2.

For the Mo–Si system, three intermediate phases Mo_3Si, Mo_5Si_3, and $MoSi_2$ are reported. The latter phase presents two modifications, namely a low, hexagonal h-$MoSi_2$ modification and a high, tetragonal one t-$MoSi_2$ which is isomorphous to WSi_2. The phase transformation occurs at 1900 °C [13].

The ternary Mo–W–Si phase diagram contains two total ternary solid solutions $(Mo,W)_5Si_3$ and $(Mo,W)Si_2$, and no ternary compound [14].

Crystallographic data of all the intermediate phases from Pearson's handbook [15] are gathered in Table 1.

One can notice that the cell parameters for the isomorphous phases are very close to each other. As a consequence, the corresponding diffraction peaks will be difficult to differentiate.

Experimental procedures

The thin films of Mo and/or W elements were prepared in a multi-target sputtering deposition system with a base pressure of $\sim 10^{-8}$ mbar; a constant pressure of 1×10^{-3} mbar argon was maintained during the deposition. The metals were deposited onto monocrystalline silicon substrates orientated (100). To improve the homogeneity of the deposition, the substrate was rotating during deposition to improve the homogeneity of the layer.

Both binary and ternary systems were investigated. For ternary systems, two sets of samples were prepared. The first set was achieved by sequential depositions of Mo and W with various thickness ratios and various stacking order, and the second one was obtained by co-deposition of Mo and W with various quantity ratios. Altogether, 11 samples were prepared; their characteristics are given in Table 2. For all the samples, the total thickness of the deposit is 100 nm.

Table 2 Characteristics of the studied samples: staking order and layer thickness for the sequential depositions, atomic percentages of the elements for the co-depositions

Sequential depositions			Co-depositions	
Stacking order	Mo/e/nm	W/e/nm	Mo/at.%	W/at.%
Mo/Si	100	0	25	75
W/Si	0	100	50	50
W/Mo/Si	25	75	75	25
	50	50		
	75	25		
Mo/W/Si	25	75		
	50	50		
	75	25		

The samples were characterized during heating from 100 to 900 °C in high vacuum ($\sim 10^{-4}$ Pa) using in situ X-ray diffraction measurements. The diffractograms were recorded every 20 °C in the [20°–60°] 2θ range, with a step size of 0.4° and an acquisition time of 50 s. The heating rate was 10 °C/min. The diffractometer was used with a copper Kα anticathode ($\lambda = 1.54$ Å) in the θ–2θ geometry.

Results and discussion

Binary systems

The authors first investigated the binary systems to compare our results with the literature data. Figure 1 presents

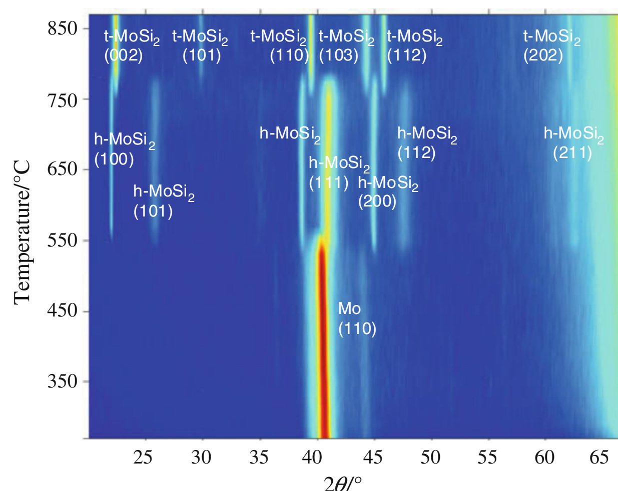

Fig. 1 In situ X-ray diffractograms obtained for the Mo/Si sample from 300 to 900 °C

the in situ X-ray diffractograms obtained for the binary sample Mo/Si. In this figure, colors are representative of the intensity of the diffraction peaks. The maximum intensity corresponds to the red color.

The peak at $2\theta = 40.51°$ which characterizes molybdenum is present from room temperature up to 560 °C. At this temperature, the hexagonal form of $MoSi_2$ (h-$MoSi_2$) appears and this phase undergoes a polymorphic transformation towards its tetragonal form (t-$MoSi_2$) at 780 °C. These temperatures of phase formation are in concordance with those reported by Guivarc'h et al. [9]. The tetragonal form of $MoSi_2$ is found to be stable at least up to 900 °C and still exists after the cooling of the sample. Even when this heat treated sample is annealed at 550 °C for 24 h, the tetragonal form of $MoSi_2$ is maintained. These results disagree with the binary Mo–Si phase diagram in which the tetragonal form of $MoSi_2$ only exists for temperatures higher than 1900 °C [13]. Thus, this high temperature form of $MoSi_2$ seems to be stabilized at room temperature in thin films. This stabilization was never reported in literature.

The X-ray diffractograms obtained for the binary sample W/Si are shown in Fig. 2. The peak which characterizes the tungsten at $2\theta = 40.26°$ is present from room temperature to 900 °C. The formation of the tetragonal phase t-WSi_2 starts at 820 °C.

By contrast with results previously reported in literature on thin films in the W–Si system [10–12], no hexagonal phase was observed at low temperatures for WSi_2. The hexagonal WSi_2 phase was observed in literature for samples of W on Si which were arsenic-ion implanted [10] or for samples constituted of amorphous mixture of W and Si [11, 12].

Ternary systems

Sequential deposits

For the samples prepared by sequential deposition, the mechanism of phase formation only depends on the stacking order, whereas the temperatures of the phase formation vary with the metal thickness ratios. These temperatures are reported in Table 3.

W/Mo/Si samples The in situ X-ray diffractograms obtained for the W (25 nm)/Mo (75 nm)/Si sample are presented in Fig. 3. Both Mo and W are evidenced at low temperature. At 560 °C, a hexagonal phase which could correspond either to $MoSi_2$ or WSi_2 is formed. Since the phase formation occurs at the same temperature as that observed in the binary Mo/Si system, the authors can

Table 3 Temperatures of phase formation for samples with sequential deposition

Stacking order	Mo/e/nm	W/e/nm	T_f/°C	
			Hexa-$W_{1-x}Mo_xSi_2$	Tetra-$W_{1-x}Mo_xSi_2$
Mo/Si	100	0	560	780
W/Si	0	100	–	820
W/Mo/Si	25	75	560	690
	50	50	560	700
	75	25	560	720
Mo/W/Si	25	75	–	790
	50	50	–	800
	75	25	–	810

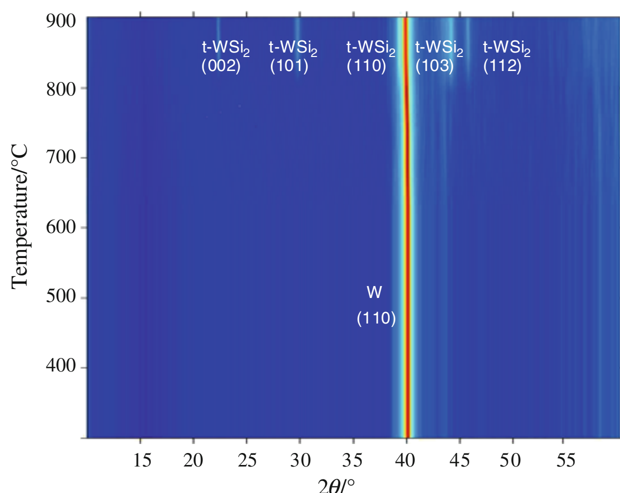

Fig. 2 In situ X-ray diffractograms obtained for the W/Si sample from 300 to 900 °C

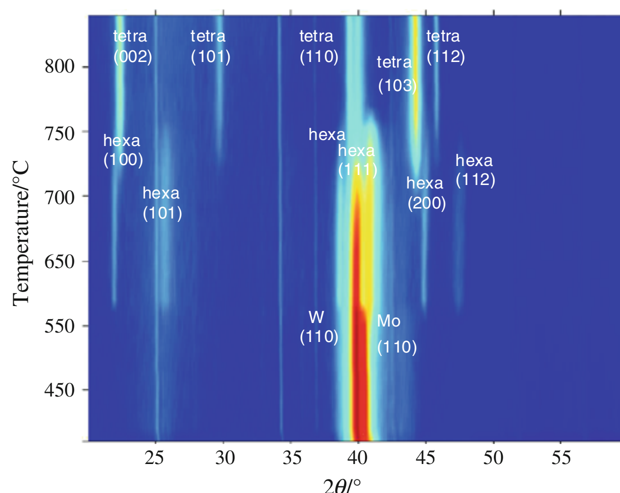

Fig. 3 In situ X-ray diffractograms obtained for the W (25 nm)/Mo (75 nm)/Si sample from 300 to 900 °C

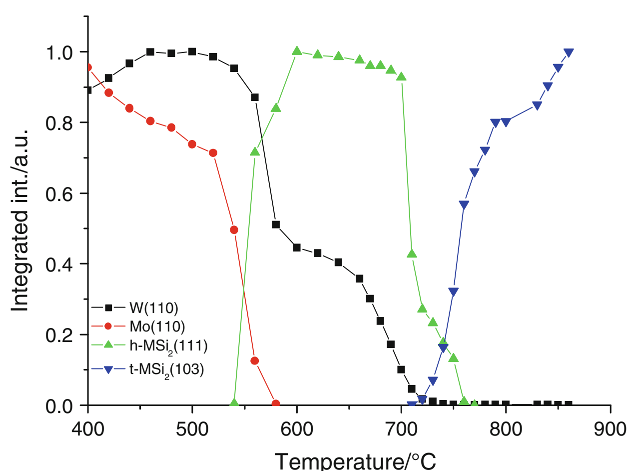

Fig. 4 Evolution of the normalized intensities of the most intense XRD peak for each phase present in the W (25 nm)/Mo (75 nm)/Si sample versus temperature

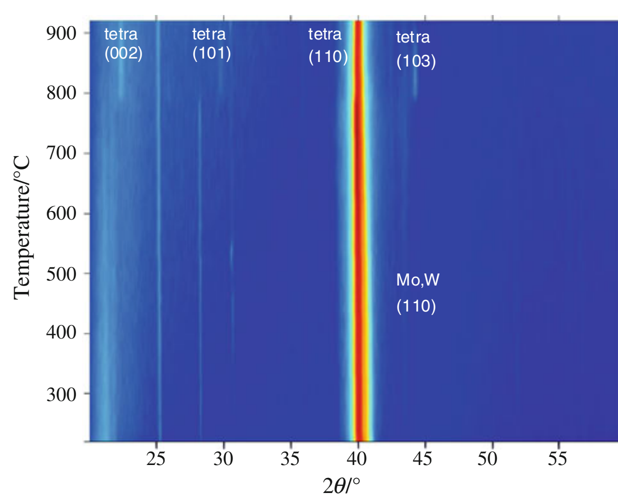

Fig. 5 In situ X-ray diffractograms obtained for the Mo (50 nm)/W (50 nm)/Si sample from 300 to 900 °C

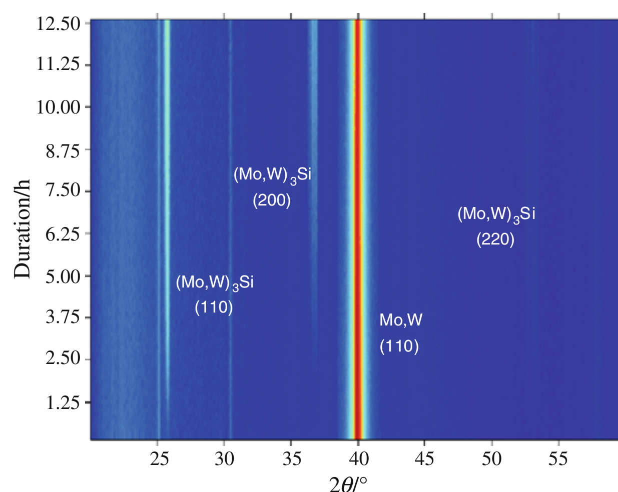

Fig. 6 In situ X-ray diffractograms obtained for the Mo (50 nm)/W (50 nm)/Si sample during an isothermal annealing at 900 °C

assume that this phase is h-$MoSi_2$. This assumption agrees with the disappearance of the Mo peak.

At 720 °C, the h-$MoSi_2$ phase transforms into the t-$MoSi_2$ phase. Since the temperature of the phase transformation is lower than that observed for the binary Mo–Si system, the authors can suggest that the phase which undergoes the transformation is a solid solution h-(Mo,W)Si_2. This assumption is supported by the results presented in Fig. 4 which shows the evolution of the normalized intensity of the most intense XRD peak for each phase present in the sample versus temperature. Indeed the volume fraction of the hexagonal phase, which is proportional to the normalized intensity, still increases in spite of the vanishing of molybdenum. This increase goes with a consumption of W shown by the decrease of the W peak intensity.

Table 3 shows clearly that the temperature of phase transformation from the hexagonal structure to the tetragonal one, decreases when the thickness of Mo is lowered. This observation could agree with the fact that the hexagonal phase is not stable for high W content. Since the phase formation of h-$MoSi_2$ occurs at the same temperature for all the samples with the W/Mo/Si sequence, the stability range of the h-(Mo,W)Si_2 is reduced when the W content is increased.

Mo/W/Si samples The in situ X-ray diffractograms obtained for the Mo (50 nm)/W (50 nm)/Si sample are presented in Fig. 5. The first phase appears at 800 °C. It corresponds to a tetragonal form of silicide. Since the temperature of formation is lower than that observed for the binary W–Si samples, this phase could correspond to a solid solution (Mo,W)Si_2. Both the diffraction peaks of Mo and W are visible up to 900 °C. An isothermal annealing performed on this sample at 900 °C for 12 h shows the formation of an additional phase $(Mo,W)_3Si$ (see Fig. 6). This could be due to a reaction between (Mo,W)Si_2 and the remaining Mo and/or W.

Figure 7 shows the evolution of the normalized intensity of the most intense XRD peak for each phase present in the sample, namely Mo(110), W(110), t-$(Mo_xW_{1-x})Si_2$(103) and $(Mo,W)_3Si$(110) versus temperature. Mo and W diffraction peaks cannot be distinguished. The decrease in their intensity at about 800 °C corresponds to the formation of t-$(Mo_xW_{1-x})Si_2$. At higher temperatures, both the volume fraction of (Mo,W) and t-$(Mo_xW_{1-x})Si_2$ decrease whereas the $(Mo,W)_3Si$ phase is formed.

The existence of a solid solution based on Mo_3Si has not been reported so far. Even though this ternary phase is not

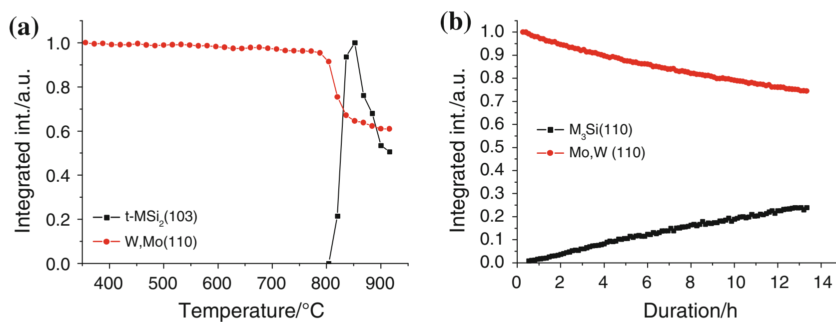

Fig. 7 Evolution of the normalized intensities of the most intense XRD peak for each phase present in the Mo (50 nm)/W (50 nm)/Si sample, versus temperature. **a** Heat treatment from 300 to 900 °C, **b** isothermal annealing at 900 °C

depicted in the Mo–W–Si ternary phase diagram [14], its existence is not surprising since a homogeneity range is observed for Mo_3Si in the Mo–Si binary phase diagram [13].

Table 3 shows that it is not possible to get the hexagonal form of the silicides with the Mo/W/Si stacking order.

Moreover, the temperature of formation of the tetragonal form decreases when the thickness of W increases.

Table 4 Temperatures of phase formation for samples prepared by co-deposition

Mo/at.%	W/at.%	T_f/°C	
		Hexa-$W_{1-x}Mo_xSi_2$	Tetra-$W_{1-x}Mo_xSi_2$
25	75	–	680
50	50	680	700
75	25	580	720

Co-deposition samples

The mechanism of phase formation is similar for all the samples prepared by co-deposition. However, the temperatures of the phase formation vary with the Mo/W ratio. These temperatures are reported in Table 4.

The in situ X-ray diffractograms obtained for these samples are given in Fig. 8. Except for the sample with highest content in W, the first phase which appears is h-(Mo_xW_{1-x}). This phase then transforms into t-(Mo_xW_{1-x}). In agreement with the results obtained for the W/Si binary system, the h-(Mo_xW_{1-x}) phase can not be formed when the W content is too high.

Figure 9 shows the evolution of the normalized intensity of the most intense XRD peak for each phase, namely Mo(110), W(110), t-(Mo_xW_{1-x})Si_2(103) and h-(Mo_xW_{1-x})Si_2(111) versus temperature for the sample containing 75 at.% Mo.

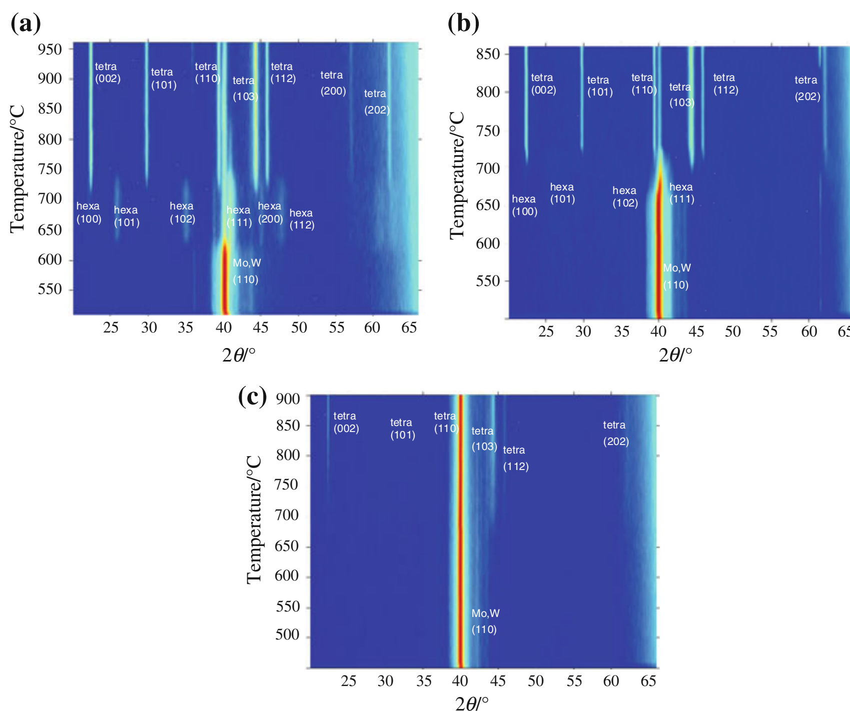

Fig. 8 In situ X-ray diffractograms recorded in the range 300–900 °C for the samples obtained by co-deposition. **a** 25 at.%W, **b** 50 at.%W, **c** 75 at.%W

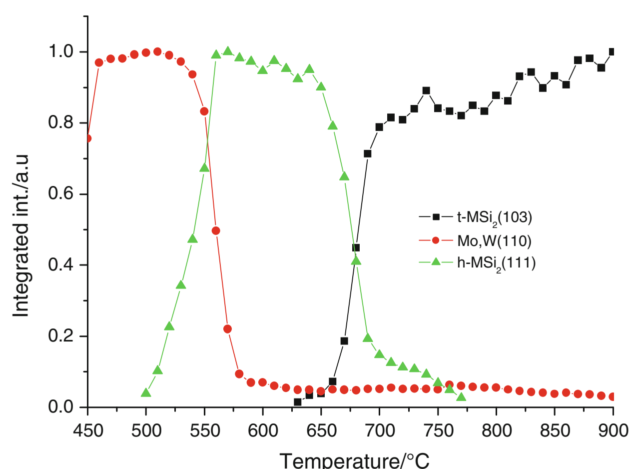

Fig. 9 Evolution of the normalized intensities of the most intense XRD peak for the phases present in the sample containing 75 at. % Mo prepared by co-deposition

Mo and W diffraction peaks cannot be distinguished. The decrease in their intensity at about 550 °C corresponds to the formation of h-(Mo_xW_{1-x})Si_2 which transforms into t-(Mo_xW_{1-x})Si_2 at about 700 °C.

One can observe from Table 4 that the temperature of formation of the hexagonal form increases with the W content. When this content is too high (75 at.%), this hexagonal form cannot be formed, the tetragonal one appears directly. The temperature of transformation from the hexagonal form to the tetragonal one decreases when the content in W increases. Thus, the stability range of the hexagonal form decreases when the content in W increases. This observation agrees with all the results previously reported in this study.

Conclusions

The phase formation in the ternary thin films system Mo–W–Si was studied in this work. Two kinds of samples were prepared by sputtering: the first ones were achieved by sequential depositions of Mo and W with various thickness ratios and various stacking order, and the second ones were obtained by co-deposition of Mo and W with various quantity ratios.

The main results can be summarized as follows. In all the samples, the first phase formed is (Mo,W)Si_2. The tetragonal form of (Mo,W)Si_2 is stabilized in thin films with respect to the bulk materials. For temperatures higher than 900 °C, in presence of tungsten, the t-(Mo,W)Si_2 transforms into (Mo,W)$_3$Si. The mechanism of formation of (Mo,W)Si_2 depends on the deposition procedure, namely sequential or by co-deposition. For the former one, the mechanism depends on the stacking order (W/Mo/Si or Mo/W/Si). When the hexagonal form of (Mo,W)Si_2 exists, its stability range in temperature decreases when the tungsten content increases. In all the cases, the authors observe that the temperature of formation of the tetragonal form increases when the molybdenum content increases.

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