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Mono- and multilayered opalline superlattices: application to nanotechnology of 2D ordered array of nanoobjects and 3D metalattices

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Abstract

We consider the development of a prospective way for fabrication of well-ordered 2D array of epitaxial nanodots and quasi-3D metalattices with spatially ordered particles. Mono- and multilayered opalline superlattices were used as an inorganic nanomask for fabrication of 2D ordered array of nanoobjects and metalattices composed from metals and semiconductors by deposition of different materials onto the substrate. With the help of developed nanotechnology, 2D and quasi-3D arrays of semiconductors (ZnO), metal nanodots (Ni, Ti) and nanoobjects with characteristic size of 100–300 nm were fabricated. Their structure and properties were investigated by SPM, electron and optical spectroscopy methods. Results and perspectives are discussed and analysed.

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1. Introduction

Crystalline array of colloidal spheres has attracted much attention for both fundamental and technological reasons. Monolayered opalline superlattice can be used as a nanomask for deposition of different materials onto the substrate. This method was recently referred as "nanosphere lithography". If the colloidal spheres are robust to resist energetic particles, the

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array of voids can be transferred into the substrate by reactive ion etching or argon ion milling. This approach was used for fabrication of 2D array composed from metals and semiconductors, mainly using polystyrene beads and molecular materials (protein) as a nanomask. In this way, 2D array of Pt, Ag, Si, and magnetic nanoparticles with characteristic size of down to 10 nm were fabricated, and their properties were investigated (review in Ref. [1]).

However, for many applications and fundamental studies it is useful to establish high perfection epitaxial nanoobjects. It demands the substrates and nanomasks with special properties allowing the epitaxial process

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to occur. The substrate material and the mask (nanospheres) should be persistent to substrate cleaning procedure and thermal treatment under ultra-high vacuum (UHV) to achieve the best conditions for epitaxial growth of the materials to be deposed. It is hardly possible to fabricate epitaxial nanoobjects by the matrix of organic based materials. For this reason, an inorganic nanomask is desirable for fabrication of epitaxial nanoobjects. One of the promising candidates is opalline nanospheres.

2. The fabrication of 2D-3D ordered arrays

Fabrication of 2D/3D ordered opal matrixes (as well as 2D ordered inorganic nanomask), based on monolayered and multilayered opalline super structure of designed geometry were developed. It is supposed to be compatible with the high temperature treatments to obtain atomically clean substrate that opens an opportunity to fabricate 2D ordered array of epitaxial nanodots and metalattices. The developed nanotechnology is starting to use for successful fabrication of 2D periodic array of well-shaped ZnO quantum dots, and conductor metalattice of Ni, Ti with dimensions of 100–300 nm.

Monosized silica spheres were synthesized through by hydrolysis of tetraethyl orthosilicate (TEOS) in ethanol in the presence of ammonium hydroxide [2]. The size and uniformity of the particles being synthesized are affected by the concentration of ammonium, water, and TEOS. Using this method, the spheres with the diameter ranging between 100 and 300 nm (with the deviation down to 5%) were synthesized [3].

The developed procedure of natural sedimentation combined with capillary contraction was used to fabricate uniform monolayer of SiO₂ spheres. SiO₂ ethanol suspension was brought in between two horizontal plates with a controllable distance between them (0.1-0.5 mm), with one of the plates serving as a substrate. The solvent was evaporated at a given rate, that the evaporation interface movement rate was varied in the range of 1-2 mm per day. The SiO₂ concentration in suspension of 0.01 wt.% was using. As a result, a continuous monolayer film of ordered SiO₂-spheres formed on the greater part of the substrate area. The single crystal domains were as large as 0.6 mm in size. Multilayered opalline structures have been prepared by deposition on vertical substrate during solvent evaporation (Fig. 1a) [4], while monolayered films have been fabricated by solvent evaporation inserted between two plates, one of which is the substrate [3] (Fig. 1b). Also some of the publications have been devoted to preparation of the opalline films [5-9].

Mono- and multilayered opal superstructures were formed on the top of sapphire (or Si) substrate, followed by thermal annealing and plasma etching. As an example, the layered opalline structure image in atomic force microscope (AFM–NTMDT) is shown in Fig. 2. As can be seen, the triangular arrangement of SiO₂ spheres corresponding to either a (1 1 1) surface of a FCC system or a (0 0 0 1) surface of a HCP one is formed. The long range order of nanospheres is apparent from Fourier transform (FFT) of AFM images (see right panel of Fig. 2). Typical domain size in these samples ranges from a few hundredth μ m² for monolayered to a few tenth mm² for multilayered opal array.

For imbedding of materials into opal superlattice two different methods were used—vacuum deposition and liquid infiltration:



Fig. 1. Deposition on vertical (a) and horizontal (b) substrates (grey).





Fig. 2. AFM image (a) and fast Fourier transform (b) of opal multilayered structure with sphere diameters of 280 nm.

(1) The substrate with opal superstructure on its top is put into the growth UHV chamber, annealed to remove residual impurities and kept under optimal temperature for growth. During material deposition the film growth takes place on the substrate against the opal sphere voids. Simplified procedure includes deposition of the materials (ZnO, Ti) onto the top of monolayered opalline structure, where both modulate discontinuous (for small thickness) film on the top of the first opal layer and quantum dots in the opal sphere porous of the first sphere layer are formed.

(2) After opalline array was prepared, the void spaces were fully infiltrated with a liquid precursor—Zn(NO₃)₂·nH₂O(concentration equivalent to 20–30 nm film of ZnO), followed by thermal decomposition (at 450–600 °C) of nitrate to oxide. Two types of opal matrixes were used for infiltration: "dried" (at 150 °C) opal samples and "annealed" (5 h at 1000 °C in air)



Fig. 3. AFM image of Ti deposited onto multilayered opal matrix (left panel) and schematic (right panel) of the deposition process.

with density 1.14 g/cm³ ("higher" porosity) and 1.51 g/cm³ ("lower" porosity) respectively.

Fig. 3 demonstrates a schematic (right picture) and AFM image (left picture) of ordered Ti clusters in opal matrix (opal nanoball diameter 260 nm) obtained by the

first method. After Ti deposition one could assume two type of Ti clusters: (1) inside the SiO_2 sphere voids (estimated size about 30 nm) and (2) clusters on the topmost opalline monolayer with typical size of 150 nm. The AFM image of Ti/opal system (left panel of Fig. 3) exhibits these two types of ordered Ti clusters.



Fig. 4. AFM/MFM images of Ni film (60 nm) and nanoparticles ($D_m = 70$ nm) on opal array. Ni 60 nm film: (a) topography contrast, (b) MFM contrast, (c) quazi 3D topoimage; Ni nanoparticles on opal, (d) superposition of magnetic (yellow) and topocontrast (blue), (e) MFM FFT image, and (f) superposition of AFM and MFM images.



Fig. 4. (Continued).

Fig. 4 presents preliminary experiments with imbedding of Ni nanoparticles by ultrasonic spraying of suspension. Ni nanoparticles were prepared by electroerosion evaporation in inert media. Ni films were deposited onto opal matrix in high vacuum by thermal evaporation. As could be found from the AFM, MFM data Ni imbedding into opal matrix leads to the formation of ordered 2D structure consisting from magnetic nanoparticles.

All fabricated semiconducting and metallic superstructure were characterized and studied by atomic and magnetic (for Ni) force microscopy and electron spectroscopy techniques.

3. Electron spectroscopy data

The electronic structure, elemental and chemical composition of the interface formed upon deposition and/or infiltration of ZnO into opal matrix (bulk and monolayered) and bulk single crystalline ZnO (for comparison) have been studied by electron spectroscopy (XPS, AES and EELS methods). Experiments were performed with ESCALAB-5 (VG Scientific)

electron spectrometer. The energy resolution during XPS experiments was 1.0 eV (for Al K α line) and 0.5 eV at EELS studies.

The main features in the XPS spectra of ZnO/opal are O 1s lines corresponding to oxygen states in ZnO and SiO₂ compounds and lines due to photoemission from inner Si 2p and Zn 3p core levels which have a similar structure for both type of investigated objects—ZnO infiltrated in bulk opal matrix and ZnO deposited onto monolayered opal structures. In Fig. 5 photoemission spectra of O 1s, Zn 3p and Si 2p core levels (left side) and EELS spectra taken at energy of incident electrons of 1000 eV (right side) for ZnO and ZnO deposited into monolayered opal matrix are presented.

One can suppose from the above presented figures that electronic structure for two types of investigated samples is slightly different. As can be seen from the XPS spectra the lineshape of Zn 3p photoemission line is similar for ZnO and ZnO–opal system but shifted by approximately 1 eV to higher binding energy. A slight increase of intensity at higher binding energy peak (93 eV) is related to emission from Si 2p level due to Al K α satellite. The line widths and splitting in Zn



Fig. 5. XPS (left panel) and EELS (right panel) spectra taken from ZnO single crystal (a) and ZnO-opal (b) systems, respectively.

 $3p_{3/2}-3p_{1/2}$ doublet are the same in both systems. The maximum of O 1s line is shifted by 1.6 eV to higher binding energies for ZnO embedded in opal matrix (see inset in the left image of Fig. 5). Besides, broadening of the O 1s photoemission line could be observed. The change of the line shape and energy position is affected by superposition of O 1s lines corresponding to ZnO and SiO₂ in spectra of ZnO/opal system.

In EELS spectra presented on the right side of Fig. 5 one can find broadening of the bulk plasmon, changing its energy position (18.5 eV in ZnO and 21 eV in ZnO-opal system) and disappearance of 5 eV peak for ZnO embedded in opal matrix relative to clean ZnO sample. These broadening and shifting of the bulk plasmon are possibly related to presence and superposition of signals from SiO₂ and ZnO.

Note that in our spectroscopic measurements we could not detect a remarkable changes in the electronic structure (due to quantum size effects) between bulk single crystalline ZnO and ZnO/opal system (with

characteristic opal nanoball size of 280 nm). This fact apparently is related to moderated energy resolution of the XPS experiment for measured ZnO cluster size.

4. Photoluminescence in ZnO–opal structures

The photoluminescence (PhL) experiments were performed using a N₂ laser with the 337.1 nm wavelength emission, 900 psec pulse duration and I =23 kW output power. The emission signals were collected by a lens (aperture 0.2 rad) in a back scattering configuration. Then the luminescence is dispersed by a monochromator MDR-6 and detected by a photomultiplier with a spectral resolution better then 0.1 meV.

In Fig. 6 we present the PhL spectra ZnO film with 90 nm thickness, deposited onto glass and opal substrate (opal nanoball diameter is 280 nm) by electron evaporation technique. They illustrate the transformation of the PhL spectrum of ZnO–opal structures in dependence on the registration angles of 20° , 35° and



Fig. 6. Left panel: PhL spectra of the ZnO film with a thickness of 90 nm, deposited on glass (1) and opal at the different registration angles 20° (2), 35° (3) and 45° (4); T = 80 K. Right panel: AFM image of the ZnO film deposited on opal with nanoball diameter of 280 nm.

 45° , measured against the surface normal. For comparison, there is also PhL spectrum (curve 1) of the ZnO film evaporated on the glass substrate without opal structures. In latter the only one-exciton emission peak with a maximum at 3.33 eV is observed. However, the luminescence of ZnO–opal structures at the angles 35° and 45° (curves 3 and 4) demonstrates the splitting of the exciton line into the several narrow peaks with the maximum at 3.33; 3.373 and 3.413 eV that belong to the shorter wavelength spectral region. This effect is caused by the size quantum effect originated in the ZnO quantum dots that are formed in the opal sphere voids of the first opal layer.

Its effective excitation by the nitrogen laser is occurred at the registration angles $35^{\circ}-45^{\circ}$. The



Fig. 7. PhL spectra of opal without ZnO (1) and infiltrated ZnOmultilayered opal (2,3) systems.

absence of the short wavelength peak at 3.413 eV on the curve 4 (Fig. 6) can be explained by luminescence reabsorbtion because of ZnO film cap that is on the top of the first opal layer. These ZnO discontinues film consists of ZnO-islands with 50–60 nm lateral dimensions, and its typical luminescence spectrum (curve 2) with only smooth peaks is observed.

Fig. 7 illustrates the changes in the PhL spectra (curves 2 and 3) of ZnO/opal structures before and after annealing for improving the perfection of ZnO nanocrystals (nanodots). ZnO/opal structures for these investigations were fabricated by infiltration of ZnO into multilayered opal matrix. For comparison, curve 1 presents of the luminescence spectrum of the initial opal matrix. The photoluminescence spectra were detected at room temperature. These spectra demonstrate the bright exitonic line in ultraviolet spectral region that allows to propose a possibility ultraviolet emitters design on the base of the ZnO/opal photonic band gap structures.

5. Conclusion

The way for fabrication of 2D and quazi-3D ordered arrays of nanodots and metalattice conductors based on opal structures is presented and discussed.

Ordered arrays of semiconducting (ZnO) and metallic (Ni, Ti) nanodots are fabricated and characterized by AFM/MFM, XPS, AES, and EELS.

The luminescence of quantum dots in the exciton ultraviolet range was found on the ZnO–opal structure

with the small zinc oxide thickness deposition. The increase of film thickness up to 300 nm of deposited ZnO results in bulk like PL spectra and the size quantization of electronic functions disappears.

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