1-1-2012

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Vladimir Kasiyan

Zinovi Dashevsky

Casey Minna Schwarz
University of Central Florida

M. Shatkhin
University of Central Florida

Elena Flitsiyan

See next page for additional authors

Recommended Citation

Kasiyan, Vladimir; Dashevsky, Zinovi; Schwarz, Casey Minna; Shatkhin, M.; Flitsiyan, Elena; Chernyak, Leonid; and Khokhlov, Dmitry, "Infrared detectors based on semiconductor p-n junction of PbSe" (2012). *Faculty Bibliography 2010s*. 2837.
https://stars.library.ucf.edu/facultybib2010/2837

Authors

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Journal of Applied Physics

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Cite as: J. Appl. Phys. **112**, 086101 (2012); https://doi.org/10.1063/1.4759011
Submitted: 29 May 2012 . Accepted: 12 September 2012 . Published Online: 17 October 2012

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JOURNAL OF APPLIED PHYSICS **112**, 086101 (2012)

Infrared detectors based on semiconductor *p-n* junction of PbSe

Vladimir Kasiyan,[1] Zinovi Dashevsky,[1] Casey Minna Schwarz,[2] M. Shatkhin,[2]
Elena Flitsiyan,[2] Leonid Chernyak,[2,a)] and Dmitry Khokhlov[3]
[1]*Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel*
[2]*Department of Physics, University of Central Florida, Orlando, Florida 32816-2385, USA*
[3]*Physics Department, Lomonosov Moscow State University, Moscow 119991, Russia*

(Received 29 May 2012; accepted 12 September 2012; published online 17 October 2012)

P-n junctions based on physical vapor deposition of thin PbSe films and conductivity type inversion from *n*- to *p*-type are developed and characterized over a wide range of temperatures and bias voltages. Photosensitivity and diode characteristics in the thin film PbSe diode structures were found at temperatures up to 300 K. The values of the measured and estimated parameters of these structures demonstrate their high photodetector performance and the potential for development of IR detectors with optimal sensitivity at the highest possible operating temperature. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4759011]

In previous studies, annealing of PbS polycrystalline films in oxygen has led to a change in their conductivity type (from *n* to *p*) and now this method is widely used for the preparation of photosensitive IR resistors based on PbS layers.[1] At the same time, functional *p-n* junctions based on PbSe are very little studied and robust *p-n* junction characteristics, based on the thermal oxidation of PbSe, have yet to be reported. Since IR detector performance is strongly influenced by *p-n* junction characteristics, it is important to understand how the preparation technology can impact the device properties.

While the electrical conductivity type conversion from *n*- to *p*-type in PbSe is known, the main point of this work is in development of IR *p-n* junction PbSe detectors, which can perform with optimal sensitivity at the highest possible operating temperature. PbSe *p-n* junctions based on physical vapor deposition (PVD) of the thin films and conductivity type inversion (CTI) in them from *n*- to *p*-type are fabricated and characterized over a wide range of temperatures and bias voltages. Photosensitivity and diode characteristics in thin film PbSe diode structures are examined in the temperature range from 4.2 to 300 K.

Polycrystalline 1–3 μm thick *n*-type PbSe films with majority electron concentration of (1-4) $\times 10^{19}$ cm^{-3} and mobility of 60–120 cm^2/Vs at room temperature were grown on a silicon/silicon dioxide (Si/SiO$_2$) substrate using a PbSe source in electron beam-assisted Edwards E306A physical vapor deposition system under the vacuum of 10^{-5} Torr. The film thickness was measured by the Edwards FTM5 Digital Film Thickness Monitor with a resolution of 0.1 nm, and the deposition rate was about 0.1–0.2 nm/s. The film morphology, mean grain size, and surface roughness depend on the substrate temperature, T_s, which was kept fixed within ±3 °C.

Hall Effect measurements were carried out between 4.2 K and 300 K at the magnetic field of 1 T. The samples were mounted on a copper holder in a variable-temperature He closed-cycle Janis cryostat (model SRDK 101D) operating under the pressure of 10^{-7} Torr. Temperature stabilization was maintained at ±0.01 K by the CryoCon cryogenic control system (model 32 BB). Electric signals were measured by Keithley 2000 multi-meters and recorded using a home-made LabVIEW program.

Improvement of structural and transport properties of *n*-type thin PbSe films were made by heat treatment in argon at 400 °C for 1 h under the pressure of 1 atm in an encapsulated reactor. Note that annealing in argon does not change the type of conductivity in the samples, but leads to the increase of electron mobility to ~210 cm^2/Vs at 100 K (vs. ~150 cm^2/Vs at 100 K before annealing).

Thermal oxidation of thin PbSe films was carried out in a resistance-heated furnace and a cylindrical stainless-steel reactor containing the samples. The oxidation temperature ranged from 400 to 500 °C. The experimental setup was computer-controlled with temperature accuracy within ±1 °C. The CTI from *n*- to *p*-type was discovered in these films after treatment in oxygen at 400 °C. Titanium (Ti) contacts, prepared by electron beam PVD technique, were used for electrical measurements. The current-voltage (*I-V*) characteristics were found to be linear for all *n*- and *p*-type PbSe samples over the entire temperature range examined, thus confirming the Ohmic nature of the contacts. After oxidation, the carrier concentration, *p*, was basically constant at 7×10^{18} cm^{-3} between 80 and 300 K and was not dependent on the duration of heat treatment in oxygen. The electrical conductivity within the same temperature range was found to be between 2 and 10 Ω^{-1} cm^{-1} depending on the duration of heat treatment in oxygen.

Atomic force microscopy (AFM) and x-ray diffraction (XRD) were used to determine the quality and composition of thin film PbSe structures. AFM images displayed polycrystalline morphology with grain size ranging from 200 to 300 nm and the root mean square surface roughness between 10 and 15 nm. The XRD spectrum of PbSe film revealed a single face centered cubic (FCC) crystalline phase with a rock salt structure indicating a texture with the axis in [100] direction perpendicular to the substrate.

We propose that the mechanism responsible for CTI in thin PbSe films after oxidation is due to generation of acceptor states at the surface of *n*-type grains from oxygen

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[a)] E-mail: chernyak@physics.ucf.edu.

diffusion along the grain boundaries.[1–3] The following process, illustrated in Fig. 1(a), may accompany the thermal oxidation of thin PbSe film: oxygen chemisorption on grain surfaces and boundaries, oxygen diffusion along grain surfaces and boundaries into the grain bulk as in Fig. 1(a) (1–3), Pb and Se out diffusion from the grains as in Fig. 1(a) (4) and the formation of oxide phases as in Fig. 1(a) (5–6).[2] The schematic drawing of the thin PbSe film heterojunction is presented in Fig. 1(b).

Current-voltage characteristics and photoelectric properties were measured over a temperature range of 4–330 K using a helium gas Janis closed-cycle cryostat (model SRDK 101D) evacuated down to 10^{-7} Torr. The GaAs laser (wavelength $\lambda = 0.65\,\mu$m) with 5 mW power and InAs light emitting diode, LED (wavelength $\lambda = 2.3\,\mu$m), were employed as the light sources. The produced photo-voltage signal was measured by a SR-7265 DSP lock-in amplifier and collected by a computer-recording system based on the LabVIEW Program.

The experimental *I-V* curves for thin film PbSe diode structure as a function of temperature are plotted in Fig. 2. These *I-V* curves have also been fitted by the Shockley's formula (with the series resistance, R_s, equal to 0 within experimental accuracy),

$$J = J_S\left[\exp\left(\frac{eV}{nkT}\right) - 1\right], \tag{1}$$

where J_s is the saturation current, e is the electron charge, n is ideality factor, T is absolute temperature. The parameters J_s and n were found by standard fitting in the forward bias region. Fig. 2, inset, shows the *I-V* characteristics of thin film PbSe diode structure under GaAs laser illumination. According to this figure, the structure saves the diode characteristics up to 300 K.

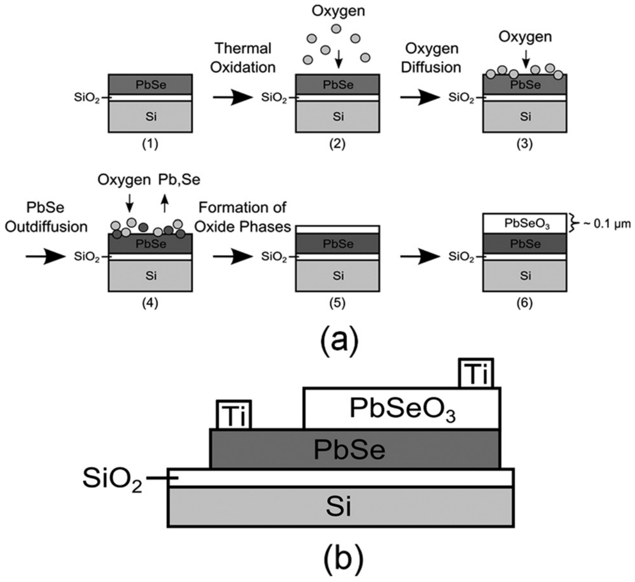

FIG. 1. (a) Model of oxidation process in thin film PbSe. Here, (1–3) represents oxygen chemisorption on grain surfaces and boundaries, oxygen diffusion along grain surfaces and boundaries into the grain bulk; (4) represents Pb and Se out diffusion from the grains; (5) represents the formation of oxide phases. (b) Schematic view of the thin film PbSe heterojunction. (Thicknesses of $PbSeO_3$ and PbSe are not shown to scale.)

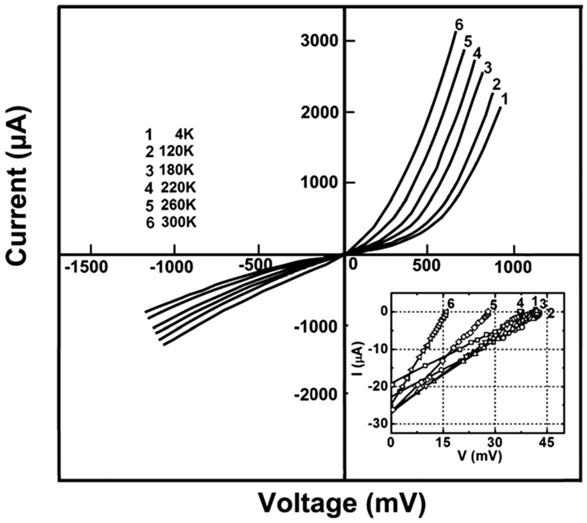

FIG. 2. Variable temperature current-voltage characteristics of the thin film PbSe diode structure. Inset: the first negative quadrant for the current-voltage characteristics of the thin film PbSe diode structure under GaAs laser illumination. Open-circuit voltage and short-circuit current are determined as intersections with x- and y-axis, respectively.

The dynamic resistance, R_d, is given by

$$R_d = \frac{nkT}{eJ}. \tag{2}$$

Calculated values of the dynamic resistance, R_d, and the ideality factor, n, as a function of temperature are presented in Figs. 3(a) and 3(b), respectively. The dark current and the thermal noise of an IR photodiode can be characterized by R_dA,[4] defined as the product of the diode dynamic resistance, R_d, at zero bias, and the diode area, A. The R_dA values allow us to estimate the specific detectivity, D^*, of these diodes.

The specific detectivity, D^*, of a photodiode is defined as[5]

$$D^*_\lambda = \frac{R_\lambda}{\left(\frac{4kT}{R_dA} + 2e^2\eta\, Q_B\right)^{1/2}};$$

$$R_\lambda = \eta e\lambda/hc; \quad Q_B(\nu_c, T) = \int_{\nu_c}^{\infty} J(\nu)\, d\nu \tag{3}$$

$$J(\nu) = \frac{8\pi\nu^2}{c^2}\cdot\frac{1}{\exp(h\nu/kT) - 1}.$$

Here, R_λ is the current-mode responsivity at wavelength λ, η is the quantum efficiency, and ν_c or λ_c are the cut-off frequency or wavelength, respectively. $J(\nu)$ is the flux density per unit frequency interval. For the black body radiation at 300 K, the typical values for the above parameters are: $\eta \approx 0.5$ and R_λ ($\lambda_c = 4\,\mu$m) ≈ 1.6 A/W. These values were used for the estimates.

The detectivity in the Eq. (3) consists of two contributions. While the first term in the denominator represents the Johnson noise, the second one stands for the background-induced noise. We, thus, estimate D^* for thin film PbSe diode structure at $T \approx 300$ K to be $\sim 1 \times 10^9$ cm Hz$^{1/2}$/W.

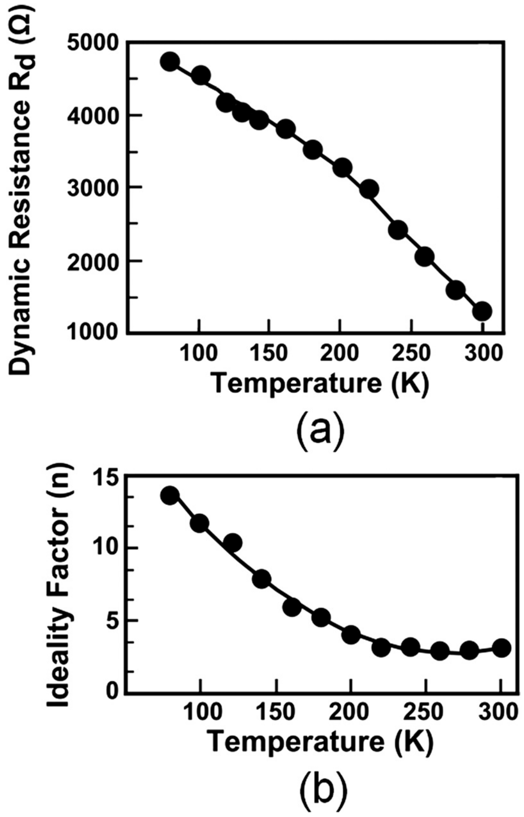

FIG. 3. (a) Temperature dependence of dynamic resistance, R_d, for the thin film PbSe diode structure. (b) The dependence of ideality factor, n, on temperature for the thin film PbSe diode.

The room temperature photoresponse for the thin film PbSe diode structure as a function of bias voltage at 1 kHz is presented in Fig. 4(a). The photosignal disappears at the forward bias close the barrier height, eV_b, with the build-in potential, V_b, experimentally estimated from the slope in Fig. 4(a) to be around 100 mV. The relative photosignal under GaAs laser ($\lambda = 650$ nm) and InAs LED (wavelength $\lambda = 2.3\ \mu$m) illumination for thin film PbSe diode structure as a function of temperature and pulse frequency is plotted in Fig. 4(b). One can see from this figure that the thin film PbSe diode structure exhibits photosensitivity up to 300 K, with the maximum at 200 K. The same behavior seen for the photosignal temperature dependence, both under GaAs laser and InAs LED illuminations, leads to the conclusion that PbSe diodes are photosensitive in the IR spectral range up to the PbSe band gap (4.3 μm). Although the dynamic resistance, R_d, for the photodetector decreases with increasing temperature (cf. Fig. 3(a)), we observe a decrease of the photosignal at room temperature versus 200 K, as in Fig. 4(b), due to thermal generation of electron-hole pairs, which, in turn, reduces the signal-to-noise ratio. Photosensitivity in the temperature range from 200 to 300 K allows using a Thermoelectric Cooler Module integrated with thin film PbSe diode structure, thus eliminating the need for liquid nitrogen cooling.

The presence of photosensitivity and rectifying characteristics in diode structures at temperatures up to 300 K demonstrates their suitability as photodetectors. The CTI from n- to p-type in thin PbSe films is observed after treatment in oxygen at 400 °C. We propose that the mechanism responsible for CTI in thin PbSe films after oxidation is through generation of acceptor states at the surface of n-type grains due to oxygen diffusion along the grain boundaries.

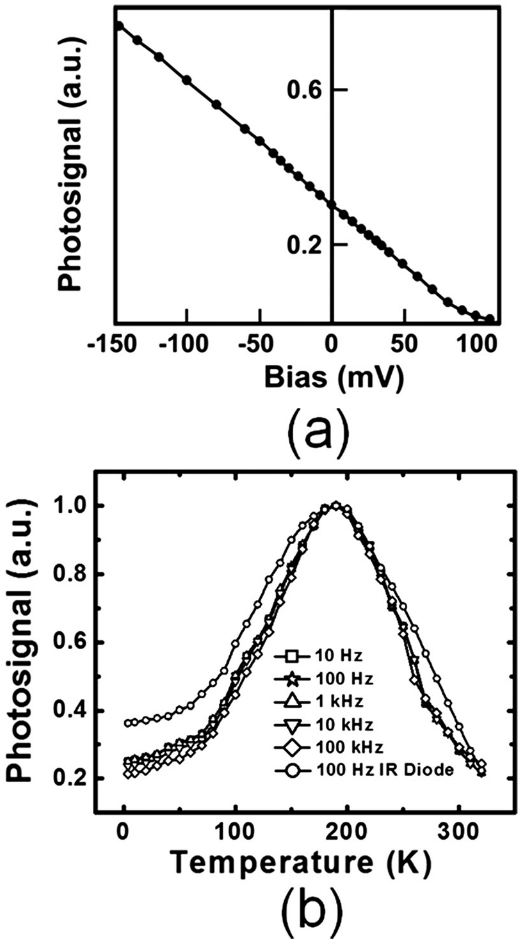

FIG. 4. (a) Photosignal of the thin film PbSe diode structure at $T = 300$ K (1 kHz; GaAs laser illumination) vs. bias voltage. (b) The relative photosignal of the thin film PbSe diode structure as a function of temperature and illumination by GaAs laser ($\lambda = 650$ nm) and InAs LED ($\lambda = 2.3\ \mu$m) with different pulse frequency.

ACKNOWLEDGMENTS

This research was supported in part by NATO under the Collaborative Linkage Grant # 984277.

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