MORPHOLOGY OF POLYMER NANOCOMPOSITES

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A computer experiment was suggested for testing of suitable methods for morphological analysis of nanocomposite films. A computer model was prepared to study three-dimensional (3D) structural properties on the basis of two-dimensional (2D) projections or sections. Some of the suitable methods are shown. A special attention is devoted to Wigner-Seitz cells and reconstruction of 3D spatial distribution.

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1 Introduction

Morphological analysis of composite or nanocomposite thin films is important both for the characterisation of the films themselves and for the analysis of their properties. These films represent class of promising materials. Composite metal/dielectric films consisting of metal particles embedded into an oxide or polymer matrix have received more and more attention in last few years due to their interesting optical, mechanical, and electrical properties. The same situation is with the nanocomposites. Composite material can be obtained by embedding metal particles into a matrix of dielectric film. It can be achieved among other methods by thermal evaporation [1], by ion-beam sputter deposition [2] or by plasma deposition techniques (e.g. [3]).

There are three possible structures of the metal containing polymer or oxide films depending on the filling factor:

- the metal particles completely insulated from each other are embedded in a polymer matrix,
- near the critical filling factor the metal-dielectric transition can be observed and metal objects form a percolation structure, and
- the metal film with polymer inclusions.

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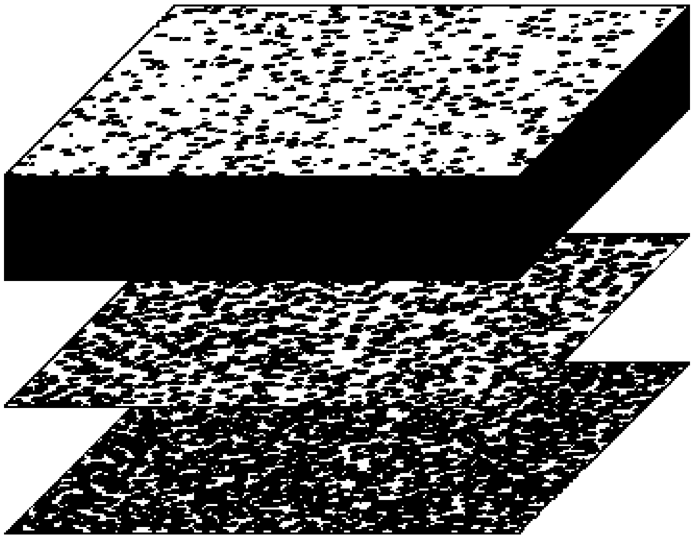

Fig. 1. Hard-sphere model, object radii are constant, filling factor 0.05, diffusion zone 0 pixels. Top shows a section, middle shows a projection for film thickness $Z = 100$, bottom shows a projection for $Z = 200$.

To make a proper analysis of prepared composite films a suitable technique for their structural description must be introduced. Theoretical approach to the problem often leads to the nearly invincible difficulties [4]; therefore, a computer experiment would be more suited for that purpose.

In our contribution, we studied the unfolding problems arising from the image analysis of the films with non-uniform structure. Our main task was to gain information about 3D spatial distribution of spherical objects in isotropic systems supposing we have 2D images only taken either from sections or from projections of the composite or nanocomposite film. A modified hard-disk model of the film was prepared for the analysis of influence of film parameters on various morphological algorithms. The older version of characterization of 3D structure was by help of statistical moments. Stronger methods are based on the usage of mathematical morphology.

2 Model

Our suggested model of composite films uses working region $2000 \times 2000 \times 200$ pixels (x, y, and z directions), pixels being the length units in our model. The number of generated objects is always the same – 2000, and the spherical form of objects is assumed in accordance with many experiments. The sphere diameters are determined by the chosen filling factor (in the range 0.05 to 0.20) of the film and by the number of objects. For the generation of the spatial distribution of objects, the 'hard-sphere technique' was used: the objects are generated randomly with a minimum distance between edges of objects which is the model parameter called the 'diffusion zone' $DZ \in \langle 0, DZ_{\max} \rangle$. The number and the size of objects determine the maximum value of the diffusion zone $DZ_{\max}$ that varies between 28 and 6 pixels for the filling factor between 0.05

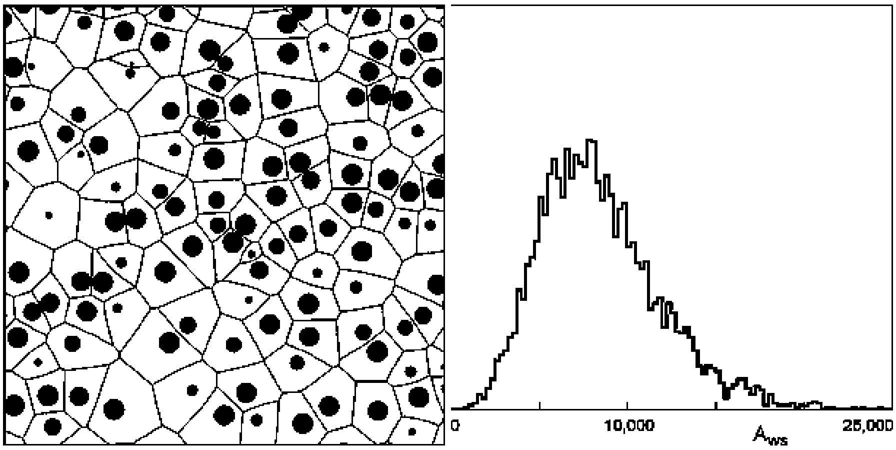

Fig. 2. Section of the hard-sphere structure with depicted Wigner-Seitz cells (on the left) and corresponding area distribution A_{WS} of WS (on the right); filling factor of the film equals 0.10, $DZ = 0$ pixels, relative frequency of the distribution on the value axis is in arbitrary units.

and 0.20, respectively. With the help of this parameter, it is possible to influence the randomness of spatial distribution of objects. The structures with higher diffusion zone are more ordered. The model is working with a fixed object diameter (see Fig. 1).

For testing the methods, which are convenient for partial reconstruction of 3D information from 2D images a simple computer experiment was prepared. Generating the composite structure we could make a random section parallel to the (x, y)-plane. In Fig. 1 we can see such random parallel section (upper plane of the film shown) and two projections of the films with different film thicknesses Z (the same effect can be achieved for hard-sphere models with two different numbers of objects). Various morphological methods can be then applied to the generated structures.

3 Spatial distribution of objects

Numerous methods can be used to characterize the spatial distribution of clusters or objects in two dimensions. For the characterization of 2D structure geometry and of spatial distribution of its objects, the quantitative morphological analysis must be performed. In the early stages of the study two simple morphological methods were used – the Radial Distribution Function (RDF) [5] and the Distribution of Nearest Neighbours (DNN) [6]. These methods work with centres of objects only, therefore they can be used for the point objects, too (e.g. in astronomy). Last years more powerful methods as Covariance (CO) [7], Chord-Length Distribution of Light segments (CHLD-L) [8], Quadrat Counts (QC), Wigner-Seitz Cells (WS) [9] often mentioned as Voronoi tessellation [10] are preferred in thin film physics. The common feature of the last methods is their complex character. They combine a greater number of object properties and produce them in integral form. In this case, the derivation of a physical meaning of the particular morphological characteristics is more complicated.

All the methods mentioned have been commonly used in 2D problems. We are trying to apply

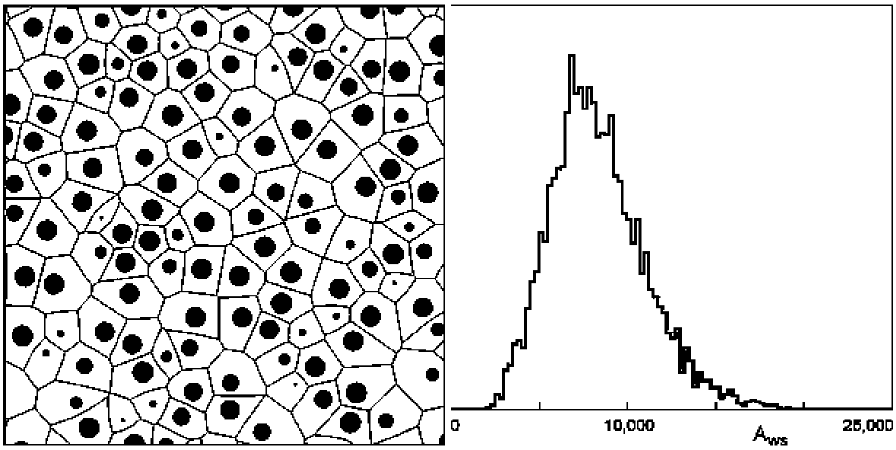

Fig. 3. Section of the hard-sphere structure with depicted Wigner-Seitz cells (on the left) and corresponding area distribution A_{WS} of WS (on the right); filling factor of the film equals 0.10, $DZ = DZ_{max}$, relative frequency of the distribution on the value axis is in arbitrary units.

them in case of 3D problems, now. The methods like RDF, CHLD-L, CO can give interesting results. They can be sensitive enough but it is very difficult to derive some relevant quantities from them.

But there is only a little knowledge about the use of the other methods like DNN, WS, etc. in three dimensions. However, there is an interesting correlation between the RDF and DNN. Both of them analyse the same kind of problems. As we had proved before [11], the RDF can be completely reconstructed from DNN of all orders i as follows

$$g(r) = \frac{1}{2\pi r} \sum_{i=1}^{\infty} w_i(r), \tag{1}$$

where $g(r)$ and $w_i(r)$ denotes the RDF and DNN of i-th order, respectively.

We are focusing on the WS method in the paper. We have tried to find out the ability of the method to describe various structures in three dimensions. In Figs. 2 and 3, we see always a section of the structure generated by our hard-sphere model with the WS drawn on the left and the corresponding area distribution of Wigner-Seitz Cells on the right. We can observe changes when the structure is more ordered (Fig. 3); the distribution function is narrower. In case of randomly distributed objects the areas have on the other hand more dispersed magnitudes with respect to their mean value $E\xi$.

If we introduce the first two central moments of random variable ξ

$$E\xi = \sum x_i p_i, \tag{2}$$

where x_i are discrete values of random variable occurring with a probability p_i, and

$$D\xi = E(\xi - E\xi)^2 \tag{3}$$

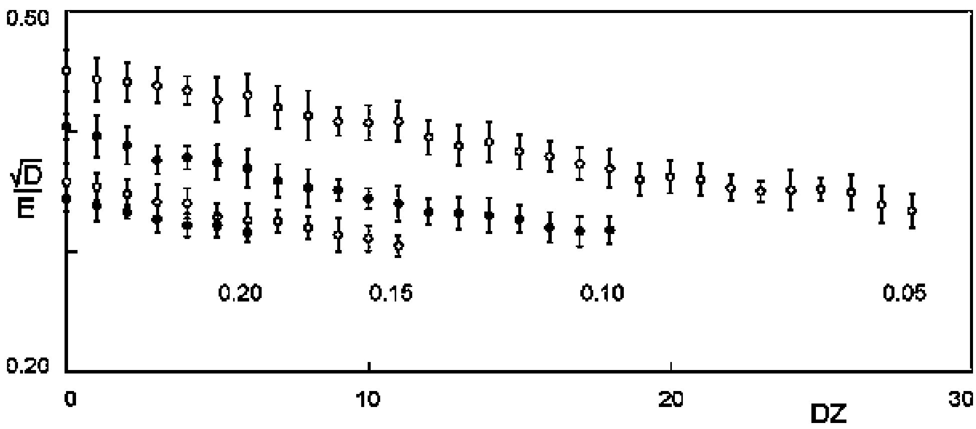

Fig. 4. Characterization of randomness of composite structure by help of the invariant $\sqrt{D\xi}/E\xi$ for various values of the filling factor. Each point includes variance of the values derived from analysis of ten sections.

we can make an invariant $\sqrt{D\xi}/E\xi$, which value is given by physical properties of studied structures only and is not influenced by non-physical parameters as the resolution of images, etc. It well characterizes randomness of object distribution in a section as well as in space. In Fig. 4 we can see results of its use for the characterization of various structures with different randomness. The randomness is well described in three dimensions by the diffusion zone DZ. Completely random structure belongs to $DZ = 0$ pixels, higher DZ means more ordered structure. However, here is demonstrated a possibility of the same characterization of given structures by the invariant mentioned above, i.e. based on the information in 2D sections only. To have results with a reasonable accuracy (see variances shown in Fig. 4) it is needed to process at least 1000 structure objects. As we showed before [12] the influence of limited number of objects is mostly more important for the possible error than the influence of digitization.

4 Conclusion

The use of different morphological methods known from 2D morphology analysis with special attention to WS is discussed in case of space analysis in three dimensions. Results of the computer experiments performed in this field are presented here. We can conclude that

- one can use both a section or a projection in case of very thin films. However, with increasing thickness of the film rapidly decreases usability of the projections (see Fig. 1),
- with increasing filling factor decreases relevance of the projections as well,
- higher filling factor causes higher ordering of the film, thus the range of possible values of diffusion zone is smaller (see Fig. 4),
- the WS method is usable for the unfolding problem. It well describes the randomness of 3D structure from the 2D information only.

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References

[1] W. Yang, Z. S. Jiang, W. N. Wang, Y. W. Du: *Solid State Commun.* **104** (1997) 479

[2] T. Ichinohe, S. Masaki, K. Kawasaki, H. Morisaki: *Thin Solid Films* **343–344** (1999) 119

[3] T. Noguchi, K. Gotoh, Y. Yamaguchi, S. Deki: *J. Mater. Sci. Lett.* **10** (1991) 477

[4] D. Stoyan, W. S. Kendall, J. Mecke: *Stochastic Geometry and Its Application*, Akademie – Verlag, Berlin 1987

[5] J. J. Metois, J. C. Zanghi, R. Kern: *Phil. Mag.* **33** (1976) 133

[6] S. H. Norrman, T. G. Andersson: *Thin Solid Films* **69** (1980) 327

[7] S. Blacher, F. Brouers, P. Gadenne, J. Lafait: *J. Appl. Phys.* **74** (1993) 207

[8] S. Torquato, B. Lu: *Phys. Rev. E* **47** (1993) 2950

[9] H. Ebeling, G. Wiedenmann: *Phys. Rev. E* **47** (1993) 704

[10] P. D. Zavattieri, P. V. Raghuram, H. D. Espinosa: *J. Mech. Phys. Solids* **49** (2001) 27

[11] R. Hrach, D. Novotný, S. Novák, J. Pavlík: *Vacuum* **50** (1998) 175

[12] S. Novák, M. Sobotka, R. Hrach: *Thin Solid Films* **373** (2000) 203