

THE STRUCTURE OF CdS NANOPARTICLES DEPOSITED FROM SOLUTION

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Abstract. The main results of structural studies of cadmium sulfide nanoparticles were given and presented data on the dependence of the structure and properties of CdS nanoparticles on their size. An X-ray analysis method was used to determine the structure and size of nanoparticles. It was found that nanostructured films and CdS nanopowders are a mixture of crystallites or domains of the cubic and hexagonal phases and have an unordered densely packed structure with an average nanoparticle size of about 5 nm.

Keywords: *cadmium sulfide, nanoparticle, sphalerite, wurzite.*

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1. Introduction

In the last two decades, there has been a growing interest in chemical deposition of CdS from solutions. Interest in the method is associated with the success of deposition of nanostructured barrier layers based on CdS films for heterostructured cascade thin-film solar cells CIGSSe (Cu-In-Ga-S-Se) (Repins *et al.*, 2008). Through the use of thin CdS films with a thickness of 10 to 100 nm as the first "window" or buffer layer in solar cells, solar cell developers managed to achieve their efficiency of up to 20%.

Since 2006, studies using CdS deposition from solutions have gone far beyond the subject of solar cells. The reason for the growing interest in the method was the possibility of synthesis of nanocrystalline particles (Jun *et al.*, 2013). It is known that if the particle size becomes less than a certain threshold value, there is a significant change in the physical properties of most solid-phase substances, including the crystal structure. This aspect is especially important when considering heavy metal chalcogenides, the electronic and optical properties of which depend on both the particle size and their structure (Oleynikov, 2010). The emergence of quantum effects with decreasing particle size has led to the emergence of the term "quantum dots" (QD). Unique optical characteristics of QD, such as blue (hypsochromic) shift of the absorption band edge and photoemission maximum with decreasing QD size, high fluorescence brightness and photostability, caused their rapid penetration into various fields of science and technology (Frigerio *et al.*, 2012).

A special place is occupied by colloidal semiconductor nanocrystals (colloidal QD). From the chemical point of view, colloidal QD is nanoparticles obtained by methods based on the processes of nucleation and growth in supersaturated solutions (Nikolenko & Razumov, 2013). One such method is chemical deposition from aqueous

solutions. At the same time, each QD is an isolated and mobile object in a solvent and stabilized by amphiphilic molecules. The ability of QD to exist in colloidal solutions makes it possible to introduce them into porous organic and inorganic matrices and thus create composite and hybrid materials (Emin *et al.*, 2011).

Due to their optical properties, cadmium chalcogenide-based QD's are promising for ultra-sensitive multi-color registration of biological objects, medical diagnostics, cytometry, in optical and electron microscopy and fluorescent analysis. To visualize biological objects or processes, QD is supposed to be injected into the object directly or with "sewn" recognizing molecules (usually antibodies or oligonucleotides) (Wang *et al.*, 2012). Nanocrystals can penetrate and be distributed over an object according to their properties. For example, nanocrystals of different sizes penetrate biological membranes differently, and since the size determines the color of fluorescence, different areas of the object are colored differently (Oleynikov *et al.*, 2007).

With the reduction of particles to nanosize, there are effects that are not peculiar to the substance in the usual state. First, the surface of the particle begins to play a large role. At the particle size CdS ~ 5 nm, the number of atoms on its surface is about 30% of the total number of atoms in the particle. A large proportion of uncompensated interatomic bonds affect the structure of the particle. For this reason, non-crystalline structures, that are not typical for large-crystal materials, may have greater stability at such small sizes (Rempel *et al.*, 2010).

α - and β - modifications of CdS crystals were first described by Klobukov and identified as wurzite (type B4) and sphalerite (type B3) structures, respectively. Designations and crystallographic parameters of two large-crystal phases according to JCPDS (Joint Committee on Powder Diffraction Standards) are presented in table 1. Both crystal structures are constructed of alternating densely-packed layers, each of which consists of sub-layers of ions of different varieties (Fig. 1).

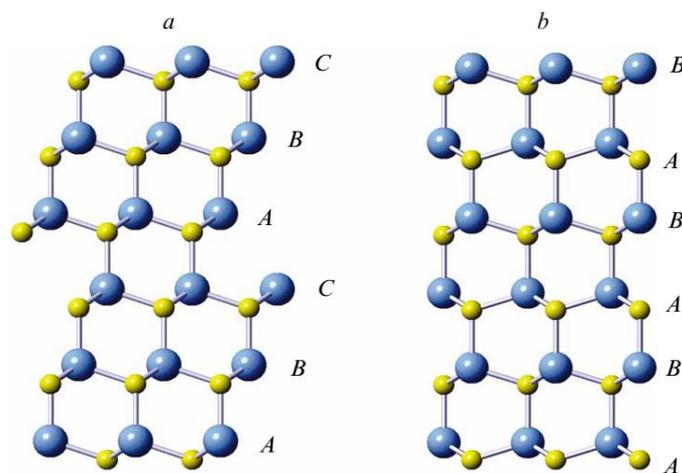


Fig. 1. Crystal structures of CdS: sphalerite (a) and wurzite (b) type

The sphalerite structure is the densest cubic packing, in which the layers are arranged normally to the four polar directions (111) of the face-centered cubic (FCC) lattice. Ions inside the double layer are connected by three bonds for each ion, and between the double layers - one bond per ion (Vorokh & Rempel, 2007). Each anion is surrounded in the plane by six similar anions, and in space - by twelve anions. Cations

are located between four anions at equal distances from them, filling half of the tetrahedral voids. Similarly, the densest packing of cations can be considered.

The structure of wurzite is characterized by hexagonal dense packing (HDP), in which the layers are normally located to the unit polar direction (001). The described modifications are characteristic of CdS crystals under normal conditions, both structures are densely packed and differ only in the sequence of alternating layers of packaging when they are superimposed on each other (Orlova *et al.*, 2011). Thus, the sphalerite structure is described as a periodic sequence of repeating ABC-fragment ...ABCABC... (see Fig. 1,a), and the structure of wurzite - as a periodic sequence of repetitive L5-fragment ...ABABAB... (see Fig. 1,b). Periodicity in the sequence of layers is a necessary condition for translational symmetry of the crystal structure.

2. Experiment

To identify the structure and size of nanoparticles, have been used SEM and x-ray phase analysis. SEM analysis show that, surface structure, form and size of clusters depend on preparing method (Fig. 2). Experimental radiographs of films with thickness from 6 to 70 nm synthesized by various methods, nanoparticles and various complex forms of CdS, taken in Cu $K_{\alpha 1,2}$ - radiation, indicate that their structures do not correspond to the structures of large-crystal modifications of CdS - wurzite or sphalerite.

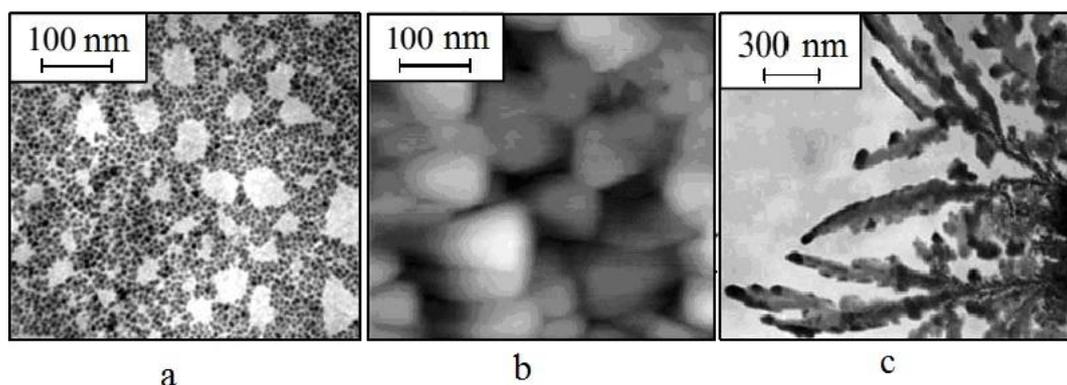


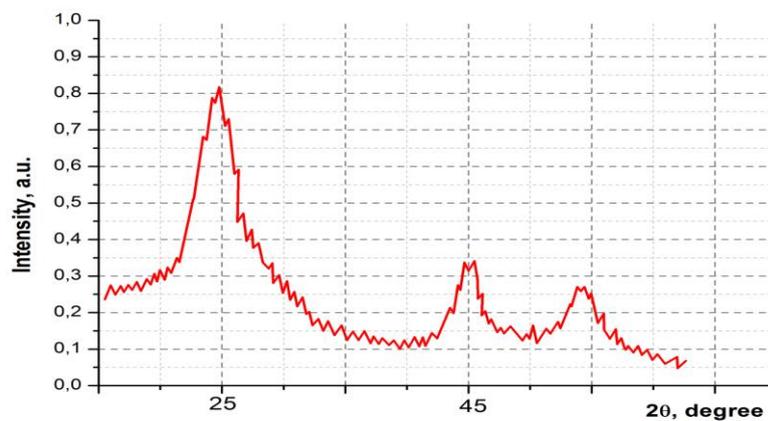
Fig. 2. Nanostructured CdS in a variety of forms. a – CdS nanoparticles; b-CdS thin films; c – dendritic structures of CdS

Almost all diffractograms of nanostructured CdS forms have the following features: the main intensity maximum is in the angle range of $2\theta \approx 26.5-27^\circ$, and at the angles of $\sim 44^\circ$ and $\sim 52^\circ$ there are two significantly lower intensity peaks (Fig. 3). Sometimes “shoulders” close to reflections [100] and [101] of wurzite structure are observed on both sides of the main maximum of the diffractogram. Of all the possible interpretations of such diffraction patterns characteristic of the CdS nanoscale state, five main ones can be distinguished:

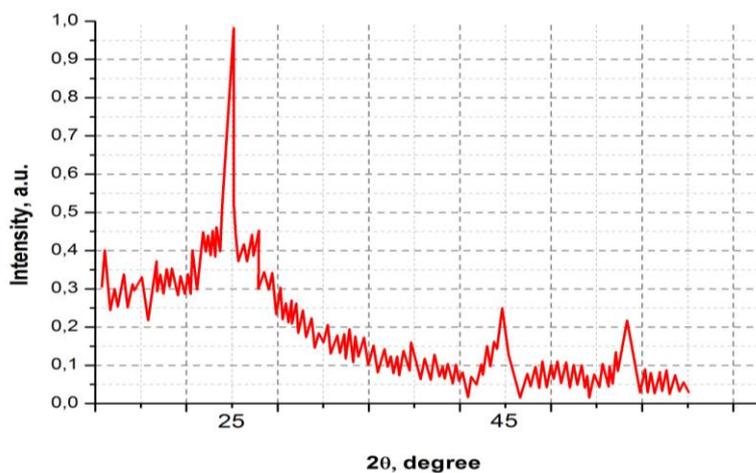
- CdS film is textured: there is a strong orientation along the C axis, directed normally to the substrate surface; in this case, the phase structure is determined in the case of powders, the structure is either cubic, or hexagonal;

- nanostructured film or CdS nanopowder is a mixture of crystallites or domains of cubic and hexagonal phases; the diffraction pattern in this case is described by a

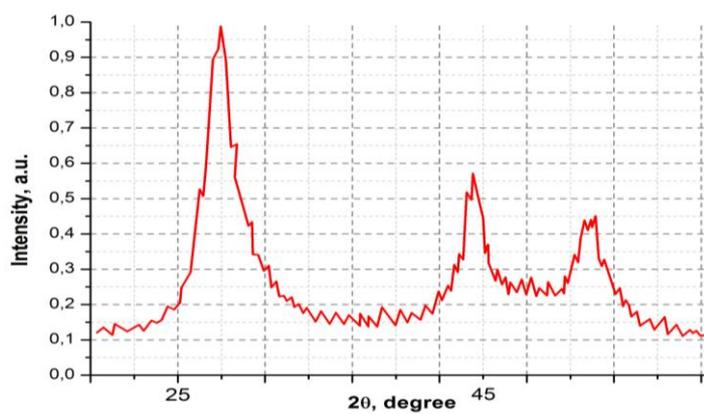
superposition of diffractograms from the two phases, taking into account their partial content;



a



b



c

Fig. 3. XRD patterns of CdS in a variety of forms. a – CdS nanoparticles; b-CdS thin films; c – dendritic structures of CdS

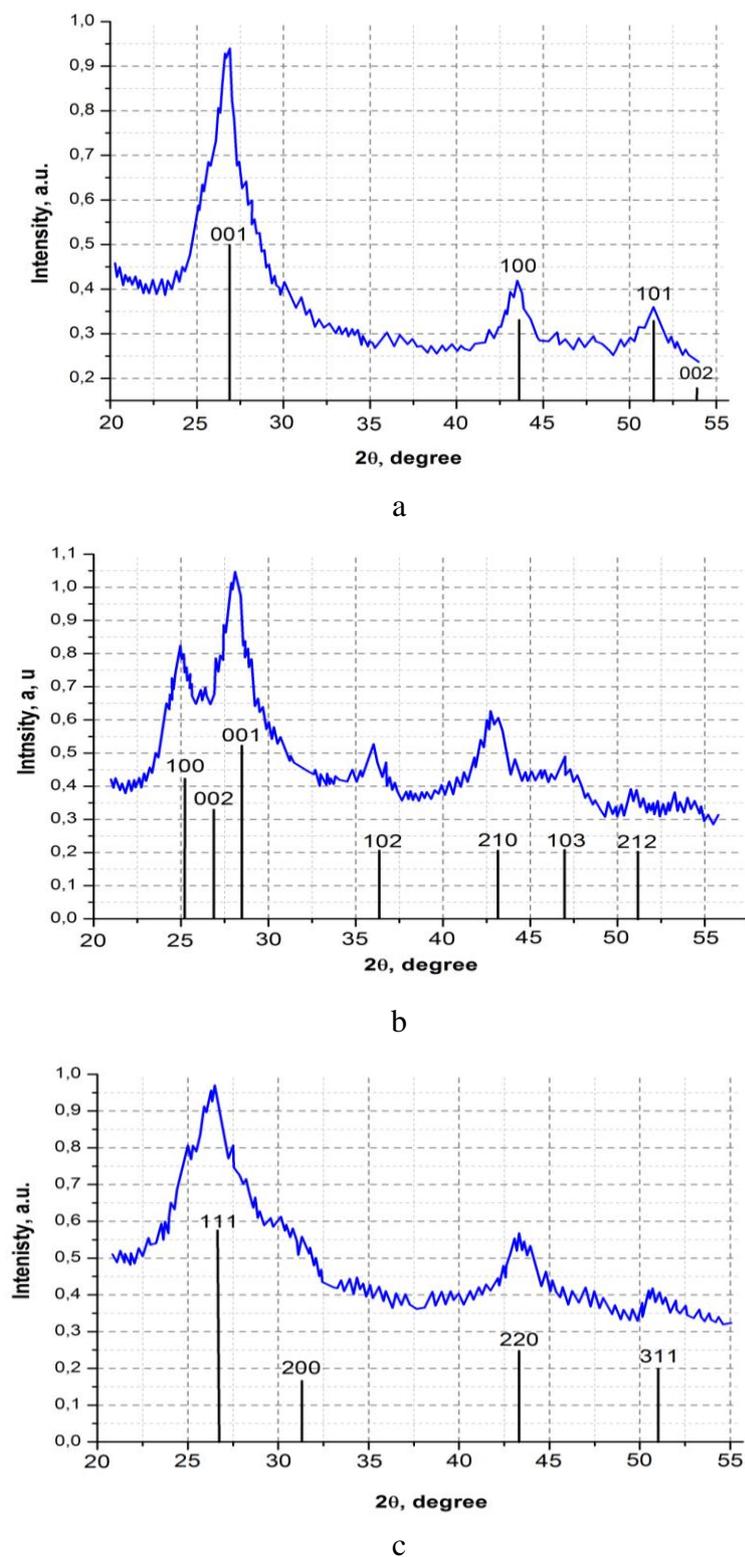


Fig. 4. Experimental X-ray diffractograms of CdS powder with linear diffraction patterns.
a - RDP-structure, space group P6; b - wurzite structure B3, space group $R\bar{6}_3mc$;
c - sphalerite structure B4, space group $F\bar{4}3m$

- the structure of thin CdS films is polytype; the structure of CdS nanoparticles is a random densest packing due to the disordering of the layer sequence, the diffraction from which corresponds to the average crystal lattice (see table. 1);

- the nanoparticle is amorphous, in this case the reflexes in the diffraction patterns represent a halo (Junkermeier *et al.*, 2007).

The main drawback of the first two interpretations of CdS diffractograms is the absence of a number of reflections both for wurzite structure (Fig. 4), for example [102] and [103], and sphalerite, for example [200]. The authors, who propose such interpretations, as a rule, do not explain the reasons for the absence of these reflections on experimental radiographs. In the case of the first interpretation, it is necessary to substantiate the well-defined (and often fixed) content of the crystal phases B3 and B4. As a rule, in order for the diffraction pattern to be successfully described by the superposition of diffractograms under any synthesis conditions, the content of the hexagonal phase should be predominant (>60%). Despite the noted shortcomings of the first two interpretations of the structure of CdS, they are dominant.

In all cases, the diffraction patterns show peaks characteristic of nanostructured CdS. In the third interpretation, in accordance with the idea of polytypism, it is assumed that there are multiple variants of alternating sequence of layers (like SiC polytypes). However, the polytypic is not peculiar coarse of CdS and in nanostructured form a new sequence of layers has not arisen, but disappears periodicity of the alternation, therefore, the notion of polytypic is not considered adequate to describe the structure of CdS nanoparticles (Vorokh & Rempel, 2010).

The fourth interpretation takes into account that the first three approaches to explaining the structure of CdS (both crystalline - type B3 or B4, and polytype) are based on the general property of atomic ordering for these types of structures - dense packing, which is put at the forefront. Some long-range order is preserved, which is due to the pronounced reflexes on diffractograms. In the fifth interpretation, on the contrary, it is assumed that there is no long-range order of atoms while maintaining the short-range order. Let us consider the last two interpretations in more detail.

Table 1. Crystallographic parameters of crystalline phases and nanostructured forms of CdS

Particle	Type of structure	map	Structure	Phase group	Atomic coordination	Cell parameters	
						<i>a</i>	<i>c</i>
α -CdS	Wurtzite B4	JCPDS-041-1049	HDP	P6 ₃ mc	$Cd\left(\frac{1}{3}\frac{2}{3}0\right)$ $S\left(\frac{1}{3}\frac{2}{3}\frac{3}{\sqrt{24}}\right)$	0.414	0.672
β -CdS	Sphalerite B3	JCPDS-041-1411	FCC	F43m	$Cd(000)$ $S\left(\frac{1}{4}\frac{1}{4}\frac{1}{4}\right)$	0.582	

3. Results and discussion

It is shown in that the specificity of diffraction patterns of nanostructured CdS is caused by disordering the sequence of packing layers. In this case, the probability that the layer is at position A, B, or C becomes uncertain. The structure of this kind is called a random dense packing (RDP). The near order, the environment of atoms, the number of nearest neighbors in all three raft-packed structures CdS - RDP, HDP and FCC - are identical, so energetically all three structures are sufficiently stable.

First, the disordering in the structure of the nanopowder CdS was found, noticing the absence of several lines from the crystal structure in powder x ray powder patterns of the CdS. He defined the structure as intermediate between amorphous and crystalline, characterized by a chaotic superposition of anionic layers.

The vast majority of data indicates that regardless of the synthesis method, there is a correlation between the structure and size of CdS nanoparticles. Thus, CdS nanocrystalline powders have an unordered dense packed structure with an average size of 5 nm nanoparticles. Dendrites obtained from a nanopowder also consist of nanoparticles of the same structure with a Gaussian-like size distribution between 2-20 nm, the peak of which is 10 nm. But at larger sizes is observed mainly structure wurzite. Thus, spherical nanoparticles and nanofibers with dimensions of 20-60 nm have a distinct hexagonal structure of wurzite. Fibers with a diameter of 100 nm have both hexagonal and possibly cubic structure, non-equilibrium under normal conditions.

The dependence of the structure on the size is also observed in the case of thin CdS films. Evaluate by diffractograms, the structure of the film with nanoscale domains can be identified as a random dense packing. With the increase in the size of the film domains to 60 nm and more domain structure corresponds to the structure of wurzite.

For isolated particles, the study of the structure is the most time-consuming, since it requires a thorough analysis of images obtained using a high-resolution transmission electron microscope (HRTEM). The images the STC-structure of CdS and its "average" of the crystal lattice in direct space have been given (Conde *et al.*, 2003). There are clearly distinguished multiple violations in alternating layers, shown on the photomicrographs. Nevertheless, the authors correlate ABA and ABC fragments with wurzite and sphalerite structures and interpret such a structure as a mixture of two phases. In a nanoparticle consisting of a dozen layers of packaging, one or two defects in the packaging actually lead to a loss of translational symmetry in the particle.

Despite the disordering, nanostructured CdS forms with RDP structure remain stable with a significant increase in temperature. When samples of thin films are heated to 720 K, the size of the domains increases and a structural transition occurs. For the first time it was found that at a temperature > 620 K the structure is gradually ordered, and above 820 K always passes into the structure of wurzite. On the diffractogram, the distinct wurzite reflex [200] from the large-crystal CdS is overlapped with the reflex of the main component of the film - nanosized particles of uncertain structure. The maximum temperature, which was synthesized CdS with RDP-structure, equal to 350 K. At temperatures of synthesis (or heating) > 500 K the structure of the CdS corresponds to the structure of wurzite, and apparently, it is more equilibrium under these conditions (Metin & Esen, 2003). Thus, crystalline CdS nanoparticles were synthesized in solution by the method of inverse micelles at high temperature. Micelle limits the size of the nanoparticle and slows down its growth rate, high temperature promotes atomic ordering. However, the HRTEM image shows that the particle is

amorphous near the surface. Under normal conditions, nanoparticles tend to form a RDP structure in which the minimization of surface energy occurs due to the entropy contribution of disordering and partial loss of translational symmetry.

The stability of structures without translational symmetry can be estimated only by the molecular dynamics method. Thus, CdS nanoparticles with wurzite and sphalerite structures were simulated by molecular dynamical calculations and computer "annealed" (re-coaxial) at a temperature of 300 K. In accordance with the function of the pair distribution of atoms in the calculated particles, it was found that as a result of relaxation, nanoparticles of size 2 nm lost their crystal structure and became amorphous (Fig. 5).

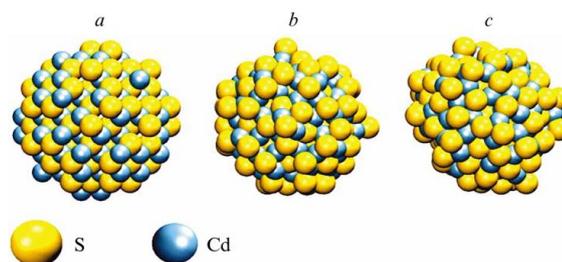


Fig. 5. Cd₁₃₂S₁₃₂ particles with a radius of 1.164 nm with sphalerite structure (a) after relaxation (b) and after "annealing" at 300 K (c)

This structure, which has a purely short-range order, is typical, according to the some authors, for particles of size < 6 nm.

The investigations showed that the structure of particles ranging in size from 3 to 9 nm has a "medium" long-range order, and this is manifested in the form of pronounced maxima on the diffractogram (Fig. 4). Namely, when scattered on stochastically alternating layers of the package, the information about the periodicity of the sequence of layers disappears. The only relevant information is that the atoms are in layers that can occupy any of the three positions in space - A, B or C, and this is tantamount to the idea that the packing layer is in all three positions with the same probability of 1/3. Therefore, RDR-structure is associated with a lattice with hexagonal symmetry, the space group P6 (C61) and the unit cell parameters $a = 0.236$ and $c = 0.334$ nm, where a - is the distance between the projections of all atoms on the packing plane, c - is the distance between the nearest dense layers of atoms of the same name (Cd or S). In the cell of the "middle" lattice, the atoms Cd and S occupy single positions 1(a); the coordinates of the atoms and the degree of filling are shown in table 1.

4. Conclusions

So, the structure of nanostructured CdS forms strongly depends on the particle size. There are two critical dimension values. With the number of atoms in a particle of the order of several thousand, the tetrahedral environment of Cd and S atoms leads to the formation of packing layers and a "medium" long-range order. This structure is typical for CdS particles < 9 nm in size and, according to the above data, is typical for particles >3 nm in size. For particles consisting of several hundred atoms, the size of ~2 nm is characterized by an amorphous structure. It is not possible to fix unambiguously the boundary separating amorphous particles from particles with RDP structure; therefore, we use the value of 3 nm as the upper boundary of the amorphous structure.

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