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Internal Friction in Semiconductor Thin Films Grown Using Sol–Gel Technology

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Abstract—A method for the efficient monitoring of the existence and composition of encapsulated nanophases in nanostructured thin films grown using sol–gel technology is suggested. The method is used to study the semiconductor film structures intended for gas-sensitive adsorption sensors. The potential for, and prospects of, studying materials and diagnosing sol–gel processes using this method are considered. © *2005 Pleiades Publishing, Inc.*

Methods based on internal friction (IF) measurements have various applications in science and engineering [1]. In this paper, we report the main results (obtained with the participation of the authors over twenty years) regarding the development of methods, based on IF techniques, for determining and monitoring the parameters of semiconductor materials. The new results are as follows:

(i) The development of methods for determining the foreign volumes of the foreign inclusions in III–V, II–VI, IV–VI, and II–V semiconductors and structures based on these semiconductors. The possibility of determining the excess metal components in GaP, GaAs, and other substrates was considered in [2]. This problem is especially urgent for the development of microelectronics, due to the need to pass to fast-response integrated microcircuits and GaAs-based circuits. The methods' sensitivity to an excess component when analyzing the temperature dependence of IF is ~0.01 vol %.

(ii) The study of singularities within the homogeneity regions of variable-composition phases. To date, the IF method has significantly complemented the classical physicochemical analysis. The theory shows that any compound is homogeneous in a certain domain of the chemical composition variability. For semiconductors, these domains are often rather narrow ($\sim 10^{-3}$ at. %); however, a variation in the composition of these demands can cause a variation of several orders of magnitude in charge-carrier concentration [3]. Under such circumstances, homogeneity regions can contain specific compositions that are unchanged when their aggregate state changes (congruent melting, sublimation, and evaporation). Previously, it was thought that the experimental determination of such compositions was impossible. However, special methods developed for the concentration of microinclusions allowed an electron-probe determination of the compositions $V_{s\max}$ corresponding to the condition of congruent melting methods. For example, $V_{s\max} = 0.500135$ [Te] (in atomic fractions) in $Pb_{1-y}Te_y$ [4]. In this case, the analytical sensitivity of an X-ray spectral microanalysis carried out for microprecipitates is higher than that of an immediate analysis of the surrounding host composition by a factor of 10^3–10^4. This fact made it possible to measure, for the first time, the dependences $V_{s\max} = f(x)$ for the semiconductor alloys $(Pb_{1-x}Sn_x)_{1-y}Te_y$ [5]. The IF method appeared to be more sensitive when applied to an analysis of microprecipitates formed under specific conditions, e.g., for $(Pb_{1-x}Sn_x)_{1-y}Te_y$ [6]. The IF method's advantage is an opportunity to obtain information about an entire sample without facing conductivity limitations. Since data on congruent-melting compositions are currently unavailable for almost all the compounds that have narrow homogeneity regions, the IF method seems a promising way to fill this gap.

(iii) Studies on the production of semiconductor materials using low-temperature halogen methods are actively being carried out in many countries (USA, Israel, Bulgaria, and others) [7]. The reaction takes place in a solvent medium, and a necessary condition for producing a high-quality material is the reaction's completeness at the synthesis stage. In [8], it was suggested that the IF method be applied to the technological control of this initial operation, which predetermines the entire process.

(iv) In [9], the IF method was successfully used when analyzing the submicroprecipitates in the doped polycrystalline layers of tin dioxide used in gas-sensitive semiconductor sensors. A technique that monitored the impurity segregation in adsorbed sensors by employing a temperature shift of the IF peak was suggested in [10].

Recently, in materials science, a special emphasis has been placed on the production and study of nanostructured materials. In semiconductor nanostructured

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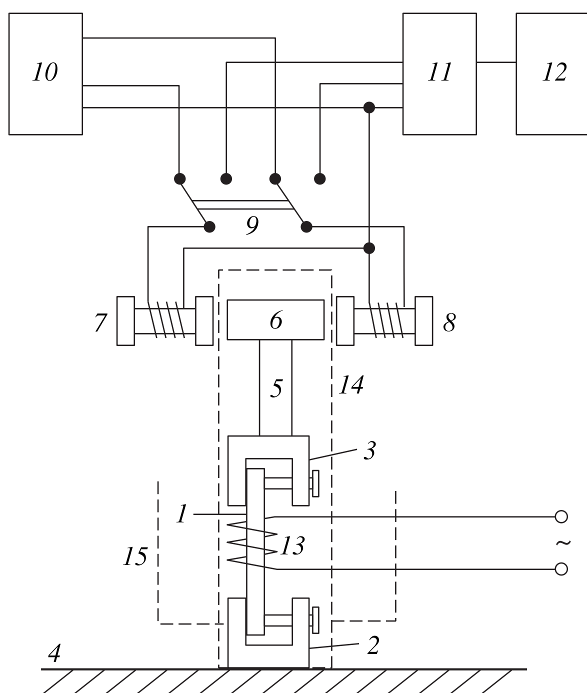


Fig. 1. The setup for internal friction measurements: (*1*) sample, (*2*, *3*) collets, (*4*) base, (*5*) pendulum, (*6*) ferromagnetic ring, (*7*, *8*) coils, (*9*) switch, (*10*) oscillator, (*11*) amplitude discriminator, (*12*) electronic counter, (*13*) heater, (*14*) vacuum-tight container, and (*15*) beaker.

materials, a variety of new effects, caused by the critical sizes of physical phenomena, begin to manifest themselves as crystallite sizes decrease. For gas-sensitive adsorption sensors, the critical size is the comparability of grain sizes with the Debye screening length. Moreover, the role of the natural microstructure, i.e., the agglomerate shape, degree of aggregation, and so on, increases in nanostructured materials.

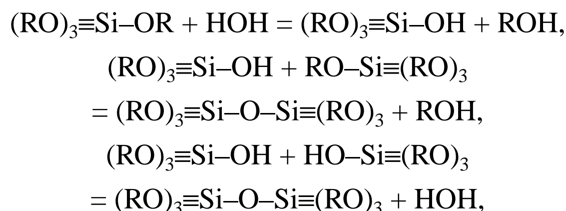
One promising method for the production of materials is sol–gel technology [11]. This method allows nanocomposite material synthesis to be attained with relative ease [12] as well as modification of the surface of sensitive layers [13]. Put in perspective, the potential of sol–gel technology is that it enables the development of a multisensor system, i.e., a system of sensors that have an unmatched response and are formed on a single substrate using a unified technological process. The requirement that there be an unmatched response to an exposure to a single gas sample and the requirement of unified implementation are mutually contradictory. This contradiction can be removed using the nonuniform spatiotemporal distribution of the gas sensitivity of thin-film structures. This nonuniformity is due to the nonuniformity in the film parameters caused by the film growth conditions (thickness, doping, and material) or in the parameters related to the film modification.

The development of this line of technology is restrained by the absence of reliable techniques for analyzing the compositions of the nanophases that arise in formed open pores and isolated voids during the structure growth.

The aim of this study is to develop a new approach to the diagnostics of the nanophases that represent a byproduct of sol–gel processes and are located in the interior microvolumes and nanovolumes of grown samples.

The entire process of film growth using the sol–gel method can be separated into three main stages: sol synthesis, film deposition, and film annealing.

To deposit nanometer films onto a semiconductor surface, specially prepared sols are used [14, 15]. We generally used sols based on tetraethoxysilane (TEOS). Film formation from TEOS-based sols is based on the hydrolysis reaction and polycondensation of TEOS hydrolysis products,



$$(RO)_3{\equiv}Si{-}OR + HOH = (RO)_3{\equiv}Si{-}OH + ROH,$$

$$(RO)_3{\equiv}Si{-}OH + RO{-}Si{\equiv}(RO)_3$$
$$= (RO)_3{\equiv}Si{-}O{-}Si{\equiv}(RO)_3 + ROH,$$

$$(RO)_3{\equiv}Si{-}OH + HO{-}Si{\equiv}(RO)_3$$
$$= (RO)_3{\equiv}Si{-}O{-}Si{\equiv}(RO)_3 + HOH,$$

where R is the hydrocarbonic radical $-C_2H_5$.

The hydrolysis and polycondensation take place simultaneously, and their degree of completion depends on many chemical and technology factors: the TEOS and water concentrations, solvent type and concentration, medium acidity (concentration of acid or other catalyst), synthesis temperature and duration, and homogenization method.

The basic objects that need to be studied are the films and modified coatings in an SnO_2–SiO_2 system, which are promising for the development of gas-sensitive adsorption sensors, including those that have an integrated design [16]. The results from an analysis of the topological features of the grown porous structures of these layers using optical, electron, and atomic-force microscopy are given in [17, 18].

However, none of the above-listed methods are efficient enough to analyze the nanophase precipitates encapsulated inside a material layer. To obtain such information, we developed techniques based on the IF method.

The method is based on a measurement of the temperature dependence of the IF using an inverted pendulum technique. A schematic diagram of the setup is shown in Fig. 1.

Sample *1* (a substrate with a formed layer), the first sample under study, is attached by one end to base *4* using collet *2*. Collet *3*, which is attached pendulum *5*, is connected to the other sample end. Ferromagnetic ring *6* is mounted on top of the pendulum. Electromagnetic coils *7* and *8* are symmetrically positioned near ring *6* and can be connected via switch *9* to low-frequency oscillator *10* or amplitude discriminator *11*, whose output is connected to electronic counter *12*. In

the former case, coils *7* and *8* are used as an activator for the mechanical vibrations of pendulum *5*, which are caused by the interaction of the magnetic field of the coils with the ferromagnetic ring. In the latter case, they are used as a sensor of ring *6* displacements. Heater *13* is arranged around sample *1*. The basic elements of the circuit are placed into vacuum-tight container *14*, which is made of fused-quartz glass. Air is evacuated from quartz container *14* in order to decrease the damping of the oscillations of pendulum *5*.

The internal friction is determined as the inverse Q factor of the oscillatory system $Q^{-1} = (1/\pi N)\ln(A_1/A_N)$, where N is the number of oscillations according to the counter, and A_1 and A_N are the amplitudes of the first and Nth oscillations.

To carry out the planned experiments, the setup was modernized so that it could measure the temperature dependences of the internal friction not only during the heating but also during the cooling of the sample. To this end, beaker *15*, which was welded to the quartz container, was filled with liquid nitrogen. In this case, cooling is due to the difference between the heat radiation fluxes from the liquid nitrogen to the sample and from the sample to the container with the liquid nitrogen.

In this study, semiconductor films consisting of nanocomposition systems based on tin dioxide were grown by a chemical method from sol solutions using sol–gel technology. The sols were ethanol solutions of TEOS, with additives of bivalent tin chloride ($SnCl_2 \cdot H_2O$) acting as a source of tin dioxide. The SiO_2 source was TEOS. In some experiments, several drops of concentrated hydrochloric acid were added to make the dispersion more complete. The film structures were grown by pouring the solution onto various substrates (silicon, glass, and glass ceramics) followed by centrifuging. The transition to gel or xerogel (dry gel) was attained by a natural evaporation of the solvent followed by an additional isothermal treatment at 600°C. Annealing of the film structures at temperatures above 500°C yields a material containing only the oxide semiconductor phases of silicon and tin. The technology of sol–gel systems and the films based on them was considered in more detail in [17].

The samples in which the solvent removal and crystallization were completed (according to the data of the differential thermal analysis and X-ray phase analysis), were analyzed using the IF method. At the same time, judging from the dynamics of the physicochemical processes in sol–gel systems, the gel network may contain nanophase inclusions consisting of water and organic solvent during its formation. However, we do not know of any techniques allowing an analysis of these structural defects, which can have a significant effect on the electrical and mechanical properties of the grown coatings. Thus, the suggested technique based on the IF method is promising for the development of operating conditions for the growth and analysis of the properties of the objects under study.

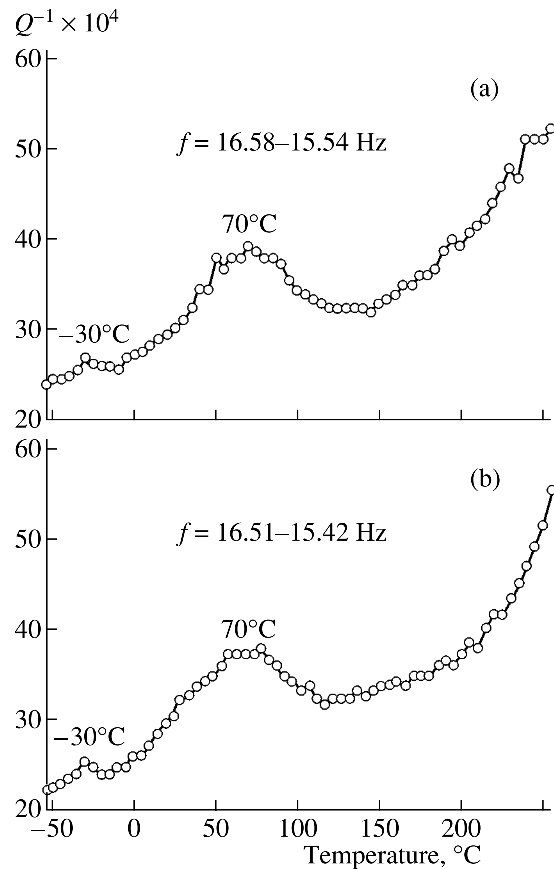


Fig. 2. Temperature dependences of the internal friction in SnO_2–SiO_2 nanocomposite films grown on glass substrates for the first (a) and second (b) sequential measurements.

The rectangular-shaped samples with a characteristic area of 12×4 mm^2 were cut and then placed into the vacuum chamber (Fig. 1). The samples in the setup were cooled to a temperatures of about –100°C followed by step-by-step heating and IF measurement. The results for the SiO_2–SnO_2 composite samples are shown in Figs. 2 and 3. These two figures show the temperature dependences of the IF for the samples formed on glass and glass-ceramic substrates, respectively, for two sequential measurements.

Figures 2 and 3 exhibit a low-temperature IF peak, which is also observed in the general case. The phase transition temperature of the inclusions in the film material is significantly lower than that of water; hence, the nanophase is a hydroalcoholic solution. The experimental data show that the peak's position is unchanged in sequential measurements of the dependences of the IF. This means that the measurement technique allows analysis of the encapsulated nanophases. A comparison of the dependences for the film structures grown on the various substrates used shows that mechanical energy

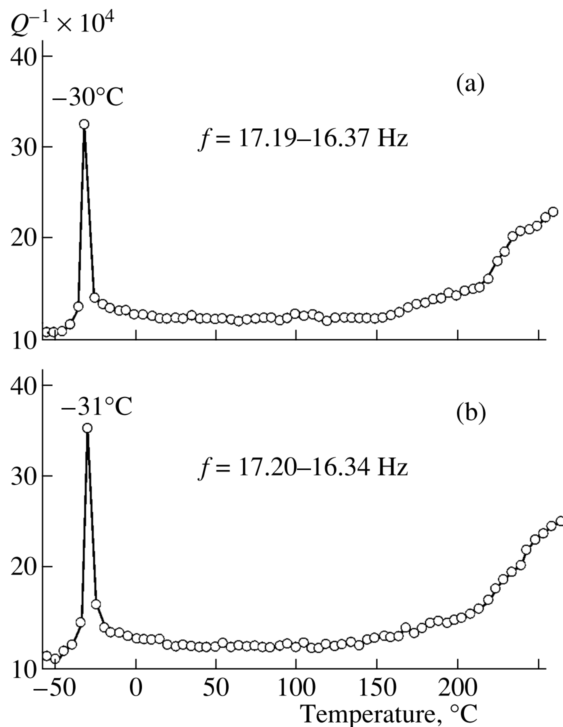


Fig. 3. The same as in Fig. 2; however, in this case, glass-ceramic substrates were used.

losses are observed in a temperature range of 40–100°C (broadened IF peak) in the samples grown on glass substrates but not in the ones grown on glass-ceramic substrates. We attribute this effect to a relaxation of the substrate–sample bonds. The absence of such losses during the glass-ceramics–film interaction can be indicative of both localized bonds (the absence of bond migration under exposure to temperature) and a short chain of atoms bonding the substrate to the film.

Thus, we have developed a method that allows efficient monitoring of the existence and composition of the encapsulated nanophases in nanostructured thin films grown using sol–gel technology. This method can serve as the basis for a new approach to the diagnostics of sol–gel processes that controls the trapping of matrix hydroalcoholic solutions, and the formation of clathrate (inclusion) compounds and phase transitions in nanoprecipitates.

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