Silicon-Based Intermediate-Band Infrared Photodetector Realized by Te Hyperdoping

Mao Wang,* Eric García-Hemme, Yonder Berencén, René Hübner, Yufang Xie, Lars Rebohle, Chi Xu, Harald Schneider, Manfred Helm, and Shengqiang Zhou*

Si-based photodetectors satisfy the criteria of being low-cost and environmentally friendly, and can enable the development of on-chip complementary metal-oxide-semiconductor (CMOS)-compatible photonic systems. However, extending their room-temperature photoresponse into the mid-wavelength infrared (MWIR) regime remains challenging due to the intrinsic bandgap of Si. Here, we report on a comprehensive study of a room-temperature MWIR photodetector based on Si hyperdoped with Te. The demonstrated MWIR p-n photodiode exhibits a spectral photoresponse up to 5 µm and a slightly lower detector performance than the commercial devices in the wavelength range of 1.0–1.9 µm. The correlation between the background noise and the sensitivity of the Te-hyperdoped Si photodiode, where the maximum room-temperature specific detectivity is found to be $3.2 \times 10^{12}$ cmHz$^{1/2}$ W$^{-1}$ and $9.2 \times 10^8$ cmHz$^{1/2}$ W$^{-1}$ at 1 µm and 1.55 µm, respectively, is also investigated. This work contributes to pave the way towards establishing a Si-based broadband infrared photonic system operating at room temperature.

1. Introduction

Broadband infrared photodetectors have been attracting the interest of many researchers due to their wide variety of applications, such as telecommunication, security equipment, environmental sensing, and biomedicine. Nowadays, commercially available photodetectors are mostly fabricated with mercury cadmium telluride (MCT, HgCdTe), PbS, and III-V quantum-well/dot (QWIP/QWID). These photodetectors exhibit high device performance in infrared light detection, but suffer from some crucial drawbacks, such as high cost, problematic environmental impact, operation at cryogenic temperatures, and especially incompatibility with the complementary metal-oxide-semiconductor (CMOS) fabrication routes. Alternatively, Si-based photodetectors overcome these disadvantages, but their infrared photoresponse is fundamentally restricted to the near infrared (NIR) spectral range due to the 1.12-eV indirect bandgap of Si ($\lambda = 1.1$ µm). Therefore, the development of a room-temperature broadband infrared Si-based photodetector is of great interest in the realm of all-Si photonic systems.

One of the most promising approaches to further extend the room-temperature optical response of Si to the short- and mid-wavelength infrared (SWIR, MWIR) range consists of introducing deep-level dopants (e.g., transition metals and chalcogen dopants) into Si at concentrations in excess of the solid solubility limit. This process leads to the broadening of the deep-level states into an intermediate band (IB) with finite width that allows for the strong optical absorption of photons with an energy lower than that of the Si bandgap. Moreover, utilizing deep-level impurities provides a path to obtain extrinsic Si-based photodetectors for room-temperature operation, which is not possible with shallow-level impurities. However, deep-level impurities such as transition metals have very high diffusion velocities in Si. Therefore, they will diffuse to the surface and form the so-called cellular breakdown, preventing the dopant incorporation and eventually the fabrication of CMOS-compatible devices. Si hyperdoped with chalcogen dopants does not exhibit cellular breakdown and has also shown potential applications for infrared photodetectors. Fortunately, due to the lack of a meticulous design of the device architecture and of the doping homogeneity, the achieved S- or Se-hyperdoped Si photodiodes show quite low sub-bandgap external quantum efficiency (EQE) and only operate in the SWIR wavelength range. Moreover, S- and Se-hyperdoped Si lose their ability to absorb infrared photons with an energy lower than that of the Si bandgap.

© 2020 The Authors. Advanced Optical Materials published by Wiley-VCH GmbH

DOI: 10.1002/adom.202001546
light even after short-duration thermal treatments at low temperatures.\[29,30\] This will compromise the application of hyperdoped Si for integration with the existing CMOS-compatible processes involving temperature-dependent steps. Unlike S and Se, Te impurities have much lower diffusivity.\[31\] Te-hyperdoped Si shows stable IR-absorption upon thermal processing up to 400 °C with a duration of 10 min.\[29,32\] Therefore, Si hyperdoped with Te holds promise for fabricating photodetectors with broad spectral response and enhanced detectivity as well as their integration into manufacturing processes.

In this work, we report on a room-temperature MWIR Si p-n photodiode working in photovoltaic mode based on Si hyperdoped with Te. The hyperdoped Si layers are homogeneous, free of cellular breakdown, and surface flat. The materials and device fabrication are fully CMOS-technology compatible. The fabricated photodiode exhibits an enhanced performance figure of merit, for example, spectral photoresponse, specific detectivity, bandwidth, and response speed. These results point out the potential of Te-hyperdoped intermediate-band Si photodetectors for room-temperature high-performance MWIR detection as the new generation of Si-based photonic systems.

2. Results and Discussion

2.1. Material Characterization

The process flow of fabricating the Te-hyperdoped Si photodetector is shown in Figure 1a,b. Detailed microstructure investigations of the Te-hyperdoped Si layer were carried out by Rutherford backscattering spectrometry (RBS) and transmission electron microscopy (TEM).\[32–34\] Single-crystalline regrowth of the Te-hyperdoped Si with a flat sample surface is achieved.
The energy probability distribution of the binding energy $E_b$ is described as the single discrete deep-level state excitation $\frac{(h\omega - E_b)^{1/2}}{h\omega}$ (Equation 1). This term convolved with a Gaussian distribution of the deep-level states energies, with a mean binding energy $E_b$ and a standard deviation $\sigma_b$ is used to describe the broadening of the deep-level states into an IB with finite width in Te-hyperdoped Si.

$$\sigma_b = \frac{1}{e^2} \left( \int \frac{(h\omega - E_b)^{1/2}}{h\omega} \exp \left( \frac{(h\omega - E_b)^{1/2}}{2E_b} \right) d\omega \right)$$

$\alpha_s$ is the absorption coefficient for the sub-bandgap absorption by assuming that electrons are promoted from Te deep-level states to the conduction band (CB) (Equation 3). The spectral fit is plotted in the inset of Figure 1g with the x-axis being the energetic distance to the CB. The energy probability distribution of the Te deep-levels suggests that the IB is not merged with the CB.

$$I = I_s \left( \frac{q(V - IR_s)}{e} \right)^{1/\eta} \frac{qV}{IR_s}$$

where $I_s$ is the saturation current, $q$ is the electron charge, $\eta$ is the ideality factor, $k_B$ is the Boltzmann constant, and $T$ is the temperature; whereas $R_s$ and $R_{shunt}$ are the series and parallel resistances, respectively. A room-temperature ideality factor of 2.1 was found by fitting the experimental data. The rectifying behavior is directly related with the n-type character of the Te-hyperdoped Si layer,

For the temperature-dependent electrical measurements, the Te-hyperdoped Si p-n intermediate-band Si p-n photodiode is placed inside a helium closed-cycle Janis cryostat with a ZnS window. Figure 2a depicts the current–voltage ($I-V$) curves at room-temperature for the Te-hyperdoped-Si p-n photodiode under dark and white-light illumination conditions with an optical power density of 20 mW cm$^{-2}$. The forward voltage corresponds to the positive bias applied to the bottom contact (p-Si substrate). As shown in Figure 2a, the Te-hyperdoped intermediate-band Si p-n photodiode exhibits a rectifying behavior. The ratio forward/ reverse current at $\pm 0.5$ V is found to be 357. Further analysis of the rectifying behavior was performed by fitting the dark $I-V$ curve using the single-diode equation as follows:

$$I = A \exp\left(\frac{-E_a}{kT}\right)$$

where $A$ is a constant and $E_a$ is the activation energy of the transport mechanism. It is worth noting that both exponential...
behaviors have been well fitted in a wide range of current. From fitting to Equation (4) in the high-temperature range ($T > 160$ K), an activation energy of 0.51 eV was deduced. This value is close to about half the silicon band gap (0.56 eV). This supports the previous interpretation of the transport mechanism that is driven by a recombination process in the depletion region in this temperature range.\[43\] At low temperature ($T < 160$ K), a smaller activation energy of 43 meV was found. Such a small activation energy together with the temperature behavior of the ideality factor support the existence of a tunneling current.\[44\] We believe that the origin of this tunneling current could be related with a multi-tunneling capture-emission process through the Te-localized states in the junction region, although further work is in progress to elucidate it exactly.

2.3. Device Characterization: Optical Properties

2.3.1. Responsivity

Figure 3 shows the temperature-dependent spectral responsivity and the band diagram of the Te-hyperdoped Si p-n photodiode. The infrared responsivity is estimated at zero bias (i.e., the photovoltaic mode) to prove the pure photovoltaic effect of the photodetector. The Te-hyperdoped Si p-n photodiode shows a strong sub-bandgap responsivity up to 5 $\mu$m, whereas the responsivity of a commercial Si photodetector reaches the noise floor as expected at wavelengths longer than 1.2 $\mu$m. As shown in Figure 3a, the Te-hyperdoped Si p-n photodiode exhibits a room-temperature below-bandgap responsivity of 79 mAW$^{-1}$ at 1.12 $\mu$m. Moreover, at the 1.55 $\mu$m-telecommunication wavelength, a room-temperature responsivity of around 0.3 mAW$^{-1}$ was obtained, which is comparable to that reported for hyperdoped Si-based photodiodes and solar cells at this wavelength.\[45,46\] The room-temperature EQE at 1.55 $\mu$m was found to be $6 \times 10^{-4}$, which is comparable to other deep level impurity-hyperdoped Si p-n photodiodes.\[18,22\] The responsivity of the Te-hyperdoped Si photodetector at different temperatures is displayed in Figure 3a–g. Different behaviors in terms of line shape and responsivity can be identified for three temperature ranges. In the region of 300–200 K, the photoresponse extends up to the MWIR range with a kink in the spectrum, where the responsivity reaches the noise floor at around 4 $\mu$m. Interestingly, as the temperature decreases, an additional broad photoresponse band spanning from 1.9 to 3.7 $\mu$m is clearly observed ($\leq 160$ K). Particularly, the responsivity extends well up to 5 $\mu$m in the temperature range of 60–20 K. As shown in Figure 3h and discussed in the previous work,\[34\] the sub-bandgap photoresponse observed here corresponds to the excitation of charge carriers from the VB to the CB through the 1B (VB$\rightarrow$IB (process II) and IB$\rightarrow$CB (process III)). Moreover, this observation of sub-bandgap optical transitions indicates that the IB is separated from the CB.

2.3.2. Detectivity

The mostly quoted performance merit for a photodetector is its sensitivity, that is, the input-output signal efficiency compared
to the output noise signal. This merit is exemplified as the noise equivalent power (NEP), which is defined as the signal power at which the photocurrent can no longer be differentiated from the noise floor, expressed as

$$\text{NEP} = \frac{I_n^{1/2}}{R_{\text{ph}}}$$  \hspace{1cm} (5)

where $R_{\text{ph}}$ is the spectral responsivity and $I_n^{1/2}$ is the root mean square of the total noise current.[8] Here, the major noise sources for the Te-hyperdoped Si photodiode are thermal noise and shot noise. The shot noise is determined by the dark current of the device, $I_{\text{dark}} = \sqrt{2qI_{\text{dark}}A_f}$, where $q$ is the electron charge. The Johnson noise in photodetector at zero bias operation is given by $I_{\text{n}} = \sqrt{4k_BT}\Delta f$, where $k_B$ is the Boltzmann constant, $T$ is the operation temperature, $\Delta f$ is the electrical bandwidth (1 Hz), and $r_0$ is the resistance product for this detector. Therefore, the specific detectivity ($D^*$) of the photodetector can be expressed as

$$D^* = \frac{\sqrt{A\Delta f}}{\text{NEP}} = R_{\text{ph}} \sqrt{A\left[2qI_{\text{dark}} + \frac{4k_BT}{r_0}\right]^{1/2}}$$  \hspace{1cm} (6)

where $R_{\text{ph}}$ is the responsivity with the units of A/W and $A$ is the photosensitive area (0.082 cm$^2$) of the detector. The calculated specific detectivity ($D^*$) of the device is shown in Figure 4. The maximum room-temperature $D^*$ of around 3.2 × 10$^{12}$ cmHz$^{1/2}$ W$^{-1}$ is achieved at 1 μm (see Figure 4a), which is above two times larger than that of Ag-hyperdoped Si photodetectors.[21] Importantly, the achieved room-temperature $D^*$ at 1 μm is comparable to that of a commercial Si Photodiode (i.e., FDS1010). Figure 4b shows the $D^*$ of the Te-hyperdoped Si photodetector at different temperatures, from 20 to 300 K. The $D^*$
related to the room-temperature sub-bandgap photoresponse is in the range of $10^{11}$–$10^6$ cmHz$^{1/2}$ W$^{-1}$, which is four orders of magnitude larger than that of Ti-supersaturated Si photodetector.$^{[19]}$ With increasing temperature, the detector exhibits a decreasing $D^*$, which is mainly due to the increase of the noise as the temperature increases. Figure 4c,d displays the comparison of the spectral $D^*$ of the Te-hyperdoped Si photodetector with a commercial photodetector at 300 and 77 K, respectively. Notably, at the wavelength range of 1.0–1.9 µm, the room-temperature $D^*$ of this prototype photodetector is around two orders of magnitude lower than that of a commercial Ge detector. Figure 4e displays $D^*$ of the Te-hyperdoped Si photodetector at 1.55 and 3.2 µm as a function of temperature. The room-temperature $D^*$ at 1.55 and 3.2 µm is around two orders of magnitude lower than that of a commercial Ge photodiode (i.e., FD10D), respectively. However, this performance can be improved by optimizing the manufacturing process. In the future, efforts must be focused towards an advanced-device design to boost the device efficiency. The device architecture can be optimized by proper surface passivation, better optical active area design for improving absorption, different contact geometries and metal electrodes for improving carrier collection, as well as antireflection-coating for improving the responsivity.

Frequency-dependent responsivity is a key factor related to the response time of the devices. Figure 4f illustrates the frequency response of the Te-hyperdoped Si photodetector (left axis: responsivity; right axis: frequency-dependent $D^*$). The measurement was performed under 1.55 µm-LED illumination with a power density of 1.6 mW cm$^{-2}$ at room temperature (left axis: frequency-dependent $R_{ph}$; right axis: frequency-dependent $D^*$).
time constant $\tau$ of 37 $\mu$s) at room temperature, which is more than two times larger than that of Ti-supersaturated Si photodetectors.\cite{19} This indicates a high bandwidth of the Te-hyperdoped Si photodetector, which also excludes the thermal (bolometric) contribution to the observed responsivity.\cite{8}

### 2.3.3. Time-Resolved Photoresponse

Another crucial parameter of a photodetector is the transient photocurrent response speed. The response speed of the Te-hyperdoped Si photodetector was measured in the photovoltaic mode at various temperatures by exposing it to a chopped short pulse in the range of 1 Hz to 10 kHz with different 1.55 $\mu$m-light intensities. The transient photocurrent was recorded by a digital oscilloscope. As shown in Figure 5a–c, the time-dependent photocurrent under varying incident light powers with modes of on-off operation at different frequencies. In general, a strong and reproducible switching behavior can be observed. Moreover, the variation of the photocurrent with different incident light powers shows an upward trend with the increase of the incident photon energy. The time-dependent photoresponse measured under $P = 0.11$ mW and $f = 1$ kHz at different temperatures is displayed in Figure 5d. The reproducible on-off behavior is revealed irrespective of temperature, which demonstrates a stable operation regime of the Te-hyperdoped Si photodetector under chopped light illumination.

The Te dopants effectively introduce deep-level states inside the Si bandgap and these states act as recombination centers. Moreover, these Te deep-level states are responsible for the rise behavior of the photocurrent. At zero voltage, the room-temperature response time for the rise process was measured to be 39 $\mu$s, the time required by the photodetector to generate a photocurrent from 10% to 90% of the peak output value after the light illumination is turned on. The decay time was found to be 42 $\mu$s.

### 3. Conclusion

In conclusion, we have fabricated a MWIR infrared photodetector based on Te-hyperdoped Si. We have demonstrated that the Te implanted Si layer is fully recrystallized after PLM and exhibits a Te-mediated broad infrared absorptance up to the MWIR region. In addition, we have investigated the figure of merit of the Te-hyperdoped Si p-n photodiodes. From the dark-current measurements, we have observed a transport mechanism based on generation and recombination dominating from 180 to 300 K. The photodiodes have been demonstrated to exhibit a sub-bandgap photoresponse spanning from 1 to 5 $\mu$m in a broad temperature range (20–300 K), where a maximum $D^*$ of around $3.2 \times 10^{12}$ cmHz$^{1/2}$ W$^{-1}$ has been achieved. At room temperature and under 1.55 $\mu$m illumination, the detectors have exhibited a broad bandwidth with a cut-off frequency...
of 4.2 kHz corresponding to a time constant of 37 µs. The room-
temperature rise time and fall time have been determined to be
39 and 42 µs, respectively. Te-hyperdoped Si is a promising
material for room-temperature Si-based infrared photodetec-
tors. Moreover, the full process, including ion implantation and
short-time annealing, is CMOS-compatible. To be competitive
with commercial infrared photodetectors, further efforts must
be made toward an advanced device design to boost the device
efficiency of this prototype of an infrared photodetector.

4. Experimental Section

Material Preparation and Characterization: A p-type double-side
polished Si (100) wafer with a thickness of 380 ± 5 µm and a resistivity
of 1–10 Ωcm was implanted with Te ions at room temperature. To obtain
a homogeneous distribution of Te ions in the implanted layer, the
sample was implanted by two sequential implantations with a dose of
1.6 × 10^{15} cm^{-2} and 6.2 × 10^{14} cm^{-2} and implantation energies of 150 and
50 keV, respectively. The implanted layer is 120 nm thick with a peak Te
concentration of 2.5 × 10^{20} cm^{-3} (0.5%), which has been calculated by the
SRIM code and then verified by RBS.[20] After ion implantation, the
sample was annealed by a spatially homogenized XeCl excimer laser with
308 nm wavelength and 28 ns duration to achieve the re-crystallization
of the implanted layer.[20–23] Micro-Raman spectroscopy and TEM were
executed to investigate the structural properties of the doped layers.
The Raman spectra were recorded in a backscattering geometry in the
wavenumber range of 200 cm^{-1} to 600 cm^{-1} with a continuous 532 nm
Nd:YAG laser excitation and detected by a liquid-nitrogen-cooled charged
couple device camera. High-resolution TEM (HRTEM) imaging
was performed with an image-C2-correction Titan 80-300 microscope
(_FEI). High-angle annular dark-field scanning transmission electron
microscopy (HAADF-STEM) imaging and spectrum imaging based on
energy-dispersive X-ray spectroscopy (EDXS) were done with a Talos
F200X microscope (FEI). Fourier-transform infrared (FTIR) spectroscopy
(Bruker Vertex 80v FT-IR spectrometer) was applied to quantify the
sub-bandgap absorbance of the obtained samples in the whole MIR
(0.05–0.85 eV, λ = 14–25 µm). The absorbance (A = 1–T–R)
was determined by recording the transmittance and reflectance spectra.
Further details about sample preparation and measurements can be
found elsewhere.[22–24]

Device Fabrication: The structure of the Te-hyperdoped Si p-n
photodiode comprises a thin Te-hyperdoped Si layer on top of the p-Si
substrate (as shown in Figure 1; Figure S1, Supporting Information).
In detail, the Te-hyperdoped Si sample was immersed into 10% hydrogen
fluoride (HF) solution to remove the native-SiO_{2} layer. Next,
a photolithography process was performed to prepare the top electrode.
A 0.084 cm^{2} illuminated area was obtained by defining fingers with a
separation of 5 µm resulting in frame-like Au top electrodes on top of the
n-type Te-hyperdoped Si layer.[23,24] The bottom electrode was made
by an In/Ga eutectic layer to form an ohmic contact at the bottom
surface with a certain distance from the sample edges in order to reduce
possible parasitic electrical conduction through the edges of the sample.

Device Measurement: A vacuum pump is used to avoid moisture
condensation at low temperatures. A Globar (SiC) source coupled with a
TMC300 Bentham monochromator equipped with gratings in Czerny-
Turner reflection configuration was used as the infrared monochromatic
source. Its intensity is spatially homogenized and was calibrated with
a Bentham pyrometric detector. The infrared light emitted from the
Globar (SiC) source is modulated by a mechanical chopper at 87 Hz
before entering the monochromator. The short-circuit photocurrent
was extracted with the help of a SR830 digital signal processing (DSP)
lock-in amplifier. For dynamic photoresponsivity experiments such as time-
resolved photoresponsivity measurements, a 1.55 µm-light emitting
diode (LED) (Thorlabs, 1550E) together with a long-pass filter at 1.3 µm
was used. The LED was powered using a homemade current-drivers
circuit coupled to the frequency of the output Transistor-Transistor
Logic (TTL) signal of the lock-in amplifier. Therefore, the frequency of
the TTL signal is adjustable to generate pulsed light and thus perform
a frequency scan of the responsivity. Moreover, the output power of
the LED is also adjustable with a maximum incident power density of
1.83 mW cm^{-2}. The cut-off frequency of the LED is 0.1 GHz, which is
sufficiently higher than that of the Te-hyperdoped Si p-n photodetector
under investigation. In the time-resolved experiments, a low-noise
current amplifier was employed to amplify the photocurrent signal from
the device under 1.55 µm-LED excitation. A digital oscilloscope was used
to record the time-resolved photocurrent.

Supporting Information

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

Acknowledgements

The authors acknowledge the ion implantation group at HZDR (Ion
Beam Center) for performing the Te implantations, Romy Aniol for TEM
specimen preparation and Elfi Christalle for SEM imaging. Furthermore,
the funding of TEM Talos by the German Federal Ministry of Education
of Research (BMBF; grant No. 03SF0451) in the framework of HEMCP
is acknowledged. M.W. thanks financial support by Chinese Scholarship
Council (File No. 201506240060) and Deutsche Forschungsgemeinschaft
(WA 4804/1-1). E.G.H. thanks financial support by the Project MADRID-PV2
(S2018/EMT-4308) funded by the Comunidad Autónoma de Madrid with
the support from FEDER Funds, and by the Spanish MINECO (Ministerio
de Economía y Competitividad) under grant TEC 2017-84378-R.
Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

CMOS compatible, hyperdoping, ion implantation, mid-wavelength
infrared photodetectors, Si photonics

Received: September 9, 2020
Revised: November 18, 2020
Published online: December 16, 2020

[1] X. Liu, B. Kuyken, G. Roelkens, R. Baets, R. M. Osgood Jr.,
W. M. Green, Nat. Photonics 2012, 6, 667.
[2] B. Y. Zhang, T. Liu, B. Meng, X. Li, G. Liang, X. Hu, Q. J. Wang, Nat.
Commun. 2013, 4, 1811.
[3] L. Vivien, J. Osmond, J. M. Fedeli, D. Marris-Morini, P. Crozat,
J. F. Damlencourt, E. Cassan, Y. Lecunff, S. Laval, Opt. Express 2009,
17, 6252.
[4] S. Park, K. Yamada, T. Tsuchizawa, T. Watanabe, H. Nishi,
H. Shinojima, S. Itabashi, Opt. Express 2010, 18, 15303.
[5] M. Casalino, G. Coppola, M. Iodice, I. Rendina, L. Sirleto, Sensors
2010, 10, 10571.
[6] A. Rogalski, Prog. Quantum Electron. 2003, 27, 59.
[7] B. Chen, Y. Wan, Z. Xie, J. Huang, N. Zhang, C. Shang, J. Norman,
Q. Li, Y. Tong, K. M. Lau, A. C. Gossard, J. E. Bowers, ACS Photonics
2020, 7, 528.
