Formation and evolution of intermixing zones in C/Si multilayer under heating

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Formation of intermixing zones, their structure and phase composition in C/Si multilayers in as-deposited state and after annealing are studied. During deposition intermixing zones of ~0.6 m thick are formed at both silicon/carbon and carbon/silicon interfaces. The zone formed at C-on-Si interlayer is denser than adjacent zone due to amorphous SiC nucleation. Both the thickness and the densities of intermixing zones increase with annealing temperature up to 800°C. Silicon carbide is revealed in Si-on-C zone at 700°C. Structure of the zones is still amorphous at 950°C.

Исследованы особенности формирования, структура и фазовый состав перемешанных зон в многослойной пленочной системе C/Si в исходном состоянии и при отжиге. При осаждении компонентов на границах раздела кремний/углерод и углерод/кремний формируются перемешанные зоны толщиной ~0.6 нм. При этом зона, которая сформировалась при осаждении C на Si более плотная благодаря тому, что в ней есть аморфный SiC. При температуре отжига 800°C размер и плотность перемешанных зон увеличиваются. При 700°C наблюдается формирование карбида кремния в зоне Si на C. Аморфная структура зон сохраняется вплоть до 950°C.

Особливості формування і еволюція перемішаних зон у багатошаровій системі C/Si при нагріванні. *І.О.Журавель, Є.А.Бугаєв, О.В.Пеньков, Є.М.Зубарев, В.А.Севрюкова, В.В.Кондратенко.*
Досліджено особливості формування, структуру та фазовий склад перемішаних зон у багатошаровій плівковій системі C/Si у вихідному стані та при відпалі. При осадженні компонентів на межах поділу кремній/вуглець та вуглець/кремній формуються перемішані зони завтовшки ~0.6 нм. При цьому зона, що сформувалася при осадженні C на Si має більшу густину, оскільки вміщує аморфний SiC. При температурі відпалу 800°C розмір та густина перемішаних зон ростуть. При 700°C спостерігається формування карбіду кремнію у зоні Si на C. Аморфна структура зон зберігається аж до 950°C.

1. Introduction

Multilayer films with layer thicknesses of nanometer scale are widely utilized as strengthening, antifriction, optical, magnetic and corrosion-inhibiting coatings in different scientific and industrial areas [1–4]. Their properties are considerably dependent on structure of their layers and interfaces.

It is well-known that during deposition of silicon-based multilayers interlayers, presenting themselves intermixing zones, can form [5, 6]. In most cases appearance of the extra layers has an influence on the properties of the multilayer coating, especially,

when the thickness of the main layers is comparable with the thickness of the inter-mixing zones. Nanoscale thickness and amorphous state of the intermixing layers make study of their composition and their structural and phase transformations under different kinds of influence more difficult. Thereupon periodical multilayers are convenient objects of the interlayer study because such multilayers form low-angle X-ray diffraction pattern [2].

Structure and composition of the inter-mixing zones in metal/silicon multilayers have been thoroughly investigated in connection with developing of X-ray optical coatings for 1−4 nm [7], 12−20 nm [5] and 38−50 nm [6] wavelength ranges. In present work the structure and composition of the intermixing zones in C/Si system were investigated. This pare of materials is a prospective alternative to Mo/Si one utilizing for development of X-ray mirrors in 22−35 nm wavelength range. C/Si multilayer is also interesting as a wear-resistant antifriction coating [8] and a precursor for nano-granulated silicon carbide [9] being a prospective material for radiation sensors and high-capacity electronic devices. In addition, the investigation of interaction processes between carbon and silicon under elevated temperatures is of a great interest in connection with the development of new silicon- and graphene-based types of heterostructures [10].

2. Method of specimen preparation and attestation

C/Si periodical multilayers were deposited by means of DC magnetron sputtering in argon environment onto polished fused silica and monocrystalline (100) silicon substrates. Graphite (99.99 %) and silicon (99.999 %) discs of 100 mm in diameter were used as the targets. Vacuum chamber was preliminary baked up and pumped out to 10^{-3} Pa pressure, argon pressure during deposition was kept at about 0.27 Pa. Layer thickness was controlled by means of properly setting the transportation velocity of the substrate holder over the targets with deposition rates of 0.08 and 0.1 nm/sec for C and Si, respectively. Before deposition the substrate was cleaned by argon ion beam ($U{\approx}1000$ V, $I = 7$ mA, $t = 10$ min). The temperature was not higher than 50°C during the deposition process. It was two types of specimens — bilayers and multilayers. Bilayers were investigated by X-ray photoelectron spectroscopy (XPS) method. Multi-
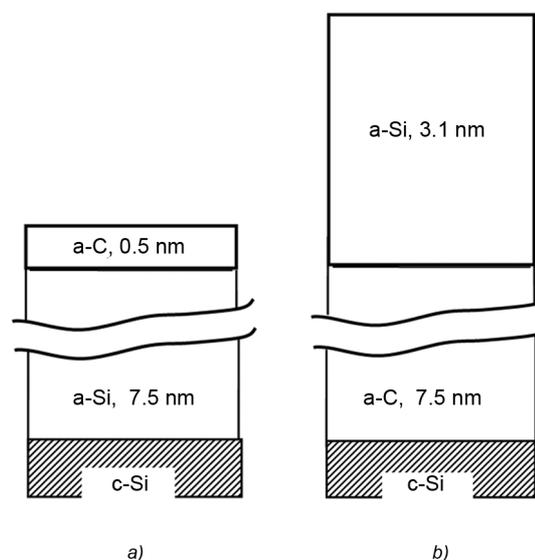

Fig. 1. Scheme of investigated specimens — Si/C and C/Si amorphous bilayers.

layers were investigated by means of low-angle X-ray diffraction (LAXRD) and cross-section transmission electron microscopy (TEM). Scheme of the specimens for XPS study is presented in Fig. 1. The thickness of top silicon layer in specimen B was selected noting that silicon reacts with oxygen on the air and about 1.6 nm of Si is consumed for SiO_2 formation.

XPS spectra were obtained using alpha (Thermo VG, U.K.) spectrometer equipped by Al Kα ($h\nu = 1486.6$ eV) monochromatic X-ray source. Vacuum in working chamber was maintained at $7.6 \cdot 10^{-7}$ Pa.

The XPS spectra were registered in the energy ranges of 275−295 eV (C1s) and 93−113 eV (Si2p). The example of the spectra of specimens A and B in as-deposited state is shown in Fig. 2.

The curves were analyzed by means of commercially available mathematical software. The individual peaks were separated

Table 1. Observed XPS spectra energy lines of Si/C and C/Si bilayers in as-deposited state

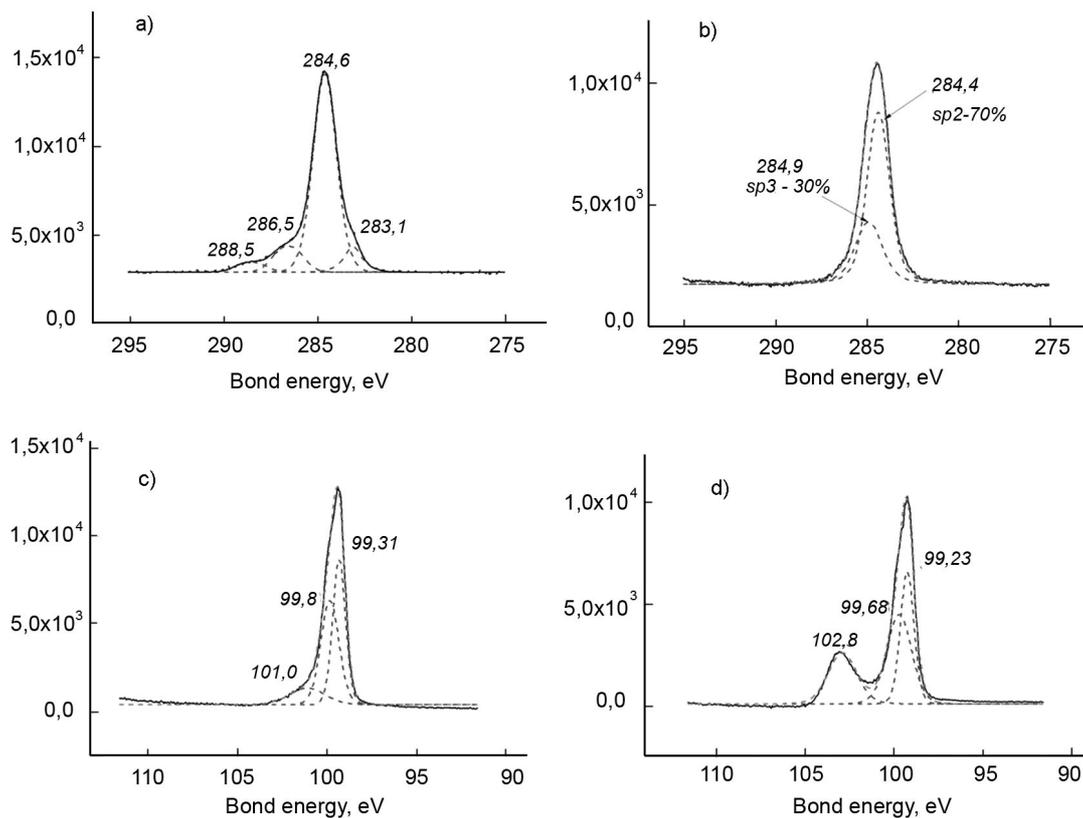| Line	Values, eV	Bond
C1s	283.0	Si–C
	284.4	C–C ($sp2$)
	284.9	C–C ($sp2$)
	286.5	C–C
	288.5	C=O
S2p	99.3	Si–Si
	99.7	Si–Si
	101.0	Si–C
	102.8	Si–O

Fig. 2. XPS spectra of different specimens in as-deposited state, type A (a, c) and type B (b,d) in C1*s* (a, b) and Si2*p* (c,d) spectral ranges.

by the approximating Voigt function after background subtraction utilizing the Shirley method. Observed lines and corresponding chemical bonds are given in Table 1.

LAXRD spectra were obtained by means of general purpose X-ray diffractometer in θ/2θ geometry at Cu–Kα1 (0.15406 nm) wavelength. Incidence radiation divergence of 0.1 mrad was provided by an asymmetrically cut Si (110) crystal monochromator. The experimental curves were fitted using X-ray_Calc software. Calculation of the fitting curves was based on the recurrence relations [12, 13] using the Fresnel equations [14].

TEM images and selected area electron diffraction patterns were obtained utilizing transmission electron microscope PEM-U at accelerating voltage of 100 kV.

The specimens were annealed in vacuum furnace equipped by six 600 W Qhalogen bulbs at ~ $7 \cdot 10^{-4}$ Pa in 300–950°C temperature range. The time of each annealing was 2 hours.

3. Results and discussion

As it was demonstrated previously [15] during deposition of C/Si multilayers the process of intermixing zone formation oc-

curs at the interfaces (Fig. 3, a). Zone thickness is ≈0.6 nm for both C on Si and Si on C interfaces. At the same time fitting of low-angle X-ray diffraction curves shows that the zones have different densities. C on Si zone has a density of ≈2.75 g/cm³ and the density of Si on C zone is ≈2.4 g/cm³. It should be noted that the density of each zone is higher then the density of carbon
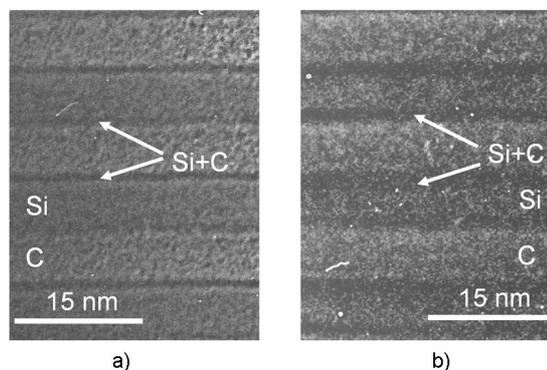

Fig. 3. Cross-sectional TEM images of C/Si multilayer in as-deposited state (a) and after annealing at 700°C (b).
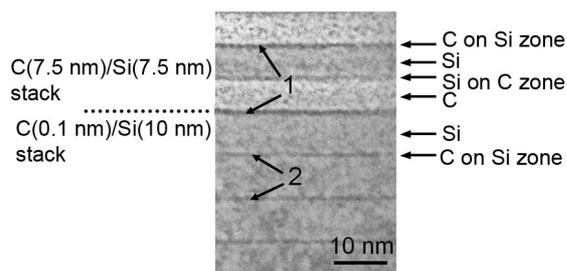
Fig. 4. TEM image of C/Si multilayer specimen composed of two stacks — C(7.5 nm)/Si(7.5 nm) and C(0.1 nm)/Si(10 nm).

and silicon layers in the multilayer. Amount of layer components that was consumed during deposition was calculated, and on that basis we can make estimation to the average composition of the both zones. It is around $C_{0.62}Si_{0.38}$ [15].

Two specimen sets were deposited to ascertain the formation features of intermixing zones in C/Si multilayer. In the first set the thickness of silicon layers was constant and amounted to ≈ 10 nm and the thickness of the carbon layers changed from the specimen to specimen from ≈ 0.1 nm to ≈ 0.4 nm with the interval of 0.1 nm. In the second set the carbon layers thickness that also amounted to ≈ 10 nm was constant and the silicon layers thickness varied from the specimen to specimen from ≈ 0.1 to ≈ 1.2 nm.

TEM study revealed that the C/Si specimens with carbon thickness of ≈ 0.1 nm represent periodical multilayers "intermixing zone/silicon" (Fig. 4), i.e. the whole deposited carbon is totally intermixed with silicon. The thickness of the intermixing zone is ≈ 0.6 nm. Low-angle diffraction

curve of such specimen can be well-fitted utilizing two-layer model. According to fitting results the density of the intermixing zone is not more than ≈ 2.56 g/cm^3 (Fig. 5, a). The intermixing zone thickness remains almost unchanged with increase of the thickness of deposited carbon. According to data of X-ray spectra fitting the intermixing zone density increases. When the carbon layer has thickness of 0.4 nm and higher, transition from two-layer "intermixing zone/silicon" to four-layer "intermixing zone/carbon/intermixing zone/silicon" occurs. Experimental LAXRD spectra can be satisfactorily fitted only by means of using the four-layer model of multilayer (Fig. 5, b). At that the density of intermixing zone C on Si amounts to ≈ 2.75 g/cm^3. Change in the intermixing layer contrast confirms an increase of the intermixing zone density (compare 1 and 2 in Fig. 4).

Formation of Si on C intermixing zone, as LAXRD spectra fitting shows, occurs in a manner similar to formation of the intermixing layer of C on Si. At the very beginning, during deposition of ≈ 0.1 nm silicon on carbon, the intermixing zone of ≈ 0.6 nm thickness and ≈ 2.27 g/cm^3 density forms. When the silicon thickness increases, the thickness of the intermixing zone doesn't change and its density increases up to 2.4 g/cm^3. Transition from the two-layer model to the four-layer (with two intermixing zones) one occurs when the thickness of silicon reaches a value of 0.6–1.2 nm.

Thus thickness of the intermixing zones, that were formed at "C on Si" or "Si on C" interfaces at the earliest stages, stay almost constant with following increase of the top

Number of layers	Layer material	Thickness, nm	ρ,g/cm	σ, nm
1	Si+C	0.6	2.70	0.75
	Si	0.92	2.27	0.30
25	Si+C	0.6	2.56	0.40

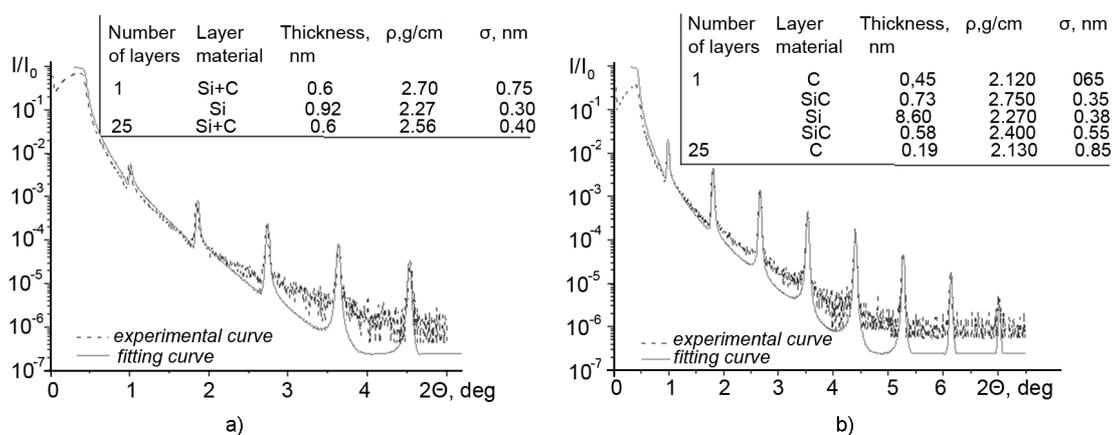| Number of layers	Layer material	Thickness, nm	ρ,g/cm	σ, nm
1	C	0,45	2.120	065
	SiC	0.73	2.750	0.35
	Si	8.60	2.270	0.38
	SiC	0.58	2.400	0.55
25	C	0.19	2.130	0.85

Fig. 5. Experimental and fitted LAXRD curves of C/Si multilayers with carbon thickness of 0.1 nm (a) and 0.4 nm (b).

Table 2. Types of chemical bonds in C/Si and Si/C bilayers

Specimen	Energy range, eV	Values, eV	Chemical bond
C on Si (A) As-deposited state	275−295 (C1s)	283.1 284.6 286.5 288.5	Si–C C–C C–O C=O
C on Si (A) As-deposited state	93−113 (S2p)	99.31 99.8 101.0	Si–Si Si–Si Si–C
C on Si (A) T_{ann} = 700°C	275−295 (C1s)	283.1 284.4 287.0	Si–C C–C (sp2) C–O
C on Si (A) T_{ann} = 700°C	93−113 (S2p)	99.38 99.78 101.6	Si–Si Si–Si Si–C
Si on C (B) As-deposited state	275−295 (C1s)	284.4 248.9	C–C (sp2) C–C (sp3)
Si on C (B) As-deposited state	93−113 (S2p)	99.23 99.68 102.8	Si–Si Si–Si Si–O
Si on C (B) T_{ann} = 700°C	275−295 (C1s)	283.0 284.4 285.0	Si–C C–C (sp2) C–C (sp3)
Si on C (B) T_{ann} = 700°C	93−113 (S2p)	99.7 100.6 103.4	Si–Si Si–C Si–O

layer thickness. At the same time density of the both zones increases with thickness of the top growing layer within the range of several tenth of nanometre.

The XPS results can be explained due to difference in the density of the intermixing zones at respective interfaces. Analysis of the data obtained on specimen A (corresponding to "C on Si" intermixing zone) shows that some amount of deposited carbon interacts with silicon, and silicon carbide is formed as a result of this interaction. This is proved by presence of corresponding maxima at 283.1 and 101 eV in the both energy ranges (Table 2). Pure carbon (284.6 eV) is also present. Thus it can be suggested that the "C on Si" intermixing zone represents a mixture of silicon, carbon and silicon carbide. If these intermixing zones are assumed to half consist of silicon carbide with the density of ≈ 3 g/cm³ and half of the mixture of silicon and carbon with the atomic composition evaluated as 1:1, then it would have a density of ≈ 2.75 g/cm³. This density value is in a good agreement with the LAXRD data.

Specimen B can be associated with the intermixing zone "Si on C". There are no

any maxima corresponding to silicon carbide formation on specimen B spectra in any of the energy ranges. Consequently, intermixing zone consists of mechanical mixture of silicon and carbon atoms. Thus the density of "C on Si" intermixing zone is higher then the density of "Si on C" one due to the presence of amorphous silicon carbide. The fact that density of the "Si on C" zone (2.4 g/cm³) is higher than the density of the both components (2.27 and 2.12 g/cm³ for carbon and silicon, accordingly) seems nontrivial if it is assumed that this zone is a mechanical mixture of the components. We can suppose that carbon composition in the intermixing zone differs from its composition in the carbon layer. This requires further study.

Heating is attended by change of the both — thickness of the intermixing zones and their density (Fig. 6). Increase of the thickness is observed for the both zones. As it has already been shown this fact is associated first of all with silicon diffusion. This assertion is supported by the silicon layer thickness decrease [15]. At the heating temperature 700°C thickness of each zone is about 1.2–1.3 nm. At the same time
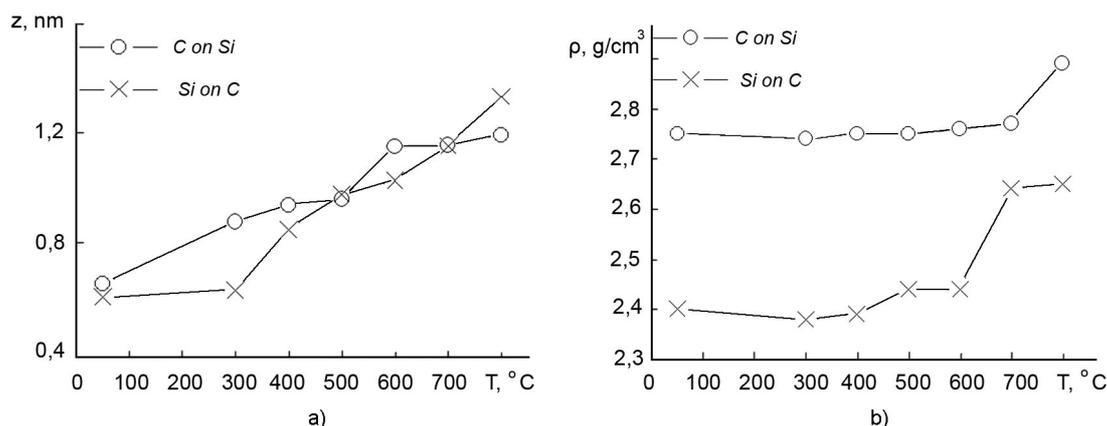
Fig. 6. Change of thickness (a) and density (b) of intermixing zones in C/Si multilayer during annealing.

the the zones density increases. According with the LAXRD fitting results the density of the "C on Si" zone is ≈2.85 g/cm^3 and the thickness of the "Si on C" one is ≈ 2.55 g/cm^3 after annealing at 700°C. The X-ray photoelectron spectroscopy results show that after heating up to 700°C silicon carbide presents either in the "C on Si" intermixing zone or in the "Si on C" one. It should be noted that after heating up to 300°C presence of silicon carbide was confirmed only for the "C on Si" zone.

As it was demonstrated previously [16] significant structural transformations take place in the C/Si multilayers at 950°C carbon reacts with silicon, that was crystallized before; nanocrystalline 3C–SiC and voids form in silicon layer. At the same time the intermixing zones are not involved in this process and keep amorphous in the entire temperature range.

4. Conclusion

Formation of the intermixing zones with thickness of ≈ 0.6 is observed on the interfaces in C/Si multilayer during deposition by DC magnetron sputtering. Such zone thickness is set after deposition of the first ≈ 0.1–0.15 nm of alter layer. The zones have different density. The density of "C on Si" zone is higher due to amorphous silicon carbide formation, which density is in turn higher than one of silicon and carbon.

During heating up to 700°C the thickness of the both zones increases from 0.6 to 1.2–1.3 nm. Simultaneously the density of the zones increases. Silicon carbide formation is observed in the "Si on C" zone.

It should be noted that evolution of the zones occurring during heating is not ac-

companied by increase of interlayer roughness. The zones are still amorphous up to 950°C. Obtained results are significant for developing the multilayer-based thermally stable X-ray optics.

References

1. C.Subramanian, K.N.Strafford, *Wear*, **165**, 85 (1993).
2. E.A.Spiller, Soft X-Ray Optics, SPIE Press Book, Bellingham (1994).
3. U.Hartmann, H.A.M. van den Berg, R.Coehoorn et al., Magnetic Multilayers and Giant Magnetoresistance, Springer-Verlag Berlin Heidelberg, Berlin (2000).
4. M.R.Etminanfar, M.Heydarzadeh Sohi, *Thin Solid Films*, **520**, 5322 (2012).
5. V.V.Kondratenko, Y.P.Pershin, O.V.Poltseva et al., *Appl. Opt.*, **32**, 1811 (1993).
6. A.V.Vinogradov, Yu.P.Pershin, E.N.Zubarev et al., *Proc. SPIE*, **4505**, 230 (2001).
7. C.Eberl, T.Liese, F.Schlenkrich et al., *Appl. Phys. A*, **111**, 431 (2013).
8. O.V.Penkov, Ye.A.Bugayev, I.Zhuravel et al., *Tribology Lett.*, **48**, 123 (2012).
9. C.K.Chung, T.Y.Chen, C.W.Lai, *J. Nanopart. Res.*, **13**, 4821 (2011).
10. X.An, F.Liu, Y.J.Jung, S.Kar, *Nano Lett.*, **13**, 909 (2013).
11. D.A.Shirley, *Phys. Rew. B*, **5**, 4709 (1972).
12. T.W.Barbee, *Opt. Engin.*, **25(8)**, 899 (1986).
13. D.T.Attwood, B.L.Henke, Low Energy X-ray Diagnostics, American Institute of Physics, New York (1981).
14. J.D.Jackson, Classical Electrodynamics, 2nd ed., John Wiley and Sons, New York (1975).
15. I.A.Zhuravel, Ye.A.Bugayev, L.Ye.Konotopsky et al., *Zh. Technicheskoy Fiziki*, **84**, 71 (2014).
16. I.A.Zhuravel, Ye.A.Bugayev, O.V.Penkov et al., *Phys. Surf. Engin.*, **12(1)**, 20 (2014).