THERMAL PROPERTIES OF SEMICONDUCTOR ZINC OXIDE NANOSTRUCTURES

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A combination of two methods — laser modulation and 3ω — has been used to determine the heat capacity, heat conductivity, and heat diffusivity of zinc oxide nanostructures. A significant difference between the thermal parameters of zinc oxide nanostructures grown by different technological methods has been revealed. It has been shown that the relatively low heat conductivity and heat diffusivity values of oxide zinc nanostructures are due to both the internal defects and the contact resistance between the film and its base — the substrate.

Keywords: *diluted magnetic semiconductors, zinc oxide, nanostructure, heat conductivity, heat diffusivity, heat capacity, contact heat resistance.*

Introduction. In the last few years, low-sized, nanostructured semiconductors have been the subject of intensive studies since they are promising for obtaining new materials with unique physical proprieties and creating nanodevices [1, 2]. As is known, zinc oxide is widely used in electronic and optoelectronic devices, as well as in hybrid solar cells [3]. The promising prospects of zinc oxide are also due to the fact that when doped with transition metals, e.g., manganese or cobalt, it passes to the class of diluted magnetic semiconductors that are of keen interest for creating a new generation of information storages and recorders, since they permit simultaneous control of their electrical and magnetic properties [4, 5].

In practice, the above materials are often used in the form of very thin films grown on substrates from silicon, sapphire, and technically important glasses. As is known [6, 7], the thermal properties of such nanomaterials may differ significantly from the properties of the crystalline materials of substrates. Therefore, it is essential that the parameters of these materials be determined for those forms and states in which they will be used. Thus, the heat transfer processes in the above structures should be considered as the critical characteristics of these structures determining their thermal properties.

A number of experimental methods for investigating the thermal properties of thin-film, nanostructural materials were developed. Most of these methods are based on the so-called ac calorimetry. These methods were proposed in [8] and improved in [9–13]. There are also experimental methods for simultaneous measurements of the heat conductivity k, the heat capacity C_p, and the heat diffusivity D of finest films [14, 15].

This work presents the results of the experimental investigation of the thermal properties of zinc oxide nanostructures with the use of two independent ac calorimeters for more accurate measurements of the thermal parameters of both the substrate–thin film nanostructure and the film itself.

Technology of Sample Preparation. For substrates, we used thin plates of nanocrystalline silicon and borosilicate glass with typical dimensions of the order of $(10 \times 5 \times 0.3) \cdot 10^{-3}$ m. One of the substrate surfaces was thoroughly cleaned by chemically pure methanol and acetone. Zinc oxide nanostructures were obtained by two independent technological methods.

1. Chemical deposition [16, 17]. High-purity (99.99%) zinc acetate serves as a zinc oxide source. Zinc oxide nanocrystals were deposited on thin plates from borosilicate glass at a temperature of 338 K, the deposition time was

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TABLE 1. Some Physical Parameters of Zinc Oxide Nanostructures

Sample number	Substrate	Method of obtaining ZnO film	ZnO film parameters	Heater parameters in the 3ω method
1	Borosilicate glass	Chemical deposition	"Pure" ZnO, $\sigma = 10^5$ Ω·cm, $h_0 = 3.0 \cdot 10^{-5}$ m	$L = 4.0 \cdot 10^{-3}$ m, $B = 28.3 \cdot 10^{-6}$ m, $r = 28.8$ Ω
2	p–Si (100)	Ultrasonic spraying pyrolysis	Mn — 5%, N — 3%, p-type, $\sigma = 0.72$ Ω·cm, $h_0 = 0.2 \cdot 10^{-6}$ m	$L = 4.0 \cdot 10^{-3}$ m, $B = 27.6 \cdot 10^{-6}$ m, $r = 27.3$ Ω
3	p–Si (100)	Same	Mn — 5%, N — 0%, n-type, $\sigma = 3.6$ Ω·cm, $h_0 = 0.20 \cdot 10^{-6}$ m	$L = 4.0 \cdot 10^{-3}$ m, $B = 27.6 \cdot 10^{-6}$ m, $r = 27.3$ Ω
4	Quartz glass	»	Mn — 5%, N — 0%, n-type, $\sigma = 3.6$ Ω·cm, $h_0 = 0.25 \cdot 10^{-6}$ m	$L = 4.0 \cdot 10^{-3}$ m, $B = 27.6 \cdot 10^{-6}$ m, $r = 27.3$ Ω
5	p–Si (100)	»	Co — 3%, n-type, $\sigma = 4.4$ Ω·cm, $h_0 = 0.5 \cdot 10^{-6}$ m	$L = 4.0 \cdot 10^{-3}$ m, $B = 27.4 \cdot 10^{-6}$ m, $r = 27.3$ Ω

24 h. Upon deposition the samples were cooled to room temperature, and then they were annealed for 1 h at an air temperature of 773 K.

2. Ultrasonic sputtering [18, 19]. To obtain doped nanocrystalline ZnO films, 0.5-molar aqueous solution of zinc acetate, 0.5-molar aqueous solution of manganese acetate, and 0.5-molar aqueous solution of cobalt nitrate were used. Films were deposited on p-type (100) silicon substrates having a temperature of the order of 673 K. Nanocrystalline ZnO films with a 5% content of manganese in ZnO nanocrystals (ZnMnO) and nanocrystalline ZnO films with a 3% content of cobalt (ZnCoO) were prepared.

The obtained nanostructures were investigated by measuring their low-temperature ($T = 10$ K) photoluminescence, and they were also subjected to microstructural analysis with the use of scanning electron microscopy (SEM XI-30 PHILIPS) and X-ray spectroscopic analysis (XRD system). The main electrical characteristics of nanocrystalline ZnO films (the type of conduction, the concentration of carriers, and the specific resistance) were determined by Hall effect measurements. Some of the parameters of the zinc oxide nanostructures are given in Table 1. The technology and methods of structural analysis used are described in more detail in [16, 18, 19].

Experimental Methods. The heat capacity and the heat diffusivity of the obtained nanostructures were measured by ac calorimetry methods [9, 11, 20] with the use of frequency-modulated electric current or a modulated light beam (semiconductor laser) as a source of thermal energy to whose action the investigated medium was subjected. The amplitude and the phase shift of the temperature wave were measured by a thermocouple or a thermistor pasted on the underside of the substrate. Ac calorimetry is most commonly used for taking accurate measurement of the heat diffusivity and the heat capacity (especially in the differential variant) for a wide range of materials, and, in so doing, it is possible to determine the thermal properties of both the whole of the film-substrate structure and the film sputtered onto the substrate [20].

The heat conductivity of ZnO nanostructures was measured by the so-called 3ω method [21] with the use of a thin metal strip sputtered onto the surface of the sample whose heat conductivity has to be measured. This film acts as both a heater and a temperature sensor. The heater ac current of frequency ω generates Joule heat with a frequency of 2ω that diffuses into the sample to a depth determined by the thermodiffusion of the sample and the current frequency. Since the resistance of the heater is proportional to its temperature, it will be modulated with a frequency of 2ω. Consequently, the voltage drop on the heater contains a third harmonic that depends on the increase in the heater temperature and can be used to determine the heat conductivity of the sample.

The most important characteristic of the experiment in modulation calorimetry is the modulation frequency used, which is largely determined by the thickness of the sample being measured and the value of its thermodiffusion. In our experiments, this frequency was 0.2–10 kHz depending on the thermal parameters of the samples being measured.

Works [9, 11, 21] describe in fair detail the method for placing investigated samples on the holder, the creation of thin-film heater/thermometer probes, the methods for fixing the measuring thermocouple, the procedure of taking measurements, and the errors in determining the thermal quantities. In the present work, only certain measuring instruments, as well as the program of computer control and measurements, were subjected to changes.

TABLE 2. Heat Capacity of ZnO Nanostructures

Sample number	C_p, J/(kg·K)		
	$T = 90$ K	$T = 150$ K	$T = 300$ K
#0	196	320	497
1	230.1	377.9	591.43
2	208.6	349.6	543.2
3	200.8	339.2	527.6
4	198.3	334.1	519.3
5	196.9	326.5	535.2

TABLE 3. Thermal Diffusivity (D) and Heat Conductivity (k) of ZnO Nanostructures at $T = 300$ K

Sample number	Substrate		ZnO	
	$D·10^6$, m^2/s	k, W/(m·K)	$D·10^6$, m^2/s	k, W/(m·K)
#0	–	–	24.5	67
1	0.55	1.0	0.38	1.4
2	87.1	138	4.37	12.7
3	82.7	136	5.25	14.3
4	0.84	1.46	5.34	15.0
5	83.9	140	6.12	16.4

Note. In Tables 2 and 3 sample #0 is a nanocrystalline ZnO film without substrate.

The absence of "standard" samples made it impossible to determine the absolute measurement error. However, on the basis of comparing the results of measurements of the thermal parameters of structurally similar specimens performed with the use of different methods, the relative measurement error for the heat capacity was estimated to be at the level of 2%, and that for the heat diffusivity and the heat conductivity, at the level of 3–5%.

Results of Measurements. The experimental data on the heat capacity of the ZnO nanostructures are presented in Table 2. For these samples, the observed increase in the heat capacity (ΔC_p) varies over the range from the minimal values of 6% to the maximal ones of 19%, and for samples No. 1 it is practically constant in the investigated temperature range. As is seen, the deviations of the heat capacity (ΔC_p) of the investigated samples from the heat capacity of the polycrystalline ZnO nanostructures, according to the known literature sources [22], markedly exceed the possible experimental errors. Similar experimental data on the heat capacity of ZnO nanostructures were presented in [23], where the heat capacity of "nano-ZnO-flakes" films at a temperature above 110 K becomes higher than for polycrystalline ZnO. The heat capacity is poorly sensitive to the presence of impurities, the more so when their concentration is less than 1%; consequently, (ΔC_p) can be due to both the structure and the change in the thermodynamically equilibrium concentrations of defects — vacancies, interface between nanocrystals, etc.

Table 3 presents the experimental data on the heat diffusivity and the heat conductivity of the investigated nanostructures. The results obtained indicate clearly that D and k in the nanostructures are much lower than in the polycrystalline zinc oxide films [22]. However, there is a significant difference between the thermal parameters of ZnO nanocrystals grown by different methods, with sample No. 1 having a lower heat conductivity value (by an order of magnitude). As in the case of C_p, the values of D and k cannot be determined by the presence of impurity atoms or the phonon-electron interaction characteristic of them. As mentioned above, in accordance with the measurements of the Hall effect, the obtained concentration of charge carriers does not exceed 10^{18} cm^{-3}.

Results and Discussion. The amplitude variation ΔC_p may be due to both the structure and the change in the concentration of defects. As is seen from Table 1, the concentration of defects is fairly small except for the ZnO films specially doped by Co and Mn. These doping elements are paramagnetic. However, the contribution of the magnetic and electronic components to the heat capacity is observed by us only at temperatures below 77 K, and only in the case of nitrogen-doped ZnMnO (sample No. 3). The temperature dependence of the heat capacity at 75 K shows a clearly defined λ-shaped peak characteristic of ferromagnetic–paramagnetic phase transitions of the second kind [24–26].

The structural investigations have shown that the investigated nanocrystalline ZnO films are polycrystals in which the average sizes of individual nanocrystallites vary from 40 to 100 nm (ZnMnO and ZnCoO). It was shown in

[27] that nanosized crystalline structures consist of two component — crystalline and interface components. The value of the ratio of the fraction of the interface component to the fraction of the crystalline component can be estimated by the expression $3\delta/d$. The vibrational and configurational entropies of the crystalline state (with long-range order), the polycrystalline state (with short-range order), and of the nanocrystalline structure (without short-range order in the interface component) will differ in degree variation as temperature functions, and, consequently, the samples will show the expected noncomparable heat capacity values.

The changes differing in amplitude in the heat capacities in nanosized ZnO films may also be due to their different density. The X-ray structural analyses of sample No. 1 and "nano-ZnO-flakes" [16, 23] revealed a lower density of these structures, and the average size of nanocrystals varies over the 250–500 m range. Actually, the relatively low density of nanosized ZnO films in this case assumes a more open atomic structure of the interface structure and, consequently, a weaker interatomic bond, which can increase the heat capacity. This argument assumes that the higher heat capacity corresponds initially to the interface component [27]. The much higher values of the interface components of the heat capacity corresponds to a large area of the interfaces. Probably, this is characteristic of only thin films of ZnO nanocrystals.

The specific features of the structure of nanocrystalline ZnO films are also responsible for the observed values of their heat diffusivity and heat conductivity. As is seen from Table 3, the obtained heat conductivity values of ZnO films are an order of magnitude lower than for volume ZnO. These values are also small compared to the powdery structures of zinc oxide [28]. Indeed, in the first case, in polycrystalline samples of ZnO D and k depend on the sizes of crystallites, their orientation with respect to the heat flow, and their density. In the second case, D and k decrease with decreasing thickness of ZnO films because of the change in the microstructure and homogeneity during the first stage of deposition. Such a considerable difference in the D and k values is primarily due to the high fraction of the surface component of the interface with respect to the volume. In particular, the relatively large fraction of surface atoms leads to an increase in the scattering surface of phonons and a decrease in their free paths, which in turn leads to a low heat conductivity proportional to the mean free path. Unlike films, the corresponding free path of phonons for free-flowing materials is much larger, and the effect from the scattering by the boundaries between particles of free-flowing materials is negligibly small. The third case is the contact heat resistance (R_i) arising between the thin ZnO film and the substrate. Undoubtedly, the actually measured heat conductivity includes also the additional heat resistance arising between the finest dielectric film and the substrate (designed for effective absorption of the frequency-modulated laser beam and excluding the shunting effect of low-resistance ZnO films on the heater in the 3ω method), as well as the heat resistance of the glue between the sample holder and the cryostat. The differential experimental technique used and the analytical procedure described in detail in [6, 11, 24] permit determining the R_i value.

The authors of [29] explain such experimental facts by the additional scattering of phonons due to the presence in them of the so-called Kapitsa effect. According to this theory, $R_i \sim T^3$ and is proportional to the acoustical-impedance ratio between the contacting media defined as products $v\rho$ (v is the mean velocity of sound, ρ is the density of the material). The impedance ratio is in our case of the order of 2.39; however, for samples No. 2–5 in our experiments at low temperatures the dependence $R_i \sim T^3$ is violated. Analogous experimental data were also obtained by us on CdS/Al_2O_3 nanostructures [30]. The experimental results presented have not yet found theoretical explanation, and in the first approximation it may be assumed that these effects are due to the strong scattering of phonons by the surface defects. It has been shown that this additional heat resistance cannot be associated with the surface itself, but must be the cause of disturbances in the near-surface region [29]. The rather large value of R_i is likely a result of the partial contact or massive disorder in the adjacent region. Up to now, there has been no convincing confirmation of this phenomenon. In many practical cases, the heat resistance of contacts between thin films of nanostructures and their base — the substrate — was found to be dominant. This thermal problem of contact resistance has just begun to be studied experimentally. Thus, the heat transfer in these structures becomes, to a greater extent, the determining factor in predicting their thermal characteristics.

Conclusions. The thermal properties of zinc oxide nanostructures grown on various substrates by two technological methods have been investigated. Measurements have shown that the ZnO nanostructures synthesized by us have, as compared to polycrystalline ZnO films, thermal parameters differing in value. The heat transfer in these structures is largely determined by the interface both between the film and the substrate and between nanocrystals.

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NOTATION

B, heater width, m; C_p, isobaric heat capacity, J/(kg·K); D, thermal diffusivity, m^2/s; d, average size of crystallites, nm; h_0, ZnO film thickness, m; k, heat conductivity coefficient, W/(m·K); L, heater length, m; r, electrical resistance of the heater, Ω; R_i, heat resistance of the contact surface between the ZnO film and the substrate, m^2·K/W; T, temperature, K; ΔC_p, additional heat capacity, J/(kg·K); δ, average thickness of the interface, nm; σ, specific resistance, Ω·cm; ω, modulation frequency of the heat flow, Hz. Subscripts: i, interface.

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