

Field-effect-assisted photoconductivity in PbS films deposited on silicon dioxide

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Lead sulfide (PbS) thin films were deposited from a chemical bath onto SiO₂/Si (*n*-type) substrates. Pseudo-metal–oxide–semiconductor devices were obtained by evaporating source and drain gold electrodes on a PbS surface and aluminum gate electrode on a Si substrate. Field-effect-assisted photoconductivity in the PbS layer was investigated at room temperature, in the 800–2700-nm-wavelength domain for different values and polarities of the drain and gate voltages. The best results were obtained for a positive gate, when both semiconductors are in depletion. An enhancement of about 25% of the photoconductive signal is obtained compared with the case when the gate electrode is absent or is not used. A simple model is proposed that explains the behavior of the dark current and photoconductive signal in PbS film with changing the gate voltage. © 2002 American Institute of Physics. [DOI: 10.1063/1.1468277]

I. INTRODUCTION

Lead sulfide (PbS) is a well-known A₄B₆ semiconductor compound with very good photoconductive properties in the infrared (IR) domain (800–3000 nm at room temperature).^{1,2} It has largely been used to manufacture photoconductive cells for civil and military applications. The standard method used for preparing PbS films is the chemical bath deposition (CBD).^{3–6} This method is less expensive, easy to handle, allowing the deposition of PbS films on a large area and on various substrates. The usual substrate for deposition is glass and electrical Ohmic contacts are made from vacuum-evaporated gold, in coplanar configuration. PbS films were also deposited on other semiconductor materials (for example on Si, Ge, or InP),^{7,8} on ferroelectrics ceramics (PZT type),⁹ or on dielectrics [silicon nitride (Si₃N₄)].¹⁰ Pseudo-metal–oxide–semiconductor (pseudo-MOS) structures were also manufactured in order to study the field-effect-assisted photoconductivity. An example is the PbS/Si₃N₄/Si structure in which the drain and source electrodes are deposited on the PbS surface and the gate electrode is on the Si substrate.¹⁰ The structure is *p*–*i*–*n*-type, PbS being the *p*-type semiconductor, while the Si substrate is *n* type. It was shown that on such structures it is possible to control the photoconductive signal in PbS by the applied gate voltage. For positive gate voltages it is possible to obtain an enhancement of the signal-to-noise ratio compared with the case when no gate electrode is used. However, it was observed that for positive drain the leakage current through the dielectric layer increases, leading to increased noise and decreased signal. The best results were obtained for negative drain and positive gate cases when both semiconductors are in depletion.

In the present article the dielectric layer is silicon dioxide (SiO₂). A pseudo-MOS structure is realized and it is

shown that significant variation of the photoconductive signal can be obtained by field effect for both positive and negative drain, on the entire sensitivity spectrum of PbS. A simple model is proposed in order to explain the experimental results.

II. SAMPLE PREPARATION AND EXPERIMENTAL METHODS

The SiO₂ layer was grown on single-crystalline *n*-type Si wafers. Thermal oxidation at 850 °C was used, in an atmosphere containing oxygen and water vapors. The final thickness of the SiO₂ layer was of about 250 nm. The PbS film was deposited by the CBD method, using lead nitrate [Pb(NO₃)₂] as the Pb²⁺ ion source and thiourea as the S²⁻ ion source.^{6,9} The deposition is performed in alkaline medium, using sodium hydroxide (NaOH), the starting solution pH being 11. Small amounts of a reducing agent (hydroxylamine chlorhydrate) and of a Bi salt are introduced in the bath in order to control the nucleation/growth process during the deposition of the PbS layer. It is known that the photoconductive properties of PbS are strongly dependent on film morphology that, in turns, depends on the bath composition.^{6,11,12} The PbS film is then photolithographic processed, leaving an area of 2.5×3.5 mm². Gold electrodes are vacuum evaporated on the PbS surface, the final active area being of 1.5×1.5 mm². After electrode deposition, the PbS films are aged at 80 °C for about 80 h in air. The final structure is schematically presented in Fig. 1.

The photoconductive measurements were performed in modulated light, using the standard setup composed by a grating monochromator (model Spex270), a lock-in amplifier (model SR830DSP), a dc voltage source (model Grundig 300), an incandescent lamp as an IR source (30 W nominal electric power), and a mechanical chopper (model Ithaco 383A). A load resistance, with a value close to the dark re-

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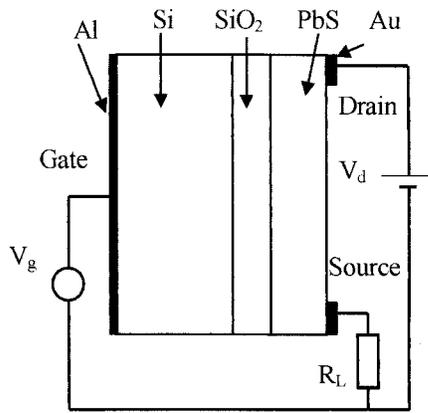


FIG. 1. Schematic of the pseudo-MOS PbS/SiO₂/Si structure and of the electrical setup used for field-effect-assisted photoconductivity measurements: V_d , drain voltage; V_g , gate voltage; and R_L , load resistance.

istance of the PbS film (usually a few hundreds k Ω), is series connected with PbS and is used to collect the photoconductive signal (see Fig. 1). For current–voltage (I – V) characteristics a Keithley electrometer, with a built-in dc voltage source (model 6517A) was used. For field-effect-assisted photoconductive measurements an aluminum electrode was deposited on the Si substrate. This will be the so-called gate electrode by analogy with the pseudo-MOS transistors manufactured using silicon-on-insulator (SOI) structures. In the present case the conductive channel is PbS, the drain and source electrodes are on the PbS surface, and the Si substrate is the gate electrode.

III. EXPERIMENTAL RESULTS

The transversal I – V characteristics, between one electrode from the PbS surface and the gate electrode, had shown that the leakage current through the dielectric layer is very low (a few pA) no matter the polarity on the PbS surface. The drain I – V characteristics are represented in Fig. 2 for different polarities and values of the gate voltage. These measurements were performed keeping the sample in the dark, thus no light was applied on the surface of the PbS

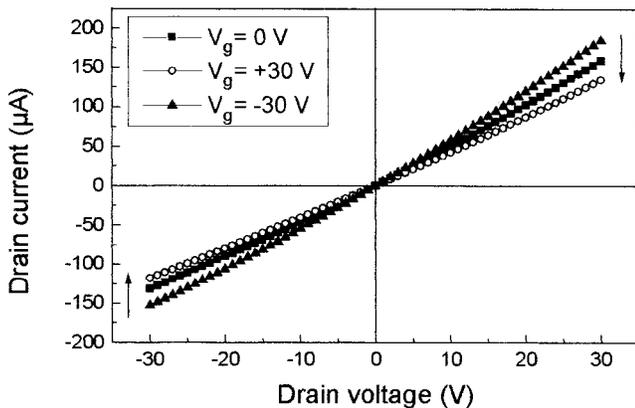


FIG. 2. Drain current–drain voltage characteristics for different polarities and values of gate voltage V_g . Arrows show the increasing of the gate voltage V_g .

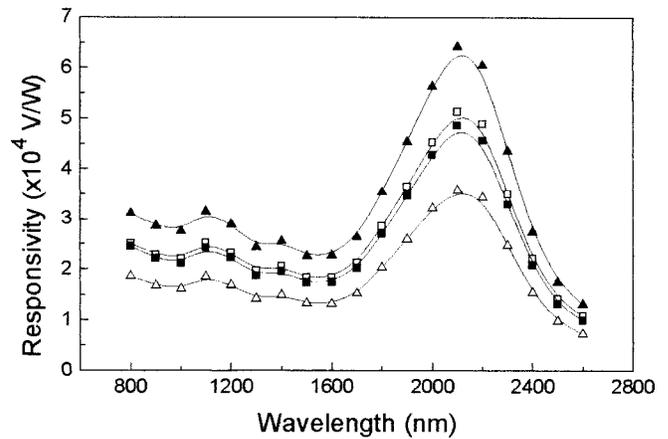


FIG. 3. Spectral distribution of responsivity in the case of PbS/SiO₂/Si heterostructures, for different gate voltages: open-squares, floating gate; solid squares, ground gate; solid triangles, $V_g = +30$ V; and open triangles, $V_g = -30$ V. Drain voltage was $+30$ V.

film. It can be observed that the value of the drain current decreases by increasing the value of gate voltage V_g .

The spectral distributions of responsivity are presented in Fig. 3 for different polarities and values of the gate voltage. The responsivity is defined as the ratio between the measured signal S , expressed in volts (V), and the incident power P_{inc} on the detector surface, expressed in watts (W):¹³

$$R(V/W) = \frac{S(V)}{P_{inc}(W)}. \tag{1}$$

The drain voltage was in all cases $+30$ V. The open-square curve was obtained for the floating gate (the gate electrode is not connected). It can be observed that for positive gate voltages the signal increases and for negative gate voltages it decreases on the entire sensitivity range of PbS. Similar results were obtained for negative drain (-30 V), but the signal variation with the gate voltage was smaller in this case.

The relative variation of the photoconductive signal is presented in Fig. 4. This was computed using the following

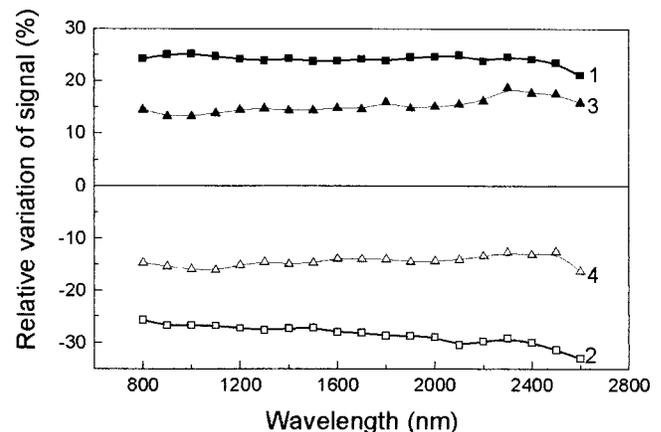


FIG. 4. Spectral distribution of the relative variation of the photoconductive signal: (1) $V_d = +30$ V and $V_g = +30$ V; (2) $V_d = +30$ V and $V_g = -30$ V; (3) $V_d = -30$ V and $V_g = +30$ V; and (4) $V_d = -30$ V and $V_g = -30$ V. Formula (2) was used for computation.

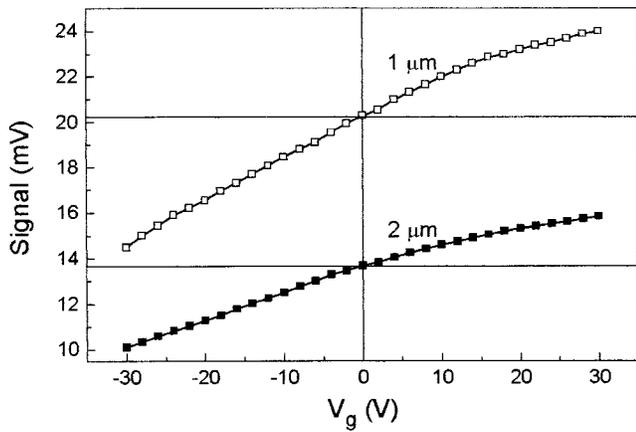


FIG. 5. Dependence of the photoconductive signal on the gate voltage ($V_d = +30$ V).

formula:

$$\Delta S(\%) = \frac{S(V_g) - S_{\text{float}}}{S_{\text{float}}}, \quad (2)$$

where $S(V_g)$ is the signal corresponding to a certain value of the gate voltage V_g and S_{float} is the signal measured when the gate is floating (is not connected). As it can be seen, the relative variation of the signal is almost constant on the PbS sensitivity range (800–2600 nm, the cutoff wavelength is 2600 nm due to the glass bulb of the incandescent lamp, when using a Nernst glower the cutoff wavelength is 3000 nm).

The wavelength was then set to a fixed value (1000 and 2000 nm) and the dependence of the photoconductive signal on the gate voltage was raised. The obtained results are presented in Fig. 5. The dependence is almost linear up to about $V_g = 15$ V and then has the tendency to saturate. These curves were raised for a positive voltage of 30 V applied on the drain electrode.

IV. DISCUSSIONS AND THEORY

The signal variation with the gate voltage can be qualitatively explained if the field effect is considered. As it is known, the chemically deposited PbS films are p type.¹ Considering that the Si substrate is n type, the studied samples are similar to $p-i-n$ structures will be considered an ideal case, with an ideal insulator and flat energy bands for $V_g = 0$ V.

Two effects can lead to signal variation with the applied gate voltage.

A. Variation of depleted region width in the PbS film

A simple model can be developed in this case. Considering positive V_g , it follows that holes will be rejected from the PbS/SiO₂ interface and depletion will occur. The PbS film can be divided in two layers in this case: one is the space-charge region, near the PbS/SiO₂ interface, which is supposedly free of charge carriers; the second one is the neutral region. The model supposes that no current will flow through the space-charge region. Thus, the current flows only through the neutral channel. It is supposed that the thickness

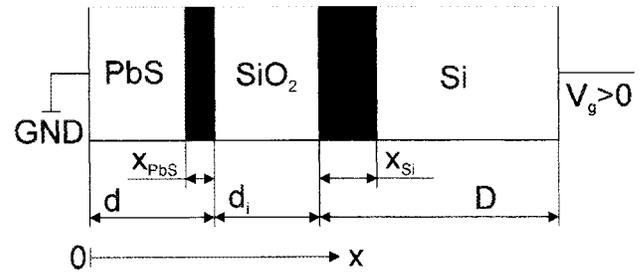


FIG. 6. Schematic of the PbS/SiO₂/Si structure with voltage V_g applied on the gate electrode. d_i is the thickness of the insulating layer, D is the thickness of the Si substrate, and x_{Si} is the thickness of the space-charge region in Si.

of this channel is constant between the drain and source electrodes. This is valid when load resistance R_L (see Fig. 1) is larger than the PbS film's dark resistance. A value of 1 M Ω was considered for R_L , larger than the value of 250 k Ω that is typical for PbS films. However, the value for R_L used in simulation is larger than that used in the measurements, thus some simulated quantities will be smaller than the measured ones (for example, the dark current). The formula that gives the dark current value is

$$I = \frac{V_d}{R_L + \frac{\rho L}{l(d - x_{\text{PbS}})}} = \frac{V_d}{R_L + \frac{\rho}{(d - x_{\text{PbS}})}}, \quad (3)$$

where V_d is the drain voltage, ρ is the PbS resistivity, L is the distance between the drain and source electrodes, l is the width of these electrodes, d is the thickness of the PbS film, and x_{PbS} is the thickness of the space-charge region in PbS. For the sake of simplicity it was considered that $L = 1$ (the distance between the PbS electrodes is equal with their width). The thickness of the space-charge region in PbS can be computed solving Poisson's equation in a simplified structure like that from Fig. 6. Thus, solving the Poisson's equation in the three materials with the appropriate boundary and continuity conditions, and taking into account that¹⁴

$$V_g + \Phi_{\text{PbS}} + V_i + \Phi_{\text{Si}} = 0, \quad (4)$$

$$x_{\text{PbS}} N_A = x_{\text{Si}} N_D,$$

the following expression for x_{PbS} will result:

$$x_{\text{PbS}} = \frac{-d_i + \sqrt{d_i^2 + \frac{2\epsilon_i^2}{qN_A} \left(\frac{1}{\epsilon_{\text{PbS}}} + \frac{1}{\epsilon_{\text{Si}} \frac{N_A}{N_D}} \right) (V_g + V_{\text{ox}})}}{\frac{\epsilon_i}{2} \left(\frac{1}{\epsilon_{\text{PbS}}} + \frac{1}{\epsilon_{\text{Si}} \frac{N_A}{N_D}} \right)}. \quad (5)$$

In Eq. (4) the first equation expresses the potential continuity at $x = d + d_i + x_{\text{Si}}$ (the border between the Si space charge and the Si neutral volume). The second equation expresses the charge conservation (the charges in the two depleted regions have to be equal). The notations are V_g is the positive voltage applied on the gate to obtain depletion, Φ_{PbS} is the surface potential at the PbS/SiO₂ interface ($x = d$), V_i is the voltage drop across the insulator, and Φ_{Si} is the surface po-

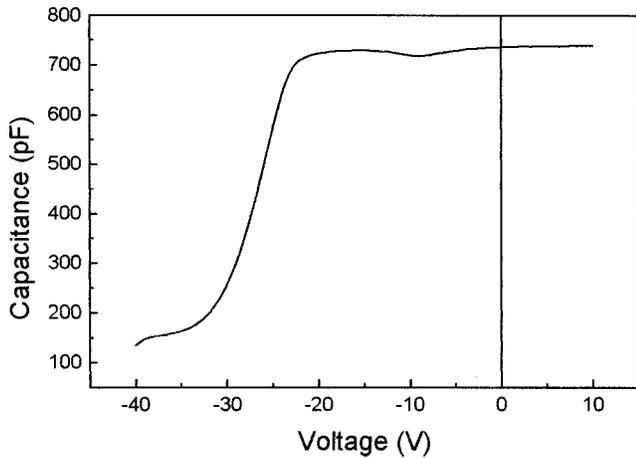


FIG. 7. C - V characteristic of the PbS/SiO₂/Si structure measured at 10 kHz.

tential at the Si/SiO₂ interface ($x=d+d_i$). In Eq. (5) the notations are ϵ_{PbS} is the dielectric constant of PbS (175), ϵ_i dielectric constant of insulator (in case of SiO₂ is 4), ϵ_{Si} dielectric constant of Si (12), N_A is the acceptor concentration in PbS (10^{16} – 10^{17} cm⁻³), N_D the donor concentration in Si (around 10^{15} cm⁻³), and q is the elementary charge. V_{ox} is a positive voltage that takes into consideration the presence of the positive charge in the SiO₂ layer. Due to this charge the structure is depleted when negative gate voltages are applied, as it can be seen from the capacitance–voltage (C – V) characteristics presented in Fig. 7. The value of V_{ox} can be as high as a few tenth of volts. We have considered a value of 30 V for further simulation.

From Eq. (5) it can be observed that increasing V_g the thickness of the space-charge region in PbS increases. The thickness of the neutral channel, that is, $d-x_{\text{PbS}}$, decreases, the resistance of this channel increases, and the current flowing through the PbS film decreases with V_g . This is shown in Fig. 8 and is confirmed by the experimental data presented in Fig. 2.

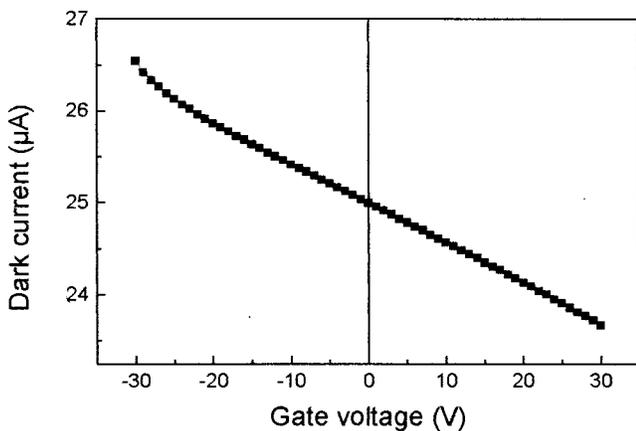


FIG. 8. Theoretical dependence of the dark current, flowing through the PbS layer, on the gate voltage applied on the Si substrate. Equation (3) was used, with x_{PbS} given by Eq. (5). Values used for the simulation: $V_d=+30$ V, $R_L=1$ M Ω , and V_g varied between -30 and $+30$ V.

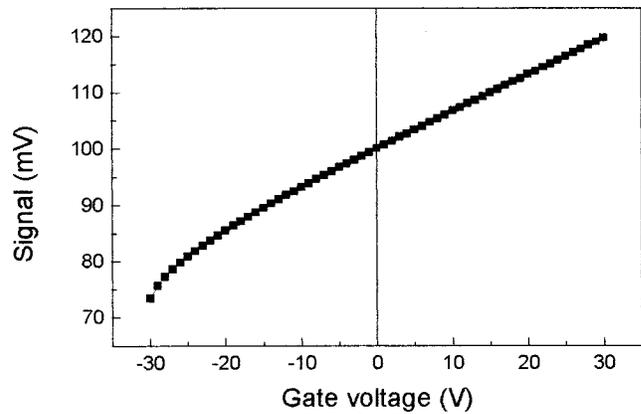


FIG. 9. Theoretical dependence of the photoconductive signal on the gate voltage, obtained using Eq. (6), for a wavelength that is uniformly absorbed in PbS. Values used for the simulation: $V_d=+30$ V, $R_L=1$ M Ω , and V_g varied between -30 and $+30$ V.

The amplitude of the photoconductive signal, in the case of the rectangular modulation of the incident light, is given by

$$\Delta v = \frac{R_L V_d}{\left(R_L + \frac{\rho}{d-x_{\text{PbS}}}\right)^2} \frac{\Delta \sigma}{\sigma^2} \frac{1}{d-x'_{\text{PbS}}}, \quad (6)$$

where $\Delta \sigma$ is the electric conductivity’s variation of the PbS film when it is exposed to light, σ is the dark electric conductivity of PbS film, x_{PbS} is the thickness of space-charge region in PbS in the dark condition, and x'_{PbS} is the thickness of the space-charge region in PbS when the film is exposed to light. Formula (6) was derived considering that the thickness of the neutral conductive channel is constant. As was mentioned above, this is valid only if the load resistance R_L is much larger than the value of the PbS dark resistance. The usual value of the dark electric conductivity for PbS is about $1.5 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$. It will be considered that the electric conductivity variation $\Delta \sigma$ is the same no matter if the gate voltage is applied or not and is given only by the variation of the charge-carrier concentration and carrier mobility under illumination. Variation of the charge-carrier concentration under illumination changes the thickness of the space-charge region, also. This is considered through x'_{PbS} , which is computed using a carrier concentration equal with N_A+n_I instead N_A , where n_I is the concentration of photogenerated carriers. This is of the order of 10^{14} – 10^{15} cm⁻³ (depending on the light intensity), while N_A is of the order of at least $(5-10) \times 10^{16}$ cm⁻³.

Returning to Eq. (6), it can be observed that the photoconductive voltage should increase with the gate voltage if the power of the incident light is constant. This is presented in Fig. 9.

The relative variation of the signal was computed using the following formula:

$$R(\%) = \frac{(\Delta v_{V_g} - \Delta v_0) 100}{\Delta v_0}, \quad (7)$$

where Δv_{V_g} is the photoconductive signal for a certain voltage V_g applied on the gate, and Δv_0 is the signal when the gate voltage is zero. A value of about 20% was obtained for R if $V_g = +30$ V. This value is very close to those obtained experimentally.

B. Variation of photogenerated holes lifetime

For large positive V_g , electrons (minority carriers) will be attracted at the PbS/SiO₂ interface (inversion). This will lead to an increase of the photogenerated hole (majority carriers) lifetime, because the recombination probability decreases. A further increase of signal can be obtained in this case. When V_g is negative, holes will be attracted to the PbS/SiO₂ interface, their lifetime will decrease and the signal will be smaller. This effect seems to contribute also to the signal variation, mainly in the extreme cases when both interfaces are in inversion (electron attracted in PbS, signal increases) or in accumulation (holes attracted in PbS, signal decreases). It cannot explain, alone, the large signal variation observed in Fig. 5, but can explain why the signal has the tendency to saturate at high gate voltages (inversion). If V_g is very large and the PbS/SiO₂ interface is definitely in inversion or accumulation, a further increase of V_g will have no effect because the negative or the positive charge already present at the interface will screen its influence.

V. CONCLUSIONS

Pseudo-MOS structures were manufactured using complex PbS/SiO₂/Si structures. Field-effect-assisted photoconductivity in the PbS layer was investigated and the following conclusions were drawn:

- (i) A signal variation of up to 50% can be obtained for positive drain and for gate voltage variation between -30 and $+30$ V.
- (ii) An increase of the signal with 25% can be obtained for positive voltage.
- (iii) Two possible effects can contribute to signal variation: (1) the variation of the depletion width region in PbS with the gate voltage, and (2) the variation of the majority carrier (hole) lifetime with the gate voltage.

- (iv) A simple model is proposed, considering that the field-effect-controlled photoconductivity is mainly due to the variation of the space-charge width in PbS.
- (v) The behavior of theoretical curves is similar to that of the experimental curves for the same range of gate voltages.

Further studies are needed to clarify why the results are not similar for positive and negative drain voltages. These structures open some interesting perspectives on PbS-based IR detectors, mainly regarding their integration with standard Si electronics.

ACKNOWLEDGMENTS

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