Temperature dependence of energy band gap and spontaneous polarization of SbSI nanowires

Marian Nowak *, Piotr Szperlich

Solid State Physics Section, Institute of Physics, Silesian University of Technology, ul. Krasińskiego 8, 40-019 Katowice, Poland

A B S T R A C T

For the first time temperature dependence of optical energy gap of antimony sulfoiodide (SbSI) nanowires has been determined. In ferroelectric phase (for 241 K < T < T_c = 292 K) the evaluated indirect forbidden optical energy gap has been fitted by $E_{gfi}(T) = [2.195(3) - 10.8(1) \times 10^{-4}T]$ eV. In paraelectric phase (T_c = 292 K < T < 344 K) the energy gap has been described by $E_{gfi}(T) = [2.152(4) - 9.3(1) \times 10^{-4}T]$ eV. It has been estimated that at the temperature of 240 K the spontaneous polarization of the SbSI nanowires has the maximum value of about 0.08 C/m^2.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

One-dimensional nanostructures have received considerable attention from the scientific and engineering communities [1]. Semiconductor nanowires exhibit novel electronic and optical properties. Therefore, they are considered to be the critical components in a wide range of potential nanoscale device applications [2]. Nanoferroelectrics are important for many applications as well as for the fundamental physics questions, too. The review papers [3,4] summarize recent advances in the quickly developing field of nanoscale ferroelectrics. Recently [5] a sonochemical method has been used for direct preparation of antimony sulfoiodide (SbSI) xerogel consisted of crystalline nanowires with lateral dimensions of about 10–50 nm and lengths reaching up to several micrometers. The maximum of dielectric constant $\varepsilon = 1.6 \times 10^4$ of this material has been measured [6] at the Curie temperature $T_c = 292(1)$ K similarly to the properties of bulk-size SbSI crystals [7,8].

The aim of this paper is to present first time the temperature dependence of optical energy gap (E_g) of the ultrasonically prepared SbSI nanowires. Additionally, the purpose of the research work is to evaluate the temperature dependence of spontaneous polarization (P_s) of this material. The presented data should be useful for theory of phase transition in systems of one dimension nanostructures. It is important because the authors of [9] have shown that nonvolatile polarization domains can be induced on

BaTiO$_3$ nanowires, suggesting that ferroelectric these nanowires may be used to fabricate nonvolatile memory devices with an integration density approaching 1 terabit/cm^2.

2. Experiment

The SbSI was prepared sonically in ethanol from the constituents (the elements Sb, S and I). Antimony (99.95%) was purchased from Sigma–Aldrich. Sublimated sulfur (pure p.a.), iodine (pure p.a.) and absolute ethanol (pure p.a.) were purchased from POCH S.A. (Gliwice, Poland). In a typical procedure, the elemental mixture with stoichiometric ratio of e.g. 1.84280 g Sb, 0.48535 g S and 1.92082 g I, was immersed at room temperature and ambient pressure in 8 ml absolute ethanol, which was contained in a 54 ml Pyrex glass cylinder. The vessel was closed during the experiment to prevent volatilization of the precipitants in long time tests. It was partly submerged in water in an ultrasonic reactor (InterSonic IS-UZP-2, frequency 35 kHz, with 80 W electrical power and 2 W/cm^2 power density guaranteed by the manufacturer). The sonolysis was carried out at 323 K for 110 min. The used experimental set up and the applied procedure were the same as the described in [5]. When the sonication was finished, a red–orange gel was obtained.

About 30 μm thick samples of as synthesized SbSI gel were deposited upon BK-7 substrates. The ethanol was evaporated from them in air at 313 K and a so-called xerogel films were obtained. Their optical transmittances (T_0) were measured using spectrophotometer PC2000 (Ocean Optics Inc.) with 600 lines grating (blazed at 500 nm). The spectrophotometer was equipped with appropriate waveguide cables as well as with the deuterium–halogen light

source DH2000-FHS (Sentronic GmbH). The sample was mounted in the optical D2209 chamber of R2205 Cryogenic Microminiature Refrigeration II-B System (MMR Technologies) based on Joule Thomson effect. Temperature was controlled with 0.1 K uncertainty using K7701 temperature controller (MMR Technologies). The multiple averaged spectral characteristics were registered in various temperatures using PC computer and the OOI-Base program (Ocean Optics Inc.). The absorbance of light in the investigated material was calculated:

$$A = \alpha w = -\log(T_{opt}) \tag{1}$$

where α represents absorption coefficient of radiation, w is the difficult to determine pathlength of light in xerogel, and T_{opt} describes optical transmittance of the sample.

Characterization of the SbSI xerogel was accomplished using different techniques, such as powder X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis, high-resolution transmission electron microscopy, selected area electron diffraction, optical diffuse reflection spectroscopy (DRS), infrared absorbance, gas chromatography, and temperature investigations of d.c. electric characteristics as well as capacity measurements. Description of the used equipment and results of these investigations were given in [5,6,10].

3. Results

Fig. 1 shows the influence of temperature on spectral characteristics of optical transmittance of film of SbSI xerogel. The fundamental absorption edge is evident. One can see its shift to longer wavelengths with increasing temperature of the sample. Fig. 2 presents typical spectral dependences of absorbance determined at different temperatures and least square fitted using numerical minimization of the following function [11]:

$$\chi^2 = \sum_{i=1}^{n} \left[(A(h\nu_i) - B\sum_{j}^{m} \alpha_j(h\nu_i) \right]^2 \tag{2}$$

where i represents photons of different energy ($h\nu_i$), α_j describes various mechanisms of light absorption, and B is the proportionality factor. The best results have been obtained for the sum of indirect forbidden absorption without excitons and phonon statistics (α_1),
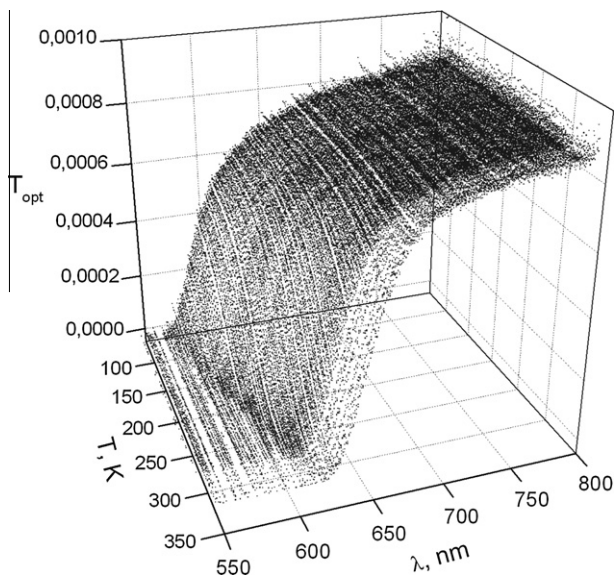

Fig. 1. Influence of temperature on spectral characteristics of optical transmittance of film of SbSI xerogel (description in the text).
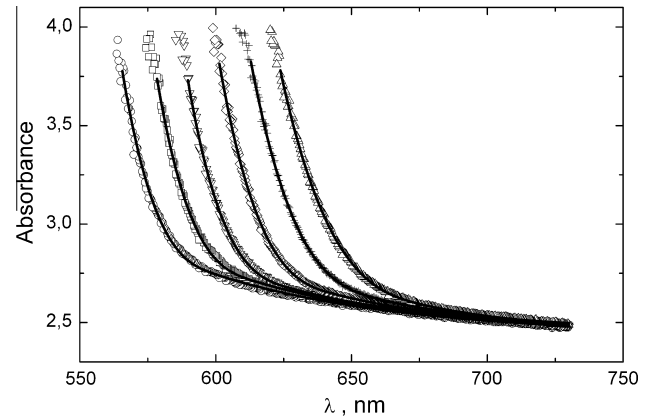

Fig. 2. Typical spectra of absorbance of SbSI xerogel determined from optical transmittance at different temperatures ($\bigcirc$ – 80 K; $\square$ – 150 K; $\bigtriangledown$ – 200.1 K; $\diamondsuit$ – 250.1 K; + – 296.8 K; and $\triangle$ – 344.1 K). Solid curves represent the least square fitted theoretical dependences for the sum of indirect forbidden absorption without excitons and phonon statistics, Urbach ruled absorption, and constant absorption term (description in the text; values of the fitted parameters are given in Table 1).

Urbach ruled absorption (α_2) and constant absorption term (α_3) [11]:

$$\alpha_1 = A_{60}(h\nu - E_{gIf})^3 \quad \text{for } h\nu > E_{gIf} \tag{3a}$$
$$\alpha_2 = A_U \exp(h\nu/E_U) \tag{3b}$$
$$\alpha_3 = A_0 \tag{3c}$$

where E_{gIf} represents the indirect forbidden energy gap, E_U is the Urbach energy, A_{60}, A_U are constant parameters. The constant absorption term A_0 is an attenuation coefficient that is considered as the sum of the scattering and absorption independent of $h\nu$ near the absorption edge. Values of the fitted parameters are given in Table 1. Figs. 3–5 present the temperature dependences of the indirect forbidden energy gap and the factors A_{60} proportional to the probability of photon absorption due to fundamental, indirect, forbidden transition in the investigated SbSI nanowires. Fig. 6 shows the adequate temperature dependences of the Urbach energy and the factors A_U (proportional to the probabilities of absorption of photons due to Urbach transitions in SbSI nanowires).

4. Discussion

The optical energy gap of SbSI xerogel is determined for unpolarized light because the nanowires are variously directed in the investigated samples (see figures in [5,10]). For light with electric field $\vec{E}$ perpendicular to the SbSI c-axis of bulk-size crystals the optical absorption edge shifts towards greater energies than for $\vec{E}$ parallel to the c-axis [7,12–14]. Since, the determined E_{gIf} values of SbSI nanowires should be appropriate for the case of plane polarized illumination with electric field parallel to the SbSI c-axis.

The mechanisms of optical absorption in SbSI xerogel evaluated using the presented absorbances and DRS data reported in [5] are the same. It should be underlined that the indirect forbidden absorption was reported for bulk-size SbSI by many investigators (see e.g. [15–18]). However, many other investigators described the optical properties of bulk-size SbSI using the Urbach absorption (see e.g. [7,13,19–22]). The value of indirect forbidden energy band gap of SbSI xerogel at 296.8 K (presented in this paper) is slightly bigger than the one derived in [5] from DRS at 297 K (Table 1). However, it is known that the reflection and transmission do not yield completely identical results for the E_g of a semiconductor. It is attributed to the fact that diffuse reflectance and optical density do not have a simple relationship.