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OPTICAL PROPERTIES

Optical Properties of Multilayer $BaTiO_3/SiO_2$ Film Structures Formed by the Sol–Gel Method

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Abstract—Multi-layer film structures $BaTiO_3/SiO_2$ with a thickness of ~1 μm containing up to 14 pairs of layers were synthesized by the sol–gel method with sequential heat treatment. It is shown that the synthesized structures are X-ray amorphous. The formation of bands in the transmission and reflection spectra caused by interference effects is demonstrated. A more regular structure exhibits a photon band gap (opacity band) in the visible range with main minimum at 636 nm and corresponding maximum in the reflection spectra. Dispersion characteristics of barium titanate films with different concentrations of initial sols were studied and an increase in the refractive index with an increase in the concentration of sol was demonstrated. For a sol with a concentration of 60 mg/ml, the refractive index in the spectral range of 390–1600 nm is 1.88–1.81. The prospects of sol–gel technology for the formation of $BaTiO_3/SiO_2$ structures for nanophotonics and solar radiation converters are discussed.

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INTRODUCTION

Interest in development and improvement of the methods for the forming multilayer film structures with periodically changing refractive indices of layers is primarily due to a wide range of applied problems which can be solved using such structures. Multilayer interference coatings, also known as Bragg mirrors or one-dimensional photonic crystals, with a reflection band localized in different areas of the optical range, are widely used in laser technology and optical instrumentation as laser mirrors, antireflection coatings, interference filters, etc. Multilayer coatings, which reflect IR and transmit visible radiation, are of considerable interest for manufacturing windows for buildings and vehicles especially in countries with high annual average temperature. Coating components (layers) may contain luminescent lanthanide ions radiating in different spectral regions. The reduction of the reflection coefficient in a wide spectral reflection region in combination with intense luminescence of doped ions in the sensitivity range of solar cells is used to increase the efficiency of photovoltaic cells with such coatings [1].

On the other hand, structures such as Bragg mirror/microresonator with excited ions/Bragg mirror are of great interest for studying fundamental problems of spontaneous emission of excited light centers in the conditions when the density of photonic states is modified [2].

Technologies of formation of multilayer structures with periodically changing refractive index using various dielectric and semiconductor materials are the subject of permanent development. There are a number of methods including magnetron and electron beam evaporation [3, 4], plasma chemical gas-phase deposition [5], electrochemical formation of porous silicon [6–8] and the sol–gel method [9–12].

Among the various methods of forming both undoped and lanthanide-doped multilayer coatings, the sol–gel method is of particular interest. The method does not require energy-demanding vacuum equipment and, accordingly, can be applied on large areas at a relatively low cost. The refractive index and the film thickness can be varied by choice of precursor, the viscosity and concentration of the sol, deposition rate, regimes of heat treatment, and other factors. An essential condition for forming a multilayer peri-

odic structure is that the sol should preserve its properties for a sufficiently long time, since any changes in the manufacturing process of the structure result in uncontrolled changes in the film thickness, which ultimately leads to a deterioration in the quality of the multilayer structure. The development of sol–gel technologies for the formation of high-quality multilayer structures is of interest. The components of photonic crystals should differ in refractive indices. Perovskites-aluminum-titanium composites, strontium titanate, barium titanate, etc., have relatively high values of refractive indices (about two); however, in contrast to titanium dioxide [9–11], their application for the synthesis of photonic crystals has not been studied in detail. The values of the refractive indices of thin films depend on the methods of their production, heat treatment modes, and other factors.

In this paper we analyze optical transmission and reflection spectra of multilayer film structures of barium titanate/silicon oxide ($BaTiO_3/SiO_2$) formed by the sol–gel method using centrifugation and heat treatment.

EXPERIMENTAL

The sol for forming films of kerogel SiO_2 included ethanol (C_2H_5OH), tetraethylorthosilicate ($Si(C_2H_5O)_4$), distilled water (H_2O), and hydrochloric acid (HCl). To prepare the sol, ethanol and distilled water were mixed, then the resulting solution was brought to pH = 1 by adding concentrated hydrochloric acid. After that, tetraethylortosilicate was added to the solution.

The sols prepared for forming films of kerogel $BaTiO_3$ had a concentration of 45, 50, and 60 mg/ml. First, a solution containing titanium isopropoxide and acetic acid was prepared, which was thoroughly mixed until all components were dissolved. Subsequent addition of barium acetate to the solution resulted in a stable film-forming sol.

Barium titanate and silicon oxide films were centrifuged at 2700 rpm for 30 s. Each layer was dried at a temperature of 200°C for 10 min, then heat treated at a temperature of 450°C for 30 min.

A multilayer structure containing 14 alternating layers of $BaTiO_3$ and SiO_2 was formed on a quartz glass substrate using a barium titanate sol with a concentration of 60 mg/ml. Transmission spectra were recorded in the process of sample preparation after the addition of each pair of $BaTiO_3/SiO_2$ layers and subsequent heat treatment. After applying 14 layers, additional heat treatment was carried out at 600°C with a duration of 30 min; then the morphology of the sample was analyzed by scanning electron microscopy (SEM).

Sample No. 2 was prepared using a modified technology of applying the layers. First, one layer of $BaTiO_3$ was applied. The second $BaTiO_3$ layer was applied after drying and heat treatment of the first layer at a temperature of 450°C for 30 min. Next, the second $BaTiO_3$ layer was subjected to drying and heat treatment at a temperature of 450°C for 30 min. After the formation of barium titanate film by this method, a silicon oxide film was formed in a similar mode. As a result, a five-layer $BaTiO_3/SiO_2/BaTiO_3/SiO_2/BaTiO_3$ structure was formed, in which each layer of the material consisted of two successive layers.

For ellipsometric measurements, single-layer barium titanate films were formed on polished monocrystalline silicon substrates with a size of approximately 15 × 15 mm, using sols with a concentration of 45, 50, and 60 mg/ml.

Thickness of films and refractive index were measured using a M-2000V ellipsometer (J. A. Woollam, Inc., United States) in the range of 350–1700 nm. The data were processed using the Cauchy model. Transmission spectra were measured on a CARY-500 Scan UV-VIS-NIR spectrophotometer (Varian, United States & Australia). X-ray diffraction studies were carried out on a DRON-3 automated X-ray diffractometer using monochromatic CuK_α radiation. Morphology of the films was analyzed using a Hitachi S-4800 scanning electron microscope.

Optical reflection spectra were recorded on a MDR-23Y monochromator equipped with a 1200 lines/mm diffraction grating. The spectral resolution was 0.5 Å. The light source was a tungsten lamp with a ribbon filament with a power up to 170W. A R9110 photoelectron multiplier (Hamamatsu, Japan) was used as a detector of optical signals. The spectra were corrected taking into account the spectral dependence of the radiation detector sensitivity, the spectral characteristics of the light source and the monochromator.

RESULTS AND DISCUSSION

Figure 1 shows dispersion graphs obtained for films formed of three barium titanate sols on monocrystalline silicon. According to ellipsometry data, the thickness of barium titanate films ranges from 48 to 63 nm and increases monotonically with increasing sol concentration (Table 1). The refractive index also depends on the concentration of sol and for the concentration of 60 mg/ml varies between 1.8–1.9.

Table 1. Thickness values of single-layer $BaTiO_3$ films obtained from sols of different concentrations measured at three points of each sample

Sol concentration, mg/ml	Layer thickness, nm
45	48; 48; 49
50	56; 57; 58
60	61; 61; 63

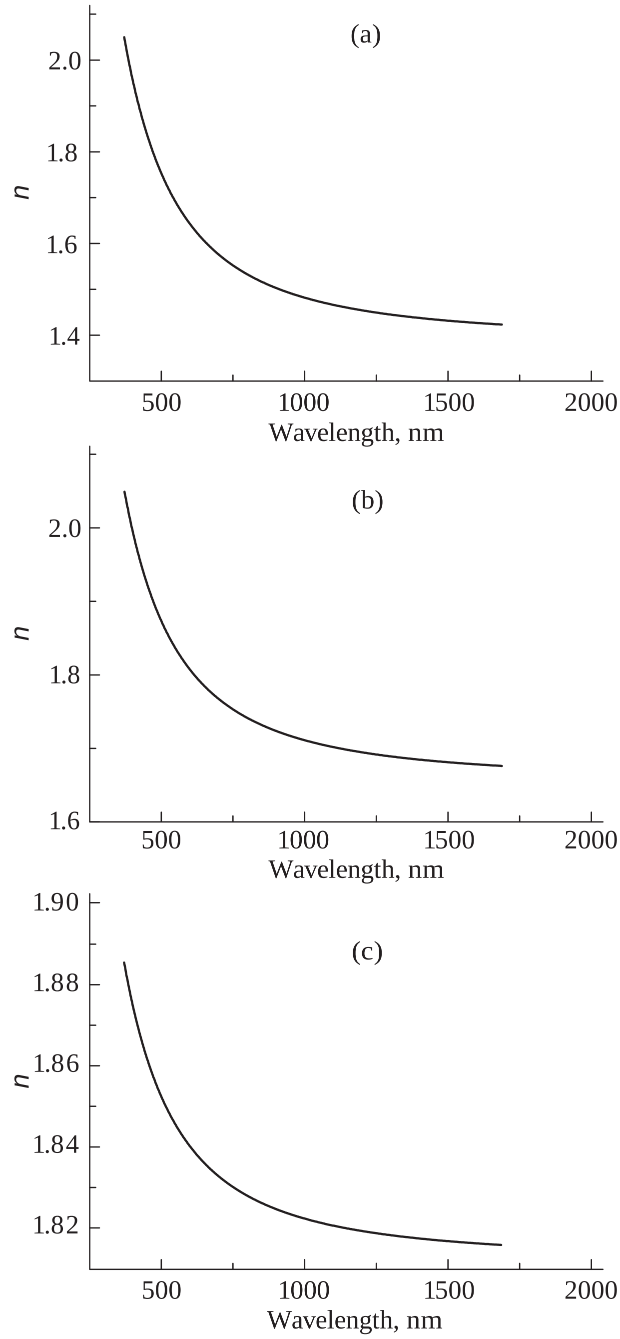

Fig. 1. Wavelength dependences of the refractive index of $BaTiO_3$ films synthesized from sols with a concentration of 45–60 mg/ml: (a) 45 mg/ml, (b) 50 mg/ml, and (c) 60 mg/ml.

Figure 2 shows a SEM image of the structure containing 14 layers. The irregularity of the structure can be caused by changes in the viscosity of the sols during the process of preparing the structure; this question requires additional research. The structure is X-ray amorphous both after heat treatment at 450°C and at 600°C.

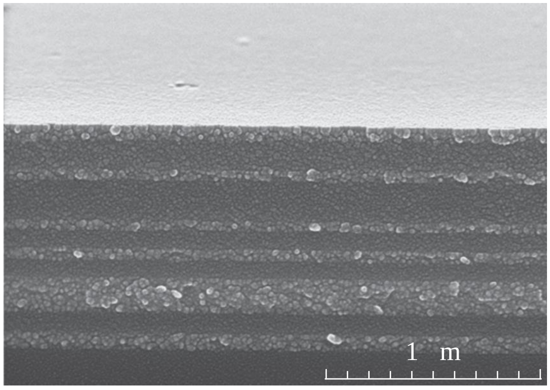

Fig. 2. SEM image of a structure containing 14 layers of $BaTiO_3/SiO_2$ after heat treatment at a temperature of 600°C.

An increase in the number of layers leads to formation of an opacity band, the intensity of which increases with the number of layers. For a final sample with 14 pairs of layers, the minimum of the band is at 693 nm (Fig. 3a) and there is a broad band in the reflection spectrum which corresponds to the opacity band (Fig. 3b). In our opinion, these bands are due to the interference of radiation on a multilayer structure. The mismatch between the transmittance minimum and reflectance maximum in the spectra (Fig. 3c) points to the insufficient quality of the structure, as evidenced by the SEM image (see Fig. 2).

An additional increase in the heat treatment temperature from 450°C to 600°C leads to a significant shift of the minimum from 693 to 652 nm and a reduction in transmittance in a broad range. As it turned out, the increase in the heat treatment temperature results in cracking of the upper layer, which reduces the transmission due to diffuse scattering. According to the modeling carried out by the matrix element method, the observed shift in the spectrum can be related to the change in the optical thickness of the films as a result of the increase in the heat treatment temperature.

Figure 4 shows a REM image of sample No. 2. After heat treatment at 450°C, this sample is also X-ray amorphous and, in comparison with sample No. 1 containing 14 layers, exhibits a more clear opacity band with a minimum at 636 nm and a corresponding band in the reflection spectrum (Fig. 5). It should be noted that the positions of extrema in the reflectance and transmittance spectra of sample No. 2 match. The observed monotonic increase in the thickness of the layers of both materials from the interface with the substrate to the sample surface (Fig. 4a) can be caused both by an increase in the viscosity of the sols and a smaller number of heat treatment operations of the upper layers compared to the lower ones. Consideration of these factors can lead to higher reproduc-

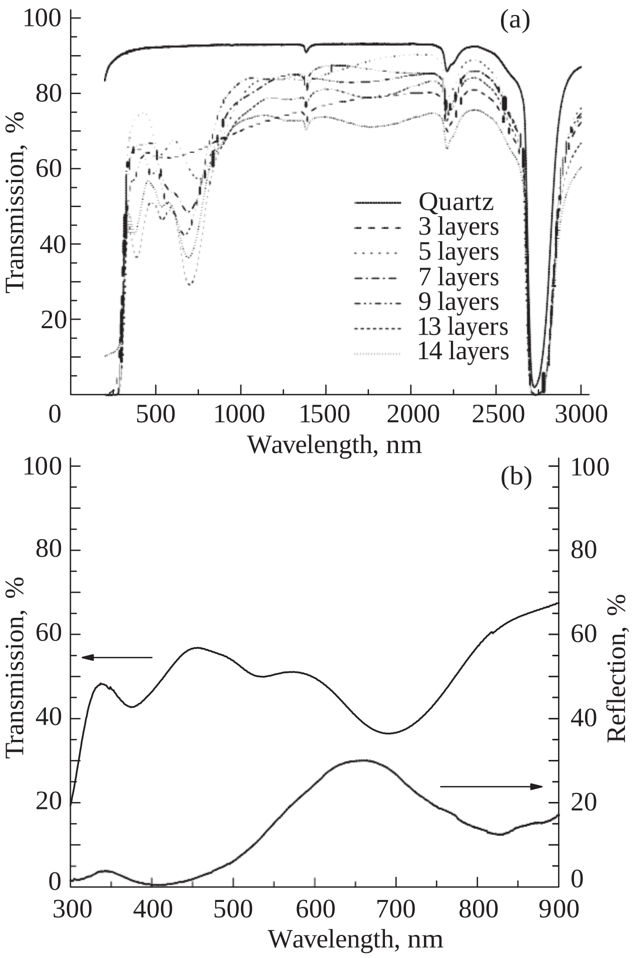

Fig. 3. Optical spectra of structures containing 3 to 14 layers of $BaTiO_3/SiO_2$ on a quartz substrate, after heat treatment of each layer at 450°C: (a) transmittance at 3 to 14 layers, (b) transmittance and reflection at 14 layers.

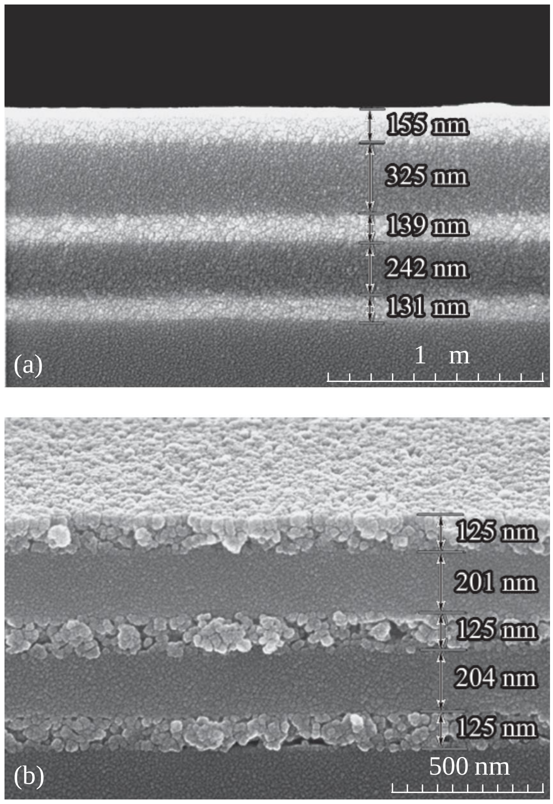

Fig. 4. SEM images of a five-layer $BaTiO_3/SiO_2$ structure (sample No. 2): (a) heat treatment of each layer at a temperature of 450°C, (b) additional heat treatment of the sample at a temperature of 800°C for 30min.

ibility of film thickness. Additional heat treatment of the formed structure at 800°C reduces the deviation in the thickness of $BaTiO_3/SiO_2$ layers (Fig. 4b).

The results obtained show that after further improvements, the sol–gel technology of forming the multilayer $BaTiO_3/SiO_2$ structures can be used to obtain single dimensional crystals and microresoantors. According to the results of the simulation carried out by the matrix element method, optimization of the synthesis of multilayer $BaTiO_3/SiO_2$ structure for achieving the thickness of $BaTiO_3$ and SiO_2 layers of about 84 and 110 nm, respectively (Fig. 6a) can be recommended for forming a photon band gap with an extremum at 636 nm, similar to the structure shown in Fig. 4, sample No. 2. The simulation was performed for films with refractive indices 1.9 (as in amorphous barium titanate film) and 1.45 for silicon oxide. According to the simulation, if the film thicknesses are maintained as constant after reaching values of about 142 nm for $BaTiO_3$ and 283 nm for SiO_2 (the average values for the layers of the structure shown in Fig. 4a, sample No. 2), the photon band gap will have an extremum at 1320 nm and 1332 nm, respectively for the structures of 5 and 14 alternating layers of $BaTiO_3$ and SiO_2.

Thus, for the multilayer structure formed by the sol–gel method consisting of 14 $BaTiO_3/SiO_2$ layers, the formation of bands in the transmission and reflection spectra due to interference effects was demonstrated. A five-layer $BaTiO_3/SiO_2$ structure on a quartz glass substrate was formed by an improved sol–gel method. The structure is characterized spectrally coinciding extrema in the transmission and reflection spectra in the optical range. Additional heating of the $BaTiO_3/SiO_2$ structure at a temperature of 800°C reduces the deviation in the thickness of both $BaTiO_3$ and SiO_2 layers. In the future, it will be of interest to study the values of refractive indices of barium titanate films formed at high processing temperatures. Taking into account the intensive luminescence of lanthanides in silicon oxide [13] and barium titanate [14] films formed by the sol–gel method and the low cost

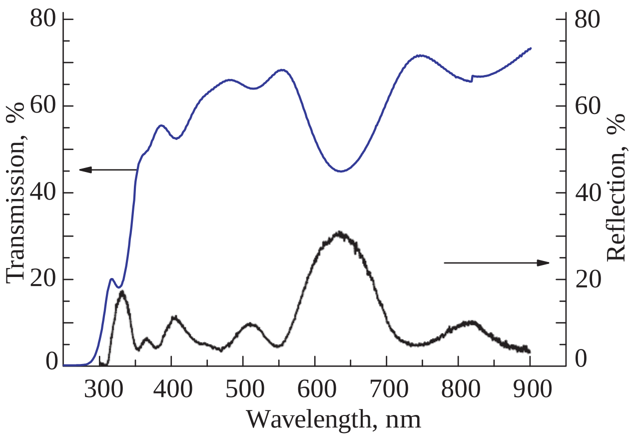

Fig. 5. Optical transmission and reflection spectra of sample No. 2 ($BaTiO_3/SiO_2/BaTiO_3/SiO_2/BaTiO_3$ films on quartz).

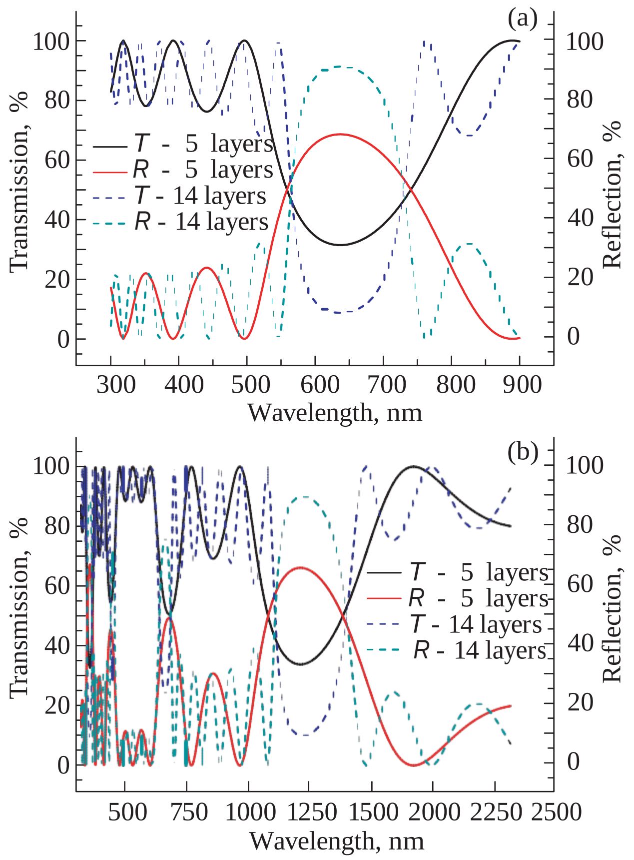

Fig. 6. Results of simulations using the matrix elements method of a multilayer $BaTiO_3/SiO_2$ structure with refractive indices of 1.9 for $BaTiO_3$ and 1.45 for SiO_2. (solid line) Five-layer $BaTiO_3/SiO_2/BaTiO_3$ structure, (dotted line) 14-layer $BaTiO_3/SiO_2$ structure (7 pairs of layers): (a) $BaTiO_3$ with a thickness of 83.8 nm and SiO_2 with a thickness of 109.8 nm, (b) $BaTiO_3$ with a thickness of 142nm and SiO_2 with a thickness of 283 nm.

of this method, the aim of further development of this technology can be the creation of lanthanide-doped luminescent $BaTiO_3/SiO_2$ structures and microresonators, as well as the development of large-area radiation converters luminesing in the visible and IR ranges for solar cells.

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