1. Introduction

High-speed and low-power flexible electronic devices such as photodetectors[1] and transistors[2] are needed in numerous applications including medical diagnostics,[2c,3] high speed communication,[4] environmental monitoring,[5] and wearable and neuromorphic computing.[6] This will also have an impact on the internet of things (IoT) where smart objects are wirelessly connected to interact with the environment and the human body.[7] The high-performing electronic devices made of compliant materials can add new capabilities in terms of high-speed communications, efficient image sensing, and so on.[4c,8] For example, the transmission rate, the transmission capacity, and the efficiency of wireless communication could significantly be enhanced if a single photodetector (PD) device could operate under wide spectra with low power consumption and latency. Furthermore, the demands for wide spectral switches[9] or memory storage[10] could be satisfied from the single PD. However, the studies so far have primarily focused on the development and characterization of high-performance flexible PDs under certain wavelength (i.e., UV[1b,10,11] visible,[12] or NIR[13] spectrum). Recently, there have been few attempts to develop ultrafast and conformable broadband PDs.[8b,14] Among these, the heterostructures based on 2D materials and perovskites have shown potential to expand the working wavelength of PDs.[14] This is owing to their direct bandgap and large absorption coefficient.[15] Specifically, perovskites have garnered more interest for optoelectronic applications as they are solution processable with low power consumption and latency. However, due to low mobility (=1–10 cm2 V−1 s−1) and poor stability,[17] their performance metrics (e.g., responsivity [R] and specific detectivity [D*]) for PDs are modest. The poor stability in ambient conditions is attributed to the adsorption of water and oxygen molecules which greatly accelerate the degradation of the perovskite photosensitive layer.[18] Efforts are ongoing to enhance the stability of perovskite-based devices exploring different encapsulations, but low intrinsic mobilities will still be a challenge. Thus, the efforts to develop next generation of flexible and high-performing PDs, with wide spectral sensitivity and robust fabrication route, are still on.

In the above context, the nanostructures and thin films of inorganic compound semiconductors such as gallium arsenide (GaAs) have shown considerable potential for optoelectronic...
devices owing to their direct bandgaps (1.42 eV), high intrinsic electron mobilities (∼8500 cm²/Vs), chemical and thermal stability, and flexibility.[8a,b,d,18] Particularly, because of the large surface to volume ratio, the compound semiconductors based 1D nanostructures have many surface trap states which enhance the photocarrier lifetime. Simultaneously, the low dimensionality of nano/microscale devices helps in the miniaturization, and limits the effective sensing area, which results in a large $R$, photovoltaic gain ($G$), and so on.[8a] This is evident from several examples related to efficient photovoltaic devices, ultrafast optical switches, high-performance UV and NIR PDs, most of which have been developed over rigid substrates and/or using single nanostructure,[8a,b,19] as it is challenging to integrate compound semiconductors-based nanostructures on flexible substrates. To this end, transfer printing technique, which allows deterministic assembly of laterally aligned photolithography-defined arrays of 1D nanostructures over plastic substrates,[28] has shown potential. Transfer printing and/or modified transfer printing approaches have been used to demonstrate various high-performance devices on flexible substrates, including both n- and p-channel transistors,[2a,21] photovoltaic and optoelectronic devices,[8c] and so on.[22]

In this work, direct roll transfer printing approach is used to integrate the arrays of well-defined and laterally aligned GaAs microstructures for high-performance flexible broadband PDs. In our previous works, direct roll transfer printing was employed to transfer silicon nanoribbons from silicon on insulator (SOI) wafer to flexible substrates.[2a,21] In this work, we have demonstrated for the first, the use of direct roll transfer printing to obtain GaAs microstructure arrays on flexible substrates. To achieve high transfer yield, we optimized the process for developing GaAs microstructures and also tuned the printing parameters. The arrays of GaAs microstructures were obtained using top-down fabrication approach, which includes the use of bulk wafer-based source materials, photolithography, and chemical etching procedures.[23] The top-down synthesis route to realise nano/microstructures is attractive owing to better uniformity control with excellent alignment and registration accuracy as compared with the bottom-up synthesis.[24] These attributes are needed to have uniform and repeatable device performance over large areas. The next step involves transferring these well-defined nano/microstructures from the source substrates (bulk wafer) to a device substrate (flexible polyimide [PI]). To this end, we have selected direct roll transfer printing as it is a single step printing method, which does not require viscoelastic polymeric stamps (typical of conventional transfer printing) to obtain nano to macro scale structures over the donor substrate. The donor substrates with GaAs microstructures are directly brought into physical contact with the semi-cured thin polyimide (PI) film over the receiver substrate.[2a,21] Owing to the strong adhesion between the fabricated microstructures and the receiver substrates (due to the semi-cured nature of PI layer), high transfer yield is achieved (∼95%). The process is compatible with roll-to-roll (R2R) fabrication, which is advantageous in terms of high throughput and large-scale electronics manufacturing. Last of all, it is worth noting that the adopted printing route can help in reducing the fabrication cost because the donor substrate (bulk GaAs wafer) can be reused multiple times after the transfer of GaAs microstructures to the receiver substrate. Following the direct roll printing step, the high-performance metal–semiconductor–metal (MSM) back-to-back Schottky contact-based PDs were realized using conventional microfabrication process. The sensing performance of the semi-insulating undoped (resistivity at RT, $>10^{10} \Omega \cdot $ cm) GaAs microstructures-based PDs was systematically evaluated in ambient conditions. Under UV (365 nm) and NIR (850 nm) light conditions, they showed high $R$ ($>10^4$ A/W), $D^*$ ($>10^{15}$ jones), photovoltaic gain, $G$ ($>10^4$), and external quantum efficiency, EQE (10%), and high dark to light current on/off ratio values ($>10^4$). Furthermore, the optimized fabrication steps were used to realize doped GaAs microstructures (carrier concentration $2.7 \times 10^{18}$ cm$^{-3}$)-based low-powered PDs (operating voltage = 1 V). These PDs showed better performance (except for current on/off ratio values) as compared with undoped microstructures-based devices (characterized under similar conditions). The PDs based on both doped and undoped GaAs microstructures showed ultrafast response/recovery (2.5/8 ms) times. Finally, the PDs were tested under mechanical bending and twisting conditions for up to 500 cycles and they showed robust device performance. This shows that the developed material and fabrication scheme holds considerable potential for large-area flexible and high-performance optoelectronic sensors/circuitry-based ultrafast optical communication.

2. Results and Discussion

2.1. Fabrication of GaAs Microstructure Array-Based Flexible Broadband Photodetectors

The fabrication process for the presented PDs is schematically shown in Figure 1. The top-down fabrication approach forms the well-defined periodic arrays of single-crystal GaAs microstructures. Figure 1a–d schematically shows the fabrication steps for array of GaAs microstructures, which includes photolithography and anisotropic wet chemical etching steps. As a first step, a thin (∼250nm) layer of plasma-enhanced chemical vapor deposition (PECVD)-assisted SiO$_2$ was deposited on a bulk GaAs source wafer (Figure 1b). Then, photolithography and dry etching steps were performed to define the geometries of the microstructures (Figure 1c). Next, the critical anisotropic chemical etching step was carried out. This step was cautiously optimized to have higher transfer yield (discussed later) during the direct roll transfer printing step (Figure 1d,e). Etching and release of GaAs microstructures by direct roll transfer printing method onto a target flexible substrate represents one conceivable route to device integration. The employed roll transfer printing assembly steps, described elsewhere,[2a] were followed for bringing the laterally aligned photolithography-defined arrays of inorganic semiconducting nanostructures on donor wafer in conformal contact with the target substrate (Figure 1f). Before printing, the target substrate was coated with a semi-cured polyimide (PI) layer to enhance the adhesion between the printed structures and the target flexible substrate. This simple yet innovative, single step process leads to a higher printing yield and registration accuracy without the need for complicated pick and place equipment. The printing approach, with yields (>95%), excellent registration accuracy (<100 nm),
and throughputs is needed for large area electronics with high device-to-device uniformity. Finally, the PDs were fabricated from the printed GaAs microstructures arrays by following conventional microfabrication steps including photolithography and liftoff (Figure 1g).

The fabrication process for GaAs microstructures includes mask layer deposition (SiO₂), conventional lithography steps, and dry (plasma) etching to define the mask geometries and wet etching. The wet etching is a critical step as it determines the final yield of the printing process. Figure 2 shows the schematic and SEM images of GaAs microstructures during various stages of chemical etching. The SiO₂ pattern had a width of 5 µm and thickness of 150 nm which served as an etching mask during the anisotropic chemical etching of GaAs. The first frame (Figure 2a) shows a strip of the SiO₂ patterned along the (011) crystalline direction on the GaAs (100) bulk source wafer. The second frame (Figure 2b) shows profiles after the start of the wet etching in a phosphoric acid and hydrogen peroxide solution according to the following equation:

\[
\text{GaAs} + \text{H}_3\text{PO}_4 + 4\text{H}_2\text{O}_2 \rightarrow \text{GaPO}_4 + \text{H}_3\text{AsO}_4 + 4\text{H}_2\text{O}
\]  

(1)

The etchant solution for GaAs is made of H₃PO₄ (85 wt%): H₂O₂ (30 wt%): H₂O = 1:13:12 by volume and kept at 40 °C. The anisotropic etching of the bulk GaAs using such a solZn of acid mixtures is well-reported.[23,25] Structures with a variety of morphologies such as reverse mesa and nanowires, can be realized using these etching technique. Generally, over-etching of the GaAs bulk wafer could lead to nanowires realised in the etching solution. In the present case, we do not want the fabricated microstructures to be released into the solution. Instead, we need rather weakly anchored microstructures on the donor substrate so that they can be transferred using direct roll printing. Therefore, the printable GaAs structures were optimized to be weakly attached at the anchor point by carefully monitoring the etching rate of the GaAs. Briefly, the process includes, first, the oxidation of GaAs and subsequent dissolution of the oxide product. Prolonged reaction times yielded sharply defined micro/nanostructures under the mask stripes (SiO₂ in the present case), as shown in the Figure 2c. Based on the obtained results, the etching rate was extracted to be \( \approx 35 \text{ nm min}^{-1} \). It was noted that if the wafer was left for higher etching times, the two side walls of each reverse-mesa structure will intersect, which then results in the collapse of the GaAs microstructures (Figure 2e) or release of microstructures in the solution. Therefore, the etching time was carefully optimized to obtain reverse-mesa sides close enough to enable efficient release of the nanostructures during direct roll transfer printing (optimization studies using Finite Element Analysis are shown below). Figure 2d shows the SEM image of an array of GaAs.
microstructures obtained using the $5 \times 50 \mu m$ SiO$_2$ mask strips and subsequent anisotropic chemical etching. Prior to direct roll transfer printing of GaAs microstructures, the oxide mask on top of GaAs microstructure arrays was etched away with a short dip in diluted HF solution.

Next, the large area transfer of as-patterned GaAs microstructures array onto PI substrates was attained using direct roll transfer printing. As mentioned earlier, the etching of the two sides of the reverse-mesa structures was carried out carefully to facilitate easy release of the microstructures from the donor substrate. This is important for the efficient and successful transfer printing of large arrays of GaAs microstructures down to nanometer scale. In this regard, we also performed Finite Element Analysis (FEA) simulation studies to optimize the printing conditions such as force and rotation speed for different width of the microstructures (Figure S1, Supporting Information). Our recent work on direct roll transfer printing showed that the applied force plays a significant role in defining the transfer yield.[2a] It was shown that a 10 N force is needed to bring the suspended silicon nanostructures in conformal contact with the target semi-cured PI layers to have a high transfer yield (>95%). However, in the previous study, printing parameters were optimized to transfer suspended Si nanoribbons (NRs) anchored at the two ends with the bulk Si. Differently from that, in the present case, the GaAs microstructures are anchored with the bulk wafer, all along their length, as shown in Figure 2c,d. In the present case, along with the force, the width (anchor side) of the microstructures also plays a critical role in defining the transfer yield. For this, first, we applied a constant compressive force (10 N) on top of the microstructure and stress distribution as well as yield strength was monitored (Figure S1a,b, Supporting Information). The maximum stress was observed at the anchor point between microstructures and bulk of the substrate. Previous studies have shown that the yield point/strength for vertically aligned top-down fabricated GaAs micropillars is $\approx 1.8$ GPa.[26] Above this, the pillars develop fractures. Accordingly, we set this as our threshold limit above which the anchor point could be broken, and microstructures can be transferred over the PI substrate. The Figure S1b, Supporting Information, shows that the width of microstructures should be $\leq 75$ nm for a 10 N of force applied over 1 cm$^2$ area. Further, for the fixed width of microstructures, we studied the minimum force required to develop strain equivalent to reach the brittle fractures (Figure S1c, Supporting Information). According to these simulations and SEM images (displaying width of $\approx 50$ nm), we applied a 10 N force using our custom-built roll system (see Experimental Section for details) to attain conformal contact of microstructures with the semi-cured PI and to have sufficient applied pressure to reach fracture limit of the anchors. The optimized transfer parameters were used to print GaAs microstructure arrays on to flexible PI with good retention of the orientation and relative position of individual microstructures with respect to each other. Strong bonding between the semi-cured PI layer and the GaAs microstructures resulted in their breakage or release from the bulk donor.

### 2.2. Electro-Optical Characterizations of Undoped GaAs Microstructures-Based Photodetectors

After printing, the standard fabrication steps were carried out to define the sensing channel regions. The high conformability
of the fabricated devices is shown using Figure 3a where the sample is conformally placed over glass tube. Figure 3b and 3c, respectively, show the optical image and schematic of a fabricated device. The length and width of the sensing channel were 40 and 50 µm (10 GaAs microstructures with each having ≈5µm width), respectively. With undoped microstructures obtained from a semi-insulating (high resistivity) bulk GaAs wafer and depositing multi-layer metals (Pd/Ge/Au) on them, the high-quality Schottky source and drain contacts were realized. The high-quality Schottky metal–semiconductor...
excitations, the peak $R$ value remained high showing the device’s applicability for wide spectra sensing (Figure 3j). Like $R$, the other PD parameters including $D^*$, EQE, $G$, and LDR showed high values under both UV and NIR illuminations. For instance, the highest $D^*$ value of $>2 \times 10^{14}$ Jones was observed at the low illuminated power intensity of 0.1 $\mu$W cm$^{-2}$ (under both UV and NIR). Further, the PDs showed negligible decrease in the $R$, $D^*$, EQE, and $G$ with increasing the incident power intensity for both UV and NIR. This small decrease can be attributed to the charge carriers scattering caused by internal-photothermal heating and enhanced carrier recombination effects.[28] Nevertheless, it is noteworthy that the PD demonstrates high performance even at the higher power intensities.

2.3. Electro-Optical Characterizations of Doped GaAs Microstructure-Based Photodetectors

Ultra-fast and low-power PDs are required for the next generation of energy efficient high-performance flexible electronics. Owing to the low charge carriers (due to lack of doping), a high 20 $V$ bias voltage was needed to drive the semi-insulating GaAs microstructures-based PDs. To improve this, the doped GaAs bulk wafer (carrier concentration $2.7 \times 10^{18}$ $\mathrm{cm}^{-3}$) was used to realize high performance PDs with low power consumption. Doping dependent adjustment of the Fermi level has been shown to enhance the GaAs NW PD performance.[198] Similar fabrication process and device dimensions, as described above for undoped GaAs microstructures, were adopted to fabricate doped GaAs microstructure-based PDs. Next, the fabricated PDs were characterized under similar conditions as described above to extract the performance parameters. For this set of experiments, the electrical measurements were performed under UV illumination only, although similar high performance was obtained under NIR light illumination (Figure S4, Supporting Information). Using the time-resolved photo response for different UV intensities at the fixed 4V, the PD performance parameters were extracted and are displayed in Figure 4. As expected, an increase of photocurrent is observed in doped GaAs microstructure-based devices with an increase of illumination power intensity (Figure 4a). The $R$, $D^*$, EQE, and $G$ associated with incident UV light power intensities are shown in Figure 4b,c,d, and e, respectively. These results indicate that $R$, $D^*$, EQE, and $G$ of the device decreased with an increase of power intensity (similar trend like undoped GaAs microstructure-based PDs). The $R$, $D^*$, EQE, and $G$ of the PD with 1 $\mu$W cm$^{-2}$ UV power intensity could reach up to $8 \times 10^4$ $A$ $W^{-1}$, $5 \times 10^{14}$ Jones, $2.7 \times 10^2$ and $2.7 \times 10^5$, respectively. On the other hand, the extracted $I_{\text{light}}/I_{\text{dark}}$ ratio and LDR values progressively increased with increasing illuminated power density. The $I_{\text{light}}/I_{\text{dark}}$ ratio and LDR under 10 $\mu$W cm$^{-2}$ of UV power intensity can reach 1.2 and 1.5.

Next, the switching speed of the PD was investigated at an illuminated wavelength of 365 nm. To evaluate the response speed of the GaAs PD, the response time (rise time) and recovery time (decay time) were extracted using the graph shown in Figure 4b. The response and recovery time were found to be 2.5 and 8 ms, respectively. Finally, we show that the 

(MS) contact is needed to decrease the level of dark current and hence to enhance the detectivity value of the PDs and to obtain a high signal-to-noise ratio.[27] Current–voltage ($I–V$) curves for the fabricated device are shown in Figure S2, Supporting Information, with the measurements conducted in the dark and different intensities of UV light illuminations. In the dark conditions, the output current, obtained at $\pm 20$ $V$, was of the order of few nanoamperes. Such a low off-device current in dark conditions is needed for higher detectivity, high value of the on/off current ratio, and high signal-to-noise ratio. The low dark current could be attributed to the high resistivity of the undoped microstructures and the high-quality of Schottky contacts formed using multi-layered contacts. Further, Figure S2, Supporting Information, shows that under light illumination, the photocurrent increases, particularly at high voltage bias, demonstrating a nonlinear and asymmetrical $I–V$ behavior. The photocurrent increases from $\approx 1$ nA (dark current) to $\approx 40$ nA (2.5 $\mu$W cm$^{-2}$) at bias voltage $V_D = 20V$. This is more than one order change in the photocurrent. Next, the electrical measurements were performed under dark conditions with varying applied voltage and intensity of UV (365 nm) and NIR (850 nm) wavelengths to verify the photodetection performance of the fabricated devices (Figure 3). Before this, the temporal response was obtained for an annealed and as-made device (Figure S3, Supporting Information) at different UV light intensities from 0.1 to 2.5 $\mu$W cm$^{-2}$. The annealed PD device showed a reasonably high sensing response as compared to the pristine device (as made). The photocurrent increased by 65% after annealing step. This could be attributed to the efficient charge transport after annealing. Thus, all further measurements were performed using annealed devices. Effect of the bias voltages and varying light intensity on important PD performance parameters including $R$, $D^*$, EQE, $G$, $I_{\text{light}}/I_{\text{dark}}$ ratio, and linear dynamic response (LDR) are extracted from the time-resolved photo response curves. The details related to the extraction of these performance parameters are given in Note S1, Supporting Information and Table S1, Supporting Information, summarizes the calculated values. As shown in Figure 3d, the photocurrent under the UV illumination as a function of time was measured at different bias voltages of 5, 10, 15, and 20 $V$. From the curves, the saturated photocurrent increases when the applied voltage is increased at the identical illumination power intensity (Figure 4). The $D^*$, EQE, $G$, and $I_{\text{light}}/I_{\text{dark}}$ associated with incident UV light power intensities are shown in Figure 4a,b,c,d, and e, respectively. These results indicate that $R$, $D^*$, EQE, and $G$ of the device decreased with an increase of power intensity (similar trend like undoped GaAs microstructure-based PDs). The $R$, $D^*$, EQE, and $G$ of the PD with 1 $\mu$W cm$^{-2}$ UV power intensity could reach up to $8 \times 10^4$ $A$ $W^{-1}$, $5 \times 10^{14}$ Jones, $2.7 \times 10^2$ and $2.7 \times 10^5$, respectively. On the other hand, the extracted $I_{\text{light}}/I_{\text{dark}}$ ratio and LDR values progressively increased with increasing illuminated power density. The $I_{\text{light}}/I_{\text{dark}}$ ratio and LDR under 10 $\mu$W cm$^{-2}$ of UV power intensity can reach 1.2 and 1.5.
PDs using doped GaAs microstructures can function at ultra-low voltage. The time-resolved photo response for different UV intensities at an operating voltage of 50 mV shows the capability of the device to detect low intensities with low power consumption. Table 1 summarizes and compares the extracted PD performance parameters for doped and undoped GaAs microstructures-based devices with the state-of-the-art photodetectors realized using GaAs and other compound semiconductors. The sensing performance of printed GaAs microstructures is further compared with other state-of-the-art sensing materials employed to detect broad band spectrum (Table S2, Supporting Information). Although the current on/off ratio and response time of the GaAs microstructure-based PDs are modest, they stand out in terms of consistent high responsivity and detectivity across the UV to NIR range.

### 2.4. Wide Range Sensing Mechanism

The measured photo response for GaAs microstructure-based PDs shows a broadband detection with wavelength ranging from 365 to 850 nm. The observed broadband detection behavior can be explained using energy band diagram (Figure S5, Supporting Information). The energy band diagrams for the Schottky contacted GaAs based PDs are shown in its equilibrium state that is, under no light illumination and no bias voltage. Upon illumination with a wavelength corresponding to photoenergy larger than that of the GaAs bandgap, large number of electron–hole pairs are generated, which leads to increase in the device current. The illuminated wavelength in the present case, under both UV (3.3 eV) and NIR (1.45 eV) light, is sufficiently high to generate electron–hole pair in GaAs ($E_g = 1.42$ eV). The presence of...
Schottky contact helps to achieve better sensing performance. For semi-insulating GaAs, high quality Schottky contacts (larger depletion width with sufficiently high barrier height) were obtained (Figure S5a, Supporting Information). This resulted in the low-dark current density. The increase in charge density in GaAs upon light illumination lowers the effective barrier height, leading to easy transport of carriers, and thus, to a significantly higher detectivity and current on/off ratio. However, because of the low doping, the high operating bias (20V) was needed to drive the photocarriers. Therefore, PDs using doped GaAs microstructures were also fabricated and they showed similar high sensing performance at much lower bias voltage of 1 V. However, for doped GaAs microstructures-based PDs, the on/off ratio was two orders lower than the devices based on undoped GaAs microstructures. This is because of the higher dark current due to difficulties in realizing high quality Schottky junctions on n-type GaAs (Figure S5b, Supporting Information). \(^\text{[38]}\) Owing to the high charge carriers and surface states in microscale materials, it is practically difficult to have high quality Schottky contacts (smaller depletion width). The smaller depletion width leads to large tunnelling current. The reduction of the surface trap concentration by surface passivation technique can help in the formation of high quality Schottky contacts. \(^\text{[39]}\) This could help increase the on/off ratio and decrease the response time down to microseconds.

### 2.5. Mechanical Stability Evaluation of Flexible GaAs Photodetectors

The reliable and robust performance of flexible PDs is critical for their applications in wearable systems, robotics, and healthcare, where these devices typically experience mechanical deformations such as bending and twisting. In this regard, the stability and reliability of presented devices was examined under different mechanical deformations. For this study, bending and twisting mechanical loadings were applied using Yuasa endurance testing system (Movie S1, Supporting Information) and subsequently, the electro-optical measurements were made. First, the samples were subjected to 500 bending cycles at a bending radius of 20 mm. After every 100 bending cycles, we measured the PD performance data shows that there is a small degradation in sensing performance due to twisting deformation over 500 cycles. The presented mechanical reliability of PDs during repeated twisting loadings was evaluated (Figure 5d–f). The presented data shows that there is a small degradation in sensing performance due to twisting deformation over 500 cycles. The mechanical reliability of PDs during repeated twisting loadings was shown in Figure S6, Supporting Information. Typical SEM images for as-made devices and after mechanical loadings are shown in Figure S7, Supporting Information. The experimental data shows NO cracks are developed in the GaAs microstructures or metal stacks or there may be minor cracks. We have observed several devices before and after mechanical loadings (bending and twisting) under SEM. Typical SEM images for as-made devices and after mechanical loadings are shown in Figure S6, Supporting Information. Typical SEM images for as-made devices and after mechanical loadings are shown in Figure S7, Supporting Information. The experimental data shows NO cracks are developed in the metal stack and GaAs microstructures after mechanical loadings. In the absence of any cracks, the minor performance degradation could be due to residual strain. This requires further in-depth analysis, which will be presented in our future works.

| Material                      | Excitation wavelength [nm] | Substrate | Bias voltage [V] | Peak R [A W\(^{-1}\)] | Peak D\(^\circ\) [Jones] | Peak EQE [%] | Peak G | Peak on/off | Response/ recovery times [ms] | Ref. |
|-------------------------------|-----------------------------|-----------|------------------|------------------------|---------------------------|--------------|--------|-------------|-------------------------------|------|
| Semi-insulating (undoped) GaAs microstructures | 365 | Flexible | 20 | 1.92 × 10\(^4\) | 2.50 × 10\(^{-15}\) | 6.44 × 10\(^{-8}\) | 6.53 × 10\(^{-8}\) | 2 × 10\(^2\) | 3/10 | This work |
| n-type doped GaAs microstructures | 850 | Flexible | 20 | 2.85 × 10\(^4\) | 3.70 × 10\(^{-15}\) | 4.16 × 10\(^{-8}\) | 9.68 × 10\(^{-8}\) | 1.18 × 10\(^2\) | 3/10 | This work |
| Single GaAs NW | 850 | Flexible | 1 | 8.14 × 10\(^4\) | 5.55 × 10\(^{-14}\) | 2.73 × 10\(^{-8}\) | 2.77 × 10\(^{-8}\) | 1.71 | 2.5/8 | This work |
| GaAs NW | 532 | Rigid | 1 | 1.12 × 10\(^4\) | 2.70 × 10\(^{-15}\) | 1.64 × 10\(^{-8}\) | 3.81 × 10\(^{-8}\) | 1.12 | 2.5/8 | This work |
| GaAs/AlGaAs /GaAs NW | 808 | Rigid | 5 | 0.75 | 1.83 × 10\(^{-10}\) | 50 | — | >10\(^2\) | 175/190 | [30] |
| GaAsSb NW | 1300 | Rigid | 0.15 | 2.37 | 1.08 × 10\(^9\) | — | — | 1.66 | — | [31] |
| InGaAs NWs | 1100–2000 | Rigid | 0.5 | 6.5 × 10\(^1\) | — | 5.04 × 10\(^{-5}\) | — | 17.3 | — | [32] |
| GaAs/GaAs NW | 855 | Rigid | 2 | 0.57 | 7.2 × 10\(^{-10}\) | — | — | 145 | — | [19a] |
| GaAs/InAs/Gr | 850 | Rigid | 0 | 1.73 × 10\(^{-3}\) | 1.83 × 10\(^{11}\) | — | — | 10\(^4\) | 0.07/0.12 | [33] |
| GaAs film/SiO | 638 | Flexible | —1 | 0.12 | — | — | — | — | — | [34] |
| SWCNT/n-type GaAs | 780 | Rigid | 0 | 274 × 10\(^{-12}\) | 7.6 × 10\(^{-12}\) | — | — | — | 1.41/0.27 | [35] |
| GaAs PDs arrays | 808 | Flexible | — | 0.41 | — | 48 | — | — | — | [36] |
| Commercial InGaAs | 800 | Rigid | —100 | — | 10\(^{-12}\) | — | — | — | — | [37] |
3. Conclusion

Nano/microstructures of III–V semiconducting materials have demonstrated enormous potential for advanced electronics and optoelectronic applications, but with devices fabricated mainly on rigid substrates. Due to the lack of suitable integration techniques, it has been challenging to transfer and integrate these nano/microstructures on flexible substrates and large areas. In this regard, the arrays of well-defined and laterally aligned printed semi-insulating (undoped) and doped GaAs microstructures, obtained here, present an important advancement. For the first time, the integration of arrays of GaAs microstructures over PI substrates has been achieved using direct roll transfer printing. It is noteworthy to mention that the optimized direct roll transfer printing technique showed excellent registration (<0.1 µm) and high transfer yield (~95%). The performance of the GaAs microstructures-based devices was systematically investigated under a wide range of illumination wavelengths (UV and NIR) and the results shows important advantages over the previous reports using GaAs thin-films, nanostructures, and more. First, high-performance undoped GaAs microstructures-based devices illustrated the capabilities of direct roll transfer printing for large-scale integration of device with high $R$ (>10^4 A/W), $D^*$ (=10^15 Jones), $G$ (>10^4), EQE (10^6%), and light to dark current on/off ratio values (>10^2) under wide spectrum (365 and 850 nm). As shown in the Figure 6, the obtained performance values are among the best reported GaAs-based PDs including the devices on rigid and flexible substrates. This high PD performance is attributed to low dimensionality of the device and high mobility of the GaAs microstructures, which resulted in an efficient charge transport, contamination free transfer of arrays of GaAs microstructures, and high quality of the Schottky contacts. These resulted in the low dark current density and thus, high detectivity and on/off ratio. However, for doped GaAs microstructures-based PDs, the on/off ratio was two orders lower than the devices based on undoped GaAs microstructures. Although the on/off ratio of the doped GaAs microstructures-based PD are not the best, their consistent high performance across the broad spectral range from UV to NIR at low bias voltage over flexible substrate is worth noting as this has not been reported so far. Further, owing to the high carrier mobility of GaAs, the response time is observed to be short (2.5 ms) for both doped and undoped GaAs. Likewise, devices showed high photoconductive gain. The obtained response time of few milliseconds represents one of the fastest responses among reported PDs in the literature. Finally, the robust operation of devices under highly bending conditions was confirmed by systematic experiments performed with bending and torsion set up. The experimental data showed negligible performance degradation under bending loading and slight decrease in performance with torsional loading up to 500 cycles. Nevertheless, it is noteworthy that the PDs continued to provide high performance and no mechanical failure of the device was observed. Thus, it was evident that the GaAs microstructures and the demonstrated integration technique have huge potential to realize the next generation of flexible high performance and broadband PDs. While the application of printed arrays of GaAs microstructures has been demonstrated for high-performance
Flexible broadband PDs, the presented approach could be followed for development of highly efficient solar cells or high-performance electronics for power devices.

4. Experimental Section

Fabrication of GaAs Array of Microstructures: Top–down fabrication process was employed to realize well-defined arrays of GaAs microstructures. The fabrication process involved patterning of 650 μm thick bulk undoped and Si-doped GaAs wafer (5 × 10^{18} cm−3) from Wafer Tech. A SiO₂ mask layer (thickness ≈250 nm) was deposited on the top of the wafer surface via plasma-enhanced chemical vapor deposition (PECVD). To define the patterns of the GaAs microstructure arrays using typical photolithography steps, a layer of photoresist (PR; S1805) was spin-cast (4000 rpm, 30 s) on top of the deposited PECVD SiO₂ on (100) GaAs bulk wafer. This was followed by soft baking at 115 °C for 1 min. A UV light exposure was carried out (MA/BA6 mask aligner from Suss Microtec) through a photomask with desired patterned lines (length of 650 μm and width of 5 μm) aligned in parallel to the (011) orientation of GaAs wafer. The exposed wafer was developed in MF-319 developer for 40 sccm CH₃/Ar flow with a chamber base pressure of 30 mTorr, 200 W RF power for 5 min). Then, the photoresist mask was dissolved using diluted HF solution. The deposited SiO₂ mask was etched using diluted HF solution. The samples with released microstructure arrays on the donor wafer were rinsed with ethanol, DI water, and dried in the fume hood respectively and prepared for direct roll transfer printing on flexible substrate.

Direct Roll Transfer Printing Technique: The direct roll transfer printing system[28] was used to transfer and integrate well-defined arrays of GaAs microstructures from bulk wafer. It is a single step process. For a successful direct roll transfer printing with high yield and high registration, an adhesion promoter of ≈1.0 μm (PI-2545 precursor from HD Microsystems) was applied on commercial PI substrate. The spin-coated PI was semi-cured by heating at 70 °C for 4 min. Subsequently, GaAs wafer with microstructures was brought into direct physical contact with the semi-cured PI receiver substrate. The applied force during roll transfer sparking was 10 N, and roll speed was 0.1 mm s−1. After NR transfer, the PI substrate was subsequently cured at 250 °C for 2 h.

Finite Element Analysis (FEA) Simulations: FEA simulations were carried out using COMSOL Multiphysics simulation software. A 2D linear elastic model of a single microstructure was implemented (Figure S1a, Supporting Information). The base of the bottom mesa structure was assumed to be fixed and a normal force was applied uniformly on the top surface of the microstructure.

Fabrication of Photodetectors: The polyimide (PI) substrates with direct roll transfer printed GaAs microstructures were used for the fabrication of MSM microstructure-based PDs. Typical photolithography and liftoff procedures were performed to form the metal contacts on the printed GaAs microstructure arrays. Sequentially, electron beam evaporation of (Pd(35)/Ge(65)/Au(200 nm)) and AuGe(14)/Ni(11)/Au(240 nm) were used to form Schottky contacts on transfer printed undoped and n-type Si doped GaAs microstructures, respectively. The fabricated devices were annealed at 150 °C for 15 min under Ar ambient in a horizontal tube furnace.

Figure 6. Comparison of flexible GaAs microstructures-based broadband PDs with state-of-the-art devices. Responsivity and detectivity comparison of direct roll transfer printed GaAs microstructure array-based PDs with other state-of-the-art GaAs and compound semiconductors-based PDs on flexible/rigid substrate. These PDs are based on different structures such as nanowires, thin film, and heterostructures.
Electro-Optical Characterization: The electrical characterization of the fabricated GaAs microstructures-based flexible PDs such as time resolved photo response, was performed in the ambient environment using semiautomated summit 12k Auto prober and semiconductor device parameter analyzer (B1500A, Agilent). A UV light emitting diode (LED) with the wavelength of 365 nm and a NIR LED (850 nm) was used for evaluating photodetection capabilities of the fabricated devices.

Mechanical Endurance Studies: The mechanical endurance studies included testing under bending and torsional loading conditions. These were conducted using a desktop endurance test machine for bending tests (Yusua System DMLHP-P150) and torsion tests (Yusua System DMLHP-TW). The devices were attached onto a flexible carrier substrate (polypropylene) to facilitate loading on the testing machines. The testing machines could repeatedly apply bending/torsional loading while controlling the bending radius/ twisting angle as well as the loading cycle duration.

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 support the findings of this study are available from the corresponding author upon reasonable request.

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broadband, flexible electronics, gallium arsenide, microstructures, photodetectors, printing

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