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SbSI Single Nanowires as Humidity Sensors

K. MISTEWICZ^{*a*,*}, M. NOWAK^{*a*}, P. SZPERLICH^{*a*}, M. JESIONEK^{*a*} AND R. PASZKIEWICZ^{*b*}

^aSolid State Physics Section, Institute of Physics — Center for Science and Education,

Silesian University of Technology, Z. Krasińskiego 8, 40-019 Katowice, Poland

^bDiv. of Microelectronics and Nanotechnology, Wrocław University of Techn., Długa 65, 53-633 Wrocław, Poland For the first time influence of humidity on photoconductivity transient characteristics are studied for antimony

sulfoiodide (SbSI) single nanowires. While negative photoconductivity is observed for SbSI gel, made up of large quantity of nanowires, only the positive effect occurs for SbSI single nanowires. Photoconductivity current response on switching on and off illumination in moist N_2 represents so-called hook anomaly.

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1. Introduction

Humidity sensing using one- and two-dimensional nanostructures is investigated in many research centers around the world. The sensors constructed from nanomaterials have received great attention because of their enormous surface-to-volume ratios. It makes their electrical properties extremely sensitive to species adsorbed on surfaces.

Antimony sulfoidide (SbSI) is a semiconducting ferroelectric. Recently, the influence of humidity on impedance spectra [1], electrical conductivity [2] and photoconductivity transient characteristics [3] of SbSI gel, made up of large quantity of nanowires, has been investigated. In order to complete investigations of the observed phenomena, the experiments with single SbSI nanowires are analyzed in this paper.

2. Experiment

Humidity nanosensors were constructed from single SbSI nanowires sonochemically prepared [2] and welded ultrasonically to Au interdigitated microelectrodes (with $l = 1 \ \mu m$ spacing), according to the technology described in [4].

Electric measurements were performed in nitrogen at pressure $p = 4 \times 10^4$ Pa and in vacuum ($p = 10^{-2}$ Pa) produced by turbomolecular drag pumping station TSH 071E (Pfeiffer). Humidities were maintained by passing nitrogen gas to the test chamber over water in special container. The humidity was determined using HIH-40003 sensor (Honeywell) with Keithley 196 multimeter. In order to control temperature, Pt-100 sensor was placed near to the investigated sample. The temperature measurements were done using 211 temperature monitor (Lake Shore). The photoconductivity transient characteristics were registered using Keithley 6517A electrometer. Argon laser (model Reliant 50s, Laser Physics) with wavelength $\lambda = 488$ nm was employed for sample illumination. The intensity of illumination (I_0) was measured using Hamamatsu S2387 photodiode in shortcircuit regime with Keithley 6517A electrometer.

3. Results and discussion

Figure 1 presents typical responses of dc photoconductivity current (I_{PC}) on switching on and switching off illumination of SbSI single nanowires in vacuum and in N_2 atmosphere of different humidities. Shape of these responses depends on the value of relative humidity (RH). After switching illumination on, the electric photoconductivity current increases fast, attains maximum, and then slowly decreases with time to a stationary value. Obviously, the rise of $I_{\rm PC}$ after switching on illumination is due to photogeneration of excess carriers in SbSI. After illumination switch off the electric conductivity current monotonically decreases due to recombination of the excess carriers. However, the first pulse in the transient characteristic exhibits a complex shape which builds to a peak, relaxes to a minimum and recovers to a saturated level (see e.g. Fig. 1d). It can be recognized as a so-called "hook anomaly", often observed for infrared detectors [5]. Spontaneous random voltage spiking often occurs in IR extrinsic detectors. The hook anomaly spikes exhibit fast



Fig. 1. Hook anomaly in photoconductivity current responses on switching on (\uparrow) and switching off (\downarrow) illumination of SbSI single nanowires (a) in vacuum ($p = 10^{-2}$ Pa) and (b, c, d) in moist N₂ ($p = 4 \times 10^4$ Pa). Characteristics were obtained for $\lambda = 488$ nm; $I_0 = 2 \times 10^{22}$ photon/(m²s); $E = 1.5 \times 10^6$ V/m; T = 280 K. Solid curves represent the best fitted dependences described by Eq. (1).

^{*}corresponding author; e-mail: krystian.mistewicz@polsl.pl

(1b)

rise times, narrow time widths and longer tails which are usually system bandwidth limited. The height distribution of the spikes and the spike rate are strongly dependent, above some threshold, on the voltage applied to the detector. In addition, they also depend on temperature and background flux levels [5]. In the case of humidity sensors constructed from SbSI single nanowires, hook anomaly pulse depends on relative humidity.

It is well known that detector response, on a step change in illumination, can be fitted by an empirical model containing three time constants [6–8]. Although, in the case of SbSI humidity sensors, the fitting of photocurrent time dependence with superposition of two exponentials is very good (Fig. 1). Therefore, transient characteristics of photoconductivity have been described by the following relations:

$$I_{\rm PC}(t) = I_{\rm PC1} \left[1 - A \exp\left(-\frac{t}{\tau_{11}}\right) \right] + I_{S1} \exp\left(-\frac{t}{\tau_{12}}\right)$$

for $t_{\rm on} < t < t_{\rm off}$ (1a)
$$I_{\rm PC}(t) = I_{\rm PC2} \exp\left(-\frac{t}{\tau_{21}}\right) + I_{S2} \exp\left(-\frac{t}{\tau_{22}}\right)$$

for
$$t > t_{\text{off}}$$

where $t_{\rm on}$ and $t_{\rm off}$ represent time of switching on and switching off illumination, respectively; I_{PC1} is the stationary value of photoconductivity current flowing under constant illumination; A, I_{S1} , I_{PC2} , I_{S2} are the preexponential factors; τ_{11} , τ_{12} , τ_{21} and τ_{22} are the time constants. The values of the selected fitted parameters are presented in Fig. 2. It should be noted that the value of I_{PC1} parameter (see Fig. 2a) increases monotonically over ten times in the relative humidity range from 0% to 54%.



Fig. 2. Influence of humidity on selected parameters of Eq. (1) fitted to the photoconductivity transient characteristics of SbSI single nanowires presented in Fig. 1.

One can see that the final settled value of photocurrent (I_{PC1}) is positive in whole range of RH (Fig. 2a). Different influence of humidity on transient photoconductivity characteristics was observed [3] in the case of SbSI gel, made up of large quantity of nanowires. It has been found that, while the value of photocurrent under constant illumination is positive in the case of small and medium RH, it is negative for RH higher than some critical value $RH_C = 39.8\%$ [3]. It has been shown in [3] that negative photoconductivity observed for SbSI gel is caused by light-induced desorption of H₂O molecules from SbSI nanowires surfaces, contacts between the nanowires, or contacts between SbSI and metal electrodes. Comparison of the results observed in the case of SbSI single nanowires nanowelded to metal electrodes with the results observed in the case of SbSI gel leads to the following conclusion. The desorption of $\rm H_2O$ molecules from contacts between illuminated SbSI nanowires, and contacts between SbSI nanowires and metal electrodes is the most important factor that determines sensitivity of the gel humidity sensors.

4. Conclusions

Photoconductivity transient characteristics measured for sensors constructed from individual nanowelded SbSI nanowires exhibit so-called hook anomaly. In the case of IR detectors, this effect depends on many factors (applied voltage, temperature, background flux levels). Concerning SbSI single nanowires, height and shape of hook pulse are functions of relative humidity.

Qualitatively different photoconductivity transient characteristics under high humidity are observed for SbSI single nanowires and gel. While negative photoconductivity is observed for SbSI gel over some critical value of RH, only the positive effect occurs for single SbSI nanowires.

Presented in this paper low power and small-sized SbSI nanosensors can find a lot of applications in environment monitoring as well as in air-conditioning systems and industrial equipments. However, the recognition of the response of this new type of sensors for different gasses is necessary to understand the adsorption processes in ferroelectric nanostructures. Such detailed investigations will be provided in near future.

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