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DIAGNOSTICS OF THE STRUCTURE AND AMORPHOUS MATERIALS GROWTH PROCESS BY NONLINEAR DYNAMICS METHOD

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It is shown that the surface structure of amorphous materials representing instant “frozen” snapshots of growth processes, has a chaotic character. This opens the possibility to estimate the structural irreproducibility and the properties of non-crystalline materials and to work out absolute new methods for structure modulation and growth processes.

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1. Introduction

The whole complex of investigation results of structural, thermodynamic, electrophysical and optical properties of hydrogenated amorphous silicon (a-Si:H) depending on the technological parameters makes it possible to draw the conclusion that there are some complicated relations between the condition of growth, structure and physical properties of the material. However, the universal and invariant characteristics, which would make it possible to describe these quantitative correlations, do not exist so far. This calls forth the necessity to work out new methods for obtaining and processing the information about the structure and growth processes of non-crystalline materials.

2. Theoretical background

We address the irreproducibility in the fabrication of solid materials by treating the development of three-dimensional structural regularity as self-organization in a nonlinear system. It has been shown that the concepts and techniques from the theory of self-organizing systems can in principle be applied to solidification, which displays bifurcations, symmetry breaking, nonequilibrium behavior, and dissipation [1]. The formation of solid-state regularity is often investigated by statistical methods. However, they have been successful only with systems near thermal equilibrium, a condition that rarely is materialized in the real world. Far more detailed knowledge of a much wider variety of structures can be gained with the tools of chaotic dynamics [2]. The role of chaotic dynamics in solidification is illustrated by the fig. 1, which represents in mathematical form the evolution of a material to the solid state. During stage 1, the material behaves in a random manner. Stage 2 is a cascade of bifurcations. The material is now characterized by having solidification nuclei correlated with each other. These correlations develop to extend over the whole system and the number of possible bifurcations increases. In stage 3, the system exhibits deterministic chaos, i.e., apparently random behavior. Mathematically, stage 3 is associated with a strange attractor, which evolves according to external conditions. With increasing correlations between different regions, the dimension of the attractor decreases. In stage 4, the strange attractor turns into simpler attractors: limit cycles and stable equilibrium points. Finally, during stage 5, the system evolves to a stable equilibrium state, which is associated with a global attractor. Note that chaos may persist throughout

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stages 4 and 5 and pass to a steady state, as can be observed in amorphous solid materials. Thus, solidification essentially includes a stage of deterministic chaos whatever the material.

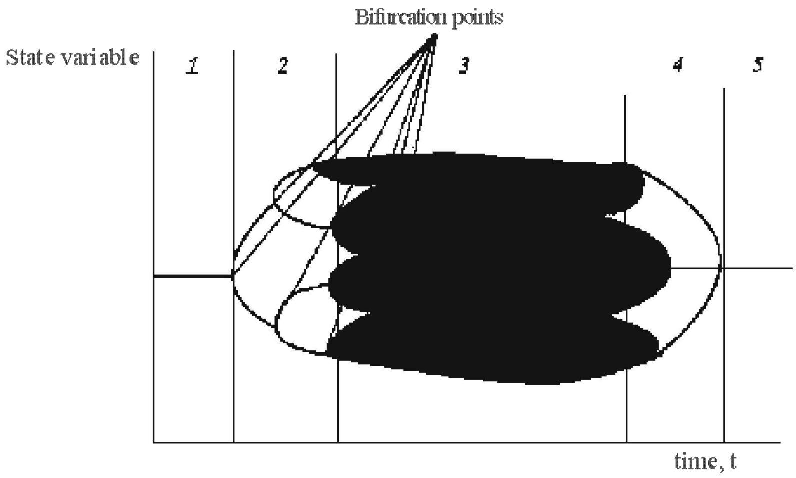

Fig. 1. Possible pattern of solidification. The stages are (1) quasi-equilibrium thermal chaos in the gas -- melt system, (2) a bifurcation cascade, (3) deterministic chaos, (4) simple attractors (limit cycles, equilibrium points, etc.), and (5) a global attractor.

The main idea of nonlinear systems modeling is that, since the observations of a dissipative system lie on a geometric object of much smaller dimension than that of the original state space, we must seek methods for modeling the evolution on the attractor itself and not evolution in the full, infinite-dimensional, original phase space [2].

The main technique of nonlinear system experimental analysis is the embedding method of Takens. While using it, it is possible to distinguish systems, demonstrating chaotic movement in low dimensional space, from systems with noise and to measure the invariant characteristics of chaotic systems. The method is based on the idea that any signal from a system comprises information about all the processes inside it, since all parts of dynamic system are interconnected and can be considered as a single whole. Therefore, the behavior of the system can be interpreted according to the measurements of any of its characteristics, which are to be carried out at regular intervals.

The obtained sequence of data is processed according to special algorithms, and attractor type and dimension, a number of degrees of freedom, Lyapunov exponents and other parameters of dynamics are defined.

As the substance at solidification changes its properties in time and in space, two variants of dynamics growth investigation are possible:

- by any characteristics of the substance *in situ*, according to ideology of embedding method. For this purpose, we can use the methods of scattering the light, ellipsometria and others. However, it is important to re-establish the temporal evolution in various points of the structure of the material. But it is impossible to solve this problem unsolved.

- by material structure, which keeps information about its previous time evolution. The first step towards the reconstruction of the spatio-temporal phase space is to consider just space series rather than temporal ones. This approach is quite legitimate if we study the “frozen” spatial disorder resulting, for example, from surface of materials. For this pure space series, all the machinery developed for time series can be directly reformulated by substituting spatial coordinate *x* for time coordinate *t*. In this way, one can calculate fractal dimension of the “space” attractor, evaluate spatial Lyapunov exponents, make models, etc. For the technologies of some materials, the surface is an instant shot of evolution process with good approximation.

We have considered the possibility of determination of the dynamics formation type by the system structure. By analogy with Lyapunov exponents, describing time system evolution λ_t, for spatial structure the concept of spatial Lyapunov exponents λ_r is being introduced. With the approach worked out in [3], it is established that the following interrelation exists between them:

$$\lambda_t / \lambda_r = C\ v, \tag{1}$$

where **C** is a positive constant, **v** is a value determined by growth rate of the material and atom diffusion in the growth surface. On the basis of this result the conclusion was made that the dynamics of material growth is defined by determined spatial and time chaos. The analysis of known experimental data confirms this conclusion.

On the basis of this interrelation between characteristics of the structure and invariant parameters of its formation dynamics was established.

On the basis of the obtained result it is possible to establish qualitative interrelation between structure parameters and characteristics of spatial-time dynamics.

Lyapunov exponents for spatial-time system $\lambda_{t,r}$ can be determined by the formula

$$\sum \boldsymbol{\lambda}_{t,r} = \sum_{\iota} \boldsymbol{\lambda}_{ri} + \sum_{j} \boldsymbol{\lambda}_{tj} \tag{2}$$

where $\Sigma\lambda_{ri}$ is the sum of spatial Lyapunov exponents, $\Sigma\lambda_{tj}$ is the sum of time Lyapunov exponents, i and j are a number of spatial and time parameters, respectively, $i+j= R_{t,r}$ - dimension of phase space of the system.

For fractal dimension of spatial-time chaos regime $D_{t,r}$ the following equation is true:

$$D_{t,r} \geq D_r, \tag{3}$$

where D_r is fractal dimension of spatial distribution.

The characteristics of material structure and growth, based on the invariants of nonlinear dynamics, can have great practical importance for modeling and control of growth processes.

By dimension of phase space and Lyapunov exponents, it is possible to judge about the extent of distance of the substance from the balance. It can be important for definition of the ways of material characteristics stabilization.

Local and global Lyapunov exponents, topological entropy make it possible to determine the limits of predictive manner of the system behavior on different spatial and time scales.

3. Experimental results

With the help of the above described Takens' procedure, the Grassberger-Procaccia algorithm, fractal dimension (D) of a-Si:H, GaAs, carbon, tungsten and other material surfaces were measured by surface profile obtained with the help of scanning tunneling microscopy and atomic power microscopy. The profile height was counted off some level accepted for zero and was measured through discrete distances. The choice of the reconstruction parameters was motivated: time of delay, the numbers of points for measurement. Then the obtained data were processed with the help of Grassberger-Procaccia algorithm, and correlation integral, correlation dimension D and its dependence on embedding dimension were defined. The typical dependence D on resolution scale (r) is shown in fig. 2 "a". It is obvious that D is not determined, however, there is a linear portion. And the slope size on this portion is saturated at increase of n. According to the approach [4], this means that the surface structure has determined chaotic distribution in which degrees of freedom are algebraically independent, and correlation length is much less that the size of the system. In addition to embedding method, the data on surface profile were investigated with the help of function of distribution, Fourier analysis, function of average mutual information.

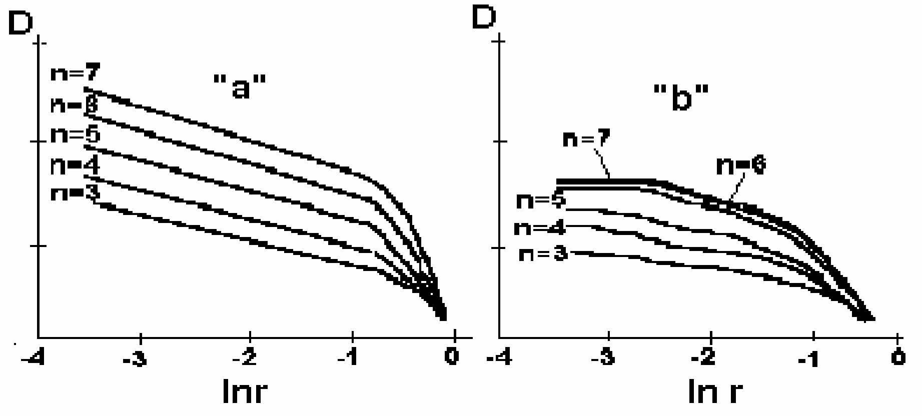

Fig. 2. Dependence D on resolution scale (r) and embedding dimension (n). The results of investigations for listed materials are the following:

Surface of a-Si:H grown in glow discharge.

Dependence D=f(n, ln r) on substrate temperature at material growth has complex feature. In all cases three different portions in the ranges Δln r: from -0,6 to 0, from -0,6 to -1,4, from -1,4 to -1,8 are observed. In all portions there are the areas with linear slope which is saturated at embedding dimension n=8. At increase of substrate temperature these portions become more marked.

Presence of the portions, having different scaling, means that fractal set, formed by the data on the profile of the surface in question, is non-uniform three-scaled in this case - and formation of the surface is determined by three different mechanisms.

Surface of carbon grown by pyrolysis.

On the diagram D=f(n, ln r) two portions, that have different maximums, are observed. Both portions are characterized by qualitatively identical behavior of D. In both cases there are areas Δln r from -2 to 1.7 and from -3.5 to -3, respectively, in which dependence D = f(n, ln r) is linear. At n=6 the slope D = f(ln r) on these portions is saturated.

Surface of crystal chip of GaAs.

On the diagram D=f(n, ln r) two portions, that have different maximums, are observed. In both cases there are areas Δln r from -0.7 to -0.4 and from -3.2 to -2.5, respectively, in which dependence D = f(n, ln r) is linear. For the first area saturation of the slope D = f(ln r) occurs at n=6 and for the second one at n=7. Thus, as in the case with carbon, two-scaled fractal set is observed, each of them having determined chaotic character and being formed by two different mechanisms.

Also dependence D = f(n, ln r) on the scale of the portion, on which the measurements were carried out, was investigated.

At passivation of GaAs surface by a diluted solution of NaOH it was found out that distribution ceases to be determined and has casual character.

Tungsten.

The sample were prepared by the following technique: cutting of a monocrystal, grinding and polishing of the surface with application of electropolishing in NaOH solution at the final stage. The character of dependence D=f(n, ln r) testifies that the surface structure has casual character. After cleaning the surface with repeated scanning, made by electronic microscope, a linear portion in the range Δ(ln r) from -2,3 to -1,9 is observed on dependence D=f(n, ln r). The slope is saturated at n=6. It shows determined character of distribution and it is possible to speak about “displaying” of ordered surface structure.

We have compared the results obtained to known experimental data on the values of fractal dimensions of the surfaces of various materials and bulk samples of porous and amorphous materials. It is established that the value D is enclosed in the interval from 2 to 3 and has fractional part. It is supposed that fractal dimensions, measured on physical properties, represent average meaning of local structure topology. Dependence D= f(n, ln r), shown in fig.2 "b", is typical of it. Thus, value D is the indicator of chaotic distribution having determined nature.

4. Conclusions

The main conclusion made from the exposed results consists in fact that the structure of surface (a-Si:H, GaAs, C), representing instant "frozen" snapshot of growth processes, has determined chaotic character. This makes it possible to evaluate the problem of structural irreproducibility and the properties of non-crystalline materials and to work out absolute new methods of structure modulating and the growth processes.

Irreproducibility.

Characteristically, chaotic dynamics is extremely sensitive to the initial conditions, so that any perturbation to them, however small it appears, grows over time and eventually reaches significant magnitude; hence the unpredictability and irreproducibility of the motion. In our opinion, it is this sensitivity in combination with both the limited precision of process variables and unavoidable fluctuations that are responsible for the structural and behavioral irreproducibility of non-crystalline semiconductor materials (such as a-Si:H) and, in some cases, single crystals.

If process variables and initial conditions are specified to a sufficiently high precision, unavoidable fluctuations become the major factor. They may have thermal or quantum character or may be caused by external agents (electromagnetic and gravitational fields, neutrinos, etc.) to which any specimen are exposed. Since instability is a concomitant of solidification, the material amplifies the fluctuations, thus acting as a source of randomness. We believe that this mechanism underlies the irreproducibility in the fabrication of semiconductor materials.

We thus arrive at the conclusion that randomness is inherent in the fabrication of an amorphous or crystalline semiconductor material. This means that it is not possible (1) to exactly reproduce a desired variety of structure and (2) to exactly predict which of the varieties will be obtained. Mathematically, one cannot change from ensembles to individual trajectories in the phase space. We see that statistical treatment provides something more important than an approximation to reality. In sharp contrast to classical theory, one can predict the probability of an event but not events themselves [5].

Proceeding from this the dynamic measures (Kolmogorov-Sinai entropy, Lyapunov exponents, average mutual information) were developed and the reproducibility limit and its dependence from a mass of growing material were defined.

Simulation principles.

Considering all the things mentioned we may presuppose that the algorithm of modulating dynamics of chaotic systems may be applied for modulating the growth processes and the structure of non-crystalline materials:

- first stage - experimental investigation of surface or volume material structure by embedding method or investigation of dynamics on the growth surface in situ;

- second stage - numerical definition of attractor type and fractal dimension, a number of degrees of freedom, Lyapunov exponents and other "dynamical parameters" of structure;

- third stage - nonlinear model building by information on the spatial distribution and characteristics of spatial compact attractor in phase space.

The advantages of this method over the existing ones consist in the fact that we don't use indirect but direct experimental data of the growth dynamics and the structure parameters.

Controlling growth processes.

The poor effectiveness of the existing means of controlling which are used in the non-regulated materials is conditioned by their incongruity to inner dynamic processes in the matter.

The above example highlights the need for a better understanding of solidification dynamics. It should be borne in mind that solidification inevitably includes a stage of spatiotemporal chaos. Accordingly, the irreproducibility problem can be treated by techniques developed for controlling chaos: chaotic driving, the amplification of external noise, stabilizing chaotic orbits, and the accelerated transition through a bifurcation point [7].

The choice of what technique will be applied should be made according to the character of the material. For example, true amorphous materials require that the control signal amplify chaos and prevent intermittency [2], a phenomenon that may result in the formation of macroscopic coherent structures. This can be achieved by chaotic driving or by amplifying externally induced noise. In the case of single crystals, it would be wise to employ the Grebogi--Ott--Yorke method of stabilizing unstable orbits on a chaotic attractor [7]. In either case, the control signal should be defined on the basis of an accurate knowledge of system dynamics.

At the same time, one should remember that it is impossible to eliminate randomness from solidification. Moreover, the existing approaches to the control of chaos have their limitations due to difficulties with measuring, modeling, and actuating. We firmly believe that a promising strategy for improving reproducibility in microelectronics processing could be framed by analogy with the reproduction of living things, which insures high fidelity despite structural diversity and strong interference from the environment.

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