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THERMAL STABILITY OF $W_{1-x}Si_x/Si$ MULTILAYERS FOR X-RAY OPTICS

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The thermal stability of multilayers (MLs) for X-ray mirrors can be increased by using a pair of materials in thermodynamic equilibrium. This was achieved by doping the W–layer by Si to decrease the driving force of interdiffusion. The $W_{0.66}Si_{0.33}/Si$, $W_{0.5}Si_{0.5}/Si$, $W_{0.33}Si_{0.66}/Si$ and, for comparison, W/Si MLs with ten bilayers were fabricated by electron-beam deposition in UHV onto oxidized Si substrates. The nominal thickness was 5.5 nm for Si and 2.5 nm for W or $W_{1-x}Si_x$ layers. The samples were heat treated by halogen–lamp rapid thermal annealing and by standard annealing in vacuum up to 1000 °C for 30 s and 25 min, respectively. Samples were analyzed by X-ray reflectivity and large angle X-ray diffraction measurements. From the results follows an increased stability of $W_{1-x}Si_x/Si$ MLs in comparison with the W/Si ones. The temperature which the sample can withstand without a serious damage increased from 500 to 850 °C with x increasing from 0 to 0.66 . As–deposited, MLs were amorphous. The crystalline bcc W or WSi_2 phases appeared at 500 °C for $x \leq 0.5$. For $x = 0.66$, a well developed WSi_2 was obtained only after annealing at 1000 °C. Hence, Si helps to keep W in the amorphous state.

1. Introduction

Multilayered X-ray mirrors are often used in the environments where the temperature and/or radiation is sufficiently intense to degrade their performance. This is not surprising having in mind that the multilayers (MLs) are inherently metastable non-equilibrium structures. The long term stability of MLs is often studied under thermal annealing or under intense X-ray, e.g. synchrotron radiation. The intense X-ray exposure causes more damage than a pure thermal annealing at the comparable temperature [1].

Great attention has been paid to the thermal stability of the Mo/Si MLs. It was shown that Mo/Si MLs structure did not change over a period of at least 20 months at the room temperature storage [2]. The instability of samples due to the interface interactions and silicide formation was observed after 300 and 400 °C treatment, for sputtered Mo/Si stacks [3-5]. The stability up to 500 °C/20 min was obtained with Mo/Si MLs deposited by e-beam evaporation at the substrate temperature of 150 – 200 °C [6]. For W/Si sputtered MLs, large structural changes have been observed after 400 °C/2h annealing [7]. For evaporated W/Si MLs, the multilayer structure persists up to 650 °C/5 s [8], however, a decrease of the period was observed after annealing at ≥ 500 °C/20 s.

The thermal stability of MLs can be increased using pairs of materials that are in thermodynamic equilibrium. According to Ref. 9 the equilibrium at the interfaces of different phases may be achieved if they are the neighbours in the phase diagram of a binary alloy system, separated by a region of their own eutectics. Obviously, the equilibrium is not obtained and the formation of silicides is inevitable at the interfaces between refractory metals W, Mo and Si. By doping the metals with Si, the driving force for Si diffusion into metal decreases (Si is the dominant diffuser) and for the combination of Si with a refractory metal disilicide ($MoSi_2$, WSi_2), the equilibrium can be achieved.

For this class of multilayers, mostly combinations $Mo_{1-x}Si_x$/Si have been studied so far. The working temperature could be increased up to 630 °C [9] with sputtered $MoSi_2$/Si MLs. Such samples could be annealed at 500 °C/1h in order to reduce their interface roughness [10]. The evaporated $Mo_{1-x}Si_x$/Si MLs with $x = 0.5$ and $x = 0.66$ were able to withstand the thermal treatment at 850 °C and 900 °C/20 min, respectively [11, 12].

Less attention has been paid to the $W_{1-x}Si_x$/Si MLs. They are studied in this paper.

2. Experimental details

Samples were fabricated in UHV apparatus with two e-beam sources, by evaporation and coevaporation of W and Si onto oxidized Si(100) substrates held at 150 °C . The thickness of the thermal SiO_2 was 500 nm. The vacuum prior to the deposition was about 10^{-7} Pa and during the deposition about 10^{-6} Pa. The deposition rates were 0.05 nm/s for both pure elements and W-Si mixtures.

The composition of the $W_{1-x}Si_x$ codeposited layers was obtained by setting of the appropriate deposition rates of the W and Si elements. The deposition rates of W and Si were derived prior the codeposition from the measurements of the thicknesses of deposited W and Si layers and time of deposition. The deposition rates of W and Si during the codeposition of $W_{1-x}Si_x$ were controlled by the mass spectrometer.

MLs with 10 bilayers were prepared starting with W or $W_{1-x}Si_x$ and finishing with Si to avoid surface tarnishing due to metal oxidation [13]. The nominal thicknesses of the layers were 5.5 nm for Si (spacer) and 2.5 nm for W or $W_{1-x}Si_x$ (reflector). Four types of MLs with different composition of the reflector layer were fabricated, namely W, $W_{0.66}Si_{0.33}$/Si, $W_{0.5}Si_{0.5}$/Si, $W_{0.33}Si_{0.66}$/Si. The composition of the last codeposit corresponds to the stable tungsten silicide WSi_2.

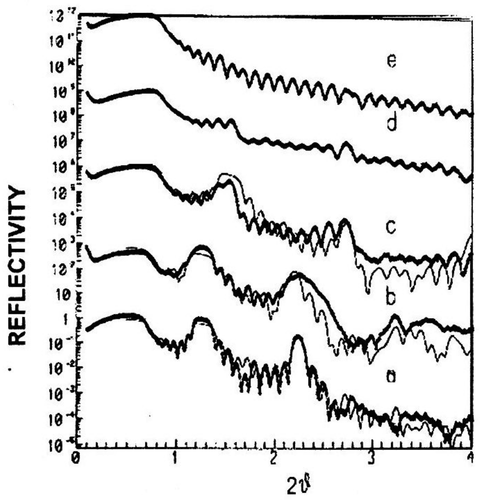
The samples were processed using rapid thermal annealing (RTA) between 500 °C/30 s and 1000 °C/30 s in a halogen lamp furnace (vacuum 10^{-3} Pa). For the comparison, also "long-term" vacuum furnace annealing at 500 °C/25 min was employed. For the analyses X-ray reflectivity measurements using the Stoe high resolution diffractometer with a double crystal monochromator and large angle X-ray diffraction (LAXD) were used. For X-ray reflectivity measurements, the CuKα_1 radiation was used.

3. *Results and discussion*

The X-ray reflectivity spectra of the as-deposited and annealed W/Si and $W_{0.33}Si_{0.66}$/Si MLs are shown in Figs. 1 and 2, respectively. The actual values of the bilayer thickness (multilayer period) $\Lambda = d_R + d_{Si}$, d_R and d_{Si} were obtained using the simulation procedure based on the Fresnel computational code [14]. Here, d_R is the thickness of the reflector W or W-Si mixture layer. The simulated spectra are also shown in Figs. 1 and 2, and the results of simulation are summarized in Table 1. The third maximum of the X-ray reflectivity curve of W/Si MLs is suppressed because of the layer thickness ratio $d_{Si}/d_R = 5.5/2.8 = 1.96$, which is close to 2. Similar, but less pronounced effect can be observed also for $W_{0.33}Si_{0.66}$/Si ML with $d_{Si}/d_R = 5.7/3 = 1.9$. The small maxima between the main Bragg maxima in the X-ray reflectivity spectra come from the interference of the waves reflected by the substrate/ML and ML/air interfaces and from the finite size of the multilayer stack.

The effect of thermal processing on the X-ray reflectivity of the W/Si, $W_{0.66}Si_{0.33}$/Si, $W_{0.5}Si_{0.5}$/Si and $W_{0.33}Si_{0.66}$/Si MLs is summarized in Table 1.

For W/Si ML, the multilayer period Λ did not change within the experimental error at 500 °C/30 s annealing. The change of layer thickness ratio d_R/d_{Si} can be explained by interdiffusion at the W/Si interfaces and will be discussed later. After annealing at 750 °C/30 s, the multilayered structure of the W/Si ML was suppressed, what hints at a strong intermixing at the W/Si interfaces. After annealing at 850 °C/30 s, the multilayered structure disappeared completely and the spectrum typical for the homogeneous thin film was observed (Fig. 1).



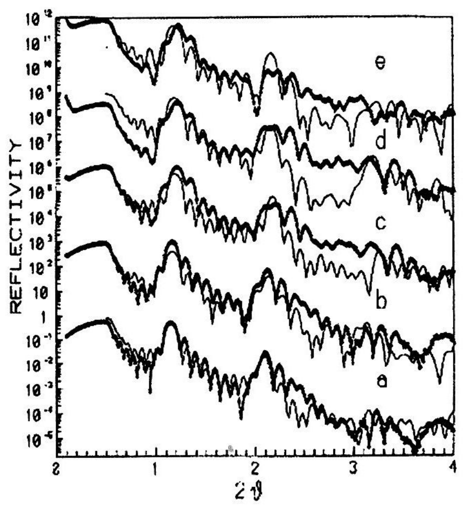


Fig. 1. X-ray reflectivity spectra of W/Si *ML: a – as–deposited, b – annealed at 500* °C/30 s, *c – annealed at 500* °C/25 min, *d – annealed at 750* °C/30 s, *e – annealed at 850* °C/30 s. *Spectra b, c, d and e are multiplied by factors of* 10^3, 10^6, 10^9 *and* 10^{12}, *respectively. The simulated spectra are shown by thin line.*

Fig. 2. X-ray reflectivity spectra of $W_{0.33}Si_{0.66}$/Si *ML: a – as–deposited, b – annealed at 500* °C/30 s, *c – annealed at 500* °C/25 min, *d – annealed at 750* °C/30 s, *e – annealed at 850* °C/30 s. *Spectra b, c, d and e are multiplied by factors of* 10^3, 10^6, 10^9 *and* 10^{12}, *respectively. The simulated spectra are shown by thin line (right).*

An increased thermal stability was found for all $W_{1-x}Si_x$/Si MLs ($x = 0.33, 0.5$ and 0.66).

The multilayered structure of $W_{0.66}Si_{0.33}$/Si ML did not change significantly at 500 °C/30 s annealing, the higher order Bragg maxima were suppressed due to the increased mixing and/or roughness at the interfaces. After 750 °C/30 s annealing a decrease of Λ was observed. As follows from simulation, this decrease of Λ results from the decrease of both layer thicknesses d_R and d_{Si}. After 850 °C/30 annealing only the first order Bragg maximum was observed, what hints at the distortion of the multilayered structure.

For the $W_{0.5}Si_{0.5}$/Si ML, Λ decreased at 500 °C /30 s annealing as follows from Table 1. After 750 °C /30 s annealing, the decrease of Λ and d_{Si} were observed. The same decrease of Λ was observed after 850 °C /30 s annealing, the layer thickness ratio d_{Si}/d_R decreased from 1.9 to 1.69. This was documented also by appearing of the 3-rd order Bragg maximum in the reflectivity spectrum.

For the $W_{0.33}Si_{0.66}$/Si ML, Λ was stable up to 750 °C /30 s annealing. At 750 °C/30 s annealing, the layer thickness ratio d_{Si}/d_R changed from 1.9 to 1.73. After annealing at 850 °C/30 s, the higher order Bragg maxima were suppressed what hints at mixing and/or increased roughness at the interfaces.

TABLE 1.
Bilayer (Λ), silicon layer (d_{Si}) and reflector layer (d_R) thicknesses obtained by simulation procedure, (c - collapsed, ML structure disappeared completely, d - distorted, ML structure is still visible).

Annealing	W/Si	$W_{0.66}Si_{0.33}$/Si	$W_{0.5}Si_{0.5}$/Si	$W_{0.33}Si_{0.66}$/Si
As deposited				
Λ [nm]	8.3	7.6	9.4	8.7
d_R [nm]	2.8	2.0	3.2	3.0
d_{Si} [nm]	5.5	5.6	6.2	5.7
500 °C/30s				
Λ [nm]	8.3	7.6	9.1	8.7
d_R [nm]	3.0	2.0	3.1	3.0
d_{Si} [nm]	5.3	5.6	6.0	5.7
500 °C/25 min				
Λ [nm]	6.7	6.4	8.6	8.3
d_R [nm]	3.2	1.7	3.1	2.9
d_{Si} [nm]	3.5	4.7	5.5	5.4
750 °C/30s				
Λ [nm]	d	6.4	9.0	8.2
d_R [nm]		1.7	3.1	3.0
d_{Si} [nm]		4.7	5.9	5.2
850 °C/30s				
Λ [nm]	d	6.4	8.9	8.2
d_R [nm]		1.7	3.3	3.0
d_{Si} [nm]		4.7	5.6	5.2
1000 °C/30s				
Λ [nm]	c	c	c	c
d_R [nm]	–	–	–	–
d_{Si} [nm]	–	–	–	–

After annealing at 1000 °C/30 s, the multilayered structure disappeared completely in all $W_{1-x}Si_x$/Si MLs and the reflectivity spectrum of homogeneous thin film was observed.

The LAXD data of as-deposited and annealed samples are summarized in Table 2, the LAXD spectra of as-deposited and annealed $W_{0.33}Si_{0.66}$/Si MLs are summarized in Fig. 3. The W, $W_{1-x}Si_x$ and Si layers in as-deposited samples are amorphous. As we have shown previously, the tungsten layers were amorphous for $d_W \leq 4$ nm, while the Si layers were amorphous at least up to $d_{Si} = 20$ nm [14]. As follows from Table 2, for W/Si ML, the crystallization of bcc W starts at 500 °C/30 s annealing. The same picture was found after annealing at 750 °C/30 s. At 850 °C /30 s annealing, the tetragonal WSi_2 is formed.

After 500 °C/30 s annealing, the early stage of crystalline bcc W or hexagonal WSi_2 was detected in $W_{0.66}Si_{0.33}$/Si and $W_{0.5}Si_{0.5}$/Si MLs, while the $W_{0.33}Si_{0.66}$/Si remained amorphous. At 750 °C/30 s annealing, the hexagonal WSi_2 phase is formed in $W_{0.66}Si_{0.33}$/Si and $W_{0.5}Si_{0.5}$/Si MLs, while in $W_{0.33}Si_{0.66}$/Si only the early stage of WSi_2 formation was observed. After 850 °C/30 s, annealing the tetragonal WSi_2 phase was found in $W_{0.66}Si_{0.33}$/Si and $W_{0.5}Si_{0.5}$/Si MLs, the early stage of tetragonal WSi_2 formation was detected also in $W_{0.33}Si_{0.66}$/Si sample.

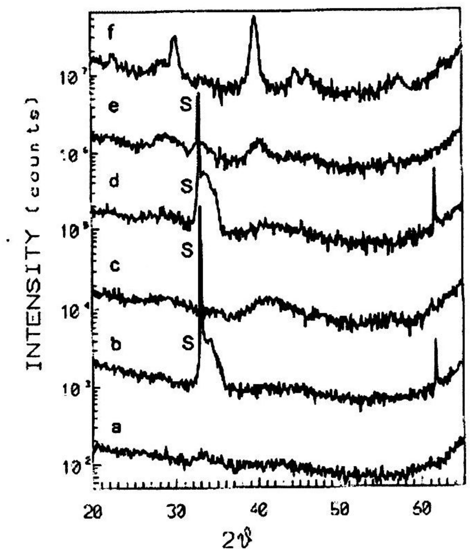


Fig. 3. LAXD spectra of $W_{0.33}Si_{0.66}$/Si *ML: a – as–deposited, b – annealed at 500* °C/30 s, *c – annealed at 500* °C/25 min, *d – annealed at 750* °C/30 s, *e – annealed at 850* °C/30 s. *f - annealed at 1000* °C/30 s; *S – substrate. Spectra b, c, d, e and f are multiplied by factors of 10,* 10^2, 10^3, 10^4 *and* 10^5, *respectively.*

TABLE 2.

LAXD data of as-deposited and annealed W/Si *and* $W_{1-x}Si_x$/Si *MLs, x=0.33, 0.5 and 0.66, (a-amorphous, *beginning of the phase formation, t-tetragonal, h-hexagonal).*

Annealing	W/Si	$W_{0.66}Si_{0.33}$/Si	$W_{0.5}Si_{0.5}$/Si	$W_{0.33}Si_{0.66}$/Si
As–deposited	a	a	a	a
500 °C/30 s	bcc W	bcc W/h–WSi_2	bcc W/h–WSi_2	a
500 °C/25 min	bcc W/*WSi_2	h–WSi_2	h–WSi_2	*t–WSi_2
750 °C/30 s	bcc W	h–WSi_2	h–WSi_2	a/*WSi_2
850 °C/30 s	t–WSi_2	t–WSi_2	t–WSi_2	*t–WSi_2
1000 °C/30 s	t–WSi_2	t–WSi_2	t–WSi_2	t–WSi_2

At 1000 °C/30 s annealing, the tetragonal WSi_2 is formed in W/Si as well as in $W_{1-x}Si_x$/Si samples.

Using the RTA, the early stage of phase formation at a given temperature was studied. In order to detect the product of prolonged annealing, the MLs were heat treated at 500 °C for 25 min. Under these conditions, the silicide phases were better developed in comparison with the 500 °C /30 s annealing.

The X-ray reflectivity data of W/Si ML annealed at 500 °C/25 min hint at an increased mixing and/or roughness at the W/Si interfaces (Fig. 1). The multilayer period Λ decreased, and higher order Bragg maxima were suppressed. A similar situation was found for $W_{0.66}Si_{0.33}$/Si ML. For $W_{0.5}Si_{0.5}$/Si ML, the 500 °C/25 min annealing results in a pronounced decrease of Λ in comparison with that observed after 750 °C/30 s or 850 °C/30 s annealing. The decrease of Λ, which was found in W/Si and $W_{1-x}Si_x$/Si ML, can be attributed to the tungsten silicide formation [8,15]. What should be explained more is the decrease of d_{Si} thickness in our samples (Table 1). It is known that Si is the dominant diffuser in the W/Si pair. This is probably valid for $W_{1-x}Si_x$/Si pair, too. Due to the presence of concentration gradient at the interfaces, there is always interdiffusion. During the heat treatment, the crystalline WSi_2 is formed from the amorphous $W_{1-x}Si_x$ mixture. This process is accompanied by the increase of the W content in the $W_{0.66}Si_{0.33}$ and in $W_{0.5}Si_{0.5}$ matrix, which remain amorphous. Further, WSi_2 formation is determined by the Si diffusion at the W-Si/Si interfaces. Therefore, the d_{Si}/d_R ratio decreases. As shown for the sample $W_{0.33}Si_{0.66}$,/Si, where the composition of the amorphous W-Si mixture in the multilayer is close to WSi_2, the interdiffusion at the interfaces is suppressed, and only small decrease of d_{Si}/d_R ratio and Λ were observed.

Summarizing the experimental data, we observed increased thermal stability of $W_{1-x}Si_x$/Si MLs, in comparison with W/Si samples. Two effects can be responsible for that. One is the increased stability of the amorphous $W_{1-x}Si_x$ mixture against crystallization in comparison with the amorphous W. This is evident with the $W_{0.33}Si_{0.66}$/Si ML, where well developed tetragonal WSi_2 phase was observed only after 1000 °C/30 s annealing.

The second effect is the suppressed intermixing at the $W_{1-x}Si_x$/Si multilayer interfaces due to the doping of W by Si. With $W_{0.33}Si_{0.66}$/Si sample, where the composition of the reflector layer corresponds to the stable WSi_2 silicide, there is no need for the diffusion of Si to compensate the changes of stoichiometry due to the silicide crystallization. Only the minor changes of the multilayered structure at least up to 850 °C/30 s heat treatment were observed.

4. Conclusion

Electron beam evaporated $W_{1-x}Si_x$/Si MLs, processed by rapid thermal annealing during 30 s, show a high thermal stability up to 850 °C/30 s for $x = 0.66$. This composition corresponds to the stable tungsten disilicide. W/Si MLs of the same period could withstand only the heat treatment at 500 °C/30 s. The increased thermal stability of the $W_{1-x}Si_x$/Si MLs is attributed: a) To the structural stability of the amorphous mixtures against crystallization. For $x = 0.66$, well developed WSi_2 phase appeared only at 1000 °C/30 s annealing; b) To the suppressed interdiffusion at the interfaces. For $x = 0.66$, the stoichiometry of the structure does not change due to the crystallization of WSi_2 (like for lower values of x) and there is no need for the diffusion of Si for the further growth of the tungsten silicide.

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TOPLINSKA STABILNOST $W_{1-x}Si_x$/Si VIŠESLOJEVA ZA RENDGENSKU OPTIKU

Primjenom parova materijala, koji se stavljaju u termodinamičku ravnotežu, može se povećati toplinska stabilnost višeslojeva za zrcala rendgenskog zračenja. Sloj volframa dopunjen je silicijem da bi se smanjila difuzija medu slojevima. Istraženi su višeslojevi W_{1-x} Si_x sa $x = 0.66, 0.5, 0.33$ i $x = 0.0$ radi uspoređivanja. W/Si višeslojevi sa deset dvoslojeva pripremljeni su nanošenjem uz pomoć elektronskog snopa na oksidirane Si podloge u ultravakuumu. Nominalna debljina slojeva Si bila je 5.5 nm, a W odnosno $W_{1-x}Si_x$ 2.5 nm. Višeslojevi su toplinski otpuštani. Uzorci su istraživani mjerenjem refleksivnosti i difrakcijom rendgenskog zračenja. Povećanjem x od 0 na 0.66, povisila se granična temperatura bez većeg oštećenja sa 500 na 800 °C.