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STRUCTURAL TRANSFORMATION IN C/Si MULTILAYER AFTER ANNEALING

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Amorphous C/Si multilayers were prepared by DC magnetron sputtering technique and investigated by transmission electron microscopy and low-angle x-ray diffraction methods after annealing at 650 and 950 °C. The amorphous interlayers of 0.5 – 0.6 nm thick were found at C/Si and Si/C interfaces being of different density and composition. Amorphous structure of the multilayer is stable up to 950 °C when crystallization of α-SiC occurs and voids form in α-Si layer.

Keywords: multilayer, diffusion, nanocrystals, intermixing layers, extreme ultra violet

Изготовленные методом прямоточного магнетронного распыления аморфные многослойные композиции C/Si были исследованы методами просвечивающей электронной микроскопии и малоугловой рентгеновской дифракции после отжигов при температуре 650 и 950 °C. На границах раздела C/Si и Si/C обнаружены аморфные перемешанные зоны толщиной 0.5 – 0.6 нм с различными плотностью и составом. Аморфная структура многослойной композиции стабильна вплоть до 950 °C, когда наблюдается формирование пор в слоях α-Si и кристаллизация α-SiC.

Ключевые слова: многослойная композиция, диффузия, нанокристаллы, перемешанные зоны, вакуумный ультрафиолет

Виготовлені методом прямоточного магнетронного розпилення аморфні багатошарові композиції C/Si було досліджено методами просвічувальної електронної мікроскопії та малокутової рентгенівської дифракції після відпалу при температурі 650 і 950 °C. На межах поділу C/Si та Si/C виявлені аморфні перемішані зони різної густини та складу завтовшки 0.5 – 0.6 нм. Аморфна структура багатошарової композиції є стабільною до 950 °C, коли спостерігається формування пор у шарах α-Si у та кристалізація α-SiC.

Ключові слова: багатошарова композиція, нанокристали, шорсткість, перемішані зони, вакуумний ультрафіолет

INTRODUCTION

Multilayer interference X-ray mirrors enable efficient normal incidence reflection in wide spectral range covering the hard and soft X-rays and the extreme ultraviolet (EUV). Silicon/carbon multilayers have a great potential to be used in the 17 – 35 nm spectral range with wide application in solar and plasma physics, spectroscopy, EUV lasers and image acquisition in high resolution microscopy and astrophysics [1, 2]. During a long time a great deal of solar astrophysicists' and plasma theoreticians' attention is attracted to the Sun and, especially to processes that occurs in solar corona [3]. Investigation of plasma emission in EUV wavelength region is very important because of information about plasma electron temperature and density. X-ray spectroscopy of coronal plasma that contains a number of strong He and Fe lines of different degree of ionization (specifically, $л_{Fe\text{-}IX}$ = 17.1 nm, $л_{Fe\text{-}XII}$ = 19.5 nm, $л_{Fe\text{-}XIV}$ = 21.1 nm, $л_{Fe\text{-}XV}$ = 28.4 nm, $л_{He\text{-}II}$ = 30.4 nm, $л_{Fe\text{-}XVI}$ = 33.5 nm) makes possible verifying different theoretical models of solar corona structure [4]. The normal incidence interference C/Si multilayer is able to provide 27% – 37% reflectance in 17 – 35 nm wavelength range if layer interfaces will be smooth and sharp [5, 6]. However, the real structure of multilayer is often far away from the ideal design and efficiency of X-ray mirror application is limited. To prevent interfacial roughness development and interlayer mixing during growth of the multilayer the detailed study of its structure and composition is needed. Multilayers are intended to be used as optical elements in outer space where considerable temperature load occurs. Consequently to reach a high thermal stability of the multilayer the systematic study of its thermal degradation is required. The aim of the present study is investigation of structure, interlayer interaction features and thermal influence on structural and phase changes in C/Si multilayer.

EXPERIMENTAL PROCEDURES

The C/Si multilayers consisted of 33 dual C/Si l ayers with 7.5/7.5 nm thickness respectively were deposited by DC magnetron sputtering in argon environment onto float glass (for X-ray study) and single-crystal (100) silicon (for electron microscopy study) substrates. Vacuum chamber was preliminarily pumped out to 10^{-3} Pa. Argon pressure during sputtering was kept on 0.27 Pa. Substrates were cleaned before deposition by argon ion beam ($U \approx 1000$ V, $I = 7$ mA). Graphite (99.99%) and silicon (99.999%) disks of 100 mm in diameter were used as targets. The layer thickness was varied by transportation velocity of substrate above the targets. Deposition rates were about 0.08 and 0.1 nm/s for C and Si layers, respectively. The substrate temperature was not higher then 50 °C.

Low-angle X-ray diffraction (LAXD) measurements were made in и/2и geometry by using general-purpose X-ray diffractometer. The Cu-$K_{б1}$ (0.15406 nm) radiation with beam divergence of 0.1 mrad of incidence was provided by asymmetrically cut Si-crystal (110) monochromator. The experimental curves of low-angle X-ray diffraction were fitted using X-Ray Calc software. Calculation was based upon recurrent relation method using Fresnel's formulas. Qualitative phase analysis was made using general-purpose X-ray diffractometer. Multilayer specimens were annealed in the vacuum furnace equipped by two 750 W halogen bulbs during 1 hour. Working pressure during annealing was ~ $7 \cdot 10^{-4}$ Pa. Transmission electron microscope (TEM) PEM-U was used for cross-section image acquisition at 100 kV accelerating voltage.

RESULTS AND DISCUSSION

Electron microscopy and X-ray diffraction study has established high quality periodic structure with sharp interfaces and amorphous structure of individual layers (fig. 1 and 2). One can see dark layers between α-Si and α-C on TEM image (fig 1a). Because only haloes are present on the diffraction pattern, we can conclude that the image contrast attributes to layer density only. The intermixed layers form during the multilayer growth on the both interfaces (fig. 1a). Profile of the image reveals mixed zones with equal thickness about 0.5 – 0.6 nm and the different density (fig 1c). Interlayer on C-on-Si

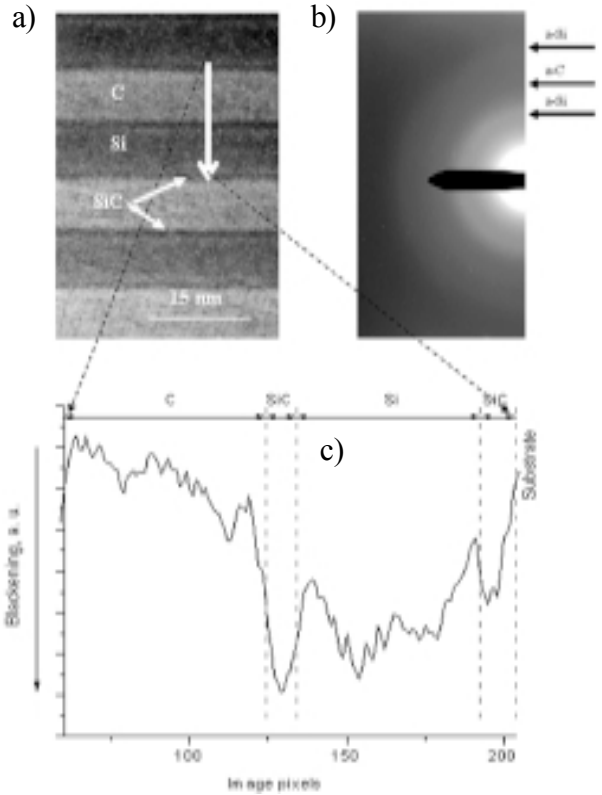

Fig. 1. The electron microscopy image (a), selected area diffraction pattern (b) and blackening profile of the image (c) of cross-sectional C/Si multilayer with 15 nm period in as-deposited state.

interface is darker and, thus, more dense than Si-on-C interlayer. Below we will write "SiC" meaning Si_xC_y alloy. LAXD study confirms the fact of dense layer formation at Si/C and C/Si interfaces. If one compare the X-ray curve of Si/C (fig. 2a) and Si/SiC/C/SiC (fig. 2b, c) compositions with the same period, the obvious difference in intensity about order of even peaks is observed (marked by arrows).

Density of the interlayers according to the best fitting of the X-ray diffraction curves is 2.75 and 2.4 g/cm^3 for C-on-Si and Si-onC interfaces, respectively. That density values are higher than for bulk Si (2.33 g/cm^3) and lower than for bulk SiC (3.1 – 3.2 g/cm^3) [7]. It's interesting to know what kind of composition of mixed zones is. The thickness of multilayer coating obtained from deposition rates is lower than the thickness calculated from product of the multilayer period to its number. Contraction of the multilayer is about 0.5 nm. It is a result of carbon-silicon chemical interaction. The interlayer thickness, the average zone density and multilayer contraction were used to determine the average C:Si interlayer atomic composition. The atomic composition was evaluated as 3:2 and about 0.5 nm of carbon and silicon layers were consumed by the interlayers.

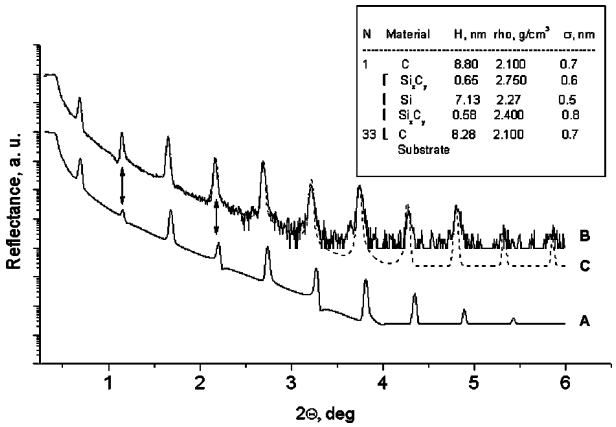

Fig. 2. Calculated (A, C) and experimental (B) low-angle X-ray diffraction patterns of C/Si multilayer (A) and C/SiC/Si/SiC ones (B, C) with 16.1 nm period in as-deposited state. The curve A is shifted down for the better comparison.

There is not another composition as SiC in the carbon-silicon system [7] and it is possible that the mixed zones are SiC and the zones are enriched by carbon with different concentration.

Peak calculated reflectivity for the C/SiC/Si/SiC mirror is 24% at 28 nm wavelength for normal incidence in contrary to 25% for C/Si multilayer with ideal design.

Thermal annealing of the multilayer during one hour at 650 °C leads to the period increasing and growth of the interlayers. There is a shift of the diffraction peaks to the low angles in the X-ray curves (fig. 3) which correspond to 4.5% period increase.

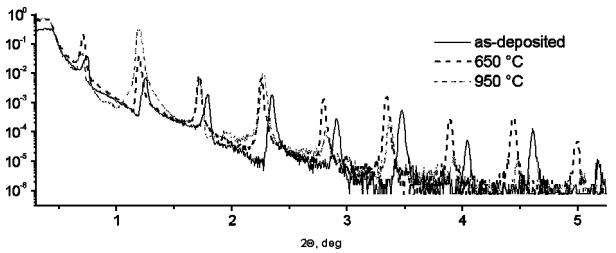

Fig. 3. Low-angle X-ray diffraction curves of the C/Si multilayer in as-deposited state (–) and after annealing at 650 °C (---) and 950 °C (···).

The thickness of intermixing layers increases during heating in different proportion, the interlayer Si-on-C grows more than the C-on-Si one (fig. 4) reaching thickness of 1.2 and 1 nm, correspondently. Simulation of the X-ray curve (fig. 3) corroborates the increase of interlayer thickness and reveals the Si layer consumption more considerably than the C layer. It may be attributed to the diffusion process of silicon to the lower dense zone and through the

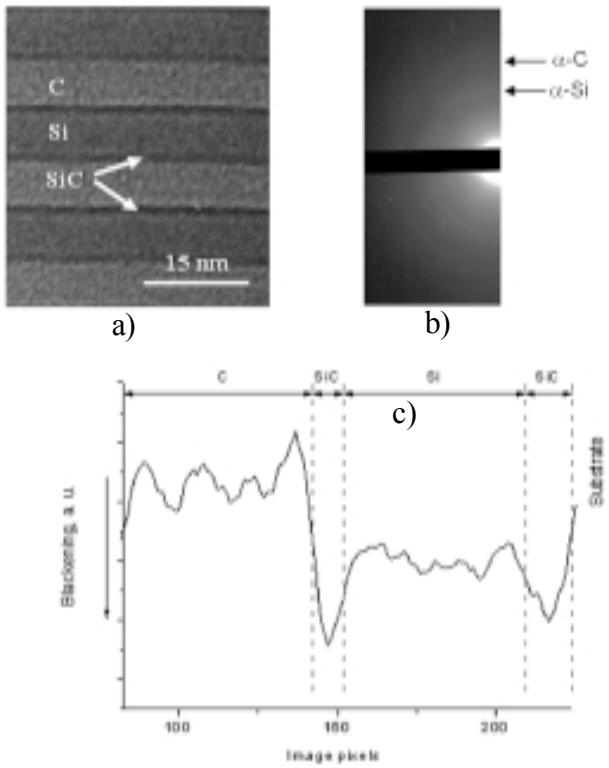

Fig. 4. The electron microscopy image (a), selected area diffraction pattern (b) and blackening profile of the image (c) of cross-sectional C/Si multilayer with 15 nm period after annealing at 650 °C.

dense zone into the carbon layer and graphitization of the carbon layer. It is known [8] that the growth of SiC during carbonization of monocrystalline Si is controlled by diffusion of Si trough the SiC layer. Consumption of carbon layer during SiC growth is compensated by graphitization process taking place in the carbon/silicon multilayer at this temperature [9, 10]. The graphitization of amorphous carbon, seemingly, is responsible for the period increase because the SiC formation leads to the volume contraction and has to be accompanied by period decreasing.

Electron microscopy and X-ray diffraction data indicate activation of diffusion process at 950 °C (fig. 5). Analysis of the X-ray diffraction pattern (fig. 3) reveals decreasing of multilayer period and the change of density of all layers. The carbon density decreases down to 1.85 g/cm^3 and density of mixed zones substantially increases up to 3 g/cm^3 that is very close to 3.2 g/cm^3, the bulk density of SiC. In contrary, density of silicon layers appears to be far from 1.85 g/cm^3 bulk value (tabl. 1). Decrease of carbon density is easy explained by graphitization process that is well known from literature [9, 10]. Increasing of the mixed zone density is explained as

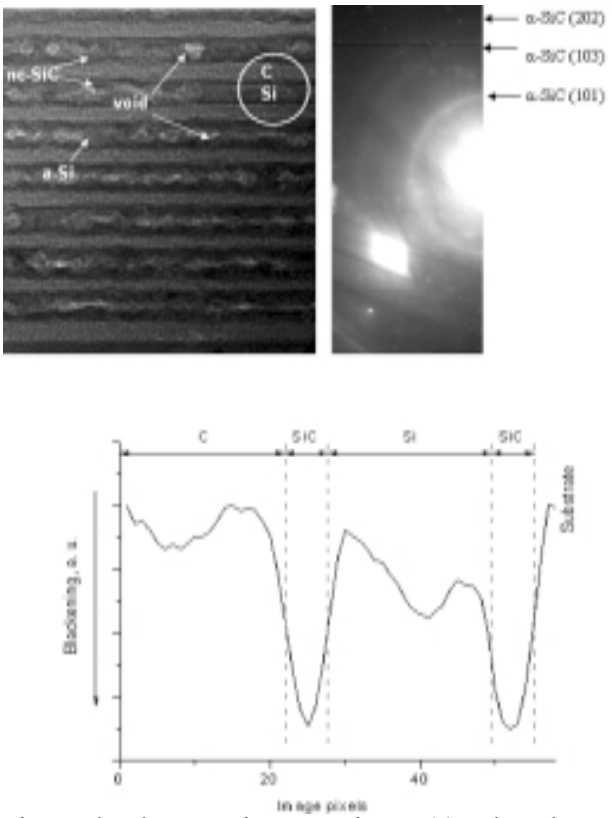

Fig. 5. The electron microscopy image (a), selected area diffraction pattern (b) and blackening profile (white circle) of the image (c) of cross-sectional C/Si multilayer with 15 nm period after annealing at 950 °C.

Table 1

Results of low-angle X-ray diffraction patterns fitting of C/Si multilayer with 15 nm period and N = 33 after 950 °C annealing

N	Material	*H*, nm	c, g/cm^3	y, nm
33	SiC	1.5	3	0.7
	Si	6.3	1.85	1
	SiC	1.5	3	1
	C	6.5	1.85	0.7

a result of crystallization process of α-SiC (2H-SiC [11]) that is displayed by electron diffraction (fig. 5b, tabl. 2).

Table 2

Measured and tabular [11] data of reflections in selected area diffraction pattern in fig. 5b

Experimental *d*	Reflection plane	*d* (ASTM)
2.386	100	2.357
1.455	103	1.420
1.187	202	1.180

The reason of silicon density decreasing is not obvious. At the first glance the contrast in the electron image is diffraction one that is typical for polycrystalline materials. However, one can see in the fig. 5a the absence of dark sections in Si layer: crystals with atomic planes oriented at the Bragg angles to the electron beam. Thus we can suppose that the contrast inside the silicon layers is caused by electron absorption only and bright sections in the image are voids in silicon layer. Some voids are faceted and some sections of multilayer have amorphous structure (white circle in the fig. 5a), therefore it can be concluded that process of carbide crystallization is inseparably linked with crystallization of silicon. The SiC nanocrystal formation by the reaction of carbon whith polycrystalline Si is more favorable than reaction with amorphous silicon [12].

The following diffusion process might be proposed (fig. 6). During heating the amorphous silicon crystallite nucleates and grows until it reaches amorphous SiC interlayer. The silicon carbide nanocrystals arise at interphase boundary. The SiC crystallization process should be accompanied by the equalization of carbon and silicon concentration and densification of local area. We suggest the voids form as a result of consumption of Si crystallite due to fast diffusion of silicon along the crystal boundary. The void formation accompanies well known process of SiC formation as carbonization of monocrystalline silicon [13].

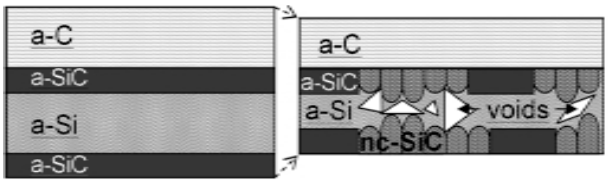

Fig. 6. Destruction of the silicon layer and void formation after annealing at 950 °C.

CONCLUSION

The C/Si multilayer in as-deposited state presents four-layer structure with two Si_xC_y intermixing layers and smooth interfaces. The Si_xC_y interlayers with thickness of 0.5 – 0.6 nm have different composition and density lower than bulk SiC. Interlayer formation pure influences on multilayer mirror reflectivity in EUV wavelength range. During thermal annealing up to 650 °C interlayers rise with different rate and their density grows, and the multilayer period increases by a few percents, probably, as a result of graphitization of α-C. At the temperature of 950 °C silicon carbide nanocrystals (α-SiC) are formed and voids in the silicon layer occur as a result of silicon diffusion and growing SiC nanocrystalls.

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