



# Role of interfacial layer as PANI–silicene in Si-based photodiodes

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## ABSTRACT

Silicene is a 2D monoatomic sheet of silicon and can be used for various applications such as degradation, therapy, and biosafety. Polyaniline (PANI) is a conducting polymer employed for electronic devices. In this study, we synthesized PANI–silicene composites and operated as an external interfacial layer between Al and different type substrates of *p*-Si and *n*-Si to compare Schottky-type photodiodes of PANI–silicene/*n*-Si and PANI–silicene/*p*-Si. The silicene structures were investigated using X-ray diffractometry (XRD) and scanning electron microscopy (SEM) techniques. Also, the light power intensity dependent of PANI–silicene/*n*-Si and PANI–silicene/*p*-Si photodiodes carried out in the range 0–100 mW/cm<sup>2</sup> and *I*–*t* measurements utilized to determine the response time of the photodiodes. Basic parameters of devices such as ideality factors barrier, height, and series resistance were obtained by Norde and Cheung methods and thermionic emission (TE) theory from *I*–*V* graphs. While the PANI–silicene/*n*-Si exhibited high ideality factor values of 5.49, the PANI–silicene/*p*-Si photodiodes showed a low ideality factor of 1.48. The photodiode parameters such as detectivity and responsivity were calculated as  $6.40 \times 10^9$  Jones and 38.9 mA/W for *n*-Si substrate and 78.2 mA/W and  $8.81 \times 10^9$  Jones for *p*-Si substrate. The case of basic electrical properties for PANI–silicene composite interlayer-based photodiodes was analyzed in detail.

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## Introduction

It is well known that silicene is a two-dimensional allotrope of silicon, and it is similar to graphene but composed of silicon atoms to be arranged in a honeycomb lattice, and it is a single layer of atoms, just like graphene, making it a nanomaterial with unique properties and potential applications [1]. The Poisson ratio of graphene is lower than silicene and also the ultimate stress, the bulk modulus, and the Young's modulus of silicene are obtained to be lower than for graphene [2]. While in-plane stiffness constant ( $C$ ), and Poisson ratio ( $\nu$ ) are  $62 \text{ J/m}^2$  and  $0.3$  for silicene,  $335 \text{ J/m}^2$  and  $0.16$  for graphene, respectively [2, 3]. The graphene bulk modulus is determined to be 3.5 times higher than silicene [3, 4]. Silicene and graphene have unique band structure features, and there are conduction and valence bands, both of which have linear distributions, intersecting at the Brillouin region, the points  $K$  and  $K_0$ , and Fermi energy. It is reported that the silicene has two different band structures buckled and flat. Both forms of silicene have a zero  $\pi$ - $\pi^*$  gap at the  $K$  point and electronic properties like graphene [3, 5, 6]. Electronic properties of silicene also enable to use of various devices such as photodiodes and photodetectors. Its direct bandgap in certain configurations allows for efficient light emission and absorption, which is crucial for developing efficient optoelectronic devices [7, 8].

In recent years, conductive polymers have attracted the attention of researchers due to their high conductivity [9, 10]. Thus, conductive polymers have been used frequently in device applications such as energy storage devices, supercapacitors, organic solar cells (OSCs), light-emitting diodes, sensors, etc. [11–19]. PANI is also a fascinating and versatile polymer belonging to the family of conducting polymers. Because it is renowned for its unique combination of electrical conductivity and processability, many researchers commonly studied PANI in the field of materials science [20]. PANI has been used in applications across various industries, including electronics, energy storage, corrosion protection, sensors, and biomedical devices [21]. In electronic devices, it has been used as a component in capacitors, batteries, and electromagnetic shielding due to its high electrical conductivity [22]. Due to ongoing research and advancements in polymer science, PANI continues to attract the attention of

researchers to explore new ways to tailor its properties and applications. Its combination of electrical conductivity, tunable behavior, and ease of synthesis make PANI a versatile and promising material for a wide range of future technologies [23].

The Schottky barrier helps in efficient and fast carrier collection, resulting in rapid response times and high-speed operation of Schottky photodiodes compared to traditional  $p$ - $n$  junction photodiodes [24]. These behaviors of the Schottky photodiode such as fast response and low noise make suitable applications for optical communication systems, fiber-optic communication networks, laser rangefinders, high-frequency and high-speed applications, and high-speed photodetector [25, 26]. As soon as enough energy strikes the surface of the Schottky photodiode near to metal, it generates hole-electron pairs in the semiconductor. Then, these hole-electron pairs are separated and collected due to the existence of the Schottky barrier [27]. The external interlayers such as conjugated polymer, metal complex ligands, or biomaterials are used in Schottky photodiodes to improve their performance and enhance their spectral sensitivity range [28, 29]. The interlayers provide spectral sensitivity adjustment, reduce dark current for high signal-to-noise ratio, increase responsivity, passivate surface dangling bonds, and barrier height adjustment [30]. Yıldırım et al. used propolis between  $n$ -Si and Au for UV-photodetector, and they reached  $0.113 \text{ A/W}$  responsivity and  $4.04 \times 10^9$  Jones detectivity values [31]. Havigh et al. employed matrix-polymer of carbon and polyvinylpyrrolidone (PVP) composites for UV-Vis photodetector applications, and they obtained  $0.69 \text{ A/W}$  responsivity,  $5.60 \times 10^{10}$  Jones detectivity and  $53.76 \times 10^3$  on-off ratio for UV region [32]. Imer et al. investigated Ru(II)-pydim complex as an interface layer between  $p$ -Si and Al for photodetection applications. The authors achieved  $0.131 \text{ A/W}$  responsivity and  $1.63 \times 10^{11}$  Jones detectivity values for visible light [33].

In this study, we synthesized PANI-silicene composites and used an external interfacial layer between Si (for  $n$ -type and  $p$ -type) and Al to accomplish the Al/PANI-silicene/ $n$ -Si and Al/PANI-silicene/ $p$ -Si photodiodes. Detailed characterization and comparison were performed based on various diode parameters, detectivity, and responsivity for fabricated photodiodes in detail.

### Material and method

The utilized semiconductor wafers were oriented (100) crystalline plane for *p*-type Si and *n*-type Si with resistivity ranging from 1 to 10 Ω cm, carrier concentrations of  $7.5 \times 10^{16} \text{ cm}^{-3}$ , and thicknesses of 400 μm. They were then cut into 2 cm<sup>2</sup> pieces and underwent a cleaning process using an ultrasonic cleaner with isopropanol and acetone. To eliminate the SiO<sub>2</sub> layer formed on the silicon wafer’s surface due to Si–O interactions, the pieces were briefly immersed into a solution of HF:H<sub>2</sub>O (1:1) for 30 s, and subsequently dried with nitrogen. A thermal evaporator was employed to obtain back contacts on the back of the pieces with 100 nm Al metal under pressure of  $5 \times 10^{-6}$  torr. Following this, the *n*-Si/Al and *p*-Si/Al structures were annealed at 550 °C in a nitrogen atmosphere for 10 min to achieve ohmic contact. For preparing the silicene, physical exfoliation of 100 mg Si microparticles was performed by sonicating in a mixture of 100 mL

deionized water and isopropanol with an equal volume in a nitrogen flow-controlled cabin for 4 h. Centrifugation at 5000 rpm and 12000 rpm were subjected to the resulting Si particles for 15 min, then the collected silicene was left to dry at 50 °C in a vacuum oven. For obtaining PANI-silicene composites, the silicene and PANI were individually mixed in 2 mL of N-methyl-2-pyrrolidone (NMP) solution each of 1 mg, and sonicated for 5 min [34]. The solution was applied in three layers onto the *n*-Si/Al and *p*-Si/Al samples using a spin coater at 2000 rpm rotating speed for 40 s. Subsequently, the PANI-silicene/*p*-Si and the PANI-silicene/*n*-Si were conveyed to a thermal evaporation system, where another Al metal with 100 nm thickness was deposited onto them through a hole array mask with  $7.85 \times 10^{-3} \text{ cm}^2$  areas. This process was employed to obtain rectifying Schottky contacts. Figure 1a depicts the visual representation of the fabricated devices with a measurement system, and Fig. 1b shows a schematic energy band diagram. As seen in

**Figure 1** a The visual representation of the measurement system along with the created devices and b schematic energy band diagram of Al/PANI-silicene/*p*-Si or *n*-Si devices.

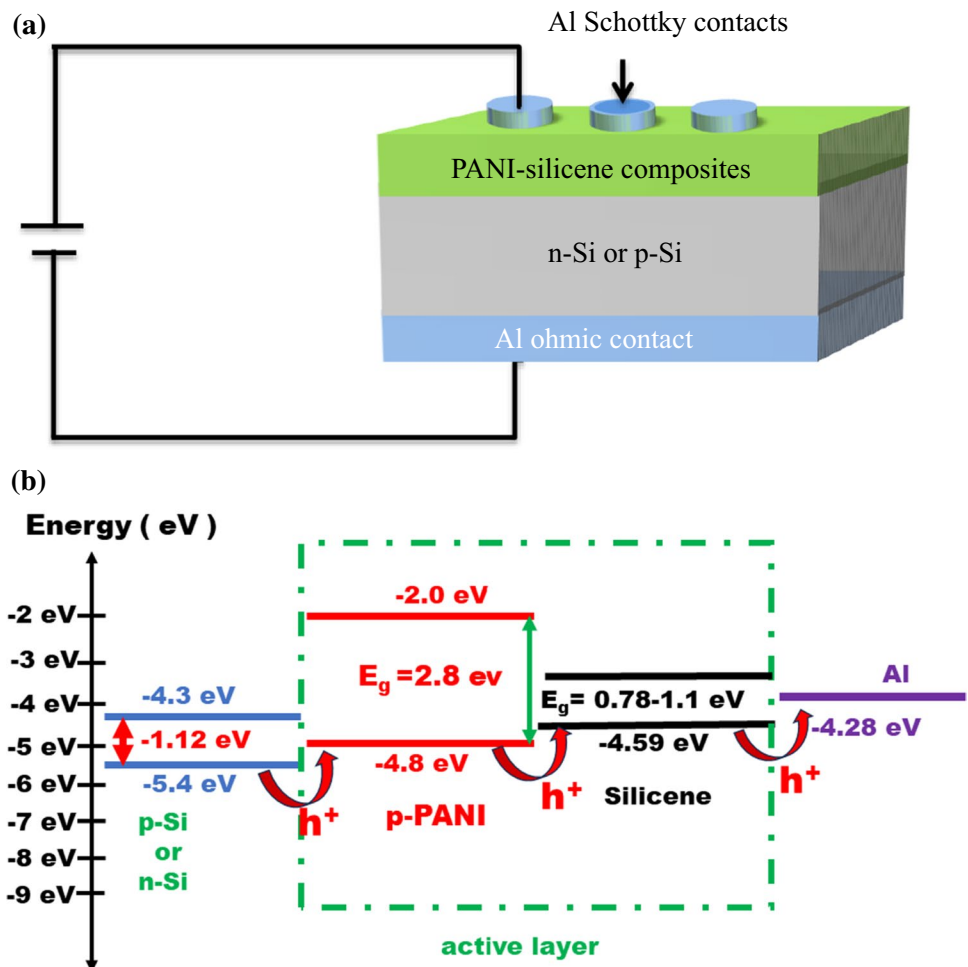


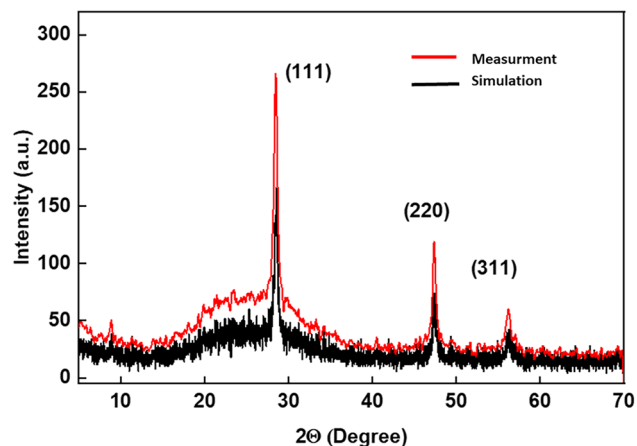
Fig. 1b, PANI, has low band energy ( $E_g = 2.8$  eV); as a result, it can be activated in visible light [35]. In addition, the band structure of silicene (in the absence of spin–orbit interaction) has a zero gap at the Fermi energy, and the work function of silicene is 4.59 eV [36, 37]. According to the simulation model of the new silicene crystal with the rectangular lattice related to the experimental result, the energy band structure is calculated, and a real direct bandgap of silicene is 0.78 (for silicene crystal with the rectangular lattice related)–1.11 (for zigzag dumbbell silicene) eV [38, 39]. Here, the different bandgap from that in the silicene crystal with the hexagonal lattice may be due to the difference in combining energy. Moreover, the interesting electronic properties of the lowest energy 2D polymorphs of silicene make them promising candidates for optoelectronic applications.

Malvern Panalytical Aeris X-ray diffractometry (XRD) operated at 600 W was employed for the crystalline structure of silicene. SEM images of the silicene were taken by ZEISS EVO LS10 with Bruker energy-dispersive X-ray spectroscopy (EDS) detector. The obtained devices underwent characterization using the Fytronix FY-7000 measurements system, where  $I-t$  (current–time) and  $I-V$  (current–voltage) measurements were conducted under dark and illumination. This characterization process allowed for a comprehensive understanding of the electrical behavior and performance of the devices in different light conditions.

## Results and discussion

The crystallinity of the prepared silicenes was examined by XRD analysis (Fig. 2). As shown in Fig. 2, the peaks of (111), (220), and (311) at the XRD pattern of silicene can correspond to Fd-3m (227) space group centrosymmetric cubic crystal. These results are in good agreement with JCPDS Card No. 73-1665 and confirm the silicene structure. The  $a$ ,  $b$ , and  $c$  parameters for the unit cell were determined as 5.431 Å, 5.431 Å, and 5.431 Å, respectively. In the previous article, Baytemir et al. [34] indicated that the silicene nanosheet has a hexagonal honeycomb lattice structure using an HRTEM image, and Yildiz et al. reported that the FTIR of PANI-silicene composites is similar to PANI [40].

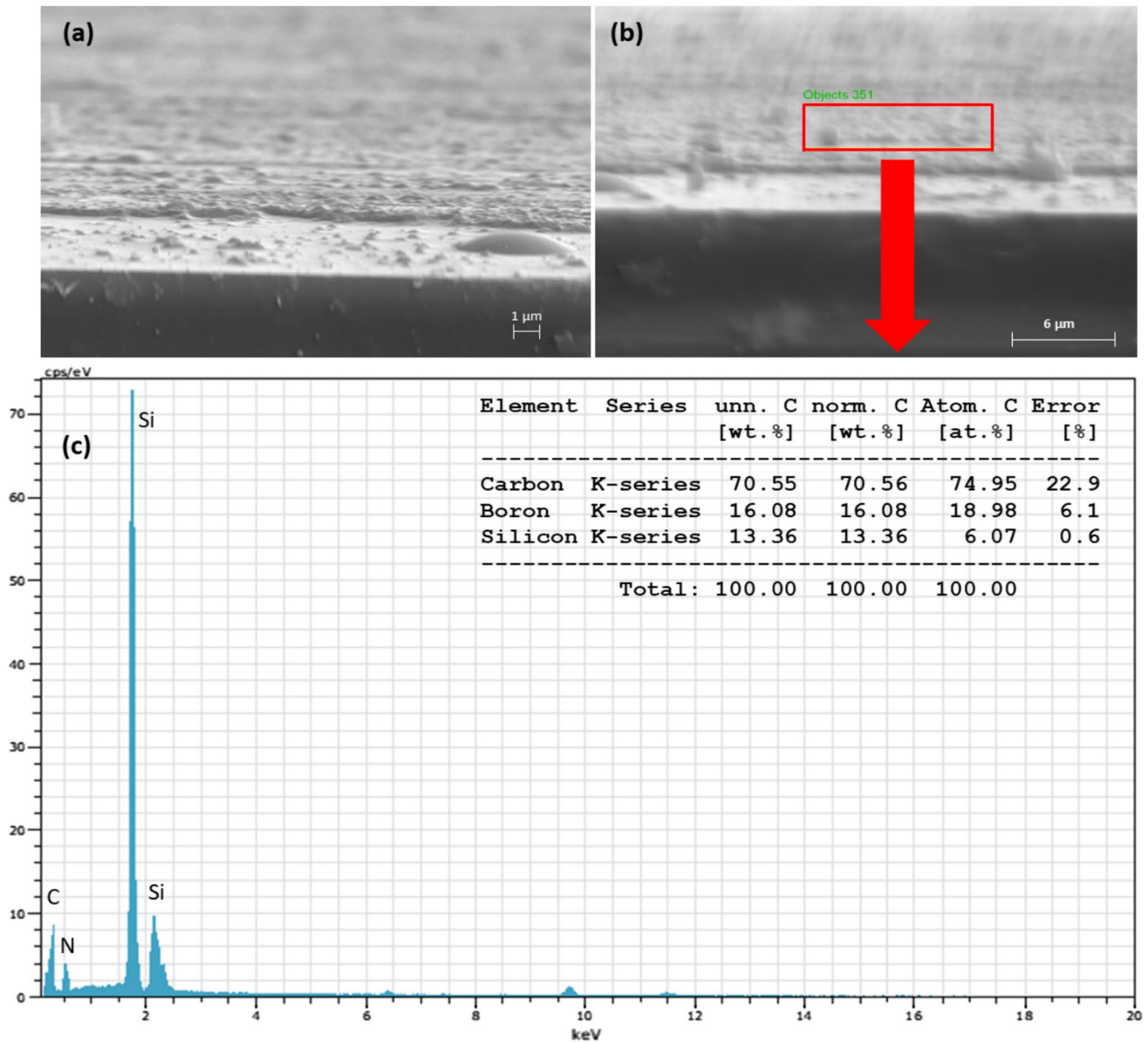
The surface morphology of the PANI-silicene film on the Si surface are shown in Fig. 3a and b from cross



**Figure 2** XRD pattern of the silicene structures.

section. The silicon substrate and PANI-silicene layer can be seen in Fig. 3a with approximately 300 nm thicknesses. The morphology of the surface looks almost homogenous for a wide area. Figure 3b shows the EDS region on SEM images. Figure 3c displays the EDS spectrum and the weighted atomic and molecular distribution of the silicene layer. The C, N, and Si are detected from the EDS spectrum. These results can be confirmed for PANI and silicene, separately by previous literature [41, 42].

The work functions of the  $p$ -Si,  $n$ -Si, and Al are 4.1 eV, 4.6 eV, and 4.3 eV, respectively. By these values, rectifying contact between Al and  $p$ -Si can easily be composed because metal has a higher work function value than semiconductor. However, it is hard to compose a rectifying contact between Al and  $n$ -Si. The external PANI-silicene layer or natural oxide layer between Si and O can help to compose barrier height or rectifying property. Figure 4 indicates  $I-V$  plots of Al/PANI-silicene/ $p$ -Si and Al/PANI-silicene/ $n$ -Si photodiodes. Figure 4a and c shows  $I-V$  of Al/PANI-silicene/ $n$ -Si for forward and reverse biases, respectively. The current increased by increment voltage and light power density at forward and reverse biases. Normally, reverse bias currents of a diode are around  $\mu$ A level instead of mA level. The high reverse bias current and increasing current with voltage can be attributed to the conducting behavior of PANI and non-forming a good rectifying behavior. However, the Al/PANI-silicene/ $n$ -Si heterojunction can be thought of as a photodetector due to the high increase in the level of photocurrent at forward and reverse biases. Figure 4b and d shows  $I-V$  plots

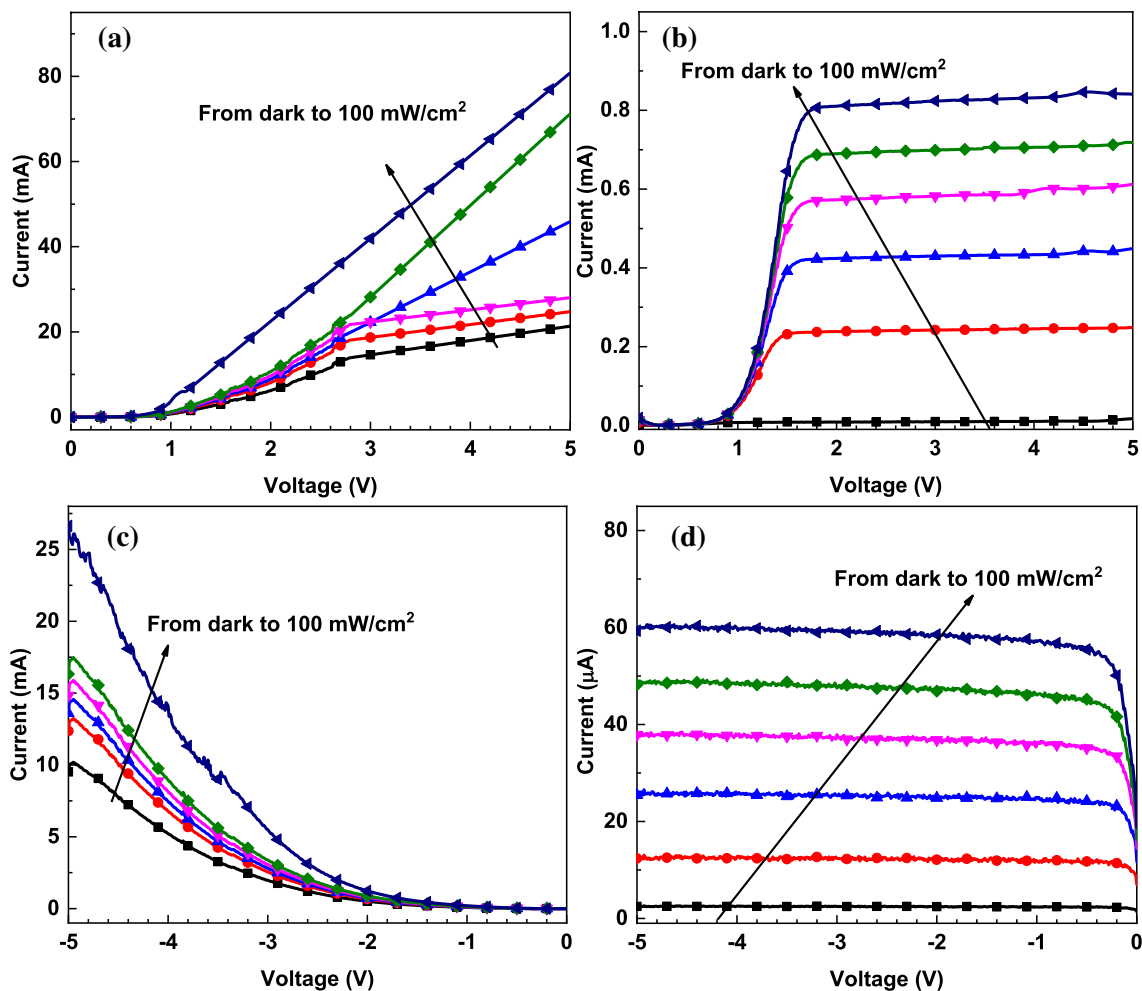


**Figure 3** **a** SEM image of the silicene film on the Si substrate. **b** SEM image of the surface for EDS square. **c** EDS spectrum of the silicene square part of **b**.

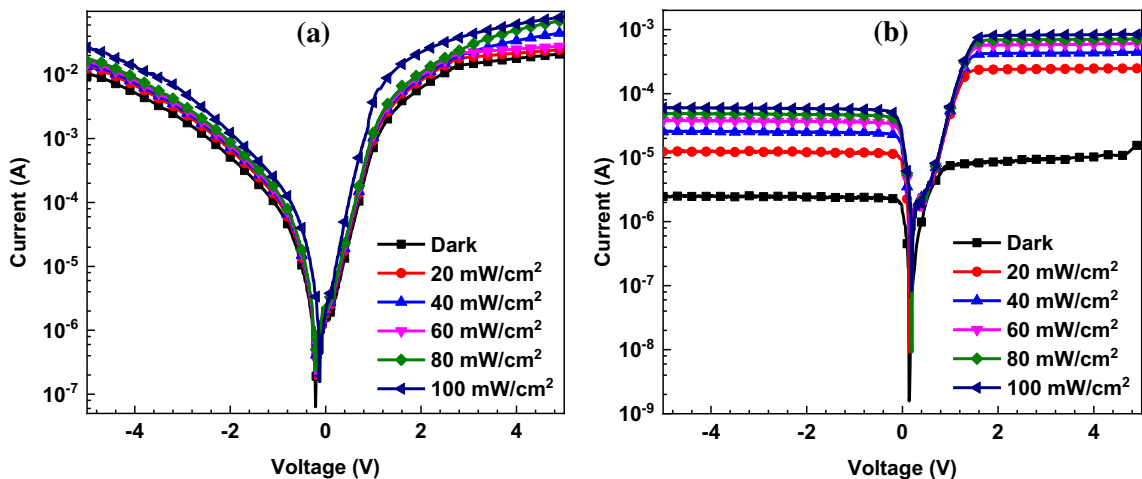
of the Al/PANI–silicene/*p*-Si for forward and reverse biases. With an increase in light power intensity under both forward and reverse biases, the current values demonstrated an upward trend. However, the current values reached a constant value both at reverse biases (around  $-0.20$  and  $-0.50$  V) and forward biases (around  $1.50$  and  $1.80$  V). While the reverse bias characteristics clearly exhibit a photodiode characteristic, the forward bias characteristics indicate a phototransistor-like characteristic. This kind of behavior can be attributed to the external PANI-silicene layer [43]. The

determined threshold voltages of Al/PANI–silicene/*n*-Si and Al/PANI–silicene/*p*-Si photodiodes are  $0.70$  and  $0.25$  V, respectively. The high threshold values of the photodiode with *n*-Si semiconductor according to the photodiode with *p*-Si can be attributed to work function differences [44, 45].

Figure 5a and b displays the  $\ln I$ - $V$  plots of the Al/PANI–silicene/*p*-Si and Al/PANI–silicene/*n*-Si photodiodes, respectively. These plots represent the characteristics of the devices under different light power densities, ranging from dark conditions to  $100$  mW/cm<sup>2</sup> by



**Figure 4** The forward biases *I-V* plots for **a** Al/PANI-silicene/*n*-Si and **b** Al/PANI-silicene/*p*-Si photodiodes, reverse biases *I-V* plots of **c** Al/PANI-silicene/*n*-Si and **d** The reverse biases of Al/PANI-silicene/*p*-Si photodiodes.



**Figure 5** *ln I-V* plots of the **a** Al/PANI-silicene/*n*-Si and **b** Al/PANI-silicene/*p*-Si photodiodes.

20 mW/cm<sup>2</sup> intervals. According to Fig. 3, both photodiodes gave the response to increasing light power for reverse and forward biases due to the effect of external layers of PANI-silicene composites as well as the metal–semiconductor interface [46]. Furthermore, the displacement of the *I*–*V* characteristics toward the positive voltage region under the influence of light can be ascribed to the augmentation of charge carriers in the interface of the devices caused by the density of light power [47].

Diverse device parameters can be derived from the semi-logarithmic *I*–*V* characteristics using the techniques, including TE theory, Norde, and Cheung methods [48]. The expression of current can be found below depending on the saturation current (*I*<sub>0</sub>), ideality factor (*n*), Boltzman constant (*k*), charge of electron (*q*), medium temperature (*T*), and voltage (*V*) [49, 50]:

$$I = I_0 \exp\left(\frac{qV}{nkT}\right) \left[ -\exp\left(-\frac{qV}{kT}\right) \right] \tag{1}$$

where *I*<sub>0</sub> is given by following equation depending on Richardson constant (*A*<sup>\*</sup>) for 32 A/cm<sup>2</sup> K<sup>2</sup> in the case of *p*-type Si and 112 A/cm<sup>2</sup> K<sup>2</sup> for *n*-type Si, barrier height ( $\Phi_b$ ), device area (*A*), *k* and *T*.

The *I*<sub>0</sub> values were determined from semi-logarithmic *I*–*V* plots of the Al/PANI–silicene/*n*-Si and Al/PANI–silicene/*p*-Si photodiodes and given in Table 1. The *I*<sub>0</sub> values exhibited variations when the substrate types were changed, attributed to differences in work functions for *p*-Si and *n*-Si substrates. By using saturation current, the barrier height and ideality factor can be calculated by following equations for  $V \geq 3kT/q$  [51, 52]:

$$I_0 = AA^*T^2 \exp\left(-\frac{q\phi_b}{kT}\right) \tag{2}$$

The values of  $\Phi_b$  and *n* formulas  $V \geq 3kT/q$  can be determined by following formulas by help of above equations:

$$n = \frac{q}{kT} \left( \frac{dV}{d \ln I} \right) \tag{3}$$

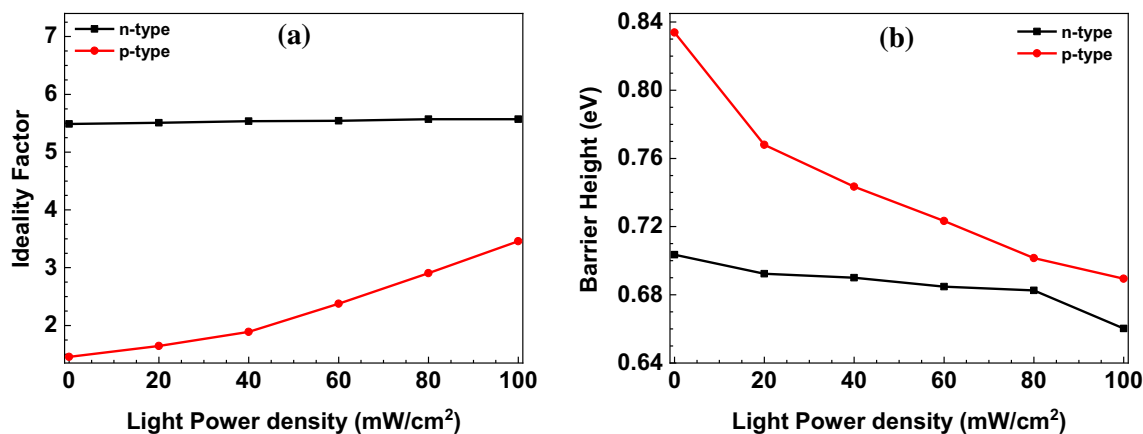
and

$$\phi_b = \frac{kT}{q} \ln \left( \frac{A^*AT^2}{I_0} \right) \tag{4}$$

The obtained  $\Phi_b$  and *n* values are tabulated in Table 1 both the Al/PANI–silicene/*n*-Si and Al/PANI–silicene/*p*-Si photodiodes at dark measurements conditions. When Al/PANI–silicene/*n*-Si has a high value ideality factor of 5.49, the Al/PANI–silicene/*p*-Si has a low value of 1.46. The high *n* values can depend on interface states, the presence of an external interfacial layer, barrier inhomogeneity, or series resistance [53, 54]. The  $\Phi_b$  values of Al/PANI–silicene/*n*-Si and Al/PANI–silicene/*p*-Si photodiodes were determined to be 0.70 and 0.83 eV, respectively. The differences in the  $\Phi_b$  values for changing substrate types can be depended on the work function differences. The changes at the  $\Phi_b$  and *n* values for increasing light power density of the Al/PANI–silicene/*n*-Si and Al/PANI–silicene/*p*-Si photodiodes are introduced in Fig. 6a and b, respectively. As the light power density increased, the *n* values showed a linear rise, while the  $\Phi_b$  values exhibited a general decrease. The increasing *n* values could be attributed to elevated barrier inhomogeneity or interface states and a reduction in series resistance because of an influx of charge carriers at the diode interfaces [55]. Additionally, the decreasing trend in  $\Phi_b$  values could be attributed to an increase in saturation currents as well as the photocurrent of the diodes. However, the increment at the *n* values and decrement at the  $\Phi_b$  values of Al/PANI–silicene/*n*-Si changed slightly. This result also can be ascribed to work function variations between Al metal and Si semiconductors. In other words, work function differences between Al with *p*-Si and *n*-Si caused an effect on the transition of the current in the junction, and thus both  $\Phi_b$  and *n* values exhibited different changing profiles with light power density [56].

**Table 1** The device parameters of the PANI–silicene/*n*-Si and PANI–silicene/*p*-Si photodiodes

Substrate type	Saturation current ( <i>I</i> <sub>0</sub> )	<i>n</i> ( <i>I</i> – <i>V</i> )	<i>n</i> Cheung	$\phi_b$ ( <i>I</i> – <i>V</i> ) (eV)	$\phi_b$ Cheung (eV)	$\phi_b$ Norde (eV)	<i>R</i> <sub>s</sub> Cheung (kΩ- <i>H</i> ( <i>I</i> ))	<i>R</i> <sub>s</sub> Cheung (kΩ-d <i>V</i> /dln <i>I</i> )	<i>R</i> <sub>s</sub> Norde (kΩ)
<i>n</i> -type	1.23 × 10 <sup>-7</sup>	5.49	5.51	0.70	0.66	0.76	0.10	0.22	0.03
<i>p</i> -type	2.29 × 10 <sup>-10</sup>	1.46	1.38	0.83	0.84	0.86	39.31	37.72	122.13

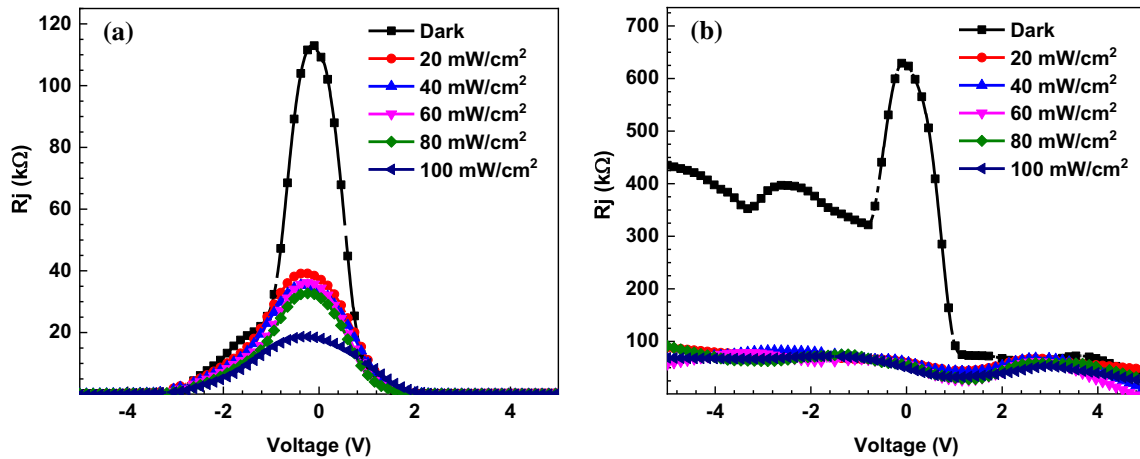


**Figure 6** **a** The ideality factor and **b** barrier height changes of Al/PANI–silicene/*n*-Si and Al/PANI–silicene/*p*-Si photodiodes depending light power density.

The obtained results can be compared with previous literature for various Schottky devices. Some researchers employ Si as semiconductor, others use ITO, GaAs, etc. Hacıismailoglu et al. fabricated Ni/*n*-GaAs Schottky diode (without interlayer) by electrodeposition technique for photovoltaic applications; they calculated ideality factor and barrier height to be 1.05 and 0.70 eV, respectively [57]. Barkhordari et al., employed PVP:ZnTiO<sub>3</sub> composites as an interlayer between Al and *p*-Si to obtain Schottky-type photodiodes, and they determined ideality factor and barrier height as 5.81 and 0.687 eV [58]. Wang et al. fabricated Gr/GO/*n*-Si Schottky silicon photodiode and obtained the ideality factor and barrier height of the device to be 2.19 and 0.88 eV [59]. Dhivar et al. reported that the charge transport behavior of metallohydrogel of Mg (II) ion using pentaethylenhexamine (PEHA) (Mg@PEHA)-based Schottky diode structures and displayed bipolar resistive switching behavior at room temperature for a resistive random-access memory (RRAM) device using Mg@PEHA. This device demonstrated excellent performance with a high ON/OFF ratio of approximately 100 and remarkable endurance of over 5000 switching cycles, but the ideality factor and barrier height of the ITO/Mg@PEHA/ITO device were calculated to be 51.83 and 0.026 eV [60]. Also, Karmakar et al. were indicated that the charge transport behavior Mg (II) metallohydrogel with trimethylamine (Mg@TMA) and Mg (II) metallohydrogel with 3-amino-1-propanol-based metallohydrogel (Mg@3AP)-based metal–semiconductor–metal structures and displayed bipolar resistive switching behavior at room temperature for RRAM device using Mg@TMA and Mg@3AP. These

devices exhibited excellent switching endurance over 10,000 switching cycles with a large ON/OFF ratio ( $\sim 100$ ) for Mg@TMA [61] and Mg@3AP [62]. While the ideality factor values were obtained to be 0.84 for Mg@TMA and 0.70 for Mg@3AP, barrier height values obtained as 0.026 eV for both ITO/Mg@3AP/ITO and ITO/Mg@TMA/ITO devices. The calculated results of the ideality factor and barrier height in this study can be comparable with various Schottky diodes, especially Si semiconductors with interlayers.

The junction resistance ( $R_j$ ) of the Al/PANI–silicene/*n*-Si and Al/PANI–silicene/*p*-Si photodiodes is determined by the relation of the  $dV/dI$ . Furthermore, it is important to know that  $R_j$  consists of both series resistance ( $R_s$ ) and shunt resistance ( $R_{sh}$ ). To ensure optimal performance of optoelectronic devices a low  $R_s$  and a high  $R_{sh}$  are essential. The  $R_{sh}$  values are obtained at reverse biases to achieve a constant or flat  $R_j$  graph, while the  $R_s$  values are chosen from the straight region of the  $R_j$  graph under positive voltage values [63]. In other words, if the  $R_j$  decreases and reaches a constant at a certain value of higher forward biases, the  $R_j$  values show  $R_s$ . However, constant  $R_j$  values represent  $R_{sh}$  values at high enough reverse biases. Figure 7a and b illustrates the  $R_j$  profile for Al/PANI–silicene/*n*-Si and Al/PANI–silicene/*p*-Si photodiodes at different densities of light powers, respectively. The trend shows a decrease in both  $R_{sh}$  and  $R_s$  values as the light power density increases, validating the correlation with changes in  $n$  and  $\Phi_b$  values. Both  $R_s$  and  $R_{sh}$  values revealed horizontal regions for higher forward and reverse biases of the Al/PANI–silicene/*n*-Si and Al/PANI–silicene/*p*-Si photodiodes.



**Figure 7** The  $R_j$ - $V$  plots of the **a** Al/PANI-silicene/ $n$ -Si and **b** Al/PANI-silicene/ $p$ -Si photodiodes.

The  $R_{sh}$  and  $R_s$  values of the Al/PANI-silicene/ $n$ -Si are  $10.95 \times 10^3 \Omega$  and  $0.28 \times 10^3 \Omega$ , respectively. For the Al/PANI-silicene/ $p$ -Si photodiode, the  $R_{sh}$  and  $R_s$  values are  $3.34 \times 10^5 \Omega$  and  $70.92 \times 10^3 \Omega$ , respectively.

Another approach for determining the series resistance ( $R_s$ ) and additional device parameters like  $n$  and  $\Phi_b$  involves employing the Cheung method, which elucidates the current using the next equation correlated with the device’s  $R_s$  value [64]:

$$I = I_0 \exp\left(-\frac{q(V - IR_s)}{nkT}\right) \tag{5}$$

where  $IR_s$  represents the voltage drop across the device attributed to  $R_s$  value. Utilizing Eq. (5), we derive two Cheung functions, which are expressed by the subsequent formulas:

$$\frac{dV}{d(\ln I)} = IR_s + n\frac{kT}{q} \tag{6}$$

$$H(I) = IR_s + n\phi_b \tag{7}$$

When plotting both  $H(I)$  and  $dV/d\ln I$  against current, linear plots emerge because of the inherent relationship between Cheung functions and current. The plot of  $dV/d\ln I$  aids in determining the  $n$  value through the  $y$ -axis crossing point and one of the  $R_s$  value by the slope of the plot while the  $H(I)$  against  $I$  plot facilitates extraction of another  $R_s$  and  $\Phi_b$  values. The Cheung graphs of the Al/PANI-silicene/ $n$ -Si and Al/PANI-silicene/ $p$ -Si photodiodes are illustrated in Fig. 8a and b, respectively. The extracted

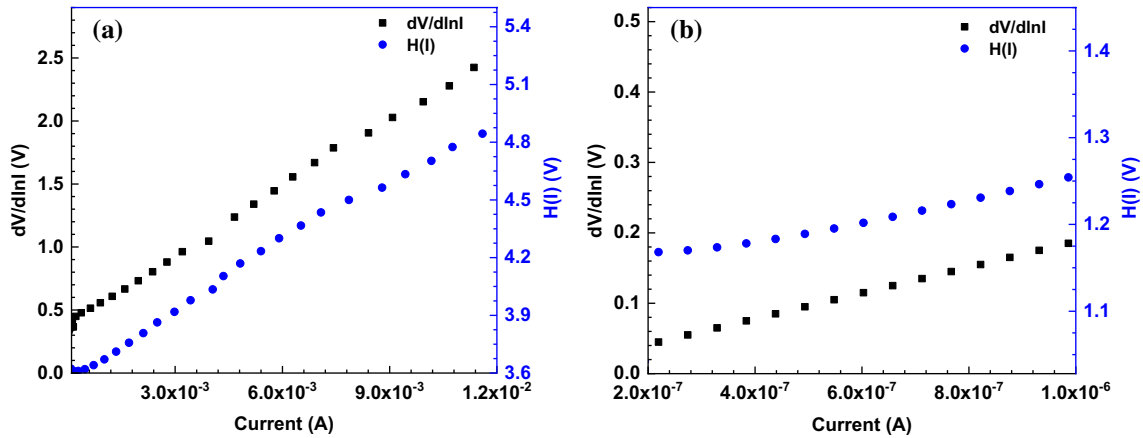
$n$ ,  $R_s$ , and  $\Phi_b$  values from the Cheung method are compiled in Table 1. Discrepancies between the TE theory and Cheung method values for  $\Phi_b$  and  $n$  arise from non-ideal device structures and approximative variations [65]. Notably, the calculated  $R_s$  values align with the  $H(I)$ - $I$  and  $dV/d\ln I$ - $I$  graphs of each device, confirming the stability of the Cheung method [66]. Moreover, the  $R_s$  values for the Al/PANI-silicene/ $n$ -Si photodiode surpass those of the Al/PANI-silicene/ $p$ -Si counterpart because of interface states between Al metal and  $n$ -Si and greater barrier inhomogeneity in the interface. It is important to acknowledge that the disparities between directly calculated  $R_s$  values and those obtained through the Cheung method can be dependent on approximation variations [67].

The utilization of the Norde method presents an alternative means to enhance the consistency of diode parameters, allowing for the calculation of  $R_s$  and  $\Phi_b$ . The Norde function is expressed by the next formula [67].

$$F(V) = \frac{V}{\gamma} - \frac{kT}{q} \ln\left(\frac{I(V)}{AA^*T^2}\right) \tag{8}$$

where  $\gamma$  represents an integer greater than  $n$  which is obtained by TE theory, and  $I(V)$  signifies the current. The calculation of  $\Phi_b$  and  $R_s$  values is accomplished through the following formulas derived from the Norde function:

$$\phi_b = F(V_0) + \left[\frac{V_0}{\gamma} - \frac{kT}{q}\right] \tag{9}$$



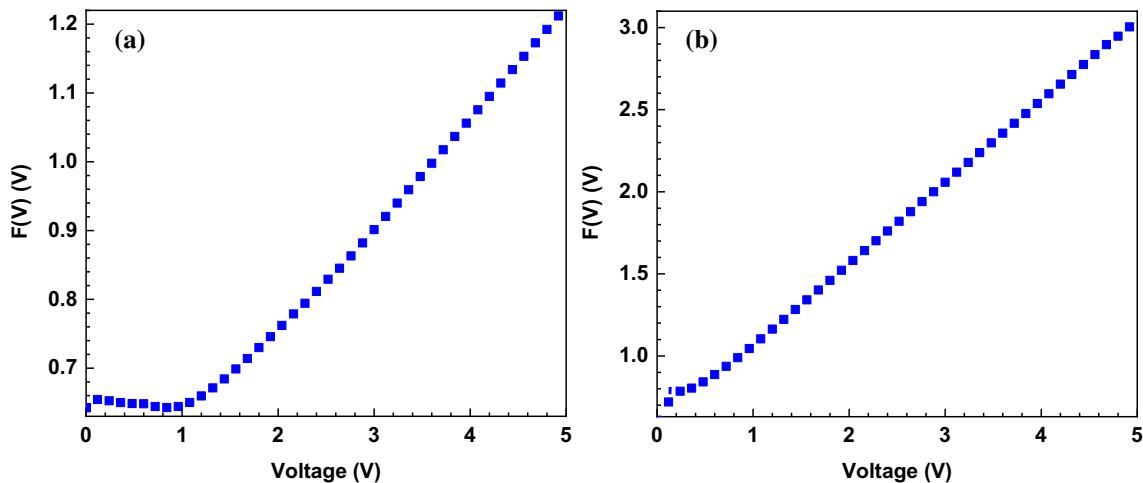
**Figure 8** Cheungs plots of the **a** Al/PANI-silicene/*n*-Si and **b** Al/PANI-silicene/*p*-Si photodiodes.

$$R_s = \frac{\gamma - n kT}{I q} \tag{10}$$

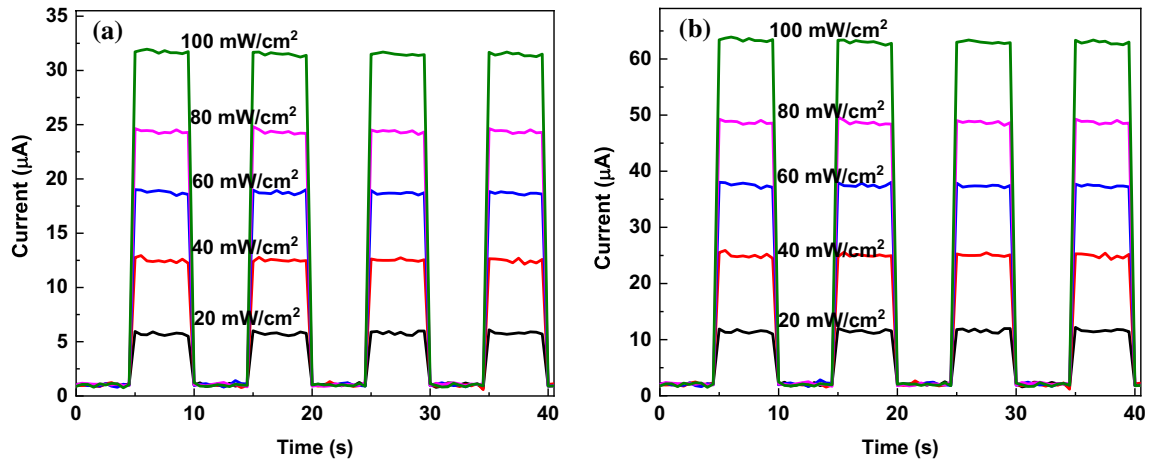
where  $V_0$  is the minimum voltage value dependent minimum  $F(V)$  value.

Figure 9a and b depicts the  $F(V)$ - $V$  characteristics of Al/PANI-silicene/*n*-Si and Al/PANI-silicene/*p*-Si devices. The resulting  $\Phi_b$  and  $R_s$  values are presented in Table 1, showcasing a favorable alignment with the calculated  $\Phi_b$  and  $R_s$  values from both TE theory and the Cheung method. Minor divergences can be ascribed, once more, to non-ideal diode structure as well as inherent approximation discrepancies unique to each device, and similar results were indicated by other researchers [29, 68].

Current transient measurements of a photodiode provide crucial insights into their dynamic behavior and performance characteristics. These measurements involve monitoring the changes in current flow through the photodiode over time, typically in response to variations in incident light intensity or applied voltage. By analyzing these transient responses, various photodiode properties such as photosensitivity, responsivity, and speed of response can be understood. Figure 10a and b displays current transient graphs of the Al/PANI-silicene/*n*-Si and Al/PANI-silicene/*p*-Si photodiodes for light power on and off situations in 5 s at  $-2$  V, respectively. Both photodiodes have exhibited an immediately increasing profile when the light is on and a decreasing profile when the light is off.



**Figure 9** The  $F(V)$ - $V$  graphs of the **a** Al/PANI-silicene/*n*-Si and **b** Al/PANI-silicene/*p*-Si photodiodes.



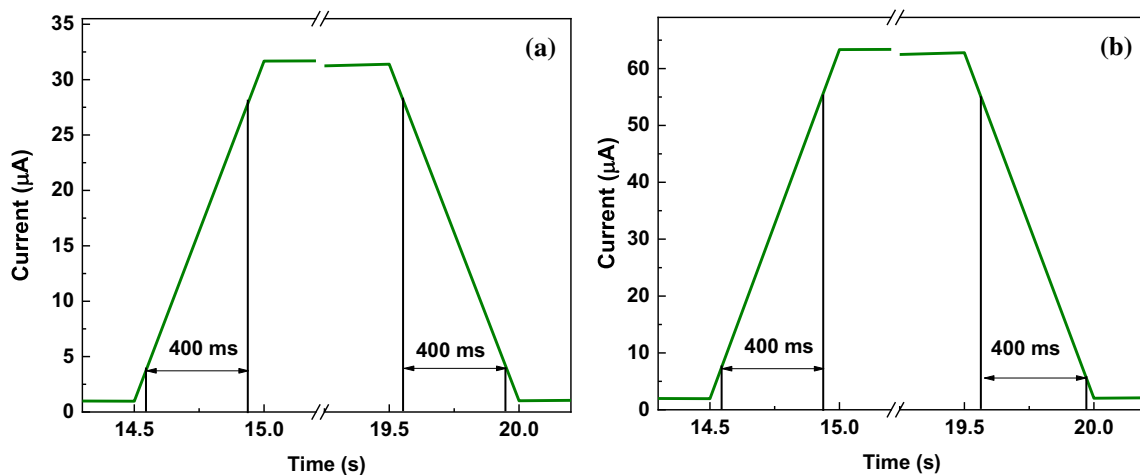
**Figure 10** The  $I-t$  characteristics of the **a** Al/PANI-silicene/ $n$ -Si and **b** Al/PANI-silicene/ $p$ -Si photodiodes depending on light power density.

The response time of a photodiode shows reaction speed to changes in light power density, and it is an important parameter for detection performance [69]. Figure 11a and b shows the response time of Al/PANI-silicene/ $n$ -Si and Al/PANI-silicene/ $p$ -Si photodiodes for 100 mW/cm<sup>2</sup> light power density. Both devices exhibited 400 ms rise and fall times, implying fast photoresponse for optoelectronic applications.

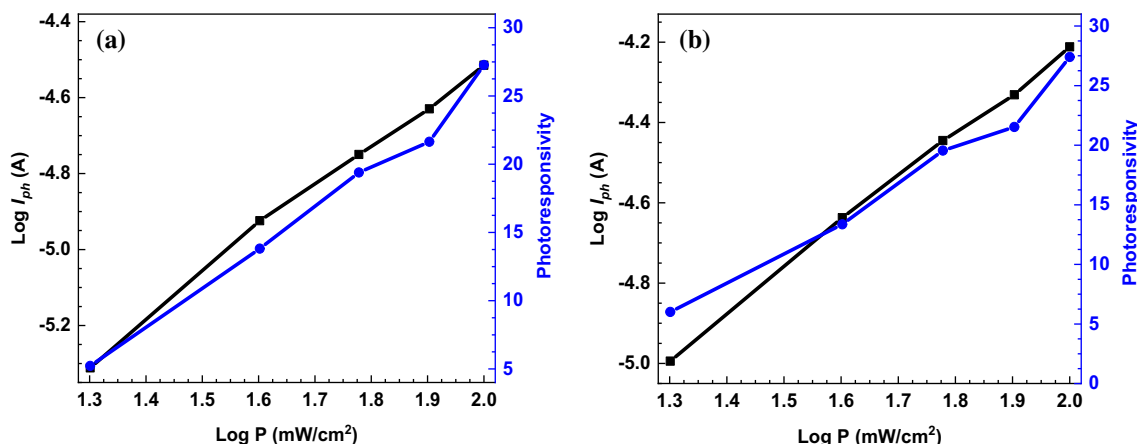
In order to examine how photoconduction changes with varying illumination intensities, we constructed a double-logarithmic plot of photocurrent ( $I_{ph}$ ) against light density ( $P$ ). The underlying photoconduction mechanism can be investigated through the utilization of the below equation:

$$I_{ph} = \alpha P^m \tag{11}$$

where  $m$  stands for the power exponent, and  $\alpha$  represents a constant. The  $m$  value is determined by the slope of  $\text{Log}I_{ph}-\text{Log}P$  plots. If the  $m$  value is greater than unity and exhibits linear behavior, the related device reveals a photoconductive mechanism [70]. Power-dependent photoresponsivity and  $\text{Log}I_{ph}-\text{Log}P$  plots of the Al/PANI-silicene/ $n$ -Si and Al/PANI-silicene/ $p$ -Si photodiodes are indicated in Fig. 12a and b, respectively. Both current and photoresponsivity have generally linear variations with increments of light power density. The  $m$  values were determined as 1.12 and 1.11 for Al/PANI-silicene/ $n$ -Si and Al/PANI-silicene/ $p$ -Si photodiodes, respectively.



**Figure 11** Response time of **a** Al/PANI-silicene/ $n$ -Si and **b** Al/PANI-silicene/ $p$ -Si photodiodes for 100 mW/cm<sup>2</sup> light power density.



**Figure 12** The  $\text{Log} I_{ph}$ - $\text{Log} P$  graphs of the **a** Al/PANI-silicene/*n*-Si and **b** Al/PANI-silicene/*p*-Si photodiodes.

These  $m$  values clearly confirmed that both devices can be used for applications of optoelectronic [71].

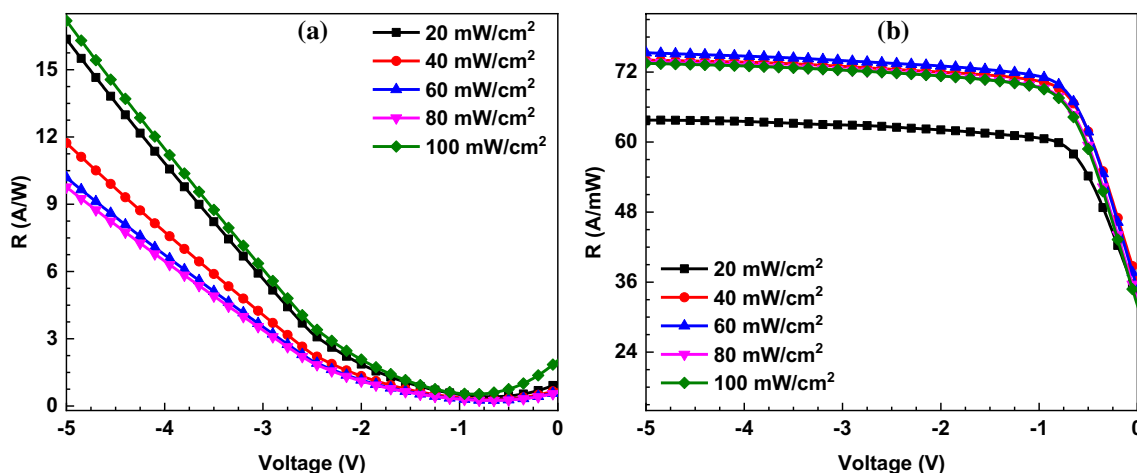
The responsivity serves as a key parameter for the effectiveness of a photodiode or photodetector, quantifying its sensitivity to incident light. This parameter can be mathematically expressed using the following equation [72]:

$$R = \frac{I_{ph}}{PA} \quad (12)$$

Figure 13a and b illustrates the alterations at responsivity of the Al/PANI-silicene/*n*-Si and Al/PANI-silicene/*p*-Si devices as a function of reverse biases, respectively. Notably, the responsivity of the Al/PANI-silicene/*p*-Si photodiode exhibited a rapid rise with minor reverse biases, followed by a

relatively stable trend as the reverse biases increased. However, the responsivity of the Al/PANI-silicene/*n*-Si increased almost linearly by increasing reverse biases after  $-2$  V. While the responsivity level of the Al/PANI-silicene/*n*-Si is around  $10^3$  mA/W, the Al/PANI-silicene/*p*-Si photodiode has  $10^2$  mA/W level. Moreover, the responsivity of each device exhibited generally a rise in correspondence with increasing light power density. This phenomenon can be dependent on the generation of excitons at the photodiode interface [73]. The applied voltage plays a pivotal role in generating these excitons, thereby facilitating the enhancement of photocurrent within the photodiode interface.

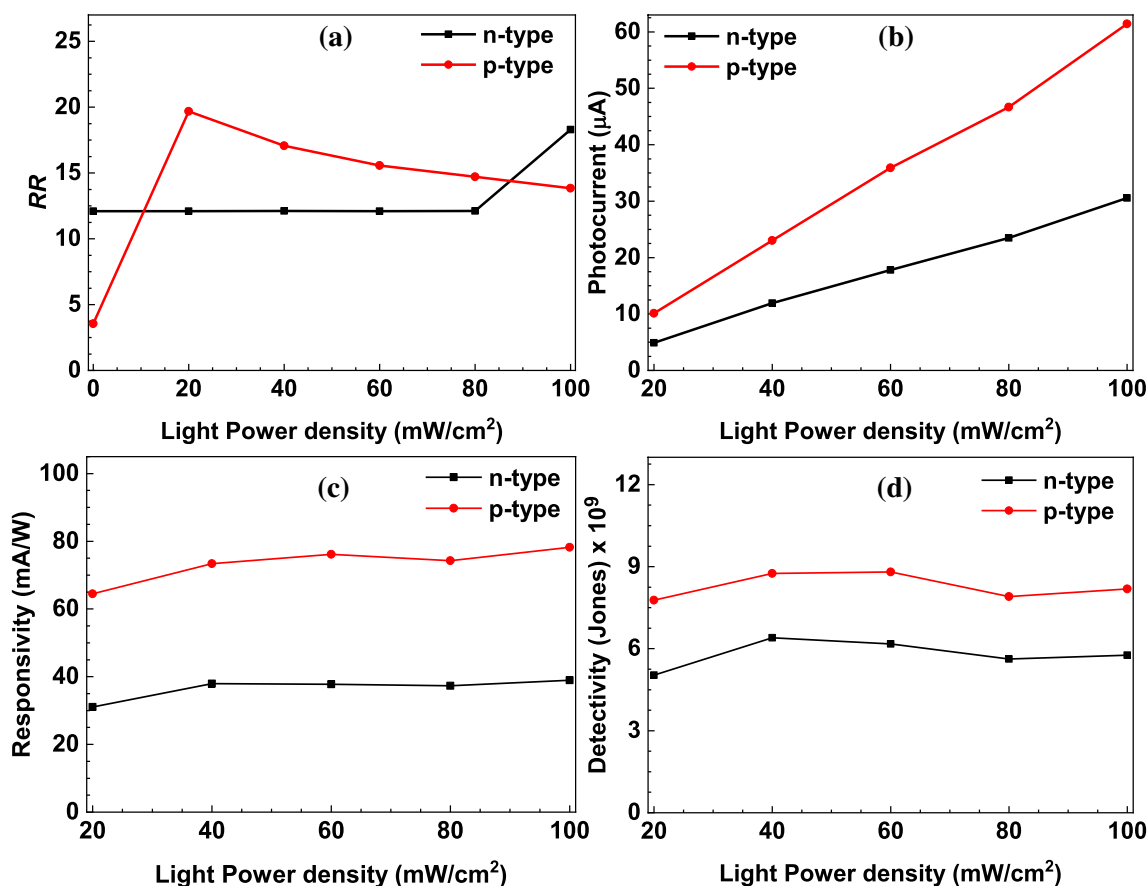
While the rectifying ratio ( $RR$ ) is important for diode characteristics, the photocurrent, responsivity,



**Figure 13** The  $R$ - $V$  of the **a** Al/PANI-silicene/*n*-Si and **b** Al/PANI-silicene/*p*-Si photodiodes.

and specific detectivity are key parameters employed in the assessment of the properties of a photodiode characteristic. The  $RR$  is obtained ratio of the currents for the same voltages at forward and reverse biases. The  $RR$  profiles of the Al/PANI–silicene/ $p$ -Si and Al/PANI–silicene/ $n$ -Si photodiodes under varying light power densities are illustrated in Fig. 14a. The  $RR$  values of the Al/PANI–silicene/ $p$ -Si photodiode slightly increased with decreasing light power density after  $20 \text{ mW/cm}^2$  because of rising current at reverse biases by power density of light. However, the  $RR$  values of the Al/PANI–silicene/ $n$ -Si photodiode stayed constant up to  $20 \text{ mW/cm}^2$  and then increased slightly. The photocurrent of a photodiode is calculated by subtracting of illuminated current from dark currents. The alterations in photocurrent, influenced by changes in light power density, are depicted in Fig. 14b for the Al/PANI–silicene/ $n$ -Si and Al/PANI–silicene/ $p$ -Si photodiodes. Notably, the photocurrent values for both photodiodes displayed an almost linear increase with the

increasing of light power. However, it is worth noting that the Al/PANI–silicene/ $p$ -Si photodiode exhibited notably higher photocurrent values in comparison. The responsivity of photodiodes shows sensitivity to the light. Figure 14c illustrates the responsivity profiles of the Al/PANI–silicene/ $p$ -Si and Al/PANI–silicene/ $n$ -Si photodiodes depending on light power density under a reverse bias of  $-2 \text{ V}$ . While both photodiodes exhibited a slight increase in responsivity with rising light power, it's notable that the Al/PANI–silicene/ $p$ -Si photodiode demonstrated higher responsivity values in comparison to the Al/PANI–silicene/ $n$ -Si photodiode. The specific detectivity of a photodiode represents to sense ability of the smallest signal that can be detected. Turning to Fig. 14d, the changes in detectivity due to increasing light power density are displayed for both the Al/PANI–silicene/ $n$ -Si and Al/PANI–silicene/ $p$ -Si photodiodes. Interestingly, the detectivity profiles of the two photodiodes exhibit similarities. Overall, the detectivity and responsivity values obtained from the



**Figure 14** a  $RR$ , b photocurrent, c responsivity, and d detectivity profiles of the Al/PANI–silicene/ $n$ -Si and Al/PANI–silicene/ $p$ -Si photodiodes depending on the light power densities.

photodiodes align well with the existing literature on photodiodes [74–76].

## Conclusion

The PANI-silicene composites were synthesized and used as interlayers of Al and both *p*-type and *n*-type silicon to manufacture Al/PANI-silicene/*p*-Si and Al/PANI-silicene/*n*-Si photodiodes. While the XRD revealed the crystalline nature of the silicene clearly, the SEM/EDS analysis confirmed the deposition of the PANI-silicene layer on Si. *I*–*V* and *I*–*t* plots of the Al/PANI-silicene/*p*-Si and Al/PANI-silicene/*n*-Si photodiodes were obtained for different light power densities from dark to 100 mW/cm<sup>2</sup>. The diode parameters were calculated by Cheung and Norde methods, and TE theory to validate the series resistance, barrier height, and ideality factor of the photodiodes. While the ideality factor values were obtained as 5.49 and 1.48 for Al/PANI-silicene/*n*-Si and Al/PANI-silicene/*p*-Si photodiodes, the values of barrier height were obtained as 0.70 and 0.83 eV, respectively. The Al/PANI-silicene/*p*-Si photodiode exhibited photodiode characteristics at the negative voltage region and phototransistor characteristics at the positive voltage region. The basic detector properties were also calculated from *I*–*t* characteristics, and results were discussed in detail for PANI-silicene interfacial-based photodiodes. While the responsivity level of the Al/PANI-silicene/*n*-Si is around 10<sup>3</sup> mA/W, the Al/PANI-silicene/*p*-Si photodiode has a 10<sup>2</sup> mA/W level. The photodiodes can be a good candidate for photodetection applications.

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## Author contributions

AK was involved in conceptualization, investigation, writing—original draft, and editing. DEY helped with writing—reviewing, and editing and also participated in supervision. NT was responsible for the investigation, writing—reviewing, and editing. MY

took part in conceptualization, investigation, and writing—reviewing.

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## Data availability

All data presented in this article will be available upon reasonable request from Dilber Esra YILDIZ as the corresponding author: desrayildiz@hitit.edu.tr.

## Declarations

**Conflict of interest** The authors declare that they have no known conflicts of interest competing interests or personal relationships that could have appeared to influence the work reported in this paper.

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