Room-Temperature Infrared Photoresponse from Ion Beam–Hyperdoped Silicon

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Room-temperature broadband infrared photoresponse in Si is of great interest for the development of on-chip complementary metal–oxide–semiconductor (CMOS)-compatible photonic platforms. One effective approach to extend the room-temperature photoresponse of Si to the mid-infrared range is the so-called hyperdoping. This consists of introducing deep-level impurities into Si to form an intermediate band within its bandgap enabling a strong intermediate band-mediated infrared photoresponse. Typically, impurity concentrations in excess of the equilibrium solubility limit can be introduced into the Si host either by pulsed laser melting of Si with a gas-phase impurity precursor, by pulsed laser mixing of a thin-film layer of impurities atop the Si surface, or by ion implantation followed by a subsecond annealing step. In this review, a conspectus of the current status of room-temperature infrared photoresponse in hyperdoped Si by ion implantation followed by nanosecond-pulsed laser annealing is provided. The possibilities of achieving room-temperature broadband infrared photoresponse in ion beam–hyperdoped Si with different deep-level impurities are discussed in terms of material fabrication and device performance. The thermal stability of hyperdoped Si with deep-level impurities is addressed with special emphasis on the structural and the optoelectronic material properties. The future perspectives on achieving room-temperature Si-based broadband infrared photodetectors are outlined.

1. Introduction

In the past decades, Si photonics, as one of the leading technological solutions for large-scale integration of multiple optical and electronic functionalities, has attracted tremendous attention due to its low cost, ultracompact device footprint, and high-density integration.[1] In integrated Si-photonic devices, the detectors should be able to detect photons with an energy below the Si bandgap (viz., 1.12 eV or wavelength longer than 1.1 μm), which can effectively propagate with minimum losses within the light waveguiding medium. Among different photodetectors, Si-based photodetectors are the most attractive candidate due to their monolithic integrability. Moreover, they can satisfy the demand for cost-effective and environmentally friendly solutions and enable the development of on-chip complementary metal–oxide–semiconductor (CMOS)-compatible photonic systems.[2,3] However, due to its 1.12 eV indirect bandgap, the photoresponse of Si is restricted to the visible (vis) and near-infrared (NIR) spectral range. This drawback fundamentally constitutes a challenge to realize broadband IR Si-based photodetectors with a variety of potential applications in telecommunications,[4] spectroscopy,[5] and integrated optoelectronics.[6] From these standpoints, extending the photoresponse of Si into the mid-infrared (MIR) spectral range is therefore a topic of great importance.

During the last years, different strategies have been adopted in the continuing quest of extending the Si photoresponse. Photodetectors based on group IV (Si–Ge) alloy heterostructures can deliver an IR photoresponse beyond the bandgap limitation of Si.[8] However, the 4.2% lattice mismatch between Si and Ge reduces the possibility of obtaining high-quality epitaxial Ge on top of Si. The resulting epilayer Ge possesses a high density of threading dislocations and high surface roughness.[9] The latter, in particular, limits the process of integrating Ge devices with Si electronics because CMOS devices require planar processing. Another approach is the intentional introduction of defects in Si by ion bombardment using Si+ ions, Ar+ ions, protons, or neutrons. This is intended to modify the band structure and generate intermediate-bandgap states in Si,[10,11] which can enable a sub-bandgap optical response. These lattice defects can induce defect-mediated extrinsic carriers without producing thermally generated free carriers.[12,13] However, defect-mediated photodetectors based on Si suffer from relatively low sub-bandgap absorption coefficients, α ≈ 0.5–50 cm−1.[10,13] Alternatively, introducing states into the bandgap by doping Si with traditional impurities, e.g., group III (B, Al, and Ga) and V (P, As, and Sb), permits photons at sub-bandgap wavelengths to be absorbed (see Figure 1).[2,14,15] Si photodetectors based on shallow-level impurities exhibit broadband IR photoresponse and operate at temperatures below 40 K (see Table 1).[14,15] The low operation temperature is required to prevent the thermal ionization of carriers from the introduced shallow-level states. This thermal ionization of carriers results in a low ratio of the optical
Although both eventually or pulsed laser mixing of a thin layer in providing high accuracy in both position and stability of hyperdoped Si with focus on the correlation between the impurity lattice location and the sub-bandgap absorption. We then conclude by outlining possible future directions for hyperdoping Si research in IR optoelectronics.

2. Extended Room-Temperature IR Photoresponse in Si Hyperdoped with Deep-Level Impurities by Ion Implantation Followed by Subsecond Annealing

2.1. Challenges for Hyperdoping Si with Deep-Level Impurities

In the last decade, laser hyperdoping has attracted interest due to the possibility of obtaining the so-called black Si, where Si irradiated by a femtosecond (fs) laser in the presence of a sulfur-bearing (SF₆) gas exhibits strong absorption spanning from the visible to the MIR range. This process results in a heavily spiked S-rich microstructure. Similarly, nanosecond (ns) laser irradiations resulting in black Si are also reported. Although both fs- and ns-irradiated materials have near-unity absorption spectra extending up to 2.5 μm, the enhanced visible absorption is attributed to the light trapping by the spiked microstructure. This is revealed by the post-laser thermal annealing process, where the absorption in the MIR decreased dramatically. To investigate the impurity-induced absorption and the role of the hyperdoped impurity in Si, issues related to the light-trapping effect of the surface structure must be avoided. Therefore, fabrication methods leading to single-crystalline and optically flat hyperdoped Si layers are needed.

Compared with conventional shallow-level impurities, some fundamental problems must be overcome to introduce nonequilibrium concentrations of deep-level impurities into Si. The equilibrium solubility limit of deep-level impurities in Si is around 10¹⁶ cm⁻³ which is several orders of magnitude lower than that of shallow-level impurities (above 10¹⁹ cm⁻³). Most importantly, such equilibrium solubility is far below the critical concentration for the formation of an IB (larger than 10¹⁸ cm⁻³). Therefore, nonequilibrium methods are needed to dope Si with deep-level impurities above the solid solubility limit. Ion implantation as an industry-standard method works in the kinetic regime and can overcome the solid solubility limit in order to hyperdope Si.

Another challenge to incorporating deep-level impurities into Si is their high diffusivity. Unlike shallow-level impurities, the diffusion coefficient of deep-level impurities is much larger. This means that long-time-annealing processes ranging from seconds to hours, such as rapid thermal annealing and furnace annealing, would lead to a strong diffusion of impurities, which tend to form clusters. Fortunately, nanosecond PLA is found to overcome this problem by incorporating the implanted impurities into the Si matrix via liquid-phase epitaxy. Importantly, ion implantation followed by PLA excels, compared with other non-equilibrium doping methods involving no ion implantation such as the pulsed laser melting of Si with a gas-phase impurity precursor or pulsed laser mixing of a thin film of impurities atop Si wafers, in providing high accuracy in both position and depth over many orders of magnitude of doping level, less lateral displacement of impurities compared to thermal diffusion, a high degree of accuracy of the impurity concentration and

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Table 1. Summary of the-state-of-the-art of IR Si photodetectors utilizing shallow-level impurities. \( \Delta E_{\text{opt}} \) is the activation energy, \( \lambda \) is the cut-off wavelength of the spectral response, NEP is the noise-equivalent power of detectors at the given temperature, \( f \) is the operation frequency, and \( T \) is the maximum operation temperature. Adapted from Sclar and Rogalski.

| Detector (n/p type) | \( \Delta E_{\text{opt}} \) [meV] | \( \lambda \) [μm]; \( T \) [K] | NEP (\( \lambda; T; f \)) \( \times 10^{-15} \) W Hz⁻¹/² |
|---------------------|------------------|-----------------|---------------------|
| Si:P (n)            | 45.6             | 28.0; 5.0       | 7.5 (28.0; 4.2; 10)  |
| Si:As (n)           | 53.8             | 24.5; 5.0       | 0.9 (23.0; 5.0; 5)   |
| Si:Sb (n)           | 42.7             | 31.0; 5.0       | 5.6 (28.8; 5.0; 5)   |
| Si:Bi (n)           | 71.0             | 18.7; 29.0      | 3.0 (13.0; 11.0; ...) |
| Si:Ga (p)           | 74.1             | 17.8; 27.0      | 1.4 (15.0; 5.0; 5)   |
| Si:Al (p)           | 70.2             | 18.4; 29.0      | –                    |

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Fig. 1. Schematic illustration of the optical response in Si. Introducing midgap states by doping Si with impurities permits photons at sub-bandgap wavelengths to be absorbed. The broadening of impurity energy levels into an intermediate band (IB) between the valence and conduction bands (CB) is caused by the increase of the impurity concentration. The IB enables the absorption of sub-bandgap photons.
control of the depth profile of impurities through the ion energy.\cite{34} Although it is also fair mentioning that both ion implantation followed by PLA and the other nonequilibrium doping methods result in similar material properties for the room-temperature photoresponse, such as high crystal quality, room-temperature sub-bandgap optical absorption, and a high fraction of substitutional deep-level impurities. Recent works on hyperdoped Si toward extending the IR photoresponse are summarized in Table 2. Further discussion of these studies will be outlined in the following subsection.

### 2.2. Hyperdoped Si with Transition Metals

Early research on hyperdoped silicon with transition metals began in earnest after the 1980s, upon unveiling its potential as an intermediate-band material for solar cell applications and IR photodetectors.\cite{35} In particular, hyperdoped Si with Ti has been studied extensively since its postulation as a material candidate for an intermediate-band solar cell.\cite{36,37,38} The formation of an IB within the Si bandgap in Ti-hyperdoped Si was first explored by both computational\cite{39} and experimental\cite{40} methods as a function of the Ti concentration. Subsequently, a strong sub-bandgap absorption with an absorption coefficient close to 10^4 cm^{-1} at 1.2 μm was reported in Ti-implanted Si above the Mott limit.\cite{41} Moreover, an extended room-temperature sub-bandgap photoresponse up to 2.5 μm in photodetectors based on Ti-supersaturated Si has also been demonstrated.\cite{42} However, a rather low room-temperature specific detectivity (D*) of 1.7 × 10^10 cmHz^{1/2}W^{-1} (660 Hz, 1.55 μm) was found (see Table 2).\cite{43}

Alternatively, another transition metal, Au, has also been shown to be adequate for the IB formation within the Si bandgap.\cite{44,45} An Au-hyperdoped Si photodetector exhibiting a room-temperature photoresponse up to 2.2 μm has been demonstrated (see Table 2). Importantly, the sub-bandgap optical activity in Au-hyperdoped Si increases monotonically with the Au implantation dose. However, the room-temperature EQE at 1.55 μm of this photodetector was found to be as low as 10^{-3}.\cite{46} Other transition metals, such as V\cite{47} and Ag,\cite{48} have also been reported as effective deep-level impurities for fabricating Si-based IB materials. A spectral photoresponse in V-supersaturated Si was reported up to 6.2 μm at 110 K,\cite{49} while a room-temperature IR photoresponse remained elusive. More recently, an IR photodetector based on Ag-supersaturated Si was demonstrated, but its room-temperature sub-bandgap photoresponse could only be extended up to 1.6 μm and the EQE at 1.55 μm was found to be 0.052 under 3 V reverse bias.\cite{50} (see Table 2).

In addition, considerable efforts have been spent on systematically exploring the possibility of creating an IB material by supersaturating Si with a variety of other transition metals (Co, Cr, Cu, Fe, Pd, Pt, W, and Zn) using ion implantation followed by PLA. However, there are some fundamental issues for Si supersaturated with transition metals. Transition metals possess very high diffusion velocities in Si.\cite{51} This indicates that a very high liquid/solid interface velocity during the resolidification process is required to trap the impurities inside the resolidified material.\cite{52} During liquid phase epitaxy driven by PLA and the rapid resolidification process, transition metals diffuse toward the surface of the material. The so-called cellular breakdown microstructure is produced, which thus impedes further recrystallization and supersaturation.\cite{53} In case of Ti-supersaturated Si, Ti atoms have been found to totally occupy nonsubstitutional sites in the Si matrix (see Figure 2), which neither contribute to donating electrons nor to the formation of the IB.\cite{50} In Au-hyperdoped Si, Au dopants result in substantial hyperdoping prior to the observed cellular breakdown.\cite{54} The Au distribution is inhomogeneous and a subsurface network

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### Table 2. Summary of the state-of-the-art of IR Si photodetectors utilizing deep-level impurities. (ΔE)_{opt} is the activation energy, λ is the cut-off wavelength, EQE is the external quantum efficiency, D* is the specific detectivity, and NEP is the noise equivalent power at room temperature.

| Detector (n/p type) | (ΔE)_{opt} [eV] | λ [μm] | EQE [λ (μm); bias (V)] | D* [cm Hz^{1/2} W^{-1}] | NEP [WHz^{-1/2}] [λ (μm); f (Hz)] |
|---------------------|-----------------|-------|------------------------|---------------------------|----------------------------------|
| Si:Ti (p)\cite{35}  | 0.21            | 2.5   | 2.7 × 10^{-7} (1.55; 0)| 1.7 × 10^{10}, 5.9 × 10^{-3} (1.55; 660) | Not reported                     |
| Si:Ag (p)\cite{36}  | 0.54            | 2.2   | 9.3 × 10^{-7} (1.55; 0)| Not reported               |                                   |
| Si:S (n)\cite{36}   | 0.36            | 1.6   | 5.2 × 10^{-7} (1.55; 3)| 1.5 × 10^{10}, 5.0 × 10^{-14} (1.2; 100) | Not reported                     |
| Si:Ag (p)\cite{36}  | 0.32; 0.62      | 1.25  | 2.3 (1.2; 12)          | Not reported               |                                   |
| Si:Te (n)\cite{36}  | 0.31; 0.59      | 1.6   | 6.0 × 10^{-7} (1.55; 1)| Not reported               |                                   |
| Si:Te (n)\cite{36}  | 0.20; 0.41      | 4.1   | 8.0 × 10^{-7} (1.55; 0)| Not reported               |                                   |

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**Figure 2.** Angular scans along the [001] direction for a Ti-implanted Si sample with a dose of 1.2 × 10^{16} cm^{-2} and annealed by PLA. The difference between the angular scan for Ti and Si indicates that Ti atoms are not located at the substitutional sites in the Si lattice.
The intensity and the width of $1\mu$m ever reported for $\text{Ge}_{25}\text{C}_{75}$ is broad. The resulting $S$-hyperdoped Si has been investigated to show a broadband IR absorption peaking at around 2.5 $\mu$m. Afterward, optical absorption in a broad wavelength range from 0.9 to 24 $\mu$m was measured. Such a high absorption coefficient is comparable to that of intrinsic Ge and $\text{I}_3\text{As}_{2}\text{Ga}_{43}\text{As}[53]$ and in turn 12 orders of magnitude higher than that for undoped Si (10$^{-9}$ $\text{cm}^{-1}$) at wavelengths longer than 1.5 $\mu$m. In the following, recent work on chalcogen-hyperdoped Si will be reviewed.

Sulfur was the first chalcogen element devoted to dope Si at a concentration greater than its solubility limit.[54] The resulting S-hyperdoped Si showed a sub-bandgap optical absorption in the range of 1.2–2.5 $\mu$m, with an absorption coefficient as high as 10$^5$ $\text{cm}^{-1}$. Afterward, optical absorption in a broad wavelength range from 0.9 to 24 $\mu$m was measured.[55] This broad MIR optical absorption band was found to have a maximum absorption peaking at around 2.5 $\mu$m (≈0.5 $\text{eV}$), which is in good agreement with the reported results on the impurity levels (0.6 $\text{eV}$) induced by S in Si at low concentrations.[56] The intensity and the width of this MIR absorption band were measured to be proportional to the doping S concentration.[55] Therefore, the extended IR photoresponse in S-hyperdoped Si layers was associated with an IB within the Si bandgap arising from known S deep energy levels. Furthermore, as a proof of concept, a p–n photodiode was fabricated by implanting nonequilibrium S concentrations on top of a p-type Si substrate. As a result, an extended IR photoresponse up to 1.25 $\mu$m (see Table 2) and an enhanced gain were measured at room temperature.[56] Bob et al.[57] found that the remaining S atoms in the doped layer and the carriers decreased with increasing number of laser shots. Sullivan et al.[58] used soft X-ray emission spectroscopy (XES) to measure the electronic structure of Si supersaturated with S (up to 0.7 at%), where a significant modification of the local electronic structure concurrent with the change in the macroscopic electronic behavior was observed. Fabbri et al.[59] investigated the luminescence properties of S-hyperdoped Si using depth-resolved cathodoluminescence spectroscopy. In their work, a strong luminescence from intragap states related to Si self-interstitials and a S-related luminescence at 0.85 $\text{eV}$ were observed, both of which show a strong dependence on the S concentration.

Beyond S, Se-hyperdoped Si has been demonstrated to exhibit a strong room-temperature sub-bandgap optical absorption covering the NIR and MIR spectral ranges.[52,55,57] By combining computational and experimental methods, the origin of the sub-bandgap optical absorption was found to be related to the presence of an IB involving transitions between the IB and the CB, rather than absorption of free carriers. The density functional theory results indicated that the Se impurity levels broaden into an IB as the Se concentration increases.[56] In addition, the experimental results obtained by extended X-ray absorption fine structure spectroscopy indicated that the sub-bandgap absorptance was directly correlated to the Se atoms in a point defect-like structure.[61]

It is known that chalcogens are double donors in Si, and especially Te introduces deep donor states in the upper half of the Si bandgap, which are in turn closer to the CB compared to those for S and Se.[62] This feature of Te offers important advantages for further extending the photoresponse toward the MIR range over its S and Se counterparts. However, attaining a Te hyperdoping level in Si comparable to the one reported for S and Se is challenging as Te possesses a larger atomic radius together with a higher formation energy than that of S and Se. Therefore, little attention has likely been paid to Te-hyperdoped Si, and the material properties have not yet been studied in detail as compared with S- and Se-hyperdoped Si. More recently, single-crystalline and epitaxial Te-hyperdoped Si layers with Te concentrations ranging from four to five orders of magnitude above the solid solubility limit have been synthesized by ion implantation followed by PLA.[18,63,64] As shown in Figure 3a,b, neither Te surface segregation nor nanoscale Te agglomerates were detected despite the high doping concentration of more than 10$^{20}$ cm$^{-3}$. The absorptance of the Te-hyperdoped Si layers has been quantified by Fourier transform infrared spectroscopy,[18] where a strong room-temperature broadband IR absorption up to 25 $\mu$m was observed (see Figure 3c). Moreover, the absorptance intensity in the IR region of Te-hyperdoped Si was found to be enhanced by more than 20 times that of Au-hyperdoped Si.[34] The absorptance increases with the Te concentration, which is consistent with previous reports on S- and Se-hyperdoped Si.[17,65] A clear evolution of the discrete energy levels toward the formation of an IB as a function of Te concentration was evidenced. Importantly, a p–n photodiode fabricated on Te-hyperdoped Si atop a p-type Si substrate was demonstrated[18] where a Te-hyperdoped Si layer with the impurity concentration below the IMT was chosen to render a better balance between light absorption, carrier mobility, and lifetime.[66] The Te-hyperdoped Si p–n photodiodes revealed a strong sub-bandgap responsivity up to 4.1 $\mu$m in the whole temperature range, whereas the responsivity from a commercial Si p–i–n photodiode at wavelengths longer than 1.3 $\mu$m reached the noise floor (Figure 3d).

Despite the high optical absorption, the room-temperature photoresponsivity of chalcogen-hyperdoped Si shows no improvements as the doping concentration increases above a certain value (e.g., above 0.36% for the case of S-hyperdoped Si).
This is explained by the overlap of the IB with the CB, which is known to broaden with increasing doping concentration. This overlap causes a shift of the Fermi level position toward the CB, preventing the generation of measurable photocarriers. Because of the tradeoff between the absorption, the impurity concentration, and the carrier lifetime, the impurity concentration leading to the optimum material and device properties was found to be far below the threshold impurity concentration for the IMT. This indicates that the overlap between the IB and the CB must be avoided. Another strategy to boost the room-temperature photoresponsivity relies on introducing additional dopants into the n-type hyperdoped material to act as acceptors such as B atoms to lower the Fermi level via the so-called carrier compensation method.[21] However, this resulted in a significant decrease in the mobility and lifetime of carriers due to the increased scattering probability, having direct implications in the device performance. In addition, the short recombination lifetime will be a limitation. Investigations based on the carrier recombination dynamics in chalcogen-hyperdoped Si with sub-picosecond resolution by optical-pump/terahertz-probe measurements[66] revealed that the carrier lifetime is of the order of hundreds of picoseconds and it decreases with increasing impurity concentration.

2.4. Thermal Stability of Si Hyperdoped with Deep-Level Impurities

Si hyperdoped with deep-level impurities is known to exhibit unique optoelectronic properties. However, the material is thermodynamically metastable and thus prone to subsequent thermal treatments that could lead to an impairment of its physical properties. Its thermal stability is one of the requirements of great importance for the integration of hyperdoped Si with the existing CMOS-compatible processes involving temperature-dependent steps. In this regard, several studies have been reported focusing on the changes of optoelectronic properties upon thermal treatment.[41,45,55,61,67]

By using Rutherford backscattering spectrometry combined with channeling, Yang et al.[45] found that the substitutional fraction of Au atoms in Au-hyperdoped Si layers dramatically decreases upon postannealing treatments at temperatures higher...
than 400 °C for only 3 min. Consequently, the sub-bandgap optical absorption decreases. In addition, the thermal stability of S-hyperdoped Si has been examined in detail by Simmons et al.\cite{64} They found that the sub-bandgap absorption decreases monotonically with the anneal temperature and anneal duration. The S-hyperdoped Si loses its ability to absorb IR light after a subsequent thermal treatment. Similar studies have been conducted on the thermal stability of other chalcogen-hyperdoped Si\cite{58,61} Particularly, for Te-hyperdoped Si, a comprehensive study regarding the subsequent thermal treatments has recently been reported.\cite{64} The results indicated that Te-hyperdoped Si is thermally stable up to 400 °C with a duration of 10 min, and that this even helps in further improving the crystalline quality and the room-temperature sub-bandgap absorption (see Figure 4).\cite{64}

At higher temperatures, however, Te atoms were found to move from the substitutional sites forming inactive clusters and precipitates that impair the optical properties.

The findings in the aforementioned works\cite{45,55,58,61} suggest that a metastable local atomistic configuration of deep-level impurity atoms in the Si host is responsible for the sub-bandgap absorption. There is a one-to-one correlation between the substitutional deep-level impurities and the unique properties. These results provide further insight into the underlying physical state transformation of deep-level impurities in a metastable compositional regime caused by post-synthesis thermal annealing as well as technical considerations toward the fabrication of hyperdoped Si-based micro-/optoelectronics.

The general attributes of a hyperdoped Si material for an efficient room-temperature IR Si photodetector can be summarized as follows: i) nonequilibrium dopant concentrations giving rise to an intermediate band within the Si bandgap which does not merge with either the CB or the valence band, ii) a high-quality single crystal with a high concentration of impurities occupying substitutional positions in the Si lattice providing high optical activation of impurities, and iii) long-term thermal stability. Limitations include i) segregation of the impurities toward the material surface during liquid phase epitaxy driven by PLA, ii) cellular breakdown originating from the liquid phase epitaxy at high impurity concentrations and consequential extensive residual defects, and iii) a carrier lifetime in the range of hundreds of picoseconds.

3. Future Perspectives

Ion implantation followed by nanosecond PLA has been demonstrated to be an effective nonequilibrium method to fabricate high-quality hyperdoped Si with deep-level impurities. However, the missing scalability of PLA inhibits both the industry application and the wafer-scale integration of the resulting Si-based IR photodetectors. In the quest for achieving wafer-scale room-temperature Si-based IR photodetector arrays, other methods should be explored. More recently, ion implantation followed by millisecond flash lamp annealing (FLA) has emerged as an alternative approach for hyperdoping Si with Se, not only bulk Si\cite{67} but also Si nanowires.\cite{68} The Se-hyperdoped Si nanowires recrystallize via a bottom-up template-assisted solid phase growth and exhibit a strong room-temperature IR photoresponse at 1.5 μm when configured as a photodiode device. Unlike ns-PLA, ms-FLA allows for the fabrication of wafer-scale IR photodetector arrays based on chalcogen-hyperdoped Si together with the required scalability for industry applications. However, its applicability for supersaturating Si with transition metals is limited because the solid phase epitaxy induces an interface breakdown at much lower concentrations as compared with the liquid phase epitaxy driven by PLA.

On the other hand, the reported room-temperature IR responsivity and EQE of photodetectors based on deep-level impurity hyperdoped Si have been found very low despite the high absorption coefficient. Therefore, future efforts should be devoted to increasing responsivity, EQE, response speed, and noise reduction. This can be tackled by engineering device architectures (i.e., the design of optical active area and electrode geometry) and by depositing an antireflection coating (ARC), together with surface passivation. To this end, we envision a planar design of an array of lateral p–i–n photodiodes based on hyperdoped Si that is compatible with large-scale Si technology (Figure 5). This lateral design of photodiodes is suitable for the integration with active devices making use of planar processes and allows for

**Figure 4.** a) Sub-bandgap absorptance of as-fabricated Te-hyperdoped Si samples with an annealing duration of 10 min. at different temperatures. The absorptance of an as-fabricated sample and the pure Si substrate is also included as a reference. b) Integrated absorptance (A_int) from 0.20 to 0.87 eV of the post-synthesis annealed samples as a function of annealing temperature. Reproduced with permission.\cite{64} Copyright 2019, American Physical Society.
the incorporation of countless p-i-n photodiodes in the form of large-scale arrays. In terms of device performance, the p-i-n photodiode offers several advantages over its p-n counterpart, such as higher EQE, wider broadband range, and faster response times when operated under a reverse voltage. To meet this latter requirement, the thickness of the hyperdoped Si layer should be thin enough (viz., the thinner, the better) to keep the transit time of photogenerated carriers short, which thus leads to high-speed photodiodes. In addition, the introduction of the intrinsic region (i) sandwiched between the p-doped and n-hyperdoped regions leads to an increase of the minority carrier current and lower capacitance because of the wider depletion width. The net generated electric current is also expected to be higher than that of p-n photodiodes with the same amount of input light energy. Another important aspect of the photodiodes is the design of the electrode. We propose an interdigitated electrode array with an interdigital gap smaller than the minority carrier diffusion length for vertical illumination of the array of p-i-n photodiodes (Figure 5b). The interdigitated electrode would provide low leakage current and high reliability. Its design consists of a metal comb-like structure aligned atop the p-type region and a complementary comb-like structure made of a semitransparent conductive electrode resting on the n-type region or hyperdoped Si. These two complementary comb-like electrodes are separated by an ARC layer covering the intrinsic region of the p-i-n photodiode.

The planar device architecture is envisioned to be applied to chalcogen-hyperdoped Si, where the n-type doping is guaranteed along with the understanding of the electrical and optical properties. These structures have also been shown to be thermally stable upon postannealing treatments, which ensures that the post-thermal-processing steps can be used toward the device scalability and final device architecture. Yet, transition metals suffer from i) interface breakdown phenomena originating from solid phase epitaxy which is driven by FLA, ii) thermal stability, and iii) lack of a defined type of doping and optical activation because most of the transition metals are known to occupy interstitial positions in Si, except for Au, which occupies substitutional sites in the Si lattice and allows for heavily p-type doping. This indicates that the use of transition metals for the envisioned p-i-n photodiode planar architecture is rather limited.

4. Conclusion

In summary, the introduction of deep-level impurities at concentrations in excess of the solid solubility limit is one of the most promising approaches to deliberately extend the IR photoresponse of Si. This leads to the formation of an IB that allows for the strong sub-bandgap optical absorption. Due to the low solubility and high diffusion coefficient of deep-level impurities in Si, the combination of ion implantation and PLA can be applied not only to overcome the solubility obstacle, but also to incorporate more impurity atoms into substitutional sites. Compared to the use of transition metal impurities, hyperdoping Si with chalcogen impurities can result in stronger sub-bandgap optical absorption in a broader IR range without forming cellular breakdown or precipitates. The sub-bandgap absorption has been found to be reduced upon post-thermal annealing above 400 °C and directly correlated to the substitutional deep-level impurity atoms in the Si host. Future work in extending IR Si photoresponse by ion implantation should include further fabrication, characterization, and optimization of devices. Ultimately, other methods, i.e., ion implantation followed by FLA, for producing wafer-scale hyperdoped Si-based IR photodetector arrays will be of great help to advance the field.

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Conflict of Interest

The authors declare no conflict of interest.
Keywords

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