The Influence of the Phase Transition in the Energy of Photonic Band Gap in the Opal Based Composites.

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Abstract: - We have prepared composites by means of the full filled method of the opal matrix with vanadium dioxide or with silver iodine, which have photonic properties and a semiconductor-metal phase transition in the interval of temperatures of 55-75 °C (VO₂) or a semiconductor-super ionic material transition in the interval of temperatures of 110-160 °C (AgI). From the study of the optical spectra on reflection of these composites it has been determined that the composites has a wide photonic band gap in the visible range of the spectrum, and its energy changes the value during the phase transition. It has been measured in the synthetic composites the thermal displacement during the phase transition, the position of the photonic band gap, the displacement has been compared with the change of the refraction index in both VO₂ and AgI polycrystalline films.

Key-Words: - Photonic crystals, Semiconductor-metal phase transition, Superionic, Thermal Hysteresis.

1 Introduction
The present work has been devoted to the study of the optical properties of the photonic crystals, in a concrete way to the synthetic composites based on opal matrix and materials with phase transition (vanadium dioxide and silver iodine). The basic property of the photonic crystal with a periodic three-dimensional structure, is the existence of the photonic band gap, that is to say the spectral interval in which the propagation of the electromagnetic wave is forbidden for some (or for all) the direction of the wave vector [1,2]. The use of material with semiconductor-metal phase transition (VO₂) or semiconductor-super ionic material (AgI) as material to fill the hollows in opal matrix will allow us to manipulate the parameters of the photonic band gap [3].

2 Sample preparation
The vanadium dioxide (VO₂) has semiconductor-metal phase transition of the first type [4,5], the equilibrium temperature of the phases is $T_c = 67 ^\circ$C. To upwards value of $T_c$ this material is a metal with tetragonal symmetry in the lattice, under the $T_c$ it is a semiconductor with monoclinic symmetry [4]. During the phase transition into the VO₂ takes place a strong change of both the electrical and optical properties [5,6]; that is to say the change of the electrical conductivity and the optical constants (dielectric constant -ε- and refraction index -η-). During the phase transition the new phase (metal) appears as nuclei in the bulk of the old phase (semiconductor); these nuclei grow if the temperature of the sample increases to higher values that $T = T_c + \Delta T$. If the temperature falls to smaller values that $T = T_c - \Delta T$, the new phase (semiconductor) also appears in the bulk of the old phase (metal). For single crystal the $\Delta T$ value is ~2-3 °C and the hysteresis loops (of conductivity or optical constants) during the phase transition is narrow and has the thermal...
branches (heating and cooling) practically vertical. The hysteresis loop of the VO$_2$ polycrystalline film is wider (20-30 °C) and it presents a displacement of the branches because the temperatures. This can be explained, considering that the film consists of a great number of crystalline grains with different sizes and defects. As a consequence, this takes to a strong distribution of the number of elementary loops (that is to say, the elementary loop is the loop of each concrete grain of the film) with respect to the widths and to the positions in the temperatures scale. The main loop of the VO$_2$ film, which is built by the sum of all elementary loops, is wider and has more displaced branches because the temperature.

The silver iodine (AgI) has a semiconductor-super-ionic material phase transition with the equilibrium temperature of the phases at $T_c = 140$ °C. During the phase transition, if the growing temperature gives place to the fusion of silver sub-lattice, then the big increase of the conductivity of the sample favors the appearance in parallel of both the electronic conductivity, the ionic conductivity, and the displacement of the optical absorption border with direction toward greater wavelengths (from ultraviolet to blue). The AgI film also presents the thermal hysteresis with a wide loop (30-40 °C).

For the synthesis of the composites, we have used as initial matrix the synthetic opals with cubic lattice structure and face-centered. This lattice has been built with solid and homogeneous spheres of amorphous SiO$_2$ by close-packed. It is necessary to notice that near to 26 % of the total volume of the opal matrix are holes linked among spheres; those which are possible to fill with another material. The average diameter of the spheres is 230±5 nm. The opals have a "poly-domain"-type structure, the size of a domain with high degree ordering of spheres is in the interval of 30-100 μm. The Fig.1 present the image of the superficial morphology of a part of this domain in synthetic opal, the image was obtained by means of an atomic force microscope model Quesant-250.

Fig. AFM-image of the opal surface (1μm x 1μm).

The formation of the VO$_2$-based composite has been carried out in two stages: in the first one, the holes of the opal matrix have been filled with a V$_2$O$_5$ and nitric acid solution. In the second one the V$_2$O$_5$ was reduced to VO$_2$ by thermal annealing in vacuum. The formation of the AgI-based composite has been carried out for immersion of the opal matrix in silver iodine melt in vacuum. The difference between the synthetic composite and the initial opal consists in that in the composites the holes among spheres have been filled with VO$_2$ or crystalline AgI, which present phase transition.

3 Methodology
The domains can be separated by visual inspection from the composite because highlight on the surface like brilliant stains of light reflected in the red range of the electromagnetic spectrum. The wavelength of the light at maximum of reflection is determined by the Bragg's formula: $\lambda_m = 2 \cdot d_{111} \cdot n$, where $d_{111}$ is the space period of the structure in the direction [111], $n$ is refraction index of the composite, the beam of light usually falls on the normal direction of the plane (111) of the photonic crystal surface. In the study process, the image of this domain has been projected with big amplification (~10-20 times) toward the optical slit of the spectrometer. The use of the slit allows us to choose different areas of the domain for measurements of the spectra.
4 Results and discussion
The Fig. 2 shows the measured spectra of like-mirror reflection of light for a domain of the VO₂-opal composite, which correspond to the semiconductor phase (T=15 °C) and metal (T=75 °C) of the VO₂. The intense and wide maximum in the reflection spectra of the light are a consequence of the Bragg's diffraction for electromagnetic wave in the space-periodic structure and demonstrate the existence of the photonic band gap for photonic states in the direction [111]. It is possible to see that the maximum of reflection $\lambda_m=639$ nm, which corresponds to the energy of the photonic band gap, moves during the semiconductor-metal phase transition toward short wavelengths ($\lambda_m=598$ nm) diminishing the intensity.

The Fig. 3 present the loop of thermal hysteresis of the position of the maximum in the reflection spectra of the VO₂-opal photonic composites.

Qualitatively, this displacement of the maximum of the reflection spectrum has good agreement with the change of the refraction index $\nu$, in the VO₂ film during its phase transition from the semiconductor to the metal states. It is known that with the increase of the temperature the real part of the $\nu$ diminishes its value. In Fig.4 is demonstrated the above-mentioned and the hysteresis loop of the $\nu$ is presented for the VO₂ polycrystalline film, which has been obtained with an ellipsometer model ELX-02C with variable angle and rotational analyzer; the measurements were made in the range of temperatures for the phase transition. As a result of the displacement of the reflection index value, the maximum of Bragg's reflection moves toward short wavelengths of the spectrum.

![Fig.4 The thermal hysteresis loop of $\nu$ in VO₂ film.](image)

We have measured also the analogous spectra of reflection for the AgI-opal composite, which correspond to the semiconductor phase (low temperatures) and to the phase of the superionic material (high temperatures), see Fig.5.

However it is necessary to notice that in the last case (AgI), the displacement of the maximum of reflection is smaller and when the temperature increases, this maximum moves in the opposite direction to the displacement of the maximum of the VO₂, that is to say in the direction of greater...
wavelengths of the spectrum: from 605 nm up to 620 nm.

Fig. 5 Reflection spectra from (111) plane of AgI-opal before (T=20 °C) and after (T=150 °C) during the semiconductor-superionic material phase transition respectively.

From these spectra we have built for different temperatures the thermal hysteresis loop of the energy of the photonic band gap, see Fig. 6.

Fig. 6 The thermal hysteresis loop of PBG of AgI-opal.

The displacement of the maximum in the reflection spectrum with increase of the temperatures has good agreement with the character of the change of the refraction index N of the movie of AgI during its phase transition of the state semiconductor to the super-ionic one.

Fig. 7 The thermal hysteresis loop of N from AgI film.

The Fig. 7 shows our ellipsometric measurements of the hysteresis loop of N from a AgI polycrystalline film. As it continues from this figure, increasing the temperature, the value of the real part of the N increases.

We also notice that the hysteresis loops, obtained for the energy of the photonic band gap in a domain of the VO2-opal composite (Fig.3) or AgI-opal (Fig.6), are wider and have extended branches (of heating and cooling) with respect to the temperature, if we compare with the narrow loops and with practically vertical branches for single crystals. At the same time those loops are narrower and its branches extend in smaller proportion with respect to the temperature, if we compare with the loops of VO2 or AgI polycrystalline films. This means that the effects of the size take place in composites (the size of the holes in opal is the cause of the wide loop of the composite in comparison with the single crystal loop) and also that the sizes of the crystals inside the opal holes are bigger in comparison with the sizes of the grains in the polycrystalline films. Also the equilibrium temperature of the semiconductor-metal phases in VO2-opal composite practically is similar to the Tc of the VO2 single crystal, this indicates a stoichiometry of the material, which full the opal holes; it is known that the stoichiometry deviation for oxygen or for vanadium is the main cause for decreasing the phase transition temperature in...
VO₂. However, we cannot conclude this on the composite AgI-opal, where the equilibrium temperature of phases is smaller than Tc in the single crystals or AgI films. This means that it has not been possible to reach the stoichiometry during the synthesis of AgI in the holes of the opal. The absence of stoichiometry in the material diminishes the Tc from 145 °C to 120 °C, and produces narrow hysteresis loop and increases the value of displacement of the branches of the loop.

5 Conclusion
On this way, presently work has been studied the directed photonic crystal, which is a three-dimensional periodic lattice of SiO₂ amorphous spheres opal (with a period ~230 nm) with crystalline material in the holes among spheres. The crystalline material (VO₂ or AgI) presents a phase transition, due to this transition takes place a strong change of the value of its optical constants (dielectric constant -ε- and refraction index -N-) and as a consequence the optical properties of synthetic composites (for example the energy of the photonic band gap). The advantage of this composite is the high dielectric contrast due to the high value of the refraction index of the material of filler and also its strong change of properties during the semiconductor-metal or semiconductor-superionic material phase transition. The studied materials can be used to manipulate the beams of light at selected interval of wavelengths.

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