IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Growth of thin Ag_2S films on silver layers: in situ ellipsometric and conductivity studies

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 6237

(http://iopscience.iop.org/0953-8984/6/31/023)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.147
The article was downloaded on 12/05/2010 at 19:07

Please note that terms and conditions apply.

J. Phys.: Condens. Matter 6 (1994) 6237–6244. Printed in the UK

Growth of thin Ag_2S films on silver layers: *in situ* ellipsometric and conductivity studies

S Russev†, L Vassilev†, V Vulchev‡, L Lutov‡ and Tz Argirov†

† *Faculty of Physics, Sofia University, 5 J Bourchier Boulevard, 1126-Sofia, Bulgaria*

‡ Faculty of Chemistry, Sofia University, 1 J Bourchier Boulevard, 1126-Sofia, Bulgaria

Received 21 March 1994

Abstract. The growth of thin Ag_2S films on silver layers from diluted H_2S gas has been studied by means of *in situ* ellipsometric and DC conductivity measurements. The experimental data from the ellipsometric studies were explained by means of a model consisting of silver and Ag_2S films and a thin layer of H_2O of variable thickness on top of them. The variation in the conductivity of the silver layer could be explained on the basis of the decreasing thickness of the silver layer when a thin Ag_2S film grew on it, together with the increasing reflection of the current carriers from the grain boundaries.

1. Introduction

Thin silver layers have been extensively studied with regard to both their electrical and their optical properties (Chopra 1969, Schumacher 1993). Silver layers have also been proposed as H_2S, SO_2 or Cl_2 detectors based on the change in the surface optical properties when a thin film of Ag_2S or AgCl grows (Brudzewski 1992). The process of film growth on silver surfaces in the presence of diluted H_2S gas has been studied by means of ellipsometric measurements (Tamai 1989) in connection with the application of silver as an electrical contact material. However, in these studies the Ag_2S film thickness has been evaluated at each step by removing the samples from the reaction chamber and consecutive ellipsometric measurements.

Recently we have developed a computer-controlled ellipsometric set-up, which allowed us to record the polarization state of the reflected light in each tenth of a second. So it was possible to study the growth kinetics of the Ag_2S film on the silver surface from diluted H_2S gas, which is the scope of the present paper. Together with the ellipsometric studies, the influence of the growing Ag_2S film was studied by direct measurement of the silver layer conductivity during the process.

2. Experimental details

Silver layers have been grown onto glass substrates via chemical deposition. Three types of solution, containing glucose (40 g l^{-1}) and Roschelle salt (40 g l^{-1}), containing $AgNO_3$ (16 g l^{-1}) and containing $AgNO_3$(10 g l^{-1})+25% NH_3, have been sprayed simultaneously onto the substrates at room temperature. The films deposited thus possess a thickness of about 140 nm.

 © 1994 IOP Publishing Ltd

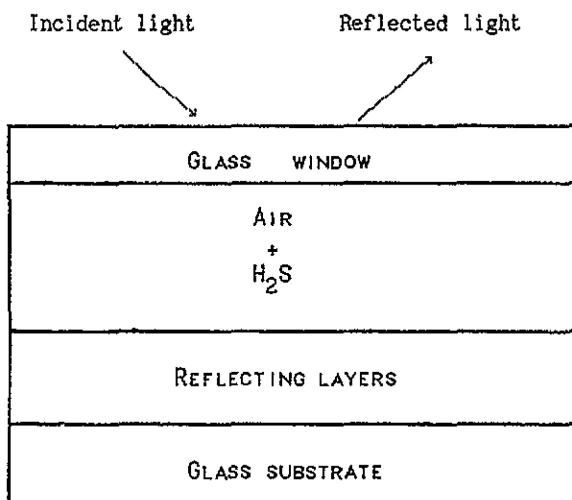

Figure 1. Schematic drawing of the experimental cell, in which the process of Ag_2S film growth is carried out.

Each sample, with four voltage probes soldered with indium, was mounted in a glass chamber, which allowed temperature stabilization, controlled gas flow and ellipsometric monitoring (figure 1).

Time-resolved conductivity and ellipsometric measurements have been performed using a computer-controlled set-up. Four-probe resistivity measurements were used to determine the resistivity variation. The resolution is 1 μV (Prema multimeter attached to the microcomputer via an IEEE 488 bus).

A rotating-polarizer ellipsometer using an He–Ne laser (λ = 632.8 nm) as a light source and at a fixed angle of incidence $\phi = 65°$ was used to determine the change in the polarization state of the reflected light during the Ag_2S film growth (Azzam and Bashara 1977). To prevent a drop in the H_2S concentration due to the reaction in a small sample chamber (of volume approximately 60 ml), a large glass container (30 l) was used for the preliminary preparation of the necessary concentration. The gas was continuously mixed to avoid H_2S segregation. A small pump then moved the gas in a closed cycle through the sample chamber. A buffer volume (2 l) after the pump ensured stable flow in the system. The gas mixture possessed 50% relative humidity in each experiment.

3. Results

The variation in the polarization state is described by means of the so-called ellipsometric angles Ψ and Δ. Ψ is connected with the change in the azimuth of the polarization ellipse, while Δ gives the change in the phase of the reflected light. These two quantities are related to the optical properties of the system via the expression

$$\tan\Psi \exp(\mathrm{i}\Delta) = \frac{R_p}{R_s} \tag{1}$$

where R_p and R_s are the generalized Fresnel reflectance coefficients for parallel (p) and perpendicular (s) polarization of incident and reflected light (Azzam and Bashara 1977).

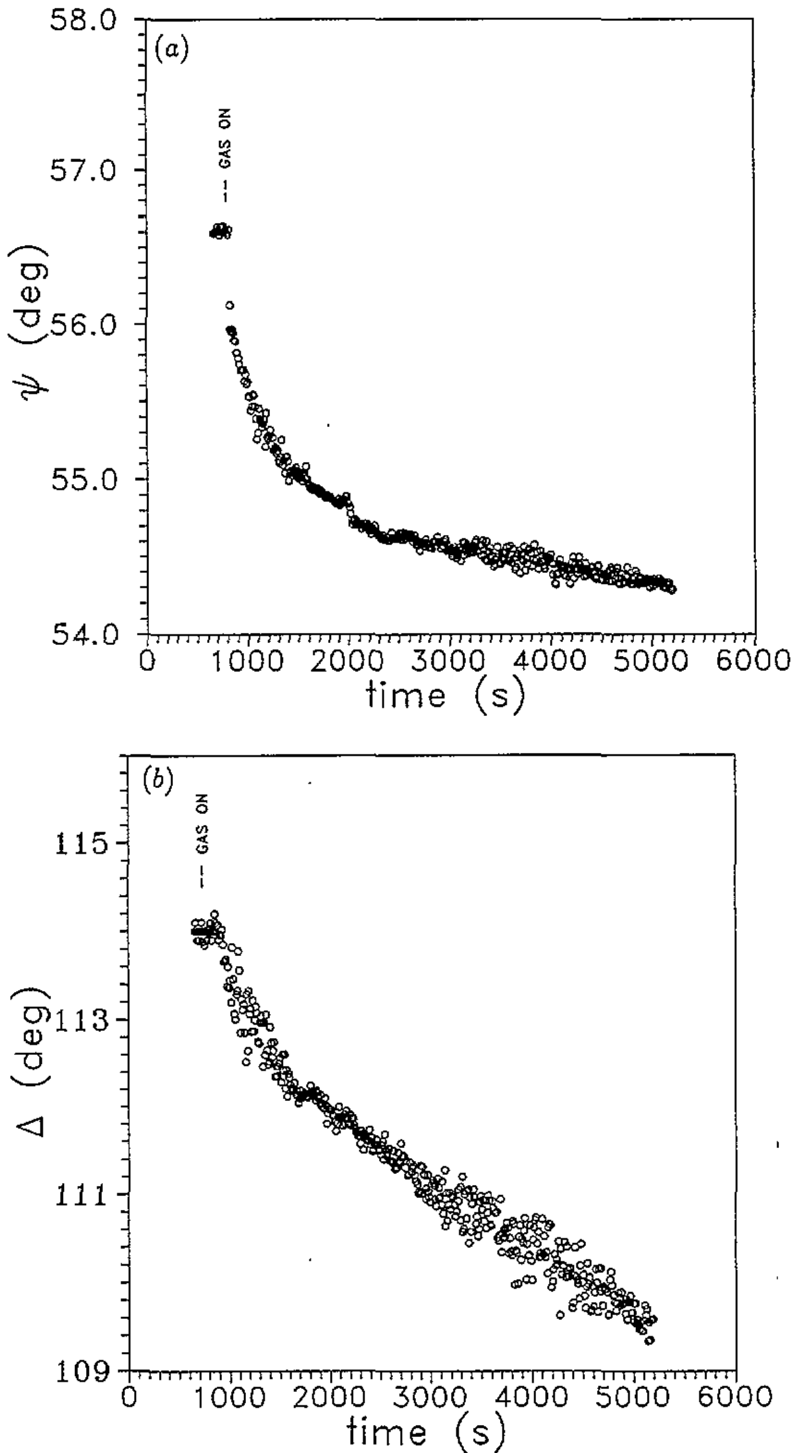

Figure 2. (*a*) The variation in the ellipsometric angle Ψ with time after a gas containing H_2S is let into the sample holder. (*b*) The same as (*a*) but for the other ellipsometric angle Δ. A substrate temperature of 35 °C, a gas temperature of 25 °C and a H_2S concentration of 180 ppm were maintained during the experiment.

We have performed several experiments, using different concentrations of H_2S gas, ranging from 20 to 180 ppm, and different substrate temperatures from 25 to 60 °C. In this paper we shall discussed the common features in these experiments, illustrated by the data for one of the samples. Typical results for the variations in the ellipsometric angles with time are presented in figure 2. The decrease in both ellipsometric angles with time after gas exposure is in qualitative agreement with the behaviour of the system due to the growth of Ag_2S layer (Tamai 1989). Our absolute values differ somewhat from the real value because the chamber has a glass window. One has to keep in mind that the change in the slope of both curves is not directly connected with the change in the sulphuration speed, because the connection between the layer thickness and the ellipsometric angles is non-linear. It should be mentioned that the fluctuations in the ellipsometric angles with time are connected with the process itself, being much larger than the apparatus noise.

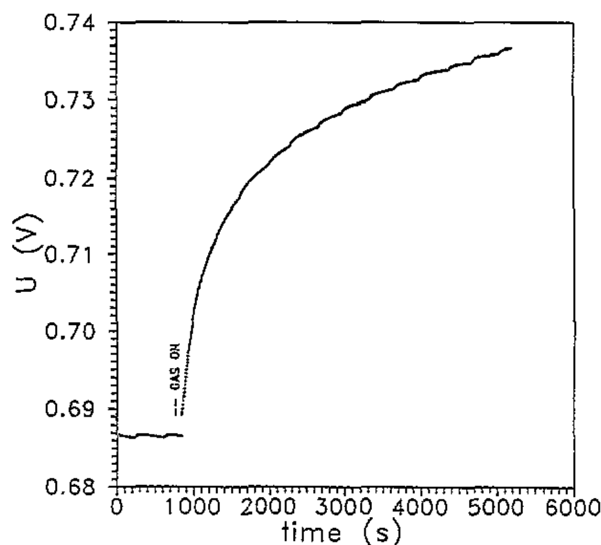

Figure 3. Variation in the voltage drop on the measuring probes with time for the same sample as in figure 2. The small step-like variations are due to the substrate temperature regulation.

In figure 3 is presented the variation in the voltage drop on the measuring probes for the same sample. A steep increase in the sample resistivity was observed after the H_2S gas was let into the chamber. The increase ΔU in the voltage drop varies in time, but its variation can be approximated by the formula $\Delta U = \text{constant } t^{\alpha}$,where $\alpha = \frac{1}{2}$ for the initial process ($t < 3000$ s) and $\alpha \approx \frac{1}{3}$ for the later process of sulphuration. Such behaviour is expected for thin insulating film growth, when the growth is limited by the diffusion of one of the components through the growing film (Tchebotin 1982).

4. Discussion

The ellipsometric angles Ψ and Δ in the case of two or more parallel layers can be presented as a function of their optical constants $N_j = n_j - ik_j$, their thicknesses d_j, the incidence angle ϕ and the wavelength λ of the polarized light:

$$\tan\Psi \exp(i\Delta) = f(N_j, d_j, \phi, \lambda). \quad (2)$$

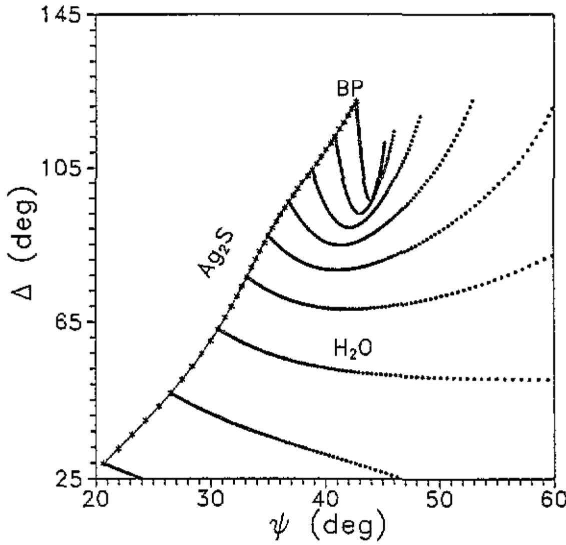

Figure 4. Model calculations for the variation in the ellipsometric angles Ψ and Δ from a Ag_2S film on a Ag layer. The solid line with asterisks labels every nanometre of the film grown. If a thin water film is spread onto the top, this will lead to a change in the ellipsometric angles values as presented by the open circles; each open circle corresponds to an additional nanometer of a water film.

The right-hand side function in equation (2) gives the ratio R_p/R_s in equation (1), once N_j, d_j, ϕ and λ are given. The explicit formulae for calculating that function for an arbitrary number of layers can be found in the monographs devoted to ellipsometry by Azzam and Bashara (1977) and Rzhanov *et al* (1979). In order to interpret our experimental data, we have calculated the ellipsometric angles for a variable thickness of the Ag_2S film on the silver layer, using complex optical constants $N_F = 2.670 - 0.910i$ for Ag_2S and $N_{Ag} = 0.341 - 3.375i$ for silver (Tamai 1989). This calculation has shown that for an Ag layer thickness above 100 nm the silver layer is strongly absorbing and we can neglect the reflection from the Ag–glass substrate interface. The results from the calculations are presented in figure 4 as a solid line; the asterisks on it label every nanometre of Ag_2S film grown (it actually reproduces the data from Tamai (1989). BP indicates the basic point, i.e. reflection from a clean silver surface. We could not fit our experimental data to this curve; that is why we performed a more complicated structure calculation, consisting of a silver substrate, an Ag_2S film and a water film on top of them (figure 5). The optical constant of H_2O is real and coincides with its index of refraction at 35 °C: $n_{water} = 1.332$. These calculations are shown as open circles in figure 4, each open circle labels every nanometre of water film on the Ag–A_2S structure at a given Ag_2S thickness.

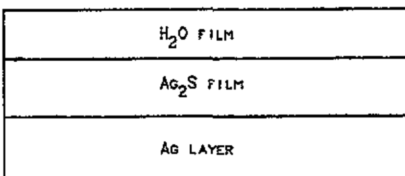

Figure 5. A model for the reflecting layers in figure 1.

In order to compare the experimental data presented in figures 2(*a*) and 2(*b*), we still have to take into account that the glass window of the experimental cell (see figure 1) changes the polarization state of the incident and reflected light. For this purpose, before and after the experiment involving the Ag_2S film growth, we measured the ellipsometric angles Ψ_1 and Δ_1 with the glass window and the Ψ_2 and Δ_2 without it, from which we deduced the correction factors

$$k_\Psi = \frac{\tan \Psi_1}{\tan \Psi_2} \qquad k_\Delta = \Delta_1 - \Delta_2$$

after which all experimental data Ψ_e and Δ_e were corrected according to (Rzhanov *et al* 1979)

$$\tan \Psi = \frac{\tan \Psi_e}{k_\Psi} \qquad \Delta = \Delta_e - k_\Delta.$$

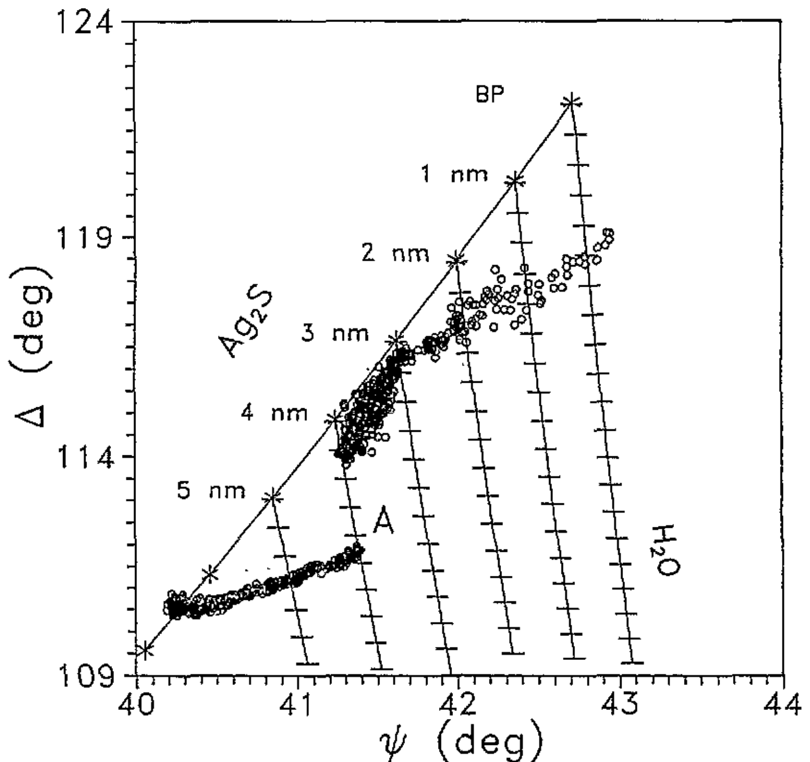

Figure 6. Comparison between the model calculations (the solid lines with asterisks correspond to the Ag_2S–Ag system and the solid lines with horizontal bars for every nanometre of H_2O as a top film) and the experimental results (represented by open circles). A denotes the beginning of the second process of sulphuration carried out on the next day.

The corrected data for Ψ and Δ are presented in figure 6 together with the calculated values for the initial stages of the Ag_2S film growth. On comparison of the experimental

results (represented by open circles in the figure) with the model calculations, it is obvious that at the initial stages of sulphuration the silver surface is covered with water film several nanometres thick. In the process of Ag_2S film growth, the water film diminishes in thickness to abut 1 or 2 nm (the upper set of open circles in figure 6). Upon cutting off the H_2S gas flow, the growth of the Ag_2S film ceases. We performed a new sulphuration process on the next day (the lower set of open circles, starting at A in figure 6). The same trend of variation in the top water film was observed; its thickness was about 4–5 nm at the beginning and diminishes in the process of Ag_2S film growth. The variations in the Ag_2S film and water film thicknesses with time are presented in figure 7. As can be seen from the figure, the initial stages of the sulphuration process are connected with a rapid increase in Ag_2S film thickness and a corresponding rapid decrease in the water film thickness. The time dependence of the Ag_2S film thickness d can be well approximated by the formula d = constant t^{α}, where $\alpha \doteq \frac{1}{2}$, which is in good agreement with the results from the conductivity measurements. For later stages ($t > 3000$ s) the exponent α decreases and approaches the value of $\frac{1}{3}$. At the same time the calculated variation in the water film thickness largely fluctuates with time, which may be partially due to inhomogeneities in the thickness of this film. So the exact values for the calculated water film thickness from equation (2) should be treated with care.

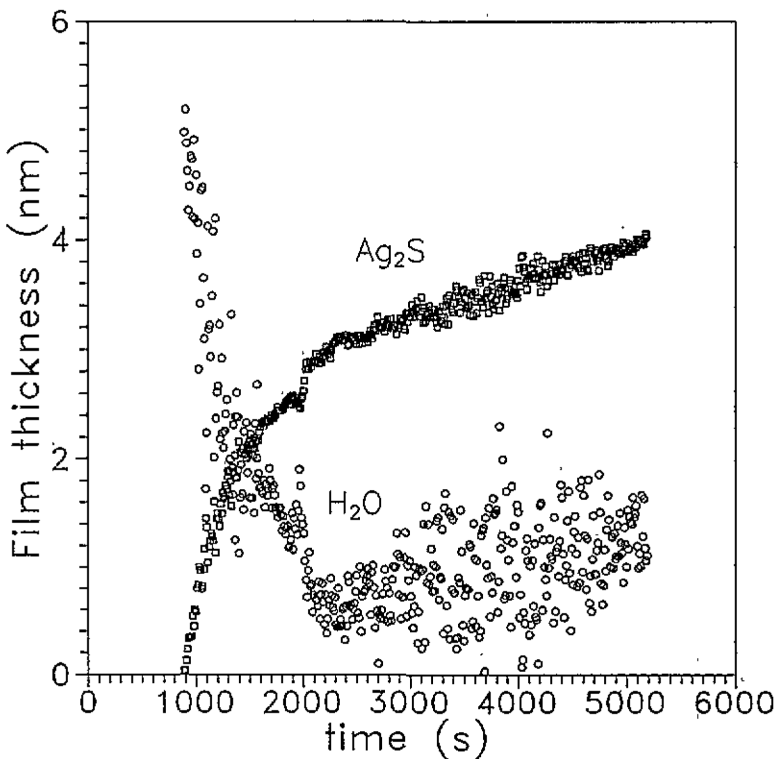

Figure 7. Evolution with time of the Ag_2S film thickness (□) and H_2O film thickness (○) as obtained from the ellipsometric studies and model calculations.

In order to interpret our resistivity measurements (figure 3), we have applied the formula for the resisitivity of silver layers with thickness D below 200 nm (Schumacher 1993):

$$\rho = A + \frac{B}{D} \tag{3}$$

where $A = 1.84\ \mu\Omega$ cm and $B = 5.3\ \mu\Omega$ cm nm. The first term A comes from the bulk resistivity, while B takes into account scattering from the layer's surface and polycrystalline grain boundaries. Our first attempt to explain the variation in the resisitivity with time was as a simple consequence of the diminishing silver layer thicknes when the Ag_2S film grew on it. The relative increase in the total resistance, as calculated from the data presented in figure 3 is 0.07, which implies that the change in the silver layer thickness is 10 nm, about three times the value obtained from the ellipsometric measurements (a Ag_2S film 4 nm thick needs the silver from a 2.8 nm Ag film). This contradiction can be eliminated if we consider the parameter B in equation (3) as a variable. This parameter can be represented in the form (Schumacher 1993, Knäbchen 1991)

$$B = K\frac{R}{1-R} \tag{4}$$

where K may be regarded as a constant in our case and R is the averaged reflection coefficient of the scattering grain boundaries. For silver layers on a glass substrate it was estimated that $R \leqslant 0.06$ (Schumacher 1993). In the process of sulphuration of the silver surface the grain boundaries are decorated first (Tamai 1989); so the presence of sulphur or its compounds may effect the electrical properties of the grain boundaries, and hence it can lead to changes in the reflection coefficient R. If we assume that the variation in the silver layer thickness is the variation obtained from the ellipsometric studies, then this can account for only one third of the observed change in the resistivity of the silver layer resistivity. Then the other two thirds are to be attributed to a doubling of the reflection coefficient R defined in equation (4), i.e. its increase from 0.06 to 0.12 during the process of sulphuration.

Acknowledgments

This work was supported by grant F-232 from the Bulgarian National Science Fund.

References

Azzam R M A and Bashara N M 1977 *Ellipsometry and Polarized Light* (Amsterdam: North-Holland)
Brudzewski K 1992 *Sensors Actuators* B 9 59
Chopra K L 1969 *Thin Film Phenomena* (New York: McGraw-Hill)
Knäbchen A 1991 *J. Phys.: Condens. Matter* 3 6989
Rzhanov A V, Svitashev K K, Semenenko A I, Semenenko L V and Sokolov V K 1979 *Foundation of Ellipsometry* (Novosibirks: Nauka) (in Russian)
Schumacher D 1993 *Surface Scattering Experiments with Conduction Electrons (Springer Tracts in Modern Physics 128)* (Berlin: Springer)
Tamai T 1989 *IEEE Trans. Components, Hybrids, Manuf. Technol.* 12 43
Tchebotin V N 1982 *Solid State Chemical Physics* (Moscow: Nauka) (in Russian)