Germanium quantum dot infrared photodetectors addressed by self-aligned silicon nanowire electrodes

Yaolong Zhao¹³, Lingfei Li²³, Shuaishuai Liu¹, Junzhuang Wang¹⁴, Jun Xu¹, Yi Shi¹, Kunji Chen¹, Pere Roca i Cabarrocas³ and Linwei Yu¹⁴

¹ National Laboratory of Solid State Microstructures/School of Electronics Science and Engineering/Collaborative Innovation Center of Advanced Microstructures, Nanjing University, 210093 Nanjing, People’s Republic of China
² Department of Information Science & Electronic Engineering, Zhejiang University, Hangzhou 310058, People’s Republic of China
³ LPICM, CNRS,Ecole Polytechnique, Institut Polytechnique de Paris, F-91128, Palaiseau, France

E-mail: wangjz@nju.edu.cn and yulinwei@nju.edu.cn

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Abstract
Germanium quantum dots (GeQDs), addressed by self-aligned and epitaxial silicon nanowires (SiNWs) as electrodes, represent the most fundamental and the smallest units that can be integrated into Si optoelectronics for 1550 nm wavelength detection. In this work, individual GeQD photodetectors have been fabricated based on a low temperature self-condensation of uniform amorphous Si (a-Si)/a-Ge bilayers at 300 °C, led by rolling indium (In) droplets. Remarkably, the diameter of the GeQD nodes can be independently controlled to achieve wider GeQDs for maximizing infrared absorption with narrower SiNW electrodes to ensure a high quality Ge/Si hetero-epitaxial connection. Importantly, these hetero GeQD/SiNW photodetectors can be deployed into predesigned locations for scalable device fabrication. The photodetectors demonstrate a responsivity of 1.5 mA W⁻¹ and a photoconductive gain exceeding 10² to the communication wavelength signals, which are related to the beneficial type-II Ge/Si alignment, gradient Ge/Si epitaxial transition and a larger QD/NW diameter ratio. These results indicate a new approach to batch-fabricate and integrate GeQDs for ultra-compact Si-compatible photodetection and imaging applications.

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(Some figures may appear in colour only in the online journal)
help to achieve a maximal exposure of the active GeQD region to the incident light signals shedding from top or lateral sides. In addition, Si-based heterojunction photodetectors are widely explored in recent years [2–4], a high quality epitaxial GeQD/Si heterojunction interface with a type-II band alignment is highly desirable as it will facilitate a rapid separation of photo-generated electrons and holes. So far, individual GeQDs can only be electrically addressed by using scanning probes or the tips of conductive atomic force microscope through vertical tunneling junctions [5, 6]. This has been very convenient for fundamental research but rather difficult to implement for scalable optoelectronic applications, not to mention that the insulating dielectric layer existing on the surface of GeQDs also hinders an efficient photocarriers extraction out of the photoactive nodes.

On the other hand, a narrow SiNW connection to the GeQD node is also beneficial as this will help to suppress the emergence of threading-dislocations (TD) at the lattice mis-matched epitaxial Ge/Si interface. Though GeQDs can be mass-produced via chemical solution processes [7–9] or annealing [10–12], arranging them into precise locations with individual electric connections remains a challenge. In parallel, GeNWs are also widely explored to fabricate infrared photodetectors [13–19], and recently hetero Ge/Si nanowires (hNWs) were produced via metal droplet catalyzed vapor–liquid–solid (VLS) growth with alternated germane (GeH₄) and silane (SiH₄) gas supplies [20–24]. These VLS-grown GeNWs or hNWs are mostly vertical NWs that require post-growth transferring and re-arrangement by using nanoprobe/manipulators for device connection, which is a technical challenge for scalable device applications. In contrast, if a pair of self-aligned SiNW electrodes can be aligned precisely to contact the individual GeQDs, with a high quality epitaxial Ge/Si interface, it could help to achieve a scalable integration of individual GeQDs for high density infrared photodetection with high spatial resolution.

In this work, we explore a new self-transformation strategy to produce GeQD islands connected epitaxially by a pair of narrow SiNW electrodes, via metal droplet assisted conversion of a bilayer of a-Si/a-Ge thin film into hetero Ge/Si island-chain NWs (hiNWs) [25, 26], in a low temperature fabrication <300 °C and with a precise location control. The narrow SiNW connections contact the GeQDs through a high quality threading-dislocation-free hetero-epitaxial interface with a width <50 nm. The as-fabricated GeQD photodetectors achieve a responsivity of 1.5 mA W⁻¹ and photoconductive gain >10² at 1550 nm wavelength, indicating a promising approach to incorporate individual GeQDs for high density and high resolution photodetection in Si-based optoelectronics.

The GeQDs were produced via an in-plane solid-liquid-solid (IPSLS) growth [25–34], led by indium (In) droplets...
with a stacked a-Si (top)/a-Ge (bottom) bilayer thin film feeding, in a plasma-enhanced chemical vapor deposition (PECVD) system. As sketched schematically in figure 1(c), the In droplets were first formed by H₂ plasma treatment of In stripes at 250 °C, which are prepatterned on glass or oxide-coated wafer substrates via lithography, evaporation and lift-off procedure. Then, a-Ge and a-Si thin films were deposited sequentially to cover the sample surface at <150 °C (to keep the In droplets frozen). After that, the sample was annealed at 300 °C in vacuum ambient for ~60 min to activate the in-plane movement of the molten In droplets. During this course, a-Si/a-Ge bilayer was absorbed by the In droplets to produce crystalline NWs behind. Due to a unique nanoscale droplet dynamic process [26], the absorption depth into the bilayer precursor can be self-modulated to produce periodic and discrete GeQDs connected by narrow SiNW chains. While the detailed growth mechanism has been explained in our previous work [26, 33], we here focus on the critical role of the a-Ge bottom layer thickness \( t_{a-Ge} \) in tuning the GeQD/SiNW diameter ratio and the compositional contrast in the hiNWs. As shown in figures 2(a)–(c), with the increase of the bottom a-Ge layer thickness from 1.6 to 10 nm, the GeQD islands in the hiNWs become more prominent, with an increased diameter ratio \( r = D_{QD} / D_{NW} \) from 1.1 to 3.4, which provides great convenience for subsequent electric contact and device fabrication. At the end, the remnant a-Si/a-Ge layers can be selectively removed by a low temperature H₂ plasma etching. More experimental details are provided in our previous works [26].

A key capability of this in-plane growth of hiNWs is to convert a uniform amorphous a-Si (top)/a-Ge (bottom) bilayer thin film, with initial Ge content ratio well below <30%, into self-condensed and phase-separated crystalline GeQD islands connected by narrow SiNW chains. Their growth results from a unique rolling dynamics driven by the In droplets that can modulate their absorption depth automatically and periodically into the a-Si/a-Ge bilayer. As shown in figures 2(a)–(c), the variation trends of the GeQD/SiNW diameter ratio and the Ge content in the hiNWs against increased a-Ge layer thickness are summarized in (d). Scale bars in the SEM images in (b) and (c) are for 100 nm and 200 nm, respectively.
accompanied with a higher Ge content detected in the QD island nodes that can reach as high as 90%, much higher than the initial Ge content in the flat amorphous bilayer. These evolution trends are summarized in figure 2(d). Interestingly, even for the NWs grown with the thinnest 1.6 nm a-Ge layer, which has a seemingly uniform diameter as seen in the SEM image in figure 2(a), a clear self-modulation of Ge composition is still observed, varying from <1% to more than 30% in the brighter regions corresponding to the Ge-rich segments in the dark field transmission electron microscopy (TEM) characterization. On the surface of the Ge-rich island nodes, a thick amorphous oxide layer is found as highlighted in the inset to its right. Note that the ability to convert uniform and low Ge content bilayer thin film into self-condensed QDs with higher Ge content and wider diameters provides an important basis to batch-manufacture GeQD nodes, with narrow Ge/Si epitaxial interface (<50 nm), for constructing high quality infrared photodetectors.

The structural and composition properties of a selected Ge-rich QD node was examined by using aberration-corrected high resolution TEM (HR-TEM) and presented in figure 3. The growth direction of this specific hiNW is found to be along (111) orientation, according to the HR-TEM lattice imaging and the calculated FFT spots presented in figures 3(d) and (e), respectively. The bright and dark regions observed in this specific QD node arise from the different Ge and Si atom densities and thus different electron scattering contrast. These observations are also consistent with the elementary mapping of the Si and Ge atom signals shown in figures 3(b) and (c), respectively. It is important to note that the narrow Ge/Si transition interface (with a width <50 nm) is coherent and TD-free, indicating a high quality epitaxial connection and smooth hetero interface transition between the Ge-rich QD nodes and the SiNW segments.

To characterize the infrared photocurrent response in the GeQDs photodetector, two parallel hiNWs grown along the guiding edges were chosen and connected by two Au/Ti electrodes by using electron beam lithography (EBL), with a source (S)/drain (D) electrode separation of 800 nm. The photocurrent mapping was carried out in an experimental setup as diagrammed schematically in figure 4(a), where the photocurrent signal was recorded under a constant bias of

Figure 3. (a) TEM image of a selected GeQD node with bright and dark contrast arising from the phase-separated Ge-rich and Si-rich regions, as confirmed by the HAADF-STEM elementary mapping of Si and Ge atom signals in (b) and (c). (d) presents the aberration-corrected high resolution TEM lattice image of the epitaxial Ge/Si transition interface, while the calculated FFT patterns are provided in (e). Scale bars in (b) and (c) are for 50 nm, and for 5 nm in (d).
V_{DS} = 5 \, \text{V}, \text{while the scanning laser beam @1550 \, \text{nm} was focused onto a spot size of } D_{\text{laser}} \sim 1.22 \times \lambda_{1550}/N_0 = 4.7 \, \mu\text{m by using an objective lens with a numerical aperture of } N_a = 0.4. \text{Under a calibrated laser power of 4 mW, the photocurrent mapping signal was obtained via a lock-in amplification system operating at 700 \, \text{Hz and shown in figure 4(b), as an overlapping semi-transparent layer upon the corresponding SEM image. The structural details in the center region marked by a red dashed rectangle are provided in the SEM characterizations shown in figure 4(c). Specifically, there are two GeQDs, as highlighted by greenish tinges in the upper and the bottom panels, found in each hiNW channel. The average diameter of the GeQDs is around } w_{QD} \sim 30-40 \, \text{nm}. \text{Note that, the existence of embedded GeQDs in the hiNWs were further confirmed by EDS analysis. As seen in figure 4(b), the photocurrent response is more important in the channel regions with two GeQD-embedded hiNWs. In addition, the dispersal photocurrent responses arise from the scattering effects of nearby uneven surface or edge lines, which can scatter the top-incident laser light towards the photactive hiNW channels. Meanwhile, the photocurrents under 1550 \, \text{nm illumination are found to increase sub-linearly, which can be fitted by a power law of } I \sim P^\alpha, \text{as plotted in figure 4(d), with an exponent close to unity, in the range of 0.93–1. This indicates that the photocurrents are still in a linear response regime with little local recombination loss in the GeQD nodes. In addition, the photocurrent under 3.3 mW illumination is found to increase with the bias voltage, but not in a linear way, as witnessed in figure 4(e), which could arise from the non-Ohmic contact between the SiNW segments and the metal electrodes.}

Considering the crystalline SiNW segments chartered in figure S2, by themselves, have negligible absorption at 1550 \, \text{nm, the photocurrent signals can be assigned solely to the photo responses from the Ge-rich QD nodes in the hiNWs. Meanwhile, the highest Ge concentration detected in the QDs is } \sim 90\%. \text{At such alloy composition the optical absorption coefficient at 1550 \, \text{nm is estimated to be } \alpha_{QD} \sim 10 \, \text{cm}^{-1} \text{ according to [35] that is, two orders of magnitude lower compared to that of pure c-Ge of } \alpha_{c-Ge} \sim 459 \, \text{cm}^{-1}. \text{Furthermore, as inferred from the EDS scans in figures 2(b) and 2(c), the Ge content in the GeQD is not uniform, and only a portion of the GeQD has a relatively high Ge content >90\%. Taking this into account, the effective volume of the GeQD active for the absorption of 1550 \, \text{nm photons should be considerably smaller than their apparent size measured in the SEM observation, say with an estimated dimension ratio of } f_{0.9\text{Ge}} \sim 0.4. \text{Taking the typical QD dimensions of } w_{QD} \sim 35 \, \text{nm wide, } l_{QD} \sim 40 \, \text{nm long and a thickness of } t_{QD}\sim I_{QD}, \text{the incident laser power upon a single QD node can be roughly estimated to be } P_{\text{in}} = P_{\text{laser}}S_{QD} \sim 0.2 \, \mu\text{W}, \text{where } S_{\text{in}} \text{and } S_{\text{QD}} \text{are the laser power density and the projected surface area of the QD, respectively. Then, the responsivity under 5 \, \text{V bias is calculated to be } R_{QD} = I_{\text{ph}}/P_{\text{in}} \sim 1.5 \, \text{mAM}^{-1}. \text{If the effective absorption achieved in a single Ge-rich QD is estimated, according to Beer–Lambert’s law, to be } P_{\text{abs}} = (1 - e^{-\alpha_{QD}wl_{QD}})P_{\text{in}}f_{0.9\text{Ge}} \sim 2 \times 10^{-12} \, \text{W}, \text{the photocurrent gain of the QD photodetector can be roughly estimated to be } G = \frac{I_{\text{ph}}/q}{P_{\text{abs}}/hv} \sim 10^2, \text{where } hv \text{and } q \text{are the photon energy and the elementary charge, respectively.}

In the Ge-rich QD nodes, the photo-generated electrons will be trapped by the slow surface or interface states in the outer Ge oxide shells [14, 16–18], as depicted schematically in figure 1(d), while holes will be driven by the bias field, to give rise to the photocurrent signal. The bulky active GeQD nodes, with a wider diameter compared to the SiNW chains, which cannot absorb the 1.55 \, \mu\text{m photons, is an advantage in view of achieving a wider light absorption cross section, while the type-II band alignment, as sketched in figure 1(b), is also a convenient way to separate the photo-generated electrons and holes at the hetero-junction interface.}

However, the relatively lower photoconductive gain of our GeQDs, compared to that reported for GeNW
In summary, GeQD infrared photodetectors have been demonstrated based on a low temperature (<300 °C) growth and self-segregation process of hetero GeQD/SiNW complex structure, with tunable geometry and precise location control. A responsivity of 1.5 mA W\(^{-1}\) and a photoconductive gain \(>10^2\) (to 1550 nm wavelength) have been achieved, indicating a promising way to integrate individual GeQDs into Si CMOS circuits for high density infrared communication, imaging and photodetection applications.

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ORCID iDs

Jun Xu @ https://orcid.org/0000-0002-0469-9766
Linwei Yu @ https://orcid.org/0000-0002-0801-5210

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