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Quantitative Detection of the Contrast of Electron Microscopic Images of Amorphous Nanomaterials with the Complex Chemical Composition

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Physically strict detection of the contrast of electron microscopic images of amorphous nanomaterials has been proposed. The necessity of separation of the contribution to the contrast of different types of electron scattering by sample atoms, namely, resilient coherent, resilient non-coherent, and non-resilient, has been revealed. Simple analytical correlations for the determination of the contribution to the electron microscopic contrast of three different scattering types have been deduced.

Keywords: Nanomaterials, Amorphous, Contrast, Scattering, Electron, Atom.

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1. INTRODUCTION

Modern electron microscopy gives wide possibilities for the investigation of the structure of nanomaterials. Typical features of the electron microscopy are the following: high resolution on the level of separate atoms, locality of the analysis on the level of units of nanometers, immediacy, complexity of application of different techniques, transition rate from one monitoring mode to another, possibility of modeling of different external influences on the sample in the microscope column directly, etc. Therefore, electron microscopic (EM) investigations allow to estimate rapidly and with a sufficient degree of probability and to quantitatively measure a number of important structure-operating parameters of nanosystems [1-3]. But in the majority of the cases, this concerns the study of crystalline objects. In the case of the disordered amorphous nanomaterials, quantitative EM methods are developed much worse, and much less theoretical and experimental works are devoted to the analysis of these questions. In the overwhelming majority of modern publications, analysis of EM images of amorphous substances is performed on the descriptive level [4, 5]. Strict description of the nanostructure of such objects provides for determination of a number of quantitative parameters from the EM changes. Especially, this concerns amorphous substances of complex chemical composition. In such samples, formation of the EM images is conditioned by the complex action of a number of reasons, namely, by the presence of atoms with different scattering possibilities of electrons; possibility of the local phase separation with distinction of different phases in both chemical composition and structure; difference in the diffraction contributions of different neighboring local regions; variation of the geometric thickness; local changes of the atomic density in the sample; presence of nanopores; manifestation of a high level of noises; absence of distinguished boundaries between image elements; anisotropy of the nanostructure, etc. During the formation of the EM image, contributions of all mentioned features of the structure of amorphous nano-objects overlap and form one contrast type which is called the amplitude or absorbed one. Therefore, the search of the methods of quantitative detection of their role in the formed general EM contrast is a very complex and promising scientific problem. In the present work, we justify the general quantitative determination of the amplitude contrast of EM images and analyze the possibility of usage of the given parameter for the quantitative analysis of nano- and microstructure of amorphous nanosystems and nanomaterials of complex chemical composition.

2. INVESTIGATION TECHNIQUE

Several different meanings of the term "contrast", namely, optical contrast, color contrast, luminance range, lighting contrast, image contrast are used in physics and photometry [6]. Therefore, to perform the quantitative analysis of EM images one should give clear physical definition of such important quantity as the amplitude EM contrast and find simple and safe techniques for its obtaining.

Different researches propose different definitions of the contrast on EM images of the objects. Here, difference in the optical characteristics of different regions of image is meant by EM contrast. Comparison of these characteristics is often carried out with respect to the certain basic value. For example, intensity of the incident electron beam I_0 is taken as such basic value in the works [7, 8]. But definition of the contrast is different there. In [7], natural logarithm of the ratio of the electron beam intensity I (which passed through the object and scattered inside aperture angle of the lens) to its basic intensity I_0 is considered as the contrast

$$K = \left|\frac{1}{\gamma}\right| \ln\left(\frac{I}{I_0}\right), \quad (1)$$

where γ is the parameter which takes into account the features of environment used for the detection of EM images. As the numerical characteristic of EM contrast [8], the value similar to the optical visibility introduced by Michelson into photometric optics [9] is used

$$K = \frac{I_0 - I}{I_0 + I}. \quad (2)$$

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Detection of the contrast using correlations (1) and (2) in practical electron microscopy causes considerable difficulties. They are connected with the complexity of the experimental registration of intensity I_0 and used rather rarely in the investigations of nanomaterials.

The value of contrast of EM images for quantitative measurements in modern electron microscopy is often specified as the change of the electron beam intensity $I_1 - I_2$ induced by its scattering inside aperture angle in different local regions of the object [10], i.e.

$$K = \frac{I_1 - I_2}{I_1} = 1 - \frac{I_2}{I_1}. \quad (3)$$

But this approach to the quantitative analysis of EM images has substantial disadvantages. Firstly, the value of K will take different values depending on that which image element we denote to be the first, and which one – to be second. Secondly, contrast by the formula (3) can be both positive and negative, while by the physical meaning it should have strictly positive value.

Thus, quantitative analysis of EM images requires the establishment of clear physical meaning of the EM contrast value. The most rigorous solution of this question is given in photometry. In this section of physics, contrast is determined as the largest difference in the illuminance of different elements of the object

$$K = \frac{B_{max} - B_{min}}{B_{max} + B_{min}}, \quad (4)$$

where B_{max} and B_{min} are the maximum and minimum illumination [11]. To our opinion, such definition of the contrast is best fitted for use in the region of analytical electron microscopy of amorphous nanomaterials. Then for EM images, as the parameter B it is necessary to take the value of "illumination" of local regions of the detecting medium, i.e. intensity of the electron beam I which forms EM image on these regions. Thus, by the analogy with correlation (4), we will call the value of K determined by expression

$$K = \frac{|I_1 - I_2|}{I_1 + I_2} \quad (5)$$

the contrast between two elements of EM images. Here I_1 and I_2 are the intensities of the electron beams which form images of two local regions of EM image. The value of numerator in formula (5) is taken by modulus in order in calculations of the contrast value it was not necessary to establish which one of two intensities I_1 and I_2 is larger, since by the physical meaning contrast always should be a positive number.

In modern electron microscopes and devices of photometric measurements, the process of registration and digitization of images is performed in such a way that to provide a linear dependence between intensity of the forming electron beam and value of optical "blackening" on the image induced of the given beam. We have to note that for reusable recording plates and matrices such dependence is typical almost for the whole intensity range of microscope electron beams which form the images [12]. For modern electron diffraction photoplates, this dependence is fulfilled only in the range of small optical blackening $D < 0{,}6\text{-}0{,}8$ (for earlier photoplates $D < 0{,}3\text{-}0{,}4$).

Thus, depending on the value of blackening of photomaterial, different mathematical approaches for the contrast calculations should be applied. Specific application of correlation (5) in the quantitative analysis of EM images is defined by the type of detecting medium of electron microscope. Traditional photoplates, phosphorus reusable recording plates, electron matrices [12] are the main of them now. The first two medium types give higher resolution and contrast of EM images, but for digitization they require photometric measurements. Two last types of detecting devices represent images directly in the form of a computer file recorded in one or another format of image conservation. In this case, level of black of each pixel of the recorded image corresponds to the intensity of the electron beam which has formed this image pixel. Therefore, for the determination of the contrast value of such images one should use directly expression (5).

In the case of light blackening of photoplates, intensity of the electron beam which forms the image is proportional to this blackening, i.e. $I = cD$, where c is the proportionality coefficient. If blackening is determined from the results of photometric measurements of photoplates, then by the determination of [4]

$$D = \lg\left(\frac{\Phi_0}{\Phi}\right), \quad (6)$$

where Φ_0 is the luminous flux incident on photometric photoplate; Φ is the luminous flux outgoing from photoplate and whose value is recorded by light-sensitive elements. Since a signal from recording light-sensitive elements of microphotometer is proportional to the flux Φ and one can suggest that digital file which we obtain as a result of photometric measurements of EM image, specifies the two-dimensional distribution of this flux. Therefore, contrast of EM images should be determined exactly through the value of this flux. At acceptable conditions, contrast of EM image on photoplates will be equal to

$$K = \frac{\left|c\lg\frac{\Phi_0}{\Phi_1} - c\lg\frac{\Phi_0}{\Phi_2}\right|}{c\lg\frac{\Phi_0}{\Phi_1} + c\lg\frac{\Phi_0}{\Phi_2}} = \frac{|\lg\Phi_2 - \lg\Phi_1|}{2\lg\Phi_0 - \lg\Phi_1 - \lg\Phi_2}. \quad (7)$$

It is more complicated to obtain expression for the contrast of EM images on photoplates when blackening value belongs to the range of D from 0,3 to 2. Here, connection between the intensity of the electron beam which forms the image and blackening should be written in the form of $D = \delta\lg(I_\tau)$. Comparing the last expression and correlation (6), one can write

$$\frac{\Phi_0}{\Phi} = (I\tau)^\tau = I^\tau \tau^\delta \quad (8)$$

or

$$I = \left(\frac{\Phi_0}{\Phi\tau^\delta}\right)^{1/\delta} = \frac{1}{\tau}\left(\frac{\Phi_0}{\Phi}\right)^{1/\delta}. \quad (9)$$

Then, for the contrast value of such regions of EM photographic images we have the following formula:

$$K = \frac{\frac{1}{\tau}\left|\frac{\Phi_0^{1/\delta}}{\Phi_1^{1/\delta}} - \frac{\Phi_0^{1/\delta}}{\Phi_2^{1/\delta}}\right|}{\frac{1\Phi_0^{1/\delta}}{\tau\Phi_1^{1/\delta}} + \frac{1\Phi_0^{1/\delta}}{\tau\Phi_2^{1/\delta}}} = \frac{\left|\frac{\Phi_2^{1/\delta} - \Phi_1^{1/\delta}}{\Phi_1^{1/\delta}\Phi_2^{1/\delta}}\right|}{\frac{\Phi_2^{1/\delta} + \Phi_1^{1/\delta}}{\Phi_1^{1/\delta}\Phi_2^{1/\delta}}} = \frac{\left|\Phi_2^{1/\delta} - \Phi_1^{1/\delta}\right|}{\Phi_2^{1/\delta} + \Phi_1^{1/\delta}}. \quad (10)$$

As seen from correlations (7) and (10), substantially different techniques of determination of the contrast numerical values correspond to two different ranges of

photoplate blackening. In the first case, at digitization of EM images besides photometric measurements of the photoplate itself, one should carry out measurements of the value of luminous flux which is directed on the photometric plate (see expression (7)). To this end, we experimentally carried out the procedure of photometric measurements of the light field of clarified table without photoplate disposed on it. By the results of such scanning, the mean value of luminous flux Φ_0 incident on the photoplate was determined. In the second case, such scanning was not necessary (see expression (10)), but we have used it for the estimation of the uniformity of distribution of the incident luminous flux over the whole area of photometric EM image. We should note that irrespective of the fact on which carrier EM image was fixed (photoplate or electron matrix) and in which region of blackening measurements are performed, the contrast value specified by formula (5) will belong to the range from 0 to 2 of relative units.

3. INVESTIGATION RESULTS AND THEIR DISCUSSION

Let us analyze the features of using of the above proposed value of EM contrast for the quantitative analysis of nano- and microstructure of amorphous materials of complex chemical composition. We note that in such objects, the EM image is formed due to the electron scattering on the studied sample within aperture diaphragm with aperture angle α. In this case, for the analysis one should separate three types of scattering, namely, resilient coherent, resilient non-coherent, and non-resilient scattering. Intensity of the electron beam which forms EM image of the local region of object due to the certain mechanism [12] is defined as

$$I = I_0 \exp(-\bar{\sigma}\rho_0 d), \tag{11}$$

where $\bar{\sigma}$ is the total averaged cross-section of the electron scattering by the corresponding mechanism within aperture diaphragm; ρ_0 is the averaged atomic density of the given local region; d is its geometric thickness.

We will designate the intensities of electron beams which form the image of local region of the sample due to the mentioned three types of electron scattering as I_{rc}, I_{rn} and I_n, respectively. Then, the total intensity of the electron scattering by local region will be equal to the sum of three intensities

$$I = I_{rc} + I_{rn} + I_n. \tag{12}$$

Substituting this expression for the total intensity of the electron scattering by two local regions into correlation (5), we obtain

$$K = \frac{|I_{1rc}+I_{1rn}+I_{1c}-I_{2rc}-I_{2rn}-I_{2c}|}{I_1+I_2} = \frac{|I_{1rc}-I_{2rc}+I_{1rn}-I_{2rn}+I_{1c}-I_{2c}|}{I_1+I_2} = K_{rc} + K_{rn} + K_n, \tag{13}$$

where $K_{rc} = \frac{|I_{1rc}-I_{2rc}|}{I_1+I_2}$, $K_{rn} = \frac{|I_{1rn}-I_{2rn}|}{I_1+I_2}$, $K_n = \frac{|I_{1n}-I_{2n}|}{I_1+I_2}$ are the fractions of contrast conditioned by different types of electron scattering in the object.

Analysis of expression (13) implies that the value of contrast on EM images consists of three components. In this case, the given components are not independent. General parameter ($I_1 + I_2$), which is specified by the total intensities of three types of electron scattering, is present in denominator of each component. Therefore, parameters K_{rc}, K_{rn}, and K_n are not the image contrasts conditioned by each scattering type separately. Such values should be specified in the following form:

$$K'_{rc} = \frac{|I_{1rc}-I_{2rc}|}{I_{1rc}+I_{2rc}};\ K'_{rn} = \frac{|I_{1rn}-I_{2rn}|}{I_{1rn}+I_{2rn}};\ K'_n = \frac{|I_{1n}-I_{2n}|}{I_{1n}+I_{2n}}. \tag{14}$$

Here, within the rigorous consideration in a general case $K \neq K' \neq K'_{rc} + K'_{rn} + K'_n$. Therefore, in the practical investigation of the contrast of EM images, one should take into account all its components K_{rc}, K_{rn}, K_n, K'_{rc}, K'_{rn}, K'_n, and total values K' and K.

Determination of the introduced values of the contrast for substances of complex chemical composition requires implementation of two main operations:

1. Averaging of the corresponding differential cross-sections of electron scattering over all chemical elements of the studied sample.
2. Integration of the intensities of resiliently coherent, resiliently non-coherent, and non-resiliently scattered electrons within aperture angle of the object lens of the electron microscope.

Each of these operations can be performed both theoretically and experimentally. The analysis we have carried out implies [12] that for some types of the contrast, theoretical calculations are the optimal ones, and for other contrast types – usage of experimental electron diffraction patterns is more preferable. Let us analyze these questions for each scattering type separately.

Contrast from the resilient non-coherent scattering. It can appear due to the variation of one of three structural parameters of local regions of the investigated sample: geometric thickness, chemical composition, and nanoporosity level. Therefore, the quantitative analysis should include consideration of all these three values. Influence on the contrast of chemical composition of local region of the studied sample is determined by the basic characteristics of electron interaction with atoms of the substance, i.e. atomic scattering amplitudes. We should note that these amplitudes are determinative parameter for the analysis of all three types of electron scattering. Therefore, to our opinion, usage of the reference values of atomic electron amplitudes $F(s)$ is the optimal method of determination of the contribution to the contrast K_{rn} of variations of chemical composition of the sample due to the change in the effective cross-section of the resilent non-coherent electron scattering $\overline{\sigma_n} = \lambda^2/8\pi \int_0^\alpha \overline{F^2(s)} s ds$.

Experimental determination of the distribution of different chemical elements in local regions of the sample should be the initial point of such analysis. Now such investigations are easily performed using modern scanning electron microscopes-analyzers which provide locality of the analysis in tens of nanometers with the accuracy to 5% [5]. Their results allow to experimentally establish the relative fractions of different chemical elements in the composition of one or another local region of the sample. If such fractions are different for two studied local regions, this will contribute to the contrast between corresponding elements of EM image.

To establish the possibility of contribution to the

contrast of different geometric thicknesses of local regions of the sample, besides of EM investigations one should carry out the study of the profile of the object surface using nanoprofilograph or atomic force microscope. If different local regions of the object have different level of nanoporosity, then they will differ by the averaged atomic density ρ. Presence of such differences can be established by registering of the dark-field EM images of the sample obtained at different position of aperture diaphragm near the central beam. If results of the given experiments establish different level of nanoporosity level of local regions, then they should have different atomic densities ρ_{01} and ρ_{02}.

Using the whole complex of the obtained results, one can find the quantitative values of the contrast contribution due to the resilient non-coherent electron scattering. In particular, for modern detecting plates with taking into account expressions (5) and (12) we obtain

$$K_{rn} = \frac{|\exp(-\overline{\sigma_{n1}}\rho_{01}d_1) - \exp(-\overline{\sigma_{n2}}\rho_{02}d_2)|}{\exp(-\overline{\sigma_{n1}}\rho_{01}d_1) - \exp(-\overline{\sigma_{n2}}\rho_{02}d_2)}. \quad (15)$$

Contrast from the resilient coherent scattering. Since structure of atomic grid of the investigated sample is unknown, then determination of the contrast due to the resilient coherent scattering K_{rc} or K'_{rc} is possible only by the experimental methods. The effective cross-section of the resilient coherent electron scattering by atoms of local region of the sample of complex chemical composition is specified by the following mathematical expression:

$$\sigma_c = \frac{\lambda^2}{8\pi}\int_0^{\alpha} F^2(s)S(s)sds, \quad (16)$$

where $S(s)$ is the structural factor of the atomic grid of local region which is experimentally determined by the methods of nanodiffraction of electrons. Correspondingly, the quantitative value of the contrast contribution due to the resilient coherent electron scattering is defined from correlation (15) in which instead of the effective cross-sections $\overline{\sigma_n}$ we substituted cross-sections σ_c of local regions of the test object.

Contrast from the non-resilient scattering. Contribution to the contrast of non-resiliently scattered electrons K_n can be found both theoretically and experimentally. But, taking into account sufficient difficulties in theoretical calculations of atomic cross-sections of non-resilient electron scattering and in their strong dependence from the real conditions of registration of the electron diffraction patterns, experimental determination method of the value of K_n should give more safe and reliable results. In this case, $\sigma_n = \lambda^2/8\pi\int_0^{\alpha}\varphi(s)sds$ is the effective cross-section of the given scattering type, where $\varphi(s)$ is the experimentally determined distribution function of the intensities of non-coherent background within aperture diaphragm. Correspondingly, the quantitative value of contribution to the contrast of EM images due to the non-resilient scattering is the following:

$$K_n = \frac{|\exp(-\sigma_{n1}\rho_{01}d_1) - \exp(-\sigma_{n2}\rho_{02}d_2)|}{\exp(-\sigma_{n1}\rho_{01}d_1) - \exp(-\sigma_{n2}\rho_{02}d_2)}. \quad (17)$$

At the presence in the studied sample of local regions, which scatter electrons by three different mechanisms, the quantitative value of the contrast of EM images will be defined by the sum of all three contributions according to correlations (15), (16), and (17).

4. CONCLUSIONS

For the quantitative analysis of the electron microscopic images, one should use the physically rigorous definition of the electron contrast, whose value does not depend on the intensity of probing beam of the electron microscope. Usage of such definition in analytical electron microscopy requires separation of the contribution to the contrast of different types of electron scattering by sample atoms within aperture diaphragm: resilient coherent, resilient non-coherent, and non-resilient. Simple analytical correlations for the determination of the contribution value to the electron microscopic contrast of these three scattering types are proposed.

REFERENCES

1. G. Lukovsky, M. Popescu, *Non-Crystalline Materials for Optoelectronics, V.1* (Bucharest: INOE publishing house: 2004).
2. M. Popescu, *Physics and application of disordered materials* (Bucharest: JNOE publishing house: 2002).
3. D. Brandon, U. Kaplan, *Mikrostruktura materialov. Metody issledovaniya i kontrolya* (M.: Tekhnosfera: 2004).
4. D.V. Shtanskiy, *Prosvechivayushchaya elektronnaya mikroskopiya vysokogo razresheniya v nanotekhnologicheskih issledovaniyah* (Zh. Ros. khim. ob-va im. D.I. Mendeleeva, 2002, V.XLVI, No5).
5. M. Watt Ian, *The principles and practice of electron microscopy* (1997).
6. K.A. Avgustinovich, *Osnovy fotograficheskoy metrologii* (M.: Legprombytizdat: 1990, ISBN 5-7088-0301-0).
7. A.N. Pilyankevich, *Prosvechivayushchaya elektronnaya mikroskopiya* (K.: Naukova dumka: 1975).
8. David C. Joy, Alton D. Romig, Joseph Goldstein, *Principles of analytical electron microscopy* (1986).
9. M. Born, E. Wolf, *Osnovy optiki* (M.: Nauka: 1970).
10. P.J. Goodhew, F.J. Humphreys, R. Beanland *Electron microscopy and analysis* (NY: Taylor & Francis: 2001).
11. *Fizicheskiy entsiklopedicheskiy slovar'* (M.: Sovetskaya entsiklopediya: 1984).
12. J.M. Zuo, *Electron detection characteristics of a slow-scan CCD camera, imaging plates and electron image resolution* (Microscopy research and technique: 2000, 49:245-268).
13. M.Y. Bobyk, E.I. Borkach, V.P. Ivanytskiy, V.I. Sabov, *Nanosystemy, nanomaterialy, nanotekhnologii* **9**, No4 (2001).