Spectral narrowing of sub-bandgap absorbance and emissivity in highly doped silicon

Zhe Li, Yan Zhang, Hao Peng, Lu Liu, Weiming Zhu and Zhijun Liu

School of Optoelectronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu, Sichuan 610054, People’s Republic of China

E-mail: liuzhijun@uestc.edu.cn

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Abstract
Doping-engineered silicon is a versatile material, well-suited for exploring new optical properties and applications in infrared spectral region below its bandgap. In this paper, we report on a doping-induced spectral narrowing phenomenon in silicon’s sub-bandgap absorbance and emissivity. By measuring silicon samples with doping concentration varied between $< 10^{12}$ cm$^{-3}$ and $4.4 \times 10^{19}$ cm$^{-3}$, we reveal that, besides the increased amplitude in absorption and emissivity, doping induces a spectral narrowing feature in both mid-infrared absorption and emission, which indicates a trade-off existing for silicon doping level in consideration of efficiency and bandwidth. The spectral narrowing effect occurs around the plasma wavelength, where the silicon changes from dielectric-like property to metal-like property with a negative permittivity. These results are helpful in further understanding free-carrier responses in silicon, and are potentially useful for developing silicon-based materials for mid-infrared applications, such as broadband bolometric sensing, thermal energy harvesting and radiative cooling etc.

1. Introduction
Silicon, the most important material in modern semiconductor industry, offers a versatile and promising platform for both fundamental and applied explorations in the field of optoelectronics [1, 2]. Based on optical interband transition, tremendous progresses have been made in silicon-based optoelectronic devices including high performance photodiodes, solar cells, biochemical sensors and photocatalytic devices [3–6]. Besides the above-bandgap applications in visible and near-infrared spectral regions, silicon recently also has attracted much attention in mid-infrared below its bandgap [7, 8]. The below-bandgap optical properties of silicon is mainly dominated by free-carriers from dopants. Depending on the doping concentration, silicon can be engineered to be fully transparent or totally absorptive, enabling an agility in material and device designs. Using high-resistivity silicon, a variety of important optical components were demonstrated including low-loss waveguides, high-Q resonators and high-speed modulators [9–12], which indicate silicon’s great potential for mid-infrared integrated photonics [13]. On the other hand, in highly doped silicon materials, interesting properties such as plasma spectral filtering and surface plasmon resonance were revealed in the mid-infrared region below silicon bandgap [14–17].

Broadband absorbance and emissivity are among the engineered properties of silicon, which have attracted considerable interest for applications in infrared sensing, thermophotovoltaics and radiative cooling [18–20]. Early in 1967, T. Satō observed high emissivity of silicon over a flat spectrum from 0.4 to 15 μm at elevated sample temperatures [21]. Meanwhile, C. H. Liebert reported a dropping behaviour of emissivity of silicon at long wavelength region [22]. More recently, broadband absorption and thermal emission have been widely reported in black silicon fabricated into various microstructures [23–26]. Although doping has been shown to play a critical role in these reported broadband absorbance and emissivity, its understanding is not yet complete as these studies correspond to some selected doping levels of silicon and consider only either absorbance or emissivity. In this paper, we investigate the effect of doping on both absorbance and emissivity of silicon in a
systematic manner, and discover a spectral narrowing feature in both absorbance and emissivity near the plasma edge. A series of n-type silicon samples with doping concentration varied from \(10^{12} \) to \(4.4 \times 10^{19} \text{ cm}^{-3}\) are characterized with Fourier-transform infrared (FTIR) spectroscopy. Our measurements reveal a doping-induced spectral narrowing feature in commonly reported broadband subbandgap absorption and thermal emission of silicon. The spectral narrowing is shown to occur around the plasma wavelength associated with free-carriers and originates from the transition of silicon from dielectric-like property to metal-like property with a negative permittivity. These results are helpful for fully understanding free-carrier dominated optical properties of doped silicon.

2. Experiments

We used six single-side polished n-type Si(100) samples, whose phosphorus doping concentrations were systematically varied as listed in table 1. The sample area size is 2 cm \(\times\) 2 cm. Resistivity of the samples was measured with standard four point probe technique [27], which changes from 0.0016 to more than 10 000 \(\Omega\text{ cm}\). Using the relation of resistivity versus donor density for n-type silicon as given in [28], doping concentrations of the samples were extracted, which decreases from \(4.4 \times 10^{19}\) to less than \(10^{12} \text{ cm}^{-3}\).

Optical absorption and emissivity of the silicon samples were characterized with a FTIR spectrometer configured into two different schemes. For the optical absorption measurement as sketched in figure 1(a), an integrating sphere was equipped with the FTIR as reported in our recent work [29]. Inner surface of the integrating sphere is coated with a high reflectance diffuse gold coating. This setup enables the measurement of hemispherical total reflectance \(R_{\text{total}}\), and total transmittance \(T_{\text{total}}\). Absorption of the sample is obtained as \(1 - R_{\text{total}} - T_{\text{total}}\). In reflection measurement, the incident light is directed to illuminate the sample placed on the top reflection port at an angle of 12°. The reflection from a reference diffuse gold mirror is used as the background spectrum. In transmission measurement, the sample is placed in the transmission port facing the incident beam, and the transmitted light is collected by the integrating sphere. Incident light entering the integrating sphere through the open transmission port is used as the background spectrum.

For the emissivity measurement as shown in figure 1(b), we followed the method described in [30]. The sample was placed in a cryostat, whose temperature is controllable from 30°C to 300°C above room temperature. Thermal emission of the sample was first spatially filtered with a circular aperture of 7 mm diameter, and then was collected and directed to the FTIR spectrometer with a ZnSe lens of 8 inch focal length. Thermal emission of a calibrated blackbody at the same temperature was used as the reference spectrum. To rule out thermal background, emission from room temperature environment was measured and subtracted from the sample and blackbody emission spectra.

Table 1. Silicon samples of different doping concentrations.

| Sample | Resistivity (\(\Omega\text{ cm}\)) | Doping concentration (\(\text{cm}^{-3}\)) |
|--------|-------------------------------|--------------------------------------|
| S1     | \(> 10\ 000\)                 | \(< 10^{12}\)                        |
| S2     | 1.9184                        | \(2.5 \times 10^{15}\)               |
| S3     | 0.1064                        | \(7.4 \times 10^{14}\)               |
| S4     | 0.0174                        | \(1.8 \times 10^{15}\)               |
| S5     | 0.0022                        | \(3.1 \times 10^{16}\)               |
| S6     | 0.0016                        | \(4.4 \times 10^{17}\)               |

Figure 1. Schematics of (a) absorption and (b) emissivity measurement setups.
3. Results and analysis

Our measured reflection, transmission and absorption spectra of the silicon samples are shown in figure 2. Reflectivity of the intrinsic sample S1 increases from 16% to about 35% as the wavelength increases. Meanwhile, its transmission gradually decreases from 90% to about 55%. Its absorption is negligibly small for wavelengths from 1.5 to 8 μm and takes a value of about 10%–32% within the band from 8 to 18 μm as originated from silicon lattice absorption as reported in [31]. As the doping increases up to \(1.8 \times 10^{18}\) cm\(^{-3}\), reflection of the sample S4 becomes flat in spectrum with a slightly decreased amplitude of about 25%. At the same time, its transmission significantly drops. It decreases from 34% to zero as the wavelength increases up to 8 μm. The resulted absorption exhibits a strong absorption of more than 60% within the band from 4 to 10 μm. As the doping further increases to \(3.1 \times 10^{19}\) cm\(^{-3}\) in sample S5, interestingly, its reflection first slightly decreases up to 10 μm wavelength, and then rapidly increases in the range of longer wavelengths. Correspondingly, its absorption is above 73% over the band of 1.5–10 μm, but decreases rapidly for wavelengths beyond 10 μm. This spectral narrowing phenomenon suggests that a trade-off exists for the doping level in silicon when considering both the absorption efficiency and bandwidth. As the doping increases to \(4.4 \times 10^{19}\) cm\(^{-3}\) for sample S6, the wavelength position where the spectral narrowing occurs shifts to a shorter wavelength of 8 μm.

Figure 3 shows the measured emission spectra and emissivity of the silicon samples at 125°C. This temperature was chosen to have distinguishable sample emission signal above the environmental background, but still low enough to prevent thermal excitation of free-carriers in silicon. It is seen that thermal emission of the samples spans a wavelength range from 3.6 to 18 μm. Emission intensities of the silicon samples are larger than that of thermal background, but less than that of the blackbody emission. The obtained emissivity of the samples increases as the doping increases. In particular, the intrinsic sample S1 has a low emissivity of less than 0.19. As the doping increases to \(1.8 \times 10^{18}\) cm\(^{-3}\) for sample S4, the emissivity dramatically increases with an amplitude of more than 0.6 and becomes flat. As the doping further increases to above \(10^{19}\) cm\(^{-3}\) for samples S5 and S6, their emissivities further increases in amplitude, but rolls off around the wavelengths of 10 μm and 8 μm.
respectively. This doping-induced spectral narrowing is similar to that measured in optical absorption as described earlier.

The above observed doping-induced spectral narrowing effect originates from free-carrier responses \[32\].

To better understand its mechanism and properties, we simulated absorption of the silicon samples with different doping concentrations using the transfer matrix method \[33\]. Thickness of the samples was assumed to be 500 μm. The complex permittivity of silicon is described with the Drude model, i.e. \[34\]

\[
\varepsilon(\omega) = \varepsilon_\infty - \frac{\varepsilon_\infty \omega_p^2}{\omega(\omega + \gamma)}
\]

where \(\omega\) represents the angular frequency, \(\omega_p\) and \(\gamma\) are the screened plasma frequency \[25, 35\] and scattering rate, respectively, which can be written as

\[
\omega_p = \sqrt{Ne^2 / m^* \varepsilon_\infty \varepsilon_0}
\]

\[
\gamma = e / m^* \mu
\]

here, \(\varepsilon_0\) is the vacuum permittivity, \(\varepsilon_\infty = 11.7\) is the dielectric constant at high frequency limit, and \(e\) is the electron charge, \(m^*\) is the effective mass of electron, which equals 0.27 times the mass of free electron in vacuum, and \(N\) represents the electron concentration. \(\mu\) is the carrier mobility, which is related to electron concentration \(N\) via an empirical relation \[36\]

\[
\mu = \mu_1 + \frac{\mu_{\text{max}} - \mu_1}{1 + (N/N_i)^\alpha} - \frac{\mu_2}{1 + (N/N_f)^\beta}
\]

where the parameters are \(\mu_1 = 68.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, \mu_{\text{max}} = 1414 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, \mu_2 = 56.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, C_r = 9.2 \times 10^{16} \text{ cm}^{-3}, C_i = 3.41 \times 10^{20} \text{ cm}^{-3}, \alpha = 0.711, \text{ and } \beta = 1.98.\]

Figure 4(a) shows the calculated free-carrier absorption of the silicon samples with different doping concentrations. For intrinsic undoped silicon S1, the absorption is zero. As the doping increases, the absorption dramatically increases, and evolves into a flat spectrum above 4.2 μm with amplitude of about 70% for sample S4 with a doping level of 1.8 \(\times\) 10^{18} cm^{-3}. As the doping level further increases to 3.1 \(\times\) 10^{19} cm^{-3} and 4.4 \(\times\) 10^{19} cm^{-3} for S5 and S6, besides the increased amplitude, the absorption start to exhibit a rolling-down behaviour at the wavelengths of 10 μm and 8 μm, respectively, which agree with our observed spectral narrowing feature in absorption and emissivity measurements. Similar dropping in emissivity of silicon was also observed by C. H. Liebert in [22]. However, its physical origin was not identified. Here, we attribute the spectral narrowing behaviour to the plasma edge effect. Figure 4(b) shows the calculated plasma wavelength \(\lambda_p\) of the five doped silicon samples. The plasma wavelength of the S5 and S6 samples are 10.67 μm and 8.95 μm, which well match the positions where spectral narrowing occur as shown in figures 2(c) and 3(b). Therefore, our observed spectra narrowing phenomenon occurs around the plasma wavelength. Physically, the doping-induced spectral narrowing can be understood from the change of silicon from dielectric-like property to metal-like property. Figures 4(c) and (d) show the calculated refractive indices of the six silicon samples. It is seen that near the plasma

\[\text{Figure 4. Calculated (a) absorption spectra, (b) plasma wavelengths, (c) real and (d) imaginary parts of permittivity of the silicon samples with different doping concentrations.}\]
wavelength, real part of the silicon refractive index changes from positive to negative, which is characteristic of a metallic property and leads to the measured rise in reflectance and decreased absorption for wavelengths above the plasma wavelength. It is noted that similar plasma edge effect has been observed in reflection spectrum of silicon in [14], which is characterized with a sharp rise in reflectivity. Here, we show that for absorbance and emissivity, the plasma edge effect leads to significant drop in their values. Therefore, when considering both efficiency and spectral performance of silicon materials in applications such as infrared sensing or radiative cooling [37, 38], a trade-off doping level needs to be taken. Finally, it is worthy to note that Fabry-Perot interference fringes arisen from the 500 μm sample thickness are present in above calculated results as shown in the purple and green shading area in figure 4(a), while they are absent in our measured results in figure 2. This discrepancy resulted from our used spectral resolution of 4 cm⁻¹, which is insufficient to resolve the interference features.

4. Conclusion

We investigated the effect of doping on sub-bandgap optical absorption and emissivity of silicon. By measuring a series of silicon samples with different doping concentrations, we observed a spectral narrowing feature in the commonly reported doping-induced broadband and strong absorption and thermal emission in silicon. This spectral narrowing phenomenon occurred around the plasma wavelength determined by the free-carrier concentration and resulted from transition behaviour of silicon from dielectric-like property to metal-like property with a negative permittivity. These results suggest that a trade-off exists for silicon doping level when considering both absorption/emission efficiency and bandwidth. Since the spectral narrowing happens within a finite spectral region around the plasma wavelength in a gradual manner instead of an abrupt one, it could be suppressed to some extent via scattering-enhanced effect by introducing sub-wavelength structures such as nanopores and nanopillars into silicon.

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ORCID iDs

Zhijun Liu https://orcid.org/0000-0002-5319-7789

References

[1] Priolo F, Gregorkiewicz T, Galli M and Krauss T F 2014 Silicon nanostructures for photonics and photovoltaics Nat. Nanotechnol. 9 19–32
[2] Thomson D A et al 2016 Roadmap on silicon photonics J. Opt. 18 073005
[3] Napiah Z A F M, Gyoubu R, Hishiki T, Maruyama T and Iiyama K 2016 Characterizing silicon avalanche photodiode fabricated by standard 0.18 μm CMOS process for high-speed operation IEEE Trans. Electron. E99.C 1304–11
[4] Yoshikawa K et al 2017 Silicon heterojunction solar cell with interdigitated back contacts for a photoconversion efficiency over 26% Nat. Energy 2 17032
[5] Wangüemert-Pérez J G, Hadji-Ellouati A, Sánchez-Postigo A, Leuermann I, Xu D X, Cheben P, Ortega-Moñux A, Halir R and Molina-Fernández I 2019 Subwavelength structures for silicon photonics biosensing Opt. Laser Technol. 109 437–48
[6] Alexander F, AlMheiri M, Dahal P, Abed J, Rajput N S, Aubry C, Viegas J and Jouiad M 2018 Water splitting TiO2 composite material based on black silicon as an efficient photocatalyst Solar. Energy Mater. Sol. Cells 180 236–42
[7] Soref R 2010 Mid-infrared photonics in silicon and germanium Nat. Photonics 4 495–7
[8] Lin H, Luo Z, Gu T, Kimmerling L C, Wada K, Agarwal A and Hu J 2018 Mid-infrared integrated photonics on silicon: a perspective Nanophotonics 7 393–420
[9] Dong B, Guo X, Ho C P, Li B, Wang H, Lee C, Luo X and Lo G-Q 2017 Silicon-on-insulator waveguide devices for broadband mid-infrared photonics IEEE Photonics J. 9 4501410
[10] Shankar R, Bulu I and Lončar M 2013 Integrated high-quality-factor silicon-on-sapphire ring resonators for the mid-infrared Appl. Phys. Lett. 102 051108
[11] Miller S A, Yu M, Ji X, Griffith A G, Cardenas J, Gauta A L and Lipson M 2017 Low-loss silicon platform for broadband mid-infrared photonics Optica 4 707–12
[12] Dong P et al 2009 Low V th ultralow-energy, compact, high-speed silicon electro-optic modulator Opt. Express 17 22484–90
[13] Fedeli J-M and Nicoletti S 2018 Mid-infrared (Mid-IR) silicon-based photonics Proc. IEEE 106 2302–12
[14] Ehsani H, Bhat I, Borrego J, Gutmann R, Brown E, Dziendziel R, Freeman M and Choudhury N 1997 Optical properties of degenerately doped silicon films for applications in thermophotovoltaic systems J. Appl. Phys. 81 432–9
[15] Chou L-W, Shin N, Sivaram S V and Filler M A 2012 Tunable mid-infrared localized surface plasmon resonances in silicon nanowires J. Am. Chem. Soc. 134 16155–8

5
[16] Gorgulu K, Gok A, Yilmaz M, Topalli K, Buyuk N and Okyay A K 2016 All-silicon ultra-broadband infrared light absorbers Sci. Rep. 6 38589
[17] Soref R, Peale R E and Buchwald W 2008 Longwave plasmonics on doped silicon and silicides Opt. Express 16 6507–14
[18] Woods S J, Proctor J E, Jung T M, Carter A C, Neira J and Defibaugh D R 2018 Wideband infrared trap detector based upon doped silicon photocurrent devices Appl. Opt. 57 D82–9
[19] Yeng Y X, Chan W R, Rinnerbauer V, Stelmakh V, Senkevich J J, Joannopoulos J D, Soljacic M and Čelanović I 2015 Photonic crystal enhanced silicon cell based thermophotovoltaic systems Opt. Express 23 A157–68
[20] J-K, Jurado Z, Chen Z, Fan S and Minnich A J 2017 Daytime radiative cooling using near-black infrared emitters ACS Photonics 4 626–30
[21] Satō T 1967 Spectral emissivity of silicon Jpn. J. Appl. Phys. 6 339–47
[22] Liebert C H 1967 Spectral emissivity of highly doped silicon Prog. Astronaut. Aeronaut. 20 17–40
[23] Wu C, Crouch C H, Zhao L, Carey J E, Younkin R, Levinson J A, Mazur E, Farrell R M, Gothoskar P and Karger A 2001 Near-unity below-band-gap absorption by microstructured silicon Appl. Phys. Lett. 78 1850–2
[24] Sher M-J, Lin Y-T, Winkler M T, Mazur E, Pruner C and Asenbaum A 2013 Mid-infrared absorptance of silicon hyperdoped with chalcogen via fs-laser irradiation J. Appl. Phys. 113 063520
[25] Gorgulu K, Yilmaz M, Topalli K and Okyay A K 2017 Wideband ‘black silicon’ for mid-infrared applications J. Opt. 19 065101
[26] Maloney P G, Smith P, King V, Billman C, Winkler M and Mazur E 2010 Emissivity of microstructured silicon Appl. Opt. 49 1065–8
[27] Schroder D K 2006 Semiconductor Material and Device Characterization (Hoboken: John Wiley & Sons Inc.)
[28] Li S S and Thurber W R 1977 The dopant density and temperature dependence of electron mobility and resistivity in n-type silicon Solid-State Electron. 20 609–16
[29] Peng H, Liu L, Zhang T, Li Z, Zhu W, Kim J H, Xu J and Liu Z 2019 Spectral diffuse scattering in porous silicon Opt. Mater. Express 9 4588–96
[30] Mason J A, Adams D C, Johnson Z, Smith S, Davis A W and Wasserman D 2010 Selective thermal emission from patterned steel Opt. Express 18 25192–8
[31] Collins R J and Fan H Y 1954 Infrared lattice absorption bands in germanium, silicon, and diamond Phys. Rev. 93 674–8
[32] Schroder D K, Thomas R N and Swartz J C 1978 Free carrier absorption in silicon IEEE J. Solid-State Circuit 13 180–7
[33] Born M and Wolf E 1999 Principles of Optics (Cambridge: Cambridge University)
[34] Basu S, Lee B J and Chang Z M 2010 Infrared radiative properties of heavily doped silicon at room temperature J. Heat Transf.-Trans. ASME 132 023301
[35] Elangovan E and Ramamurthi K 2003 Studies on optical properties of polycrystalline SnO2:Sb thin films prepared using SnCl2 precursor Cryst. Res. Technol. 38 779–84
[36] Masetti G, Severi M and Solmi S 1993 Modeling of carrier mobility against carrier concentration in arsenic-, phosphorus-, and boron-doped silicon IEEE Trans. Electron Devices 30 764–9
[37] Matt G I et al 2010 Fullerene sensitized silicon for near- to mid-infrared light detection Adv. Mater. 22 647–50
[38] Zhao B, Hu M, Ao X and Pei G 2018 Performance analysis of enhanced radiative cooling of solar cells based on a commercial silicon photovoltaic module Sol. Energy 176 248–55