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Obtaining and studying the luminescent properties of zinc oxide synthesized in a stream of high-energy electrons

For the first time, zinc oxide samples were obtained by a method based on irradiation of nominally pure zinc with a stream of high-energy electrons with an energy of 1.4 MeV and a power density of 7 kW/cm^2 in atmospheric air. The morphology of the synthesized substance was studied by transmission electron and optical microscopy. Particles of ultrafine zinc oxide in the form of needles were found at a distance (1–3) cm from the irradiation zone, with average lengths and diameters of 150 and 10 nm, respectively. Ultrafine samples are characterized by the presence of a hexagonal wurtzite structure. By optical microscopy, ZnO whisker microstructures with a diameter of ~ 1 μm and a length of 50–100 μm were detected in the irradiation zone. The photoluminescence spectrum of all samples is represented by one narrow exciton band with a maximum at λ = 380 nm and a decay time of τ < 13 ns in the absence of other bands due to intrinsic and impurity defects, which indicates the high crystalline perfection of the synthesized crystals.

Keywords: zinc oxide, radiation synthesis, nano- and microstructures, transmission electron microscopy, photoluminescence.

Introduction

Adding Zinc oxide is of scientific and practical interest due to its unique properties: wide band gap (~ 3.3 eV at 300 K), high exciton binding energy (60 MeV) and high radiation resistance. In this regard, ZnO-based materials synthesized by various methods are of interest for the creation of UV light-emitting devices, registration of gamma quanta and X-ray radiation [1–3]. Recently, special attention has been paid to highly dispersed forms of ZnO nanocrystals and thin films. Due to their improved physical and chemical properties, nanostructures have become attractive materials in the field of nanoelectronics, optoelectronics, energy and biomedicine [4–6]. Zinc oxide is a promising material for the creation of semiconductor lasers in the UV and blue ranges operating at room temperature [7]. Various methods are used to produce thin films of zinc oxide and nanostructures of other materials: molecular beam epitaxy, hydrothermal, pulsed laser spraying, magnetron deposition, chemical vapor deposition [8–11]. The literature data indicate a strong influence of the synthesis method and the presence of impurities on the luminescent characteristics of zinc oxide nanocrystals. Special attention is paid to the development of high-performance, economical and safe technologies for the production of nanopowders, thin films and multicomponent ceramics, which include electron beam and laser [11, 12]. The purpose of this work is to elucidate the possibility of radiation synthesis of ZnO nanocrystals using a powerful electron beam with energy of 1.4 MeV and a power density of 6–10 kW/cm^2 released into the air at atmospheric pressure.

Experimental

For the synthesis of ZnO, samples of pure (99.9 %) zinc in the form of granules were used, which were placed in specially prepared cells in a copper plate (crucible), measuring 40×100×10 mm, with a diameter of 8 mm and a depth of 4 mm and irradiated with an electron flux with an energy of 1.4 MeV and a power density of (6–10) kW/cm^2 generated by the ELV-6 accelerator (BINP, Novosibirsk). The crucible moved at a speed of 1 cm/s relative to an electron beam with a cross section of 1 cm^2. Thus, the surface of Zn was irradiated for 1 s. The characteristics of products deposited on a copper substrate were studied by transmission electron microscopy (TEM) on a JEOL JEM-2100F electron microscope by employees of the Scientific and Educational Innovation Center "Nanomaterials and Nanotechnology" TPU (ESNPT).

In addition to TEM, luminescent analysis of the synthesized material was applied. The source of excitation of pulsed photoluminescence (PPL) was a nitrogen laser (λ = 337.1 nm; τ = 10 ns). The PPL spectra and luminescence kinetics were recorded using the "point–by-point spectrum" method using the MDR-23 monochromator, PMTs -84 and the Tektronix DPO-3034 oscilloscope.

Results and Discussion

Zinc irradiation led to the formation of a white powder located both on the irradiated zinc surface (Fig. 1, a, zone 1) and on the surface of the copper plate (Fig. 1, a-b, zone 2), at a distance of up to 10 mm from the irradiation zone.

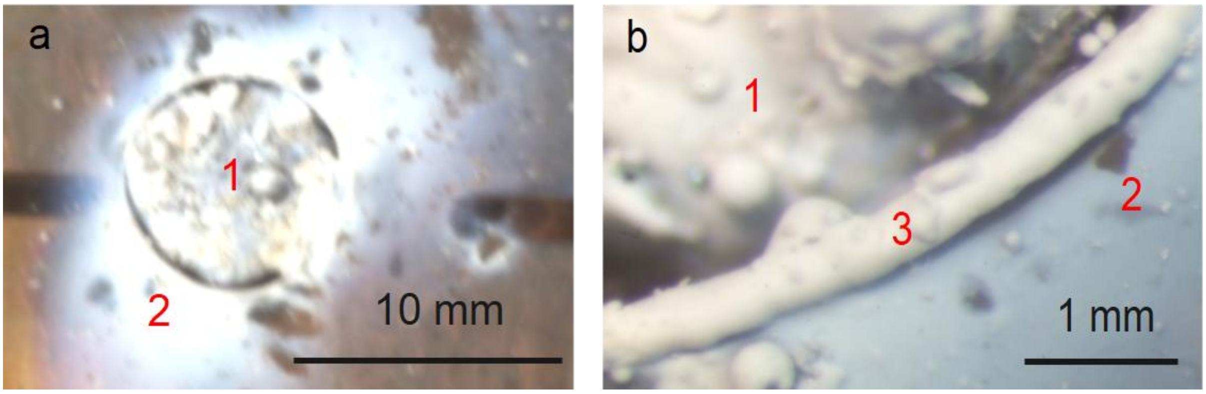

Figure 1, a-b. Photographs of a white powder formed on the surface of Zn (zone 1) and on the surface of a copper plate at a distance of up to 10 mm from the irradiation zone (zone 2).

Zone 2 was formed as a result of the effect of the supply ventilation air flow on the evaporation products formed near the irradiated zinc surface. The powder layer formed away from the irradiation zone (zone 2) was easily removed by mechanical cleaning, while the white layer, tens to hundreds of microns thick, formed on the irradiated zinc surface (zone 1) had good adhesion. At the periphery of the copper cylindrical cell, a thicker layer was formed (Fig. 1, b, zone 3), in the form of a roller.

Filamentous formations (whiskers) with a diameter of 1 μm and a length of 50–100 microns were found inside the copper cell after irradiation with an electron beam on the surface of microcrystals (Fig. 2, a-b)

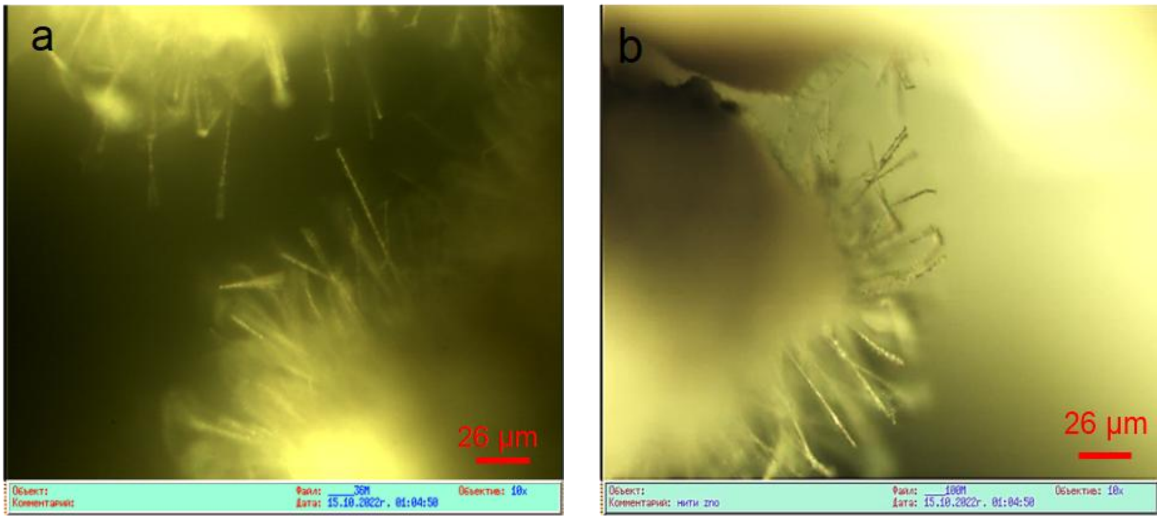

Figure 2, a-b. Image of an ensemble of filamentous structures formed on the surface of microcrystals synthesized inside a copper cell.

Figure 3a shows a high-resolution photograph (HRTEM image) of white powder nanocrystals formed on the surface of a copper plate at a distance of 10 mm from the irradiation zone, and Figure 3b shows an electronogram (SEAD image) on which several diffraction rings are observed.

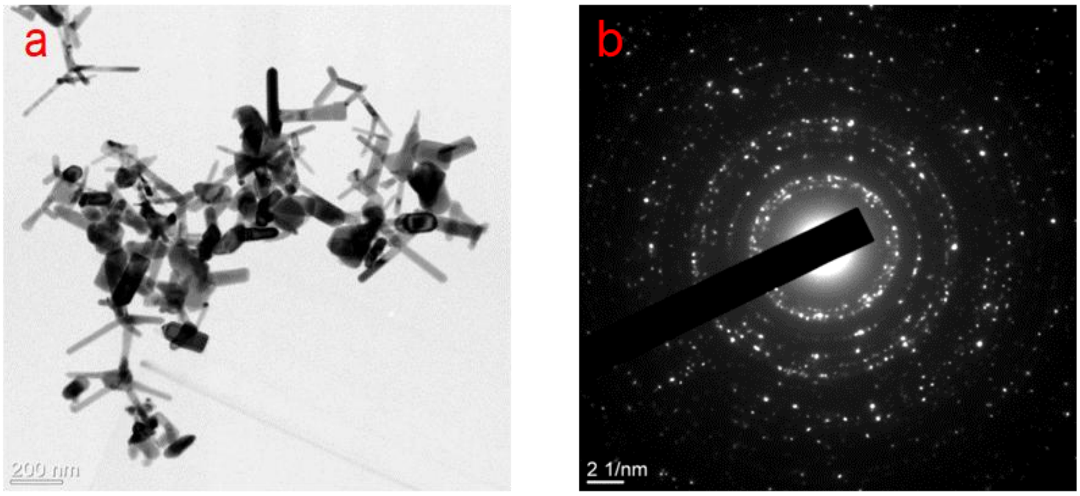

Figure 3 a — TEM — image of ultrafine ZnO powder; b — electron diffraction from the same region.

The calculation of the rings radii (r) and the corresponding interplanar distances d (Å) is given in Table. and indicates that the white powder is zinc oxide with a hexagonal wurtzite structure.

T a b l e

Calculation of the radius of the rings and the corresponding interplanar distances

No.	1/2r	1/r	r	d(Å)	h	k	l
1	7.0588	3.5294	0.284	2.84	1	0	0
2	7.647	3.5294	0.2615	2.61	0	0	2
3	8.0672	4.033	0.2479	2.47	1	0	1
4	10.420	5.210	0.191	1.91	1	0	2
5	12.268	6.134	0.163	1.63	1	1	0

The analysis of synthesized ZnO was additionally carried out by the luminescent method. The PPL spectrum and the kinetics of luminescence of zinc oxide are shown in Figure 4, a, b.

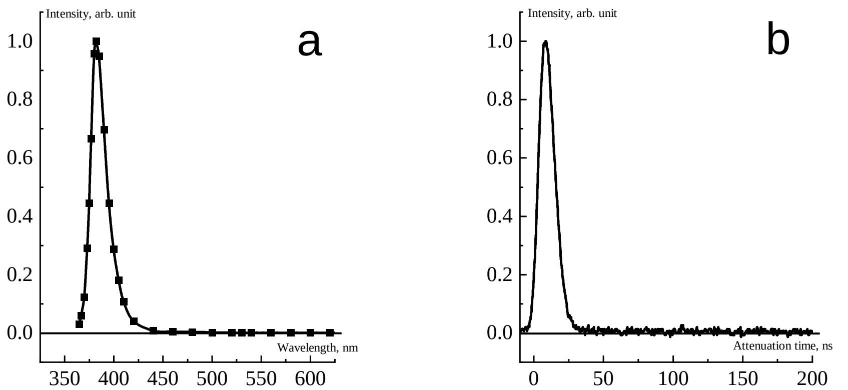

Figure 4. a — PPL spectrum; b — photoluminescence kinetics of synthesized ZnO

It can be seen that in the PPL spectrum there is one exciton band with a maximum at λ =380 nm with a decay time of $\tau \leq 13$ ns in the absence of other bands due to intrinsic and impurity defects, which indicates the high crystalline perfection of the synthesized nanocrystals.

The revealed features of the process of formation of ZnO filamentous structures correspond to the model representation of the classical Vapor–liquid–solid (VLS) mechanism by Givargizov-Chernov [13]. According to the model, the process of forming filamentous structures begins with the formation of an ensemble of metal droplets, in this case zinc, whose molecules condense on a copper substrate. Subsequently, oxygen vapor molecules from atmospheric air enter the drop, where they react with zinc and form a supersaturated liquid solution. Zinc oxide crystals fall out of the solution. A similar mechanism of growth of filamentous crystals was observed earlier by the authors of [14] when growing CdS on a SiC substrate.

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Conclusions

For the first time, a technique for the synthesis of zinc oxide nanocrystals by irradiating nominally pure (99.9 %) zinc with an electron beam with an energy of 1.4 MeV and a density of 7 kW/cm^2 released into the air at atmospheric pressure was proposed and implemented. It was found that the ZnO PPL spectrum consists of a single exciton band in the absence of bands associated with impurities and defects. The implementation of electron beam technological processes in atmospheric pressure air opens up new possibilities for obtaining high-crystalline zinc oxide nanocrystals.

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Жоғары энергиялы электрондар ағынында синтезделген мырыш оксидінің люминесцентті қасиеттерін алу және зерттеу

Алғаш рет мырыш оксидінің сынамалары номиналды таза мырышты атмосфералық ауада энергиясы 1,4 Мэв және қуат тығыздығы 7 квт/см2 жоғары энергиялы электрондар ағынымен сәулелендіруге негізделген әдіспен алынды. Синтезделген заттың морфологиясы трансмиссиялық электронды және оптикалық микроскопия арқылы зерттелді. Инелер түріндегі ультра жұқа мырыш оксидінің бөлшектері сәулелену аймағынан (1-3) см қашықтықта, орташа ұзындығы мен диаметрі сәйкесінше 150 және 10 нм болатын. Ультра жұқа үлгілер алтыбұрышты вурцит құрылымының болуымен сипатталады. Оптикалық микроскопия арқылы сәулелену аймағында диаметрі ~ 1 мкм және ұзындығы 50-100 мкм болатын ZnO вискерлі микроқұрылымдары анықталды. Барлық үлгілердің фотолюминесценция спектрі максимумы λ = 380 нм және ыдырау уақыты τ болатын бір тар экситон диапазонымен ұсынылған. $\tau < 13$ нс ішкі және қоспалық ақауларға байланысты басқа жолақтар болмаған кезде, бұл синтезделген кристалдардың жоғары кристалды жетілуін көрсетеді.

Кілт сөздер: мырыш оксиді, радиациялық синтез, нано- және микроқұрылымдар, трансмиссиялық электронды микроскопия, фотолюминесценция.

В.И. Олешко, Цзысюань Ли

Получение и изучение люминесцентных свойств оксида цинка, синтезированного в потоке электронов высокой энергии

Впервые получены образцы оксида цинка методом, основанным на облучении номинально чистого цинка потоком высокоэнергетических электронов с энергией 1,4 МэВ и плотностью мощности 7 кВт/см^2 в атмосферном воздухе. Морфология синтезированного вещества исследовалась методами просвечивающей электронной и оптической микроскопии. На расстоянии (1–3) см от зоны облучения обнаружены частицы ультрадисперсного оксида цинка в форме игл, средние значения длины и диаметров составляют 150 и 10 нм соответственно. Для ультрадисперсных образцов характерно наличие гексагональной вюрцит структуры. Методом оптической микроскопии в зоне облучения обнаружены вискерные микроструктуры ZnO диаметром ~ 1 мкм и длиной 50–100 мкм. Спектр фотолюминесценции всех образцов представлен одной узкой экситонной полосой с максимумом при λ=380 нм и временем затухания $\tau < 13$ нс при отсутствии других полос, обусловленных собственными и примесными дефектами, что свидетельствует о высоком кристаллическом совершенстве синтезированных кристаллов.

Ключевые слова: оксид цинка, радиационный синтез, нано- и микроструктуры, просвечивающая электронная микроскопия, фотолюминесценция.

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