

Ternary FePSe₃ Atomic Layers with Competitive Temperature Coefficient of Resistance for Uncooled Infrared Bolometers

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The semiconducting metal phosphorus trichalcogenides (MPX₃, X = S, Se), a new family of layered atomic materials similar to the transition-metal dichalcogenides, have recently attracted great attention owing to their 2D magnetic properties as well as their wide range of tunable bandgaps, which can lead to promising applications in spintronic and optoelectronic devices. Herein, an uncooled bolometer based on FePSe₃ atomic layers is reported, on which a competitive temperature coefficient of resistance (TCR) of $\approx -2.96\% \text{ K}^{-1}$ at room temperature is observed. In detecting infrared radiation (980–1550 nm) at room temperature using the FePSe₃ bolometer, high responsivity exceeding 10^8 V W^{-1} and specific detectivity up to 10^9 Jones are achieved, which can be attributed to the combined advantages of the competitive room-temperature TCR and natural thermal isolation between the inner layers of FePSe₃ and the environment. This result reveals a remarkable property of FePSe₃ atomic layers and paves the way toward new types of bolometers with high sensitivities.

1. Introduction

Bolometers have been widely adopted for detecting infrared (IR) radiation for a variety of applications including thermal imaging, astronomy, health care, and security. A key advantage of the bolometers is that they can work at room temperature without cooling,^[1–7] which has been a major limitation for cooled photodetectors based on low bandgap semiconductors such as HgCdTe,^[8–11] II–VI and III–V semiconducting superlattices,^[12–17] and quantum wells,^[18–24] to reduce the dark current and enhance the signal-to-noise ratio. As bolometers measure the resistance change (ΔR) caused by temperature variation (ΔT) under the infrared illumination, high temperature coefficient of

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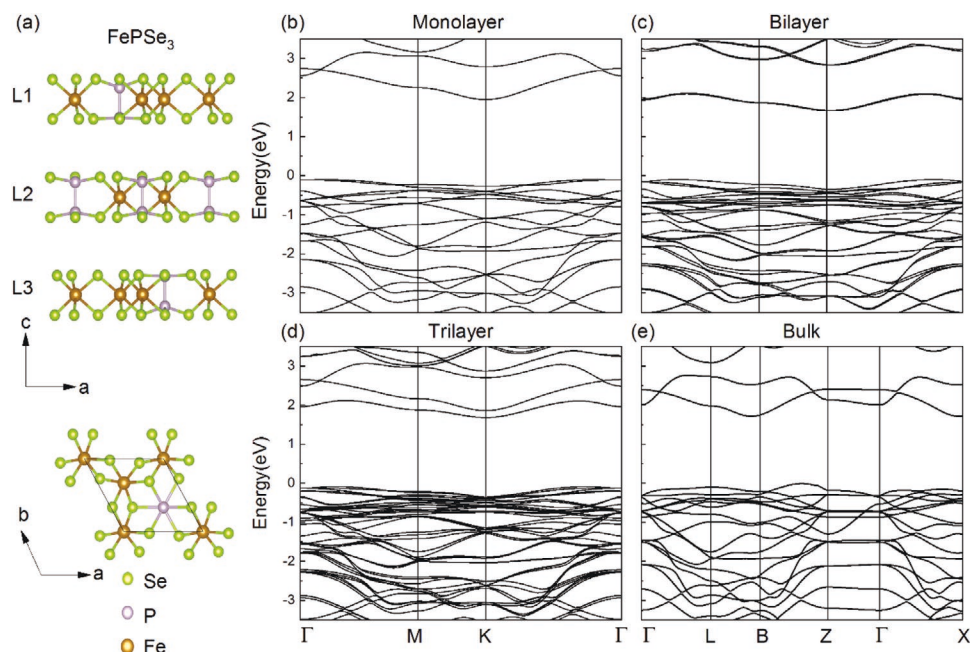


Figure 1. a) Layered structure (side view) of bulk FePSe₃ (upper) and in-plane lattice structure (top view) of a monolayer FePSe₃ (lower). The electronic band structures of the FePSe₃ material with b) monolayer, c) bilayer, d) trilayer, and e) bulk structures.

resistance (TCR) of the bolometer materials is critical. The commercially adopted materials have TCR values typically in the range of a few percent. For example, metallic Ti, Ni, or Pt have $\text{TCR} < 1\% \text{ K}^{-1}$,^[25–28] semiconducting amorphous silicon^[6,29,30] and vanadium oxide (VO_x)^[28,31,32] have TCR in the range of 2–4 and $-2\% \text{ K}^{-1}$, respectively. In addition, recently reported polycrystalline ceramic composites with large room-temperature TCR also show a promise for applications.^[33,34] Since $\Delta R = \text{TCR} \times \Delta T$, the bolometer detectivity may be limited under low infrared light intensity^[35,36] and/or poor thermal isolation of the bolometer. Therefore, a major challenge in the field is to explore new materials which can further improve the detectivity of bolometers and work under uncooled conditions.^[3–5,37,38]

The metal phosphorus trichalcogenides (MPX₃, X = S, Se) are a family of 2D layered atomic materials, similar to the transition-metal dichalcogenides, with high chemical diversity and wide range of tunable bandgaps where the bandgaps in MPS₃ (M = Mn, Fe, Ni, Zn, Cd, and In_{2/3}) and MPSe₃ (M = Mn, Fe, and In_{2/3}) range from 1.3 to 3.5 eV.^[39–43] Although the optical bandgap of FePSe₃ is ≈ 1.3 eV, it is worth noting that the Fe²⁺ ions are nearly octahedrally coordinated in the FePSe₃ crystal and the electronic configuration of the Fe²⁺ is 3d⁶(⁵D) in an octahedral ligand field. In a crystal field, the ⁵D state splits into a ⁵T_{2g} orbital triplet (ground state) and a ⁵E_g orbital doublet (excited state) when Fe²⁺ in the high spin state. The ⁵T_{2g} → ⁵E_g transition energy in FePSe₃ is located near 0.81 eV (≈ 1550 nm) at 300 K, which corresponds to an absorption band ranging from 0.75 (1650 nm) to 0.89 eV (1400 nm).^[44] This suggests that the FePSe₃ could be a promising material for near-infrared (NIR) and short-wave infrared (SWIR) detection. In particular, the conventional semiconductor bolometers must be suspended to reduce their thermal link to the surrounding for high signal-to-noise ratios. In contrast, the FePSe₃ atomic-layer stack

with the weak van der Waals (vdW) interlayer force inherits a naturally suspended structure that can reduce effectively the thermal link to the supporting substrate. Motivated by this, we present the first systematic study of the FePSe₃ bolometers with thicknesses ranging from 6 layers (6 L) to 74 L using the mechanical exfoliation and dry transfer method. A competitive room-temperature TCR of $\approx (2\text{--}3)\% \text{ K}^{-1}$ has been obtained, which is comparable to that for the current state-of-the-art commercial VO_x bolometers. Remarkably, high responsivity (R_v) exceeding 10^8 V W^{-1} and specific detectivity (D^*) up to 10^9 Jones (1 Jones = $1 \text{ cm Hz}^{1/2} \text{ W}^{-1}$) under 1550 nm light illumination have been obtained on uncooled FePSe₃ bolometers, suggesting 2D atomic layer materials are promising candidates for high sensitivity IR detection.

2. Results and Discussion

In the monolayer structure of FePSe₃, (P₂Se₆)^{4−} bipyramids are arranged in a triangular lattice and wrapped in a six-Fe ring (Figure 1a). The point symmetry group for monolayer structure is D_{3d} when the bulk is in space group R-3 (No. 148). The bulk crystals consist of ABC-stacked monolayer assemblies that are held together by van der Waals forces. Thus, the bilayer and trilayer structures are AB and ABC stacking, respectively. In the electronic band structure without spin polarization, all four modalities have an indirect bandgap, as shown in Figure 1b–e. In the few-layer form (monolayer, bilayer, and trilayer), the valence band maximum (VBM) is around Γ point and the conduction band minimum (CBM) is at K point. As the number of layers increases, the bandgap narrows down from 2.05 eV (monolayer) to 1.78 eV (trilayer). For the bulk structure, the indirect bandgap of 1.73 eV is the energy difference between

VBM along B-Z line and CBM around B point. In addition, note that we use the in-plane lattice constant (6.17 Å) from the experimental data and do not consider spin-orbit coupling and the Hubbard U correction, which may lead to that the calculated bandgap (1.73 eV) is larger than the experimental optical bandgap (1.30 eV) of bulk FePSe₃.^[45] The corresponding cutoff wavelength of FePSe₃ lies in the range from 605 to 717 nm based on the calculated bandgap values from 2.05 to 1.73 eV depending on the thickness. However, the particularity of the FePSe₃ crystal is that Fe²⁺ has a nearly octahedrally coordinated structure. The ground state and excited state of the Fe²⁺ in a crystal field are ⁵T_{2g} orbital triplet and ⁵E_g orbital doublet, respectively. To quantify the energy difference between Fe-d-*t*_{2g} (low-lying) and *e*_g (high-lying) states in FePSe₃, we estimate the relative on-site energy of each Fe-d orbital with maximally localized Wannier functions (MLWFs) obtained with the Wannier90 package.^[46] The Fe-d orbital is adopted as projections to construct WFs. Appropriate inner and outer energy windows are used during the disentanglement procedure. The calculated split value of the *t*_{2g} and *e*_g in FePSe₃ is ≈0.70 eV, which is consistent with the experimental room-temperature optical absorption for the ⁵T_{2g} → ⁵E_g transitions, i.e., actually is ascribed to the *t*_{2g} → *e*_g excitations that is a wide band ranging from 1400 nm (0.89 eV) to 1650 nm (0.75 eV).^[44] This means the optical absorption of FePSe₃ can extend to the NIR-SWIR spectra. A similar IR absorption has been reported on MoS₂ atomic layers taking advantages of the IR absorption of MoS₂ at 6–9 μm wavelengths.^[47]

The structures, quality, and average stoichiometry of FePSe₃ bulk single crystals were characterized by X-ray diffraction (XRD) patterns and energy-dispersive X-ray (EDX) spectroscopy (Figure S1, Supporting Information). The crucial peak of FePSe₃ single crystal is the XRD (003) diffraction peak located at 2θ ≈ 13.3°. In addition, the XRD pattern of the single crystal is exactly corresponding to the (00l) diffraction peaks of the FePSe₃, and no peaks of other impurity phases were observed (Figure S1a, Supporting Information). The EDX spectroscopy shows that the average atomic ratio of FePSe₃ single crystal is Fe:P:Se = 0.1977:0.2005:0.6019 ≈ 1:1:3 (Figure S1b, Supporting Information), which is consistent with the expected stoichiometric ratio of the FePSe₃ crystals. These results indicate that no significant vacancies were observed in FePSe₃ crystals as well as no traces of impurity were detected on the cleaved surfaces. **Figure 2a** shows the schematic of a multilayer-FePSe₃ bolometer device consisting of a FePSe₃ flake with two Cr/Au electrodes. The naturally suspended atomic layer structure of the FePSe₃ is illustrated schematically, which is desirable for bolometer applications. The thicknesses of the FePSe₃ flakes were measured using atomic force microscopy (AFM). Specifically, the thickness of a single-layer (1 L) FePSe₃ is ≈0.80 nm, which is consistent with literature.^[45] The AFM images and line scans taken on six FePSe₃ flakes with thicknesses of 5.04 nm (6 L), 7.85 nm (10 L), 13.73 nm (17 L), 25.72 nm (32 L), 43.87 nm (55 L), and 59.12 nm (74 L) are illustrated in Figure S2a–f and their insets, respectively (Supporting Information). The Raman spectra of these FePSe₃ flakes are exhibited in Figure 2b (43.87 nm in thickness) and Figure S4 (Supporting Information) (with flake layer numbers range of 6–74 L) in the Supporting Information. There are five characteristic Raman peaks

indexed to the FePSe₃ associated with the metal atom vibrations and the P₂Se₆ unit vibrations of D_{3d} symmetry group.^[45,48] The highest intensity peak at 210.2 cm⁻¹ is associated with the A_{1g}(ν₁) mode (the symmetric stretching vibration of the P–Se bonds). The other stretching vibration of the P–Se bonds is the A_{1g}(ν₂) mode at 163.6 cm⁻¹. The peaks at 143.5 and 176.5 cm⁻¹ are attributed to the E_g(ν₁₂) and the E_g(ν₁₁) modes, respectively, which do not involve any P–Se bond stretching. The peak at 110.3 cm⁻¹ is derived from the metal atom vibrations in the FePSe₃ crystals. With decreasing the number of layers of the FePSe₃, the Raman signal gradually weakens to the point that it is almost impossible to distinguish the signal from the noise due to the decreased amount of material (<9 L) (Figure S4, Supporting Information). On the other hand, the peak at 299.9 cm⁻¹ originated from SiO₂ becomes more prominent with decreasing FePSe₃ flake thickness due to decreasing signals from thinner FePSe₃ and increasing signal from the substrate.

The results from transport *R*–*T* curves reveal the semiconducting nature of FePSe₃ flakes (Figure 2c). The TCR of the 55 L (or 43.87 nm in thickness) FePSe₃ flake can be calculated by $TCR = (1/R_0) \cdot (dR/dT)$, and the result of TCR as a function of temperature is shown in the inset of Figure 2c. With increasing temperature, the absolute value of the decreases monotonically, which is similar to conventional bolometer materials.^[5,49] The TCR value of the 55 L (or 43.87 nm in thickness) FePSe₃ flake is as high as –12.89% K⁻¹ at low temperature of 123 K, and it can still reach a competitive value of –2.63% K⁻¹ at room temperature. To determine the relationship between the room-temperature TCR and the number of layers, we have prepared several samples with different thicknesses (6, 9, 19, 35 and 67 L) and measured their *R*–*T* curves in the temperature range of 295–353 K. The result is summarized in Figure 2d and Figure S3 (Supporting Information). Specifically, the TCR values obtained are in the range from –2.74 to –2.96% K⁻¹ at room temperature. This result, in combination with that on the two previously measured samples (35 and 55 L), indicates that the intrinsic TCR of the FePSe₃ around –2.9% K⁻¹ is nearly independent of the sample thickness. This is expected from the very weak interlayer interactions in 2D FePSe₃ atomic layers. It is worth noting that the TCR value of FePSe₃ is slightly larger than that of the commercial VO_x bolometer (typical about –2% K⁻¹).^[5] This implies that the ternary FePSe₃ atomic layers is a promising candidate material for a bolometer-type uncooled infrared detector. Based on the TCR and bandgap results described above, we can propose the operating principle of the FePSe₃ detector under the illumination of different wavelengths (Figure 2e). When the photon energy *hν* is greater than the bandgap of FePSe₃, the FePSe₃ layers could absorb photons to generate the excitons (photogenerated carriers) through interband *E_v* → *E_c* transitions, and the excitons can dissociate into free holes and electrons by the applied bias voltage between the two electrodes. Therefore, the device behaves like a photoconductor and the changes the conductivity of the FePSe₃ semiconductor channel is regarded as the photoconductive response. It should be noted that lower energy photons beyond the optical cutoff of the FePSe₃ can be absorbed via the ⁵T_{2g} → ⁵E_g transitions, resulting in the resistance decrease of the FePSe₃ channel due to the excitons dissociation to phonons (or lattice vibration) or heat (bolometric effect).

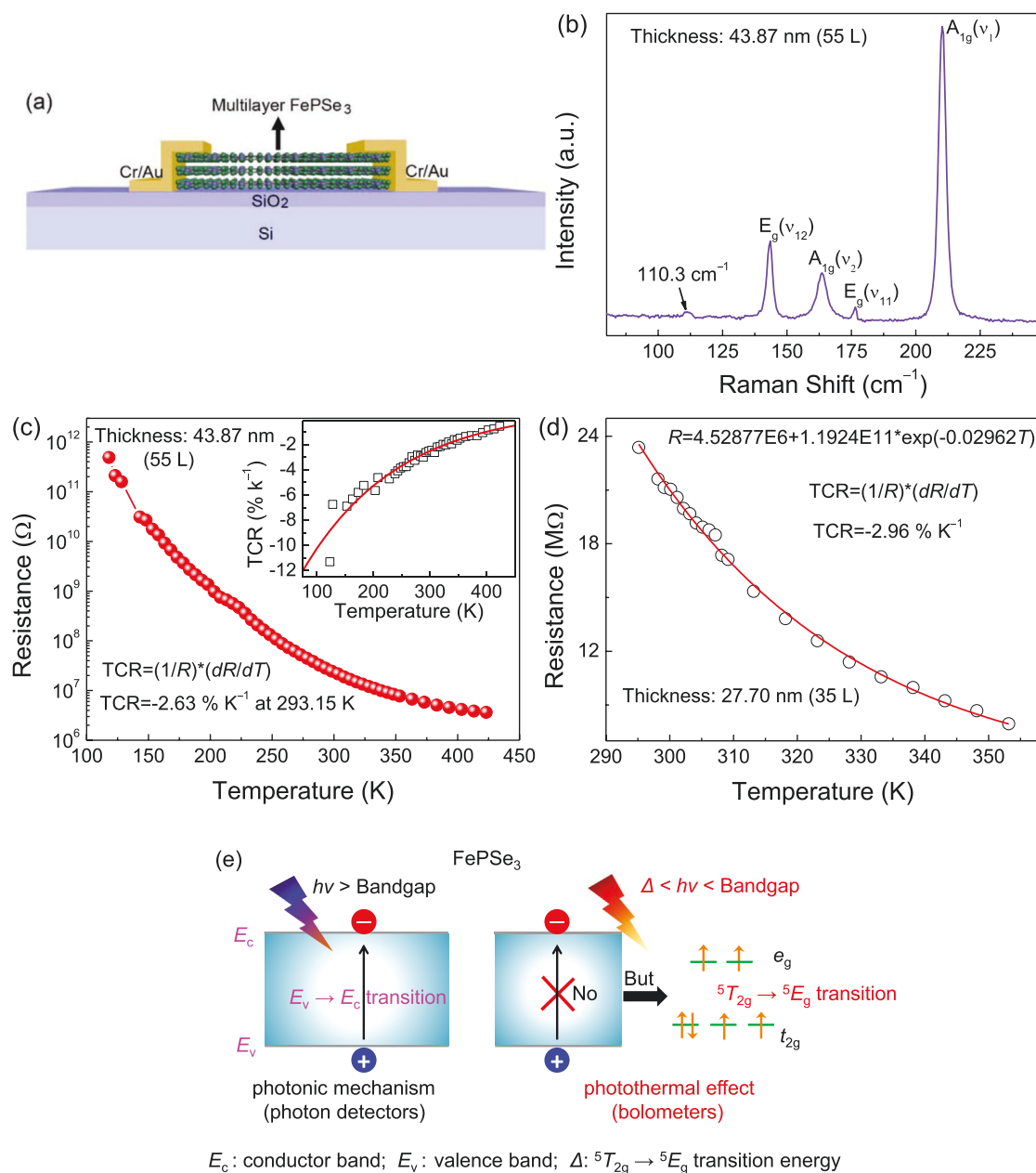


Figure 2. a) Schematic sideview of FePSe₃ bolometer device. b) Raman spectrum of the 55-layer FePSe₃ flake. Resistance R versus temperature T of the c) 55-layer FePSe₃ flakes and d) 35-layer FePSe₃ flake. Inset shows the extracted TCR of the 55-layer FePSe₃ flakes as a function of temperature. e) Schematic diagram of the operating principle of the FePSe₃ detector under the illumination of different wavelength bands.

The obtained photoresponse characteristics of the FePSe₃ devices with various layer numbers (6–74 L) are illustrated in **Figure 3a** as well as Figure S5 (Supporting Information) at various excitation wavelengths (400–1550 nm) with different optical powers. The linearity in the V_{ds} – I_{ds} curves indicates a good ohmic contact between FePSe₃ flake and Ti/Au electrode and is anticipated for a bolometer or photoconductor. The photoinduced voltage (photovoltage, V_{ph}) can be defined as the difference of the voltage in light and the dark, which is linearly dependent on the current (Figure 3b). The device can generate V_{ph} as high as 7 mV even when the incident light power is

as low as 0.075 nW, illustrating the benefit of the naturally suspended layered structure of the FePSe₃ flakes. Dynamic photoresponse measured on the FePSe₃ bolometers are shown in Figure 3c. The rise (and fall) time is defined as the time from 10% to 90% (from 90% to 10%) of the maximum photovoltage in response to IR illumination of 980 nm (blue), 1064 nm (purple), and 1550 nm (red) wavelengths, respectively. As illustrated in Figure 3d, the rise/fall times of the FePSe₃ bolometer are 0.68/0.75 and 0.76/0.91 s under 1064 and 1550 nm excitation, respectively, demonstrating promising performance for practical applications.

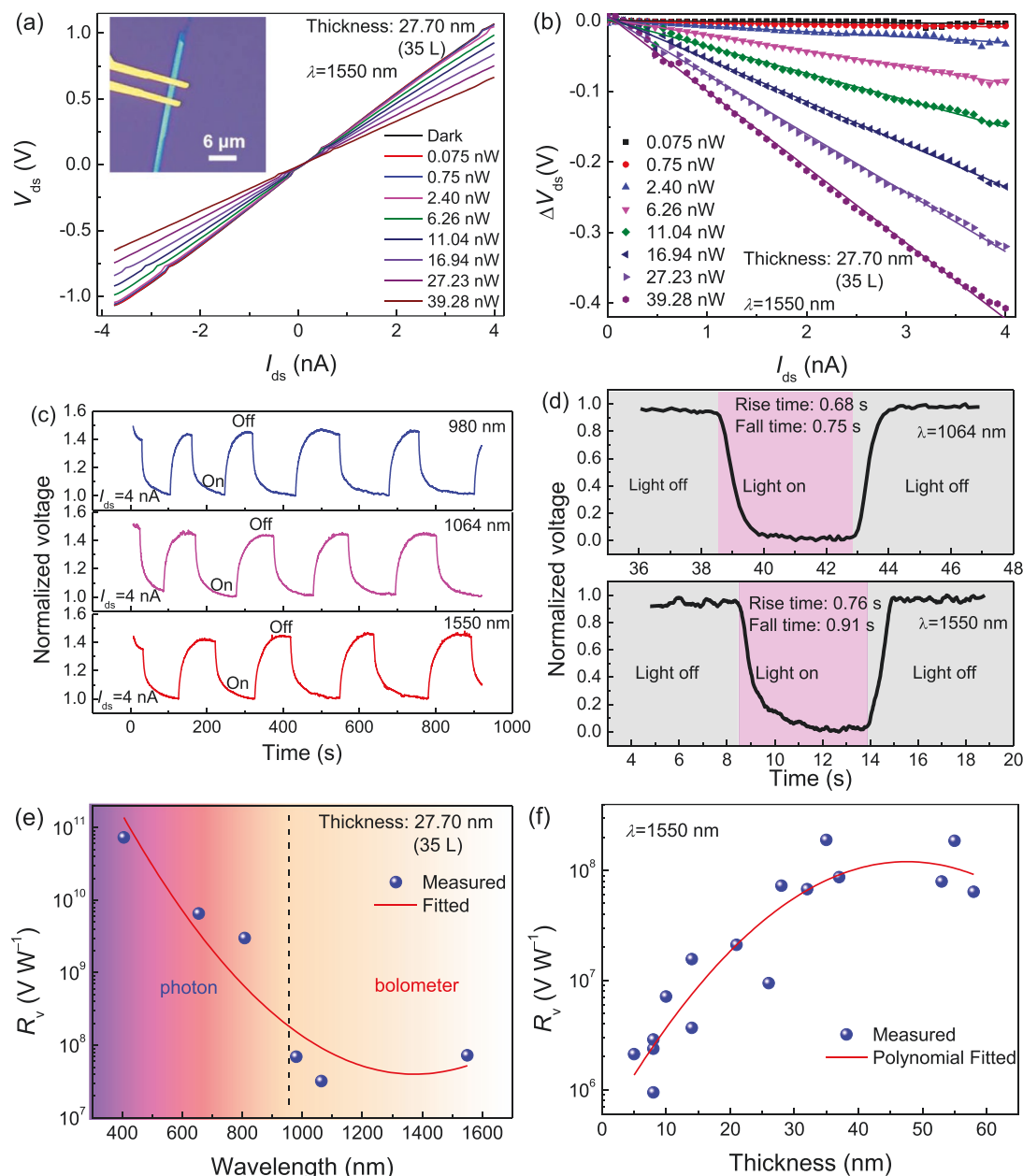


Figure 3. a) V_{ds} - I_{ds} curves of the 35 L FePSe₃ bolometer in the dark and under 1550 nm irradiation with various powers. b) Photovoltage (V_{ph}) versus current curves extracted from the V_{ds} - I_{ds} curves in (a). c) Temporal voltage response under various NIR-SWIR wavelengths of 980, 1064, and 1550 nm. d) Response time of the FePSe₃ bolometers. e) Responsivity R_v of the 35 L FePSe₃ bolometer as a function of wavelength. f) R_v versus thickness of the bolometer under 1550 nm irradiation.

An important figure of merit used to evaluate the performance of a bolometer is the voltage responsivity R_v , which is the photovoltage V_{ph} divided by the light power P_{in} : $R_v = V_{ph}/P_{in}$, where P_{in} is equal to the product of the incident optical power density P_d and the effective detection area S of the device. The R_v of devices with various layer numbers (6–74 L) at various excitation wavelengths (400–1550 nm) have been calculated (Figure 3e and Figure S6, Supporting Information). The R_v of the 35 L-thick FePSe₃ bolometer is as high as 10^{10} – 10^{11} V W⁻¹ when the excitation wavelength is in the ultraviolet–visible spectra. Remarkably, the R_v of the 35 L-thick FePSe₃ can reach

up to 5×10^7 V W⁻¹ in the NIR band. Obviously, when the energy of the incident photon is larger than the bandgap of FePSe₃ (the corresponding cut-off wavelength is ≈ 954 nm), the responsivity is significantly higher, which is not surprising considering the higher carrier energy and hence mobility. At the illumination of lower energy IR photons ($\Delta < h\nu < \text{Bandgap}$), the absorbed photon energy through the intraband $^5T_{2g} \rightarrow ^5E_g$ transitions is converted primarily to phonons (or lattice vibration) or heat in the FePSe₃. The resulting responsivity is typically lower as shown in Figure 3e. This further indicates that there are two main mechanisms for the photoresponse of FePSe₃ devices

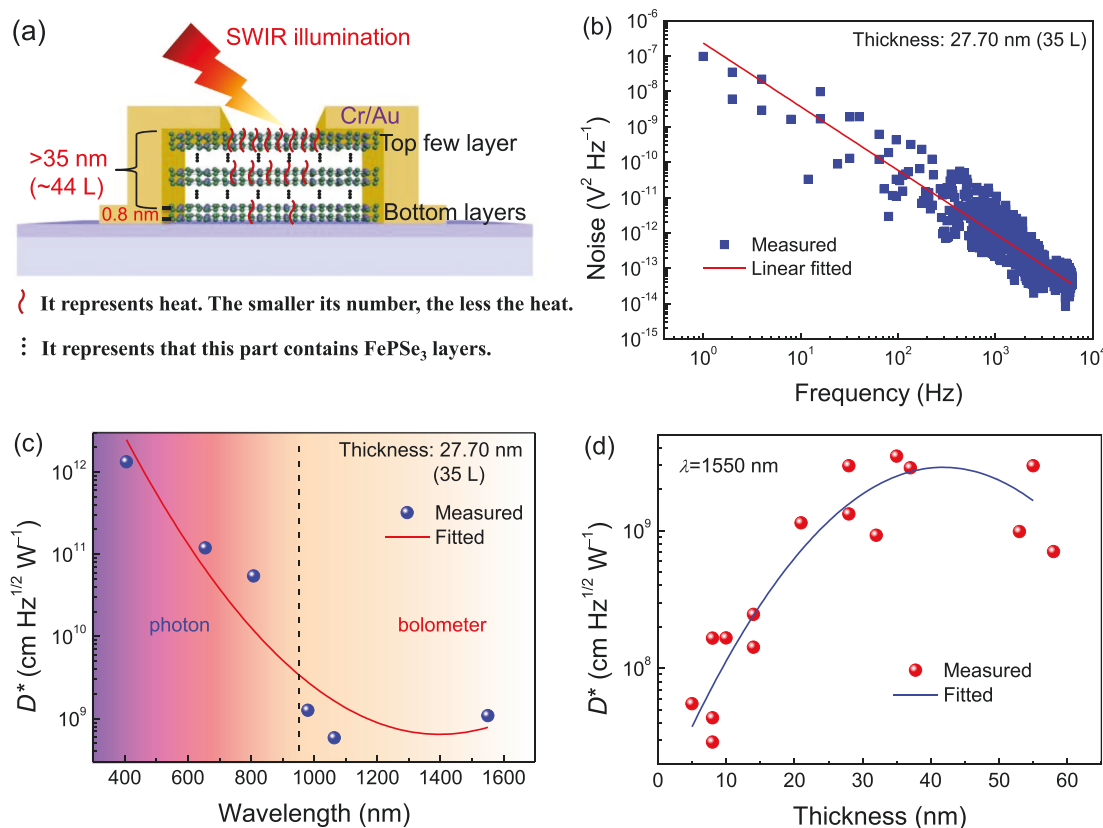


Figure 4. a) Schematic diagram shows the thermal isolated effect that the layer number of FePSe₃ flake would affect the thermal link. b) Spectrum of voltage noise power density (V_n^2) for the 35 L FePSe₃ bolometer. A linear fit (solid red line) shows that the $1/f$ noise dominates the noise level of this device. c) Specific detectivity D^* as a function of wavelength for the 35 L FePSe₃ bolometer. d) D^* versus thickness under 1550 nm irradiation.

under different incident wavelengths: the photoconductive effect at wavelengths above the optical cutoff ≈ 954 nm and the bolometric effect at longer wavelengths beyond the cutoff as proposed in Figure 2e.

To better compare the performance of the FePSe₃ bolometer, the R_v as a function of the thickness of the FePSe₃ under 1550 nm light illumination is shown in Figure 3f. The results show that the R_v value of the FePSe₃ bolometer can reach up to 1×10^8 V W⁻¹, which is 2–3 orders of magnitude higher than that of the commercial VO_x bolometer (10^4 – 10^5 V W⁻¹) in the same spectral range.^[5,49] Unlike most commercial bolometers that use a suspended structure to reduce the thermal link between the device and surrounding, no suspended structure was used for the FePSe₃ bolometers. Therefore, the high bolometric performance obtained in this work illustrates a distinctive advantage of the FePSe₃ 2D atomic layer stacks for bolometer applications. Interestingly, Figure 3f exhibits a strong thickness dependence of the R_v values. When the layer number of the FePSe₃ increases from 5 to 35 nm, the R_v value increases monotonically, which may be attributed to increasing benefit of the FePSe₃ top layers being thermally isolated, resulting in large ΔT , and hence large $\Delta R = \text{TCR} \times \Delta T$ (proportional to responsivity). At larger thickness above 35 nm (or >44 L), the R_v saturates, followed by a slightly decreasing R_v with further thickness increase. While the specific mechanism responsible for this trend needs more systematic investigation, a plausible

argument is that at a larger thickness beyond 35 nm, the IR photon absorption and therefore heating of the bottom layers in the FePSe₃ may not be as efficient as the top layers. As the bottom layers (inactive element) are in parallel to the top layers (active element) of the bolometer, a saturation of the R_v at the critical thickness around 35 nm is anticipated, at which the inactive element is negligible. Reduction of the R_v values would occur when the inactive element provides an alternative electron transfer path in parallel to the active one, as illustrated schematically in Figure 4a where a schematic shows the thermal isolated effect that the layer number of FePSe₃ flake would affect the thermal link due to the naturally suspended structure of the 2D van der Waals stacks.

To characterize the noise level of our device, the noise power density (V_n^2) spectrum of the dark voltage of the 35 L (or 2770 nm in thickness) FePSe₃ bolometer was measured and fitted with the $1/f$ noise model (the solid red line), as shown in Figure 4b. The overwhelming $1/f$ noise coming from the random temperature fluctuations is unavoidable in almost all detectors. The noise equivalent power (NEP) is defined as the signal power when signal-to-noise ratio is unity, given by $\text{NEP} = V_n^{2/2} / R_v = \text{RMS}(V_n) / R_v$ in units of W Hz^{-1/2}, where $\text{RMS}(V_n) = V_n^{2/2}$ is the root-mean-square voltage noise calculated from the spectra of noise power density. Here, the $\text{RMS}(V_n)$ value of 35 L (or 2770 nm in thickness) FePSe₃ bolometer is 2.75×10^{-10} V Hz^{-1/2}. The voltage noise spectra of other FePSe₃

bolometers with different thicknesses were measured and the $RMS(v_n)$ values were calculated as well (Figure S7, Supporting Information).

Another typical figure of merit used to evaluate the bolometer performance is the specific detectivity D^* , defined as $D^* = S^{1/2}/NEP = R_v S^{1/2}/v_n^{1/2}$. We measured the photoresponse of a series of devices with various layer numbers at room temperature and calculated the D^* values under different excitation wavelengths (Figure 4c, Figure S8, Supporting Information). The D^* value is in positive correlation with the wavelength in shorter wavelengths and almost constant in longer wavelengths. The D^* of the 35 L (or 2770 nm in thickness) FePSe₃ bolometer is as high as 10^{11} – 10^{12} cm Hz^{1/2} W⁻¹ under the illumination wavelengths range from visible to ultraviolet. The D^* as a function of the thickness under 1550 nm light illumination at room temperature is shown in Figure 4d. Similar to the relationship between R_v and thickness, the D^* increases initially as the FePSe₃ thickness increases from 5 to 35 nm and reaches a maximum value at ≈ 35 nm. Besides, the low noise leads to a potential high detection sensitivity. It is worth noting that the D^* values can reach up to 1×10^9 cm Hz^{1/2} W⁻¹ at room temperature. As we have mentioned, the commercial VO_x or other bolometers must use suspended structures to cut the thermal links of the bolometer and its surrounding to obtain high signal-to-noise ratios. The competitive performance demonstrated in the naturally suspended ternary FePSe₃ bolometers to the previously reported on the state-of-the-art commercial suspended VO_x bolometer^[5,49] suggests FePSe₃ and possibly other 2D materials are promising materials for IR bolometer applications at room temperature.

3. Conclusion

In summary, 2D FePSe₃ atomic layers with different thicknesses in the range of 5.04 nm (6 L) to 59.12 nm (74 L) have been used for fabricating high-performance uncooled bolometers. High R_v and D^* of 10^{10} – 10^{11} V W⁻¹ and 10^{11} – 10^{12} cm Hz^{1/2} W⁻¹, respectively, have been achieved on the FePSe₃ bolometers under the illumination wavelengths ranging from ultraviolet to visible spectra. In NIR–SWIR spectra, the uncooled R_v and D^* of the FePSe₃ bolometers exhibit an inverted-bell-shaped thickness dependence with the peak R_v and D^* exceeding $\approx 1 \times 10^8$ V W⁻¹ and $\approx 1 \times 10^9$ cm Hz^{1/2} W⁻¹ under 1550 nm SWIR illumination at ≈ 35 nm FePSe₃ thickness. Remarkably, the performance of the FePSe₃ bolometers is on par with the current state-of-the-art conventional bolometers that require suspended structure for thermal isolation and hence improved signal-to-noise ratios. The achieved high bolometer performance can be attributed to: 1) the competitive room-temperature TCR for FePSe₃ $\approx -(2-3)\%$ K⁻¹; 2) the broadband optical absorption extending from UV–visible to NIR–SWIR spectra associated to direct interband absorptions at ≈ 1.3 eV to lower energy of ≈ 0.75 – 0.89 eV through the $^5T_{2g} \rightarrow ^5E_g$ transitions of Fe²⁺ in an octahedral ligand field; and 3) the unique thermal isolation due to that the FePSe₃ atomic layers stacked by the weak van der Waals interlayer force inherit a naturally suspended structure that can effectively reduce the device's thermal link to the supporting substrate. Our result demonstrates that the 2D FePSe₃

atomic layers can provide a promising candidate material for high-performance uncooled bolometers for miniaturized thermal radiation detection.

4. Experimental Section

Growth, Mechanical Exfoliation, and Transfer of FePSe₃ Bulk Single Crystals: FePSe₃ bulk single crystals were synthesized using the chemical vapor transport (CVT) method.^[45] The high-purity powders of Fe (99.9+%, Alfa Aesar), P (100 mesh, 98.9%, Alfa Aesar), and Se (99+%, Alfa Aesar) at a stoichiometric ratio of 1:1:3 and 10–20 mg I₂ (99.99%, Alfa Aesar) were sealed in a 25-cm-long quartz ampoule at a pressure of less than 10^{-2} Pa. Herein, the I₂ was the transport medium. The quartz ampoule was then placed in a two-zone tube furnace. The temperature of the growth and source ends were kept at 600 and 650 °C, respectively, for 7 d before the quartz ampoule was air-cooled to room temperature. The as-grown crystal structures and quality were characterized by powder XRD using Cu-K α radiation source ($\lambda = 1.5406$ Å) (Rigaku SmartLab-9 KW). The average stoichiometric ratio of FePSe₃ crystals was examined by EDX spectroscopy (Elite Plus, AMETEK EDAX). The FePSe₃ flakes were prepared using a scotch tape standard mechanical exfoliation method from the FePSe₃ bulk single crystals onto the polydimethylsiloxane (PDMS). Then, the FePSe₃ flakes were transferred to a heavily doped p-type 285 nm-SiO₂/Si substrates by releasing from PDMS. Thus, there are some FePSe₃ flakes with different thicknesses on the SiO₂/Si substrates. The FePSe₃ samples with different thicknesses were selected according to the optical contrast using the optical microscope (Leica DM4000 M) for subsequent device fabrication, and then their thicknesses are accurately determined by AFM (AFM 5500, Keysight). The quality and the layer numbers of the FePSe₃ flakes were characterized using Raman spectroscopy with a 632.8 nm laser (LabRAM HR Evolution).

Calculation on the Electronic Band Structures of FePSe₃: The first-principles calculations were performed using the projected augmented-wave method as implemented in the Vienna Ab initio Simulation Package.^[50–52] The exchange-correlation functional was modeled by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) realization.^[53] The vdW corrections were taken into account by the approach of Dion et al.^[54] and the band structures were given by the Heyd–Scuseria–Ernzerhof (HSE06) functional including 25% nonlocal Hartree–Fock exchange.^[55] Some tunable parameters were all taken as convergence tests, and the following parameters in each analysis were kept: plane-wave cutoff energy, Γ -centered k mesh, and the thickness of the vacuum slab, which were set to 500 eV, $10 \times 10 \times 1$ ($10 \times 10 \times 10$ for the bulk structure), and 20 Å, respectively. To optimize the lattice structures, the energy and force convergence criteria were set to be 10^{-5} eV and 0.01 eV Å⁻¹, respectively. And the in-plane lattice constant was set to be 6.17 Å according to the experimental data.

Fabrication and Optoelectronic Measurement of the Devices: The FePSe₃ flakes with various thicknesses were transferred to a heavily doped p-type 285 nm-SiO₂/Si substrates preprocessed by acetone, alcohol, and piranha solution (3:1 mixture of sulfuric acid and 30% hydrogen peroxide). The electrodes of the device were made by using standard electron-beam lithography process (FEI–Novel NanoSEM50 with JC Nability–Nanometer Pattern Generation System), followed by thermal evaporation (DE400EVP, DE Technology) of a Cr/Au film (5/40 nm thick) and lift-off process. All measurements were taken in the atmosphere at room temperature. The semiconductor parameter analyzer (4200-SCS, Keithley) was used to collect the electronic transport signals. The light sources were the continuous-wave semiconductor lasers with wavelengths of 405, 532, 655, 808, 980, 1064, and 1550 nm. To make sure that incident light was collimated, the optical collimating lenses (k9) were installed to the fiber outputs of the lasers. The entire device was illuminated by the collimated incident beam in the experiments. The power of the incident laser beam was measured using a optical power/energy meter (1936-R, Newport) with UV enhanced silicon detector

(918D-UV-OD3R, Newport) at 405–1064 nm and germanium detector (918D-IR-OD3R, Newport) at 1550 nm. During the measurements, a device was placed inside the sealed metal box with a small hole (diameter of $\approx 1\text{--}2$ mm), allowing the laser to pass through and isolate the device from the room light. The incident light power (P_{in}) on the devices could be calculated by $P_{\text{in}} = P_d \times S$, where P_d is the incident power density calculated as the laser output power divided by the cross-sectional area of the laser beam and S is the actual device area measured under microscope. So the responsivity R_v can be calculated as $R_v = V_{\text{ph}}/P_{\text{in}} = V_{\text{ph}}/(P_d \times S)$. The dynamic signal analyzer (SR785, Stanford Research) was used to take the noise spectra of FePSe₃ devices. A digital oscilloscope (RTO1024, Rohde and Schwarz) and an optical chopper (SR540, Stanford Research) were used to measure the dynamic photoresponse of device.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

Keywords

2D materials, FePSe₃ bolometers, multinary metal phosphorus trichalcogenides, temperature coefficient of resistance

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- [1] A. Koh, S. R. Gutbrod, J. D. Meyers, C. F. Lu, R. C. Webb, G. C. Shin, Y. H. Li, S. K. Kang, Y. G. Huang, I. R. Efimov, J. A. Rogers, *Adv. Healthcare Mater.* **2016**, *5*, 373.

- [2] P. L. Richards, C. R. McCreight, *Phys. Today* **2005**, *58*, 41.
 [3] A. Rogalski, *Acta Phys. Pol., A* **2009**, *116*, 389.
 [4] A. Rogalski, *Infrared Phys. Technol.* **2002**, *43*, 187.
 [5] A. Rogalski, *Prog. Quantum Electron.* **2003**, *27*, 59.
 [6] H. J. Zuo, D. Y. Choi, X. Gai, P. Ma, L. Xu, D. N. Neshev, B. P. Zhang, B. Luther-Davies, *Adv. Opt. Mater.* **2017**, *5*, 1700585.
 [7] E. S. Kulkarni, S. P. Heussler, A. V. Stier, I. Martin-Fernandez, H. Andersen, C. T. Toh, B. Ozyilmaz, *Adv. Opt. Mater.* **2015**, *3*, 34.
 [8] M. Kopytko, A. Rogalski, *Prog. Quantum Electron.* **2016**, *47*, 1.
 [9] K. D. Mynbaev, A. M. Smirnov, N. L. Bazhenov, N. N. Mikhailov, V. G. Remesnik, M. V. Yakushev, *J. Electron. Mater.* **2020**, *49*, 4642.
 [10] P. Martyniuk, W. Gawron, A. Rogalski, *J. Electron. Mater.* **2013**, *42*, 3309.
 [11] A. Rogalski, P. Martyniuk, M. Kopytko, *Prog. Quantum Electron.* **2019**, *68*, 100228.
 [12] L. Ciura, A. Kolek, J. Wrobel, W. Gawron, A. Rogalski, *IEEE Trans. Electron Devices* **2015**, *62*, 2022.
 [13] X. J. Hao, Z. Deng, J. Huang, Y. Huang, H. Yang, Y. Teng, Y. Zhao, Q. H. Wu, X. Li, J. F. Liu, Y. Chen, H. Zhu, B. L. Chen, *IEEE J. Quantum Electron.* **2020**, *56*, 4300106.
 [14] A. Rogalski, M. Kopytko, P. Martyniuk, *Proc. SPIE* **2017**, *10177*, 1017715.
 [15] G. Ariyawansa, J. Duran, C. Reyner, J. Scheihing, *Micromachines* **2019**, *10*, 806.
 [16] E. Gomolka, O. Markowska, M. Kopytko, A. Kowalewski, P. Martyniuk, A. Rogalski, J. Rutkowski, M. Motyka, S. Krishna, *Bull. Pol. Acad. Sci.: Tech. Sci.* **2018**, *66*, 317.
 [17] M. Settipalli, S. Neogi, *J. Electron. Mater.* **2020**, *49*, 4431.
 [18] P. M. Mensz, B. Dror, A. Ajay, C. Bougerol, E. Monroy, M. Orenstein, G. Bahir, *J. Appl. Phys.* **2019**, *125*, 174505.
 [19] V. S. Krivobok, D. A. Litvinov, S. N. Nikolaev, E. E. Onishchenko, D. A. Pashkev, M. A. Chernopittsky, L. N. Grigor'eva, *Semiconductors* **2019**, *53*, 1608.
 [20] A. D. Shen, A. P. Ravikumar, G. P. Chen, K. A. L. Zhao, A. Alfaro-Martinez, T. Garcia, J. de Jesus, M. C. Tamargo, C. Gmachl, *J. Vac. Sci. Technol. B* **2013**, *31*, 03C113.
 [21] X. F. Wei, W. Y. Wang, J. Fang, R. He, *Physica E* **2020**, *117*, 113801.
 [22] Y. Kaya, A. Ravikumar, G. P. Chen, M. C. Tamargo, A. D. Shen, C. Gmachl, *AIP Adv.* **2018**, *8*, 075105.
 [23] A. Teke, S. Dogan, F. Yun, M. A. Reshchikov, H. Le, X. Q. Liu, H. Morkoc, S. K. Zhang, W. B. Wang, R. R. Alfano, *Solid-State Electron.* **2003**, *47*, 1401.
 [24] Z. Yang, L. J. Guo, B. Y. Zu, Y. A. Guo, T. Xu, X. C. Dou, *Adv. Opt. Mater.* **2014**, *2*, 738.
 [25] R. P. Chasmar, W. H. Mitchell, A. Rennie, *J. Opt. Soc. Am.* **1956**, *46*, 469.
 [26] F. Kohl, F. Keplinger, A. Jachimowicz, J. Schalko, *Sens. Actuator A: Phys.* **2004**, *115*, 308.
 [27] W. G. Langton, *J. Opt. Soc. Am.* **1946**, *36*, 355.
 [28] E. S. Awad, N. Al-Khalli, M. Abdel-Rahman, M. Alduraibi, N. Debbar, *IEEE Photonics Technol. Lett.* **2015**, *27*, 462.
 [29] M. Garcia, R. Ambrosio, A. Torres, A. Kosarev, *J. Non-Cryst. Solids* **2004**, *338*, 744.
 [30] A. Orduna-Diaz, M. Rojas-Lopez, R. Delgado-Macuil, A. Torres-Jacome, F. J. De la Hidalga-W, D. Ferrusca, S. Ventura-Gonzalez, C. G. Trevino-Palacios, *Proc. SPIE* **2011**, *8011*, 80111v.
 [31] L. N. Son, T. Tachiki, T. Uchida, *Jpn. J. Appl. Phys.* **2011**, *50*, 025803.
 [32] Y. Y. Su, X. W. Cheng, J. B. Li, Y. K. Dou, F. Rehman, D. Z. Su, H. B. Jin, *Appl. Surf. Sci.* **2015**, *357*, 887.
 [33] H. Li, G. Dong, K. Chu, X. Pu, Z. Li, H. Zhang, Q. Chen, X. Liu, *J. Mater. Chem. C* **2020**, *8*, 17054.
 [34] H. Li, K. Chu, X. Pu, S. Zhang, G. Dong, Y. Liu, X. Liu, *J. Alloys Compd.* **2020**, *847*, 156417.
 [35] P. W. Kruse, *Uncooled Thermal Imaging: Arrays, Systems, and Applications*, SPIE, Bellingham, WA **2001**.
 [36] A. Rogalski, *Infrared Detectors*, CRC Press, Boca Raton, FL **2010**.

- [37] A. Rogalski, M. Kopytko, P. Martyniuk, *Opto-Electron. Rev.* **2020**, *28*, 107.
- [38] A. Rogalski, M. Kopytko, P. Martyniuk, *Appl. Phys. Rev.* **2019**, *6*, 021316.
- [39] R. Gusmeao, Z. Sofer, M. Pumera, *Adv. Funct. Mater.* **2019**, *29*, 1805975.
- [40] T. A. Shifa, F. M. Wang, Z. Z. Cheng, P. He, Y. Liu, C. Jiang, Z. X. Wang, J. He, *Adv. Funct. Mater.* **2018**, *28*, 1800548.
- [41] T. Gao, Q. Zhang, L. Li, X. Zhou, L. G. Li, H. Q. Li, T. Y. Zhai, *Adv. Opt. Mater.* **2018**, *6*, 1800058.
- [42] C. C. Mayorga-Martinez, Z. Sofer, D. Sedmidubsky, S. Huber, A. Y. S. Eng, M. Pumera, *ACS Appl. Mater. Interfaces* **2017**, *9*, 12563.
- [43] R. Brec, D. M. Schleich, G. Ouvrard, A. Louisy, J. Rouxel, *Inorg. Chem.* **1979**, *18*, 1814.
- [44] E. Banda, *Phys. Status Solidi B* **1986**, *138*, K125.
- [45] K. Z. Du, X. Z. Wang, Y. Liu, P. Hu, M. I. B. Utama, C. K. Gan, Q. H. Xiong, C. Kloc, *ACS Nano* **2016**, *10*, 1738.
- [46] A. A. Mostofi, J. R. Yates, G. Pizzi, Y. S. Lee, I. Souza, D. Vanderbilt, N. Marzari, *Comput. Phys. Commun.* **2014**, *185*, 2309.
- [47] A. Goswami, P. Dhandaria, S. Pal, R. McGee, F. Khan, Ž. Antić, R. Gaikwad, K. Prashanthi, T. Thundat, *Nano Res.* **2017**, *10*, 3571.
- [48] M. Scagliotti, M. Jouanne, M. Balkanski, G. Ouvrard, G. Benedek, *Phys. Rev. B* **1987**, *35*, 7097.
- [49] C. H. Chen, X. J. Yi, X. R. Zhao, B. F. Xiong, *Sens. Actuator A: Phys* **2001**, *90*, 212.
- [50] P. E. Blochl, *Phys. Rev. B* **1994**, *50*, 17953.
- [51] G. Kresse, J. Furthmuller, *Phys. Rev. B* **1996**, *54*, 11169.
- [52] G. Kresse, J. Hafner, *Phys. Rev. B* **1994**, *49*, 14251.
- [53] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
- [54] M. Dion, H. Rydberg, E. Schroder, D. C. Langreth, B. I. Lundqvist, *Phys. Rev. Lett.* **2004**, *92*, 246401.
- [55] J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **2003**, *118*, 8207.