Highly Tensile-Strained Self-Assembled Ge Quantum Dots on InP Substrates for Integrated Light Sources

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ABSTRACT: Highly tensile-strained Ge quantum dots (TS-Ge-QDs) emitting structures with different size were successfully grown on InP substrates by molecular beam epitaxy. Dislocation-free TS-Ge-QDs were observed by transmission electron microscopy. Finite element modeling indicates a maximum tensile strain of 4.5% in the Ge QDs, which is much larger than the required strain to achieve direct band gap conversion of Ge based on theoretical prediction. Photoluminescence (PL) from a direct band-gap-like transition of TS-Ge-QDs with a peak energy of 0.796 eV was achieved and confirmed by the etch depth-dependent PL, temperature-dependent PL, and excitation-power-dependent PL. In addition, a strong defect-related peak of 1 eV was observed at room temperature. The band structure of the TS-Ge-QDs emitting structures was calculated to support the experimental results of PL spectra. Achieving PL from direct band-gap-like transitions of TS-Ge-QDs provides encouraging evidence of this promising highly tensile strained semiconductor-nanostructure-based platform for future photonics applications such as integrated light sources.

KEYWORDS: tensile strain, germanium, quantum dots, photoluminescence, self-assembled growth, quantum confinement effects

INTRODUCTION

Germanium, one of the earliest studied semiconductors, has found important applications in the current electronics and optoelectronics industry. Significant progress has been made in recent years for the Ge-based optical and optoelectrical components, such as germanium (Ge) based modulators, photodetectors, and lasers. More interestingly, it has been predicted theoretically that ~2.0% of biaxial tensile strain can convert Ge into a direct band gap semiconductor, allowing for efficient light emission. Relentless efforts have been made to introduce tensile strain into Ge. The first approach was to anneal thick Ge films on Si substrates which can introduce 0.25% of biaxial tensile strain into the Ge films due to the differences in the thermal expansion coefficients. Growing Ge thin films on InGaAs or GeSn template layers with larger lattice constants can introduce up to 2.33% of biaxial tensile strain. Micromechanical strain engineering or external stressors such as nanomembranes, bridges, and nanowires were employed to introduce biaxial or uniaxial tensile strain into Ge structures. As a result, a strong direct bandgap light emission from tensile-strained Ge thin film on an InGaAs template has been achieved from low-temperature photoluminescence (PL). Moreover, low-threshold optically pumped lasing action of tensile-strained Ge nanowires and tensile-strained Ge microbridges were demonstrated recently. However, the current devices of tensile strained Ge are still far from being practical applications, due to factors such as insufficient amount of strain and/or poor material quality of the thin films on the template layers, or the complexity of fabricating micromechanical structures, limiting the potential for large-scale integration.

Recently, self-assembled tensile-strained Ge quantum dots (TS-Ge-QDs) or Ge nanocomposites were proposed as a promising approach to achieve efficient light emission from Ge due to their unique properties which combine the advantages of direct-band-gap Ge and quantum dots (QDs). TS-Ge-QDs can hold large strain without plastic relaxation and are less susceptible to dislocations. Quantum confinement effect (QCE) can trap the electrons and holes to enhance the radiative recombination process, as well as control the discrete energy levels to tune the emission wavelength in a wide range. Furthermore, due to the δ-shape density of state (DOS), QD-based lasers possess the advantages of a low lasing...
threshold, low temperature sensitivity, and narrower line width.24–27 In our previous work and other’s reported work, the prototype model of TS-Ge-QD on InP substrate was demonstrated by molecular beam epitaxy (MBE).18,28,29 The strain distribution and growth mode of Ge QDs were analyzed. However, the optical properties, especially light emission, of TS-Ge-QDs have not been extensively investigated.

In this work, we demonstrate PL from TS-Ge-QD based structures. TS-Ge-QDs with different sizes buried in In0.52Al0.48As barriers have been grown successfully on InP substrates by MBE. The strain in TS-Ge-QDs was simulated by the finite element method (FEM) and the largest biaxial tensile strain is as high as 4.5%. PL at both room temperature (RT) and lower temperatures down to 9 K was achieved from the samples, and at 9 K a peak emission at 0.796 eV was found from the direct transition in the TS-Ge-QDs. The physical origin, size effect, temperature, and power-dependent properties of the PL spectra were investigated. As a concept validation study, III–V materials were employed to provide lattice mismatch and potential barrier for the TS-Ge-QDs. In the future, pure group IV materials, such as Si1−x−yGexSn0.5 alloys, can be utilized to realize fully CMOS-process-compatible light emitters with TS-Ge-QDs as the gain media, for light sources can be utilized to realize fully CMOS-process-compatible light emitters with TS-Ge-QDs as the gain media, for light sources

## RESULTS AND DISCUSSION

### Surface Morphology and Structural Properties of Ge QDs Samples

Figure 1b shows the surface morphology of the samples corresponding to S1 to S4 without capping for the Ge QDs. Samples with spherical Ge QDs of different sizes were grown by MBE. The average diameters of the QDs in the samples from S1 to S4 are 100, 32, 44, and 40 nm, and the average heights of the QDs in the samples from S1 to S4 are 22, 6, 9, and 7 nm, respectively. The QDs that stick together were removed from the size statistics. The morphology of the QDs in S1 was more uniform than that of the QDs in S2. The percentage of the standard deviation of diameters and heights of S1 were 8.7% and 17.6%, respectively. There are QDs with two typical sizes in S2. The size difference between S1 and S2 is the largest among the four samples.

The successful growth of Ge QDs with a capping layer were confirmed by cross-sectional TEM (XTEM) with EDX mapping and three-dimensional (3D) APT (Figure 2a–2d). The shape, growth mode, compositions of TS-Ge-QDs, and the defects in the samples are investigated. As shown in Figure 2a, the sample with Ge QDs buried in the In0.52Al0.48As matrix layers is observed. The image contrast is caused by the strain fields of QDs. The growth mode of Ge QDs on the InAlAs layer is the Volmer–Weber mode without Ge wetting layers, which is essential to avoid forming antiphase-domain (APD) defects and is significant for device applications.28 For the sample with large Ge QDs (S1), defects from the surface of Ge QDs to the InGaAs capping layer are observed (Supporting Information Figure S1). The 3D APT image shows spherical Ge QDs without wetting layers, seen in Figure 2b. This is also confirmed by the TEM EDX mapping image as shown in Figure 2c. Compared to the EDX mapping image, the phenomenon that the QDs appear tilted in the APT image is due to the distortion of the image which is an artifact due to the higher removal of ions from Ge QDs than the surrounding InAlAs matrix in APT measurements.35 The QDs have a strongly Ge-enriched core and an abrupt Ge/bottom InGaAs interface (Figure 2d). Furthermore, the intermixing between Ge QDs and the In0.52Al0.48As matrix was investigated by 3D APT. It is found that the intermixing between the III–V matrix and Ge QDs was observed near the Ge QDs/matrix interface.

### Strain Distribution in Ge QDs

The strain components of Ge QDs were simulated by FEM based on a 3D spherical cap model with a diameter of 40 nm and a height of 7 nm, respectively, which is the average size of QDs in S4 (Figure 3). The maximum value of the strain component εxx is 4.5% at the peripherals. The strain distribution of the Ge QD with the capping layer is more uniform than that of the Ge QD without the capping layer. The mean volume value of strain εxx in the Ge QD is 3.0% which is as much as 78% of the initial strain induced by the lattice mismatch between Ge and In0.52Al0.48As. Tensile strain higher than 3% in Ge embedded in InAlAs has been revealed by Raman spectroscopy and reported.30,31 The induced strain is much larger than the required amount to achieve direct band gap conversion of Ge based on theoretical
prediction. Moreover, as the diameter/height ($D/H$) ratio increases, the residual strain in Ge QDs increases which is shown in Figure 3d. The shear strain component $\varepsilon_{xy}$ (Figure 3c) is negligible in the center of the QD. It is mainly distributed around the edge of the QDs and is smaller than the normal strain component $\varepsilon_{xx}$. The shear strain in Ge QDs will suppress the conversion of Ge from an indirect band gap material to a direct band gap material. The shear strain in the capped Ge QDs is smaller than that in the uncapped one which is beneficial for the emission properties of the Ge QDs.

**PL Spectra of Ge/InAlAs QDs at Room and Low Temperature.** The optical properties of the Ge QDs samples were investigated by PL measurements. All Ge QD samples demonstrate strong and broad PL signals at RT. Figure 4a shows the RT PL of S1 ($H=22$ nm) and S2 ($H=6$ nm) with an emission peak of 0.972 eV ($\sim$1276 nm). The full width at half maximums (fwhm’s) of the peaks from S1 and S2 are 292 and 302 meV, respectively. The intensity of the PL of S2 is stronger than that of S1. Besides, a weak PL with a peak of 1.5 eV was observed, which most likely originates from the direct
band gap transition of In$_{0.52}$Al$_{0.48}$As. In order to investigate the origin of the main peak, PL spectra of the Ge QDs sample (S4) with different etching depths (EDs) are measured. The etched samples are S4 with full structure (ED = 0), S4 with the InGaAs layer etched (ED = 10 nm), S4 with the In$_{0.52}$Al$_{0.48}$As capping layer etched (ED = 110, 130, 140, 170, and 200 nm), S4 with the Ge QDs layer etched (ED = 210 nm), and S4 etched to InP (ED = 410 nm). The PL spectra of the etched samples as well as of an InP reference wafer are shown in Figure 4b. As shown by the red curve, when the InGaAs layer is etched, the main peak still exists and its intensity is stronger than that of the full structure sample, indicating light attenuation by the InGaAs layer. The PL spectra of the samples with different EDs of In$_{0.52}$Al$_{0.48}$As layer (ED = 10, ED = 120, 140, 170, and 200 nm) are similar to each other, so only the PL spectrum of the sample with InGaAs capping layer etched (ED = 10) is shown here. Interestingly, when the Ge QDs layer is further etched, shown by the blue curve, the main peak disappears, indicating that the strong emission at RT is from the TS-Ge-QD layer or the region of In$_{0.52}$Al$_{0.48}$As capping layer near the Ge/In$_{0.52}$Al$_{0.48}$As interface. When the sample is etched to the InP substrate, the PL is the same as that of the InP reference wafer.

To gain more insight into the TS-Ge-QD samples, PL measurements at 9 K were performed. Figure 4c is the PL spectrum of S1 at 9 K plotted in a logarithmic coordinate. Interestingly, in addition to the PL peak at ~1 eV observed in the RT PL spectrum, two new PL signals at lower energies of 0.480 and 0.796 eV are observed. The PL signals from the InAlAs layers and InP substrates increase at 9 K as well. The three peaks in the low energy regime are labeled as P0, P1, and P2, respectively. The P0 peak is red-shifted by as much as 410 meV with respect to the direct band gap of bulk Ge ($E_g^{\text{Ge}} = 0.890$ eV), in agreement with the fact that the band gap of Ge shrinks due to tensile strain and confirms the large tensile strain in Ge QDs as extracted from FEM simulation. P1 demonstrates less red shifts than P0 relative to direct band gap of bulk Ge. The maximum intensity of the new peak P1 is comparable to that of P2. The fwhm of P1 at 9 K is 77 meV, approximately 1/3 of that of P2.

**Quantum Confinement Effect of Ge/InAlAs QDs.** Figure 4d shows the PL spectra of TS-Ge-QDs samples with different QD sizes (samples S1–S3) whose average height varies from 6 to 22 nm. The PL spectra are fitted by Gaussian functions as shown by red curves (PL fitting curves) and green dashed curves (single peak). It is worth noting that P1 demonstrates a blue shift as the QD size decreases, while P2 almost has no dependency on size effect. With the QD size decrease from 22 to 6 nm, P1 demonstrates a blue shift of 78 meV which is attributed to the quantum confinement effect and strain of the QDs with different sizes. The PL blue shift of P1 with reduced QD size suggests that peak P1 is from the radiative recombination in TS-Ge-QDs. Considering the size dependent (Figure 4d) and etching depth dependent PL
spectra (Figure 4b) of TS-Ge-QDs, we believe that P2 is not from TS-Ge-QDs but the region near the top In_{0.52}Al_{0.48}As/Ge interface. Origins of all peaks are labeled in Figure 4c accordingly for ease of reference.

Thermal Decay Process in Ge/InAlAs QDs. To confirm whether the Ge QDs are fundamentally direct-like or indirect-like gaps, temperature-dependent PL of S1 in the range from 9 to 290 K were performed (Figure 5a). The PL intensity of P1 decreases and the peak width of P1 broadens with the temperature increase from 9 to 90 K, which is a feature of the direct band gap semiconductor and is quite different from PL of indirect band gap Ge.37 Different from P2 which demonstrates strong luminescence up to room temperature, P1 only demonstrates considerable luminescence below 100 K. The rapid thermal quenching of the P1 may be due to the existence of radiative recombination or nonradiative recombination centers in the InAlAs barriers.38 In addition to the trapping of carrier by nonradiative recombination centers near QDs, radiative-recombination centers near QDs might also trap the carriers/exciton in QDs as the temperature increases. The integrated PL intensities of P1 and P2 are extracted by peak fitting with Gaussian functions. Figure 5b shows the relationship between integrated PL intensities and 1/k_BT, where k_B is the Boltzmann constant and T is the temperature of the PL spectrum measurement. The temperature-dependent integrated PL intensity is fitted well by the following Arrhenius formula:

\[
E^0 = E^{0\text{P}1} = 44 \text{ meV} \\
E^0 = E^{0\text{P}2} = 13 \text{ meV}
\]

Figure 4. (a) RT PL spectra of S1 (H = 22 nm) and S2 (H = 6 nm). (b) RT PL spectra of TS-Ge-QD sample (S4) with different etching depths. (c) PL spectrum of S1 at 9 K. (d) PL spectra of TS-Ge-QDs with different sizes at 9 K. The red lines are the PL fitting curves, and the green dashed line is the Gaussian function to fit single peak.

Figure 5. (a) Temperature-dependent PL of S1. P3 is cut to show P1 and P2 more clearly. (b) The integrated intensity of P1 and P2 versus 1/k_BT of S1. (c) The energies of P1 and P2 of S1 vary with the temperature.
For P1, $\gamma$ is the integrated PL intensity at 0 K, $A$ is a proportional constant, and $E_g$ is the thermal activation energy. The extracted activation energies of P1 and P2 are 13 and 44 meV, respectively. The activation energy derived from temperature-dependent PL is determined by the thermal decay processes involved. The activation energy of P1 is related to the energy barrier height between ground states of Ge QDs and radiative/nonradiative recombination centers near the QDs. The small value of activation energy of P1 indicates that the major limitation of the emission efficiency of QDs at room temperature is due to the carrier recombination, possibly near the QD/matrix boundaries, giving insight to improve the optical properties of TS-Ge-QDs by reducing the recombination centers near QD/matrix boundaries in the future. The activation energy of P2 is extracted to evaluate the energy for carriers to escape from the radiative recombination centers to nonradiative recombination centers in InAlAs layers.

Furthermore, as shown in Figure 5c, the temperature induced red shift of P2 is 1 order of magnitude lower than that of P1 in the temperature range 9 to 90 K. The temperature insensitivity and broad peak width of P2 indicate that P2 might be related to deep impurity levels. The temperature-dependent energy of P1 is compared with the direct band gap of bulk Ge with Varshni’s equation

$$E_g(T, meV) = E_g(0) - 0.0036T^2/(T + 296)$$

where the direct band gap at 0 K, $E_g(0)$, is modified to 795 meV considering the strain effect or QCSE. As shown by the magenta dashed line in Figure 5c, the energy shift of P1 by temperature from 9 to 90 K is consistent with the direct band gap shift of Ge using Varshni’s equation.

**Band Alignment Type and Recombination Mechanism of Ge/InAlAs QDs.** Excitation-power-dependent PL is performed to investigate the band alignment type and the dominant carrier recombination mechanism of the Ge/InAlAs QD heterostructure. Figure 6a shows the excitation-power-dependent PL of S1 with the power range from 50 to 500 mW at 9 K. The energy of P1 shows no significant shift with decreasing power, which is a result of the minimal effect of the Coulomb interactions on the type-I band alignment. The excitation-power-dependent integrated intensities of the three peaks are well fitted with the power law $I \propto P^\gamma$ where $P$ is the excitation power. The exponent $\gamma$ is related to the recombination mechanisms. For P1, $\gamma$ is 1.23, suggesting that the recombination mechanism of P1 is exciton recombination ($\gamma \approx 1$) with an admixture of free-carrier recombination ($\gamma \approx 2$). P2 demonstrates an obvious sublinear dependence with a $\gamma$ of 0.61. Such a large difference of excitation-power-dependent integrated intensities between P1 and P2 indicates different physical origins of P1 and P2. The sublinear excitation power dependence of P2 indicates that the intensity of P2 tends to saturate at a high excitation power. This indicates that P2 might be associated with exciton bound to deep level traps. The intensity of P2 tends to saturate at high excitation power when the deep level traps are fully occupied with carriers/excitons. The possible origins of the radiative recombination centers/traps for the emission of P2 will be discussed in the next paragraph. The $\gamma$ of P3 is slightly less than 1, indicating the existence of a loss mechanism, such as nonradiative recombination centers introduced by the defects in In$_{0.52}$Al$_{0.48}$As layers.

**Discussion and Band Structure Modeling.** Figure 7 summarizes our understanding of the PL spectra based on our knowledge of the structure of the QDs shown in Figures 1 and 2. The QD size effect on light emission is found in the carrier recombination represented by the sharp peak labeled as P1 in S1. The PL intensity of P1 decreases and the peak width of P1 broadens with increasing temperature. The energy variation with temperature of P1 is similar to that of the direct band gap Ge bulk. Furthermore, the energy of P1 shows no significant shift with excitation power. Meanwhile, the $\gamma$ of the integrated intensity of P1, fitted by the equation $I \propto P^\gamma$, is 1.23.
Considering the features above, P1 is inferred to be from the direct band-gap-like transition $\Gamma_0 - LH_L$ of TS-Ge-QDs. The band alignment of In$_{0.52}$Al$_{0.48}$As/Ge QD/In$_{0.52}$Al$_{0.48}$As is type-I, and the optical recombination type in the TS-Ge-QDs is excitonic. P2 is spatially from the TS-Ge-QD layer or the region of the In$_{0.52}$Al$_{0.48}$As capping layer near the Ge/In$_{0.52}$Al$_{0.48}$As interface. Ge contamination is mainly in the region of the In$_{0.52}$Al$_{0.48}$As capping layer near the Ge/In$_{0.52}$Al$_{0.48}$As interface. The size effect is hardly found in the carrier recombination represented by P2. The energy of P2 decreases with temperature, showing less sensitivity to the temperature than that of P1. Moreover, P2 demonstrates an obvious sublinear dependence on exciton powers with a $\gamma$ of 0.61. The energy of P2 remains unchanged with the excitation power. The PL of P2 is strong and broad with an fwhm of ~300 meV at RT. Considering the optical and composition features above, P2 is most likely from the radiative recombination between the band edge and the deep level of In$_{0.52}$Al$_{0.48}$As. The deep level in the In$_{0.52}$Al$_{0.48}$As might be induced by Ge growth contamination or defects near the Ge/In$_{0.52}$Al$_{0.48}$As interface. The spatial localization of the deep levels can make the k-values in momentum space spread, resulting in the large fwhm of the P2. The emission from deep levels is often insensitive to the temperature, which accounts for the low sensitivity of the energy of P2 to the temperature. Strong and broad luminescence observed in many semiconductors such as dilute bismide and nitride is attributed to deep-level defects. P3 is from band-to-band radiative recombination of In$_{0.52}$Al$_{0.48}$As layers, since the energy of P3 is equal to the theoretical band gap energy of In$_{0.52}$Al$_{0.48}$As. P0 may be from $\Gamma_0 - LH_L$ transitions of Ge QDs. Since the PL signals are collected along the sample surface normal, most photons created by $\Gamma_0 - LH_L$ have transverse magnetic (TM) polarization which propagates in the plane of Ge QD layers, resulting in the weak intensity of P0. Besides, P0 can be observed up to ~100 K which has a similar temperature-dependent feature of P1.

To further understand the optical properties of the Ge QDs, the band structure of a 3D spherical QD is calculated as shown in Supporting Information Figure S2. The calculated QD is with a diameter of 100 nm and a height of 20 nm, which is based on the average size of the QDs in S1. It is found that, under such large strain ($\varepsilon_{LS} \approx 3.0\%$), Ge QDs have been converted into direct band gap materials even considering the QCE. The ground level of the $\Gamma$ conduction valley is ~60 meV lower than that of the L valley. Compared to the unstrained Ge/In$_{0.52}$Al$_{0.48}$As, tensile-strained Ge/In$_{0.52}$Al$_{0.48}$As shows stronger confinement of carriers, especially for electrons. The band offset of the conduction band increases from 11 meV to about 400 meV. The light hole band and the heavy hole band split for about 250 meV, due to the strains. The heterostructure is type-I band alignment with both electrons and holes confined in the TS-Ge-QDs. According to the simulation, the transition energy from $\Gamma_0$ to $LH_L$ is 0.584 eV which is lower than the energy of P1. The blue shift from 0.584 to 0.796 eV may be due to several factors. One possible reason is that the deformation potential coefficient may be changed by large tensile strains. The size of the Ge QD for the simulation is from the AFM images. The measured size of QDs is usually larger than the actual size due to the limitation of AFM tips. The intermixing between Ge and InAlAs may make the sizes of buried QDs smaller than that of surface ones measured by AFM. Considering the tip effect of AFM and QD size affected by intermixing, the calculated transition energy will be blue-shifted. Besides, the electronegativity of the In$_{0.52}$Al$_{0.48}$As layer in contact with Ge (III–Ge or V–Ge bonds) will affect the band offset between Ge and In$_{0.52}$Al$_{0.48}$As. The diffusion of the group III–V atoms into Ge-QDs may also affect the band structure significantly. Hence, more work should be done to fully understand the optical behavior of highly TS-Ge-QDs in the future.

## CONCLUSIONS

In summary, we studied the structural and optical properties of TS-Ge-QD emitting structures with different QD sizes grown on InP (001) substrates by MBE. The growth mode of TS-Ge-QDs on In$_{0.52}$Al$_{0.48}$As was demonstrated to be the V–W mode which was essential for growing high-quality samples. Dislocation-free growth of TS-Ge-QDs was confirmed by TEM. The strains in Ge QDs were simulated by FEM and the results show that the maximum tensile strain is 4.5%, which is much larger than the required strain to achieve direct band gap conversion of Ge based on theoretical prediction. Four carrier transition processes were observed from PL measurements, the transition between the ground states of electrons and heavy holes in Ge QDs, the ground states of electrons and light holes in Ge QDs, deep levels and band edge of InAlAs, and band-to-band recombination of InAlAs layers. The deep levels are in the InAlAs capping layer near the Ge/InAlAs interface. This work shows that the highly tensile strained Ge/InAlAs QDs can be a promising semiconductor-nanostructure-based platform for future photonics applications such as integrated light sources.

## METHODS

**Molecular Beam Epitaxy.** Growth was conducted by DCA MBE systems. All samples were grown on (100) semi-insulating InP substrates. Before the growth of the In$_{0.52}$Al$_{0.48}$As layer, the InP substrates were deoxidized in the group III–V chamber at 605–620 °C. The thickness and the growth temperature of the In$_{0.52}$Al$_{0.48}$As layer on the InP substrate were 200 nm and 650 °C, respectively for all samples. Then, the samples are transferred to the group IV chamber to grow the Ge QD layers. The flux rate of Ge is calibrated by both electron impact emission spectroscopy and a Q-pod quartz crystal monitor. Surface evolution of the Ge-QDs is monitored in real-time by in situ RHEED. The sizes and densities of Ge QDs are tuned by flux rate, deposition time, and the growth temperature of Ge. Samples S1 to S4 were deposited with Ge equivalent thin films thickness of 3 monolayers (ML), 0.33 ML, 2 ML, and 1 ML, respectively to tune the QD sizes. The growth temperature and flux rate of the Ge are calibrated by both electron impact emission spectroscopy and a Q-pod quartz crystal monitor. The growth temperature and flux rate of the Ge for samples S1 and S2 are 470 °C and 0.05 ML/s, respectively. The growth temperature and flux rate of the Ge for samples S3 and S4 are 450 °C and 0.1 ML/s, respectively. The higher growth temperature and lower Ge flux rate for samples S1 and S2 are to reduce the density of QDs to cause most QDs to be separated from each other to prevent the formation of the antiphase domain in the InAlAs capping layer. With a lower Ge flux rate and higher Ge growth temperature, the diffusion rate and diffusion time of Ge atoms/cores on the InAlAs surface increases, resulting in a longer diffusion length. Thus, more Ge small islands will be merged and the density of QDs is reduced. After the growth of Ge QD layers, samples are transferred to the group III–V chamber to grow the In$_{0.52}$Al$_{0.48}$As and InGaAs capping layers. The In$_{0.52}$Al$_{0.48}$As capping layers on Ge QDs layers were grown under the same conditions for the bottom In$_{0.52}$Al$_{0.48}$As layers. The top layer of the samples were 10 nm InGaAs capping layers to suppress the oxidation of In$_{0.52}$Al$_{0.48}$As.

**Photoluminescence Setup.** The optical properties of the samples were investigated in a wide temperature range of 9–290 K and a power range of 50–500 mW by an infrared modulated PL technique based on an FTIR spectrometer running in the step-scan.
mode. A 532 nm laser was selected for pumping, and a liquid-nitrogen-cooled InS detector was used for PL detection. The samples’ temperature was controlled by a closed-cycle compressor. A reflection rather than transmission PL optical path was employed for PL measurements, so as to avoid the substrate reabsorption influence on the PL spectral line shape.

Strain and Band Structure Calculations. The simulation of the strain in Ge QDs is based on the classical continuum elasticity model. The simulation of the electronic structure is based on the EMA using the real potential which is calculated by deformation potential theory. The Ge QDs are in a spherical cap shape, which was confirmed by AFM and EDX mapping. The simulation of strain is based on a 3D spherical cap model with a diameter of 40 nm and a height of 7 nm, which is the average size of S4 observed by AFM. The simulation of electronic structure is based on a cap model with a diameter of 100 nm and a height of 20 nm, which is the average of S1 observed by AFM.

The strain tensor $\varepsilon$ was calculated by the linear elastic theory which is expressed as

$$
\begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix}
= 
\begin{bmatrix}
C_{11} & C_{12} & C_{13} \\
C_{12} & C_{11} & C_{13} \\
C_{13} & C_{13} & C_{12}
\end{bmatrix}
\begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
$$

(2)

To investigate the electronic structure of Ge QDs, we consider the Schrödinger’s equation under the effective-mass approximation (EMA), as follows:

$$
\frac{\hbar^2}{2} \nabla^2 \Psi_n + V_n \Psi_n(r) = E_n \Psi_n(r)
$$

(3)

where $\Psi_n$ is the corresponding inverse effective mass tensor ($\eta = \Gamma, L, LH, HH$ refers to different band valleys), $V_n(r)$ is the corresponding intrinsic band profile. $V_n(r)$ is the corresponding strain-induced energy shift given by

$$
V_{\text{str}} = a_0 (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})
$$

(4)

$$
V_{\text{str}}[\text{nm}] = \left( \Xi_3 + \frac{1}{3} \Xi_4 \right) \Gamma + \frac{2}{3} \Xi_4 (n_{\xi \xi} + m_{\xi \xi} + \kappa_{\xi \xi})
$$

(5)

$$
V_{\text{strain}} = -P - \frac{1}{2} (Q - \Delta + \sqrt{\Delta^2 + 2Q\Delta + 9Q^2})
$$

(6)

$$
V_{\text{strain}} = -P - Q
$$

(7)

where

$$
P = -a_0 (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})
$$

(8)

$$
Q = -\frac{b}{2} (\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz})
$$

(9)

where $a_0$ is the deformation potential of the $\Gamma$-conduction band; $\varepsilon_{xx}$, $\varepsilon_{yy}$, and $\varepsilon_{zz}$ are the diagonal components of the strain tensor $\varepsilon$. $V_{\text{str}}[\text{nm}]$ is the strain-induced energy shift of the $\Gamma$-conduction valley. $\Xi_3$ and $\Xi_4$ are deformation potentials. $a_0$ and $b$ are the hydrostatic and shear deformation potentials of valence bands, respectively. $\Delta$ is the spin–orbit splitting of Ge. The parameters used for the calculation are listed in Table S1 in the Supporting Information.

### Supporting Information

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acsanm.0c03373](https://pubs.acs.org/doi/10.1021/acsanm.0c03373). Extended details on TEM analysis and band structure calculations on the Ge QDs samples (PDF)

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