Nanofine spatial dissipative structures with azimuthal lattice curvation

V B Malkov¹, O V Chemezov²,⁵, V G Pushin³, A V Malkov⁴, B V Shulgin² and O V Malkov⁴

¹Institute of High-Temperature Electrochemistry, Ural Branch of the Russian Academy of Sciences, 20, Academicheckaya str., Yekaterinburg, 620990, Russia
²Ural Federal University named after the First President of Russia B N Yeltsin, 19, Mira str., Yekaterinburg, 620000, Russia
³Institute of Metal Physics named after M N Mikheeva Ural Branch of the Russian Academy of Sciences, 18, Sophyi Kovalevskoy str., Yekaterinburg, 620108, Russia
⁴CJSC SPC ‘Rosna’, Yekaterinburg, Russia

E-mail: ⁵o.v.chemezov@urfu.ru

Abstract. The nanofine spatial dissipative structures (NSDS) were characterized by transmission electron microscopy and electron diffraction. The NSDS obtained by thermogradienly processing an amorphous selenium film by unilateral heating of its lower surface at \( T = 413 \) K preliminarily. The results indicate that the NSDS of hexagonal selenium obtained in an amorphous film possess an azimuthal curvature of the lattice and a nonlinear fan-shaped system of flexural contours on their electron microscopic image. The lattice of the above NSDS undergoes elastic – plastic rotational curvature around three mutually perpendicular directions. The lattice rotation angles of hexagonal selenium NSDS reach: around [001], – 25°, around the direction perpendicular [001] and lying in the plane of the amorphous film – 32°, around the direction perpendicular to the first two ones and not lying in the plane of the amorphous film - azimuthal curvature of the lattice, – 35°. Thus, as a result of electron-microscopic and microdiffraction studies, it was found that NSDS of hexagonal selenium with azimuthal curvature of the lattice, causing the curvature of its habitus, are in a nonequilibrium state.

1. Introduction

It is known that the formation of dissipative structures can be realized by an explosive crystallization of amorphous substances [1]. Another way of forming such structures exists – with rotational curvature of the lattice by thermogradienly processing of an amorphous film by unilateral heating of its lower surface [2, 3]. The rate of formation of the NSDS during the explosive crystallization creates difficulties in obtaining dissipative structures of a given size. Taking into account the above, the formation of NSDS of hexagonal selenium with rotational curvature of the lattice and given dimensions was carried out by the method of thermogradienly processing of an amorphous film [2, 3].

2. Experimental

The study of NSDS of hexagonal selenium was carried out by electron microscopy and electron diffraction [5–11]. NSDS of hexagonal selenium with azimuthal curvature of the lattice are formed in an amorphous Se film during thermogradienly processing of by heating its lower surface at \( T = 413 \) K.
(Figure 1 a). A characteristic detail of the electron microscopic images of NSDS is the system of bending contours [4, 9–12]. The appearance of the system of bending contours is caused either by their bending as a whole or by the rotational curvature of their lattice [2, 3, 10–12]. Systems of nonlinear fan-shaped extinction contours are present on electron microscopic images of NPDS of hexagonal selenium with a curved habit (Figure 1 a).

Quenching of NSDS of hexagonal selenium by cooling in an air was performed after completion of the thermogravity processing of the amorphous Se film. In NSDS of hexagonal selenium formed in the amorphous film during quenching, the lattice structural defects are fixed. Lattice structural defects are atoms and vacancies displaced from their equilibrium positions. The concentration of the nonequilibrium structural defects, corresponding to the temperature of one-sided heating of the lower surface of the amorphous Se film, remains in NSDS formed in the amorphous film with a sharp decrease in temperature [2, 3, 13–15]. Quenching of the nonequilibrium structural defects allows the structure of NSDS to be ‘frozen’ and exist without exchange of both energy and matter with the environment. The NSDS formed in the amorphous Se film possess all the signs of nanofine crystals after quenching.

3. Results and Discussion
In microdiffraction studies [5–8] of NSDS of hexagonal selenium with curved habitus microelectron diffraction patterns were obtained from the central parts of NSDS (Figure 1 b) and from their peripheral parts: from the ‘right’ part (Figure 1 c) and from the ‘left’ part (Figure 1 d), respectively. Table 1 show the results of the calculation of microelectron diffraction patterns of the nanofine PDS of hexagonal selenium, respectively: from the central part (Figure 1 b), from the ‘left’ part (Figure 1 c) and from the ‘right’ part (Figure 1 c). Reflections in the microelectron diffraction pattern from the central part of NSDS of hexagonal selenium with azimuthal curvature of the lattice (Figure 1 b) indicate that prismatic planes of the first kind are in the reflecting position in this part of the NSDS. The results of the calculation of microelectron diffraction patterns of the peripheral parts of NSDS (Figure 1 c and Figure 1 d) allow determining their position in the reciprocal lattice by NSDS of hexagonal selenium with azimuthal curvature of the lattice. The position of microelectron diffraction patterns from the ‘left’ and ‘right’ parts of NSDS of hexagonal selenium in its reciprocal lattice is characterized by mirror symmetry.

Comparative analysis of microelectron diffraction patterns (Figure 1 b, 1 c and 1 d); and calculations performed using standard crystallographic formulas allow to establish that the lattice of the studied NSDS of hexagonal selenium with the curved habitus undergoes elastic - plastic rotational curvature around three mutually perpendicular directions – around [001], which coincides with the smallest size of NSDS; around the direction perpendicular to [001] and lying in the plane of the amorphous film and the azimuthal curvature around the direction perpendicular to the first two ones (Figure 1 a).

The elastic – plastic nature of the rotational curvature of the lattice of NSDS with azimuthal curvature of the lattice formed in the amorphous Se film is indicated, on the one hand, by the peculiar properties of their bending extinction contours. Indeed, the bending extinction contours of NSDS of hexagonal selenium (Figure 1 a), in their peripheral part, are discontinuous. On the other hand, high values of the angles of rotational curvature of the lattice of NSDS around three mutually perpendicular directions exclude the purely elastic nature of the rotational curvature of their lattice.

Thus, as a result of electron-microscopic and microdiffraction studies, it was found that NSDS of hexagonal selenium with azimuthal curvature of the lattice, causing the curvature of its habitus, are in a nonequilibrium state. The lattice of NSDS experiences elastic – plastic rotational curvature around three mutually perpendicular directions. The lattice rotation angles of these NSDS of hexagonal selenium reach accordingly: around [001], 250, around the direction perpendicular [001] and lying in the plane of the amorphous film – 320, around the direction perpendicular to the first two – azimuthal curvature of the lattice – 350.
**Figure 1.** Electron-microscopic image of NSDS of hexagonal selenium with azimuthal curvature of the lattice (Figure 1 a). JEM-200CX JEOL Ltd, Japan. Microelectron diffraction pattern from the central part of NSDS of hexagonal selenium with azimuthal curvature of the lattice (Figure 1 b); prismatic planes of the first kind are in a reflective position. Microelectron diffraction patterns from the ‘left’ (Figure 1 c) and ‘right’ (Figure 1 d) of the peripheral parts of NSDS.

The rotation of the reciprocal lattice by NSDS of hexagonal selenium with azimuthal curvature of the lattice is the result of the rotation of selenium macromolecules – structural units that form a lattice NSDS. Accordingly cooperative movements of the structural units forming the lattice NSDS with azimuthal curvature of lattice are cooperative rotations of the selenium macromolecules around three mutually perpendicular directions.
Table 1. Interplanar distances and Miller indices for a microelectron diffraction pattern of NSDS of hexagonal selenium with azimuthal curvature of the lattice: B) from the central part; C) from the ‘left’ part; D) from the ‘right’ part, respectively.

| Part | Reflex numbers | Interplanar distances Experiment (Å) | Interplanar distances Theory (Å) | Miller indices |
|------|----------------|-------------------------------------|----------------------------------|----------------|
| B    | 1              | 3.810                               | 3.800                            | 10 1 0         |
|      | 2              | 2.977                               | 2.975                            | 10 1 1         |
|      | 3              | 2.093                               | 2.060                            | 10 1 0         |
|      | 4              | 1.739                               | 1.755                            | 20 2 1         |
| C    | 1              | 2.977                               | 2.975                            | 10 1 1         |
|      | 3              | 2.186                               | 2.167                            | 11 2 0         |
|      | 4              | 2.046                               | 2.167                            | 11 0 2         |
| D    | 1              | 2.977                               | 2.975                            | 10 1 1         |
|      | 3              | 2.046                               | 2.060                            | 0 1 1 2        |
|      | 4              | 2.180                               | 2.167                            | 2 1 1 0        |

4. Conclusion

Thus, the formation of NSDS of hexagonal selenium with azimuthal curvature of the lattice occurs in an amorphous film during its thermogradients treatment – one-sided heating of the lower surface of the amorphous film with subsequent quenching by cooling in air and is the result of all the necessary and sufficient conditions for the formation of spatial dissipative structures: a) NSDS with azimuthal curvature of the lattice are formed in a thermodynamically open system; b) this system is removed from an equilibrium; c) this system is described by nonlinear equations; c) the formation of NSDS of hexagonal selenium with azimuthal curvature of the lattice is the result of the cooperative movement of the structural units of their lattice – the cooperative rotation of selenium macromolecules around three mutually perpendicular directions [2, 3, 17–20].

Reference

[1] Shklovsky V A and Kuzmenko V M 1989 Explosive crystallization of amorphous substances *Advances in Physical Sciences* **157** 2 pp 311–38 [In Russian]
[2] Malkov V B, Nikolaenko I V, Shveikin G P, Malkov A V, Pushin V G, Shulgin B V, Malkov O V and Plaksin S V 2017 Patent RU 2637396 [In Russian]
[3] Malkov V B, Nikolaenko I V, Shveikin G P, Pushin V G, Malkov A V, Malkov O V and Shulgin B V 2018 Formation of dissipative structures in an amorphous film *Reports of the Academy of Sciences* **478** 5 pp 543–5
[4] Kvegls L I and Kashkin V B 2015 Dissipative structures in thin nanocrystalline films (Siberian Federal University: Prospekt) [In Russian]
[5] Hirsch P B, Howie R B and Nicholson D W 1968 *Electron microscopy of thin crystals* (London: Butterworths) pp 418–20
[6] Tomas G and Goringe M J 1979 *Transmission electron microscopy of materials* (New York-Chichester-Brisane-Toronto) pp 198–203
[7] Utevsky L M 1973 *Diffraction electron microscopy in metal science* (Moscow: Metallurgy) [In Russian]

[8] Andrews K V, Dyson D J and Keown S R 1968 *Interpretation of Electron Diffraction Patterns* (London) pp 39–56

[9] Malkov V B, Nikolaenko I V, Shveikin G P, Malkov A V, Pushin V G, Malkov O V and Shulgin B V 2014 Patent RU 2534719 [In Russian]

[10] Bolotov I E and Kolosov V Yu 1980 Bending of thin-film crystals of selenium, detected by extinction contours *Izv. USSR Academy of Sciences Ser. Physical* 44 6 pp 1194–97 [In Russian]

[11] Bolotov I E and Kolosov V Yu 1982 Investigation of Crystals Based on Bend-Contour Arrangement I Relationship between Bend-Contour Arrangement and Bend Geometry *Phys. Stat. Sol. (a)* 69 1 pp 85–96

[12] Kolosov V Yu 1982 *Abstract of dissertation* Electron-microscopic study of defects in crystals growing in amorphous films (Sverdlovsk: IFM) [In Russian]

[13] Damascus A and Deans J *Point defects in metals* ed. Lyubova B Ya (Moscow: Mir) 1966 [In Russian]

[14] Malkov V B, Nikolaenko I V, Shveikin G P, Malkov A V, Pushin V G, Shulgin B V, Malkov O V and Plaksin C V 2019 Patent RU 2687876 [In Russian]

[15] Bolotov I E and Prilepo V L 1983 On the vacancy mechanism of the occurrence of compressive stresses during crystallization of amorphous films *Phys. Stat. Sol. ABD* 1 pp k67- k70

[16] Prigogine I and Condepudi D 2002 *Modern thermodynamics. From heat engines to dissipative structures* (Moscow: Mir) [In Russian]

[17] Askhabov A M 1993 *Crystallogenesis and evolution of the crystal-medium system* ed. Yushkin N P (Saint Petersburg: Nauka) [In Russian]

[18] Nikolis G and Prigozhin I 1979 *Self-organization in nonequilibrium systems* ed. Chizmadzheva Yu A (Moscow: Mir) [In Russian]

[19] Mandelkern L 1966 *Crystallization of polymers* (Leningrad: Chemistry) [In Russian]

[20] Wunderlich B 1979 1984 *Physics of macromolecules* (Moscow: Mir) T 2, 3 [In Russian]