Electric tuning of direct-indirect optical transitions in silicon

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Electronic band structures in semiconductors are uniquely determined by the constituent elements of the lattice. For example, bulk silicon has an indirect bandgap and it prohibits efficient light emission. Here we report the electrical tuning of the direct/indirect band optical transition in an ultrathin silicon-on-insulator (SOI) gated metal-oxide-semiconductor (MOS) light-emitting diode. A special Si/SiO₂ interface formed by high-temperature annealing that shows stronger valley coupling enables us to observe phononless direct optical transition. Furthermore, by controlling the gate field, its strength can be electrically tuned to 16 times that of the indirect transition, which is nearly 800 times larger than the weak direct transition in bulk silicon. These results will therefore assist the development of both complementary MOS (CMOS)-compatible silicon photonics and the emerging “valleytronics” based on the control of the valley degree of freedom.

Bulk silicon has an indirect bandgap and a multiple degenerate valley structure in the conduction band. Electrons occupy the minimum energy states with the crystal momentum far from zero (near the X-point) and holes occupy the maximum energy states in the valence band at zero crystal momentum (Γ-point) (Fig. 1(a)). Since photons do not carry significant momentum and a dipole transition requires momentum conservation, an optical direct transition is not allowed in bulk silicon and a weak phonon-mediated indirect transition is dominant. To overcome this inherent constraint, many attempts have been made to improve emission efficiency by using quantum confinement1–6, doping7,8, strain7,9, and heterogeneous technology4,10,11. However, most of these approaches rely strongly on a specific fabrication process, and the origin of the improvement is not fully understood due to the lack of tunable physical parameters.

Recently, “valleytronics”, which utilize valley degrees of freedom to create new functions, have been attracting much attention12–16. Valley splitting in a silicon has been widely studied two dimensional electron systems (2DESs)17–31, quantum dots (QDs)32,33 and dopants34,35. It is known that the physical origin of the valley splitting results from the coupling of valley generated states due to the breakdown of the translational symmetry and the resultant momentum dispersion of electrons. The energy of the valley splitting at both a conventional silicon metal-oxide-semiconductor (MOS) and a Si/SiGe interface is typically several hundred microelectron volts20–29, and its magnitude can be tuned by controlling the gate electric field. Recently, an anomalously large valley splitting of a few tens of microelectron volts has been reported using a specially prepared Si/SiO₂ interface formed on SIMOX (separation by implantation of oxygen) silicon on an insulator (SOI) substrate and a large gate electric field17,18, suggesting a large momentum dispersion of the conductive electrons. Since such a large energy of the valley splitting is comparable to that of dopant impurities, we expect that these electrons can be directly dipole-coupled to holes, thereby emitting photons efficiently. However, it is not easy for such electrons to couple with holes at the interface since the large electric field makes them separate in real space. In this study we try to solve this problem by using thin silicon quantum wells (QWs) to confine both electrons and holes so that their spatial overlap is significant even in a high field, thus making it possible to maintain a large overlap in both momentum and real space.

In the present work, we form a thin silicon gated p-i-n MOS diode on a SIMOX wafer (Fig. 1(b)). The front-gate oxide (FOX) is formed by conventional thermal oxidation. The main difference between our devices and typical ultra-thin MOSFETs is the use of buried oxide (BOX), which is formed by employing high temperature thermal treatment followed by oxygen ion implantation. This treatment causes large valley splitting when electrons distribute at the BOX interface. The width and length of the gate is 200 and 400 μm, respectively. The thicknesses of the QWs are 4.3 and 6.0 nm. (Further details about device fabrication are provided in the Method section.) We find that the silicon QW diode exhibits strong and electrically-tuned direct optical transition, which would assist the development of CMOS-compatible silicon photonics36–38.
Results
First, we investigated valley splitting under unipolar conditions where only n+ contacts are used to measure the electron conduction, with reference to a previous experiment. Figure 2 shows the drain current (I_D) and its second derivative (d^2I_D/dV_FG^2) as a function of V_FG and V_BG. The bright diagonal line in the d^2I_D/dV_FG^2 panel indicates the onset of current conduction through electron ground states in the QW. For a positive V_BG value, another line structure appears at a different angle; the structure was previously studied in detail including the Shubnikov-de Haas oscillation of 2DESs under a magnetic field. From the appearance of periodic Shubnikov-de Haas oscillation and the valley degeneracy estimated by both the carrier density and two dimensional density of state, it was identified as a valley excited state arising from anomalous large valley splitting. Although there can be several possible origins for a strong NP transition such as interface states that may exist at the special interface, which will be discussed later in more detail, we believe that one probable origin of this strong NP transition is the large valley splitting. Although there can be several possible origins for a strong NP transition such as interface states that may exist at the special interface, which will be discussed later in more detail, we believe that one probable origin of this strong NP transition is the large valley splitting.

Figure 4(a) shows the TO and NP peak energies as a function of V_BG. The energy of the Stark shift is calculated using

\[ \Psi_{\alpha} = \frac{1}{\sqrt{2}} (\pm \varphi_{\alpha}) \]

where \( \varphi_{\alpha} \) and \( \varphi_{\pm} \) are the longitudinal and transverse effective mass of the conduction electrons, respectively. Valley splitting \( \Delta \) is defined in the bottom right schematic, where the Fermi surface of contact is shown as an orange line that aligns with the antibonding state (fully valley polarized). The valley splitting energy is 21 meV at V_BG = 1.06 V where the electron density is approximately 1.7 x 10^{12} cm^{-2}. For a negative V_BG value, another line structure appears at a different angle; the structure was previously studied in detail including the Shubnikov-de Haas oscillation of 2DESs under a magnetic field.

We then tested diode operation with n+ and p+ contacts and found that the diode current also has a valley-related signature (its derivative is shown in Fig. 3(a)). The onset of valley splitting is shifted slightly toward negative V_FG and V_BG values due to the bias applied to the n+ contact, but the features in Fig. 2(b) are consistently reproduced (see also Supplementary Information Sec. II-A). The appearance of valley splitting in Ipn indicates that electron mobility still has a significant effect on the bipolar current. The electroluminescence (EL) spectra taken along the constant V_BG value in Fig. 3(a) are plotted in Fig. 3(b). The spectra are mainly dominated by three features arising from the origin of their recombination. For a high negative or positive V_FG value, an impurity recombination accompanied by transverse or longitudinal optical (TO/LO) phonons (\( B^{TO/LO} \) or \( B^{LO/TO} \)) (~1.06 eV) at heavily doped contacts dominates the spectra. For a specific V_BG value, two other peaks develop. When we take these peak energies with an energy separation of ~59 meV, and the rearrangement of ground states by quantum confinement into consideration, these two peaks are assigned as a transverse optical (TO) phonon mediated free-exciton (\( T^0 \)) emission and a non-phonon (NP) free-exciton (\( T^0 \)) emission, respectively. For these gate-biases, electrons and holes recombine within an undoped QW and their EL intensity maintains a high value although Ipn is rather small. To focus on the light emission from the undoped QW channel, the EL spectra taken along the current minima, which correspond to the broken red line in Fig. 3(a), are plotted in Fig. 3(c). There is a noticeable change in the EL spectra from a negative to positive V_BG value; the peak intensity of the NP emission is small for a negative V_BG but it gradually increases from almost zero to a large positive value. The intensity of the NP peak strongly depends on V_BG and develops greatly with a positive V_BG value. Since large valley splitting appears for a positive V_BG value and its magnitude increases as V_BG increases, these results clearly indicate that a direct-indirect optical transition can be tuned by changing the gate electric field and the tunability strongly correlates with the magnitude of the valley splitting. Although there can be several possible origins for a strong NP transition such as interface states that may exist at the special interface, which will be discussed later in more detail, we believe that one probable origin of this strong NP transition is the valley-coupled state we observed in the conduction measurement, which exhibits a large valley splitting energy as impurity states do.

Figure 4(a) shows the TO and NP peak energies as a function of V_BG. The energies show an almost quadratic dependence, indicating the occurrence of a quantum confined Stark shift (Supplementary Information Sec. II-C). The observation of the quantum confined Stark shift indicates that the emission peaks are related to the confined state in the QW. The energy of the Stark shift is calculated using a single-valley effective mass approximation and plotted as a dotted line in Fig. 4(a). It should be noted that there is slight asymmetry for V_BG. We believe that this asymmetry is a result of the large valley splitting for a positive V_BG. Since valley splitting for V_BG < 0 is negligible, we can fit the energy differences as \( \alpha = \frac{E}{V_{BG}^2} \), where \( \alpha \) is a constant. In contrast, for V_BG > 0 the valley splitting is
significant. Thus it is fitted by $\delta E = \alpha V_{BG}^2 - \Delta$ and we estimate the valley splitting energy, $2\Delta$. In Fig. 4(b), the valley splitting estimated from these EL peak positions is plotted with that estimated from electrically measured data (Fig. 2(b)). They show fairly good agreement, thereby supporting our interpretation that NP transitions are mediated by the ground state of valley coupled states. Additionally, we can estimate the electric field in a QW and splitting coefficient $\gamma$ (unit in Coulomb/m) supposing a linear relation of $2\Delta = \gamma F$, where $\Delta$ is half of the valley splitting in electron volts and $F$ is the effective field for the electrons. Coefficient $\gamma$ is approximately $10^{-9}$ for BOX interfaces (Supplementary information Sec. II-C). Meanwhile, it is $2.6 \times 10^{-11}$ for the standard Si/SiO$_2$ interface in bulk MOSFETs.

To discuss the enhancement of the direct optical transition qualitatively, we plot the integrated EL intensities divided by the injection current in Fig. 5(a). The NP intensities increase with increasing positive $V_{BG}$ value and its intensity in a thinner QW is higher than that in a thicker one. Since the increase is observed only for a positive $V_{BG}$ value, we consider it to be a consequence of the large valley coupling. The larger enhancement in a thinner QW is probably due to the stronger confinement. At $V_{BG} = 80$ V, the efficiency of a NP direct transition was 16 times greater than that of a bulk indirect TO transition. In Fig. 5(b), intensity ratio $I_{NP}/I_{TO}$ is plotted for a given $V_{BG}$ value. The $I_{NP}/I_{TO}$ ratio increased by a factor of 4 at $V_{BG} = 80$ V, indicating that NP transition is now the dominant recombination, where the direct NP transition rate is 800 times greater than that under a bulk condition. We here compare our results with impurity-based luminescence in silicon. Bi in silicon has an activation energy of 71 meV and the energy splitting between the ground 1s (A$_v$) and the excited 1s (T$_v$) state is 39 meV. In Bi doped silicon, the dominant radiative process is recombination through the exciton bound at neutralized donor BiX and its NP to TO ratio BiX$^{NP}$/BiX$^{TO}$ reaches two$^{45}$, which is comparable to the value in our experiment.

To explain our experimental results semi-quantitatively based on the 2DES model, we calculated the NP emission rate based on an electric breakthrough model derived from an extended zone effective mass (EM) theory$^{19-21}$. It is known that this EM model provides similar results to other theories$^{25-27,29}$. The electric field dependence of valley splitting in the model is explained by the following

$$\Delta \sim \frac{\alpha}{2} \int |\frac{d}{dz} e^{-2ik_{z}z}| |\Psi_{a}(z)|^2$$

(1)

**Figure 2** | Transport measurements of valley splitting. (a) Drain current $I_{Dn}$ through an electron channel as a function of $V_{FG}$ at $T = 4.5$ K for $t_{SOI} = 6$ nm. In this measurement, only n-type contacts are used and constant drain voltage $V_D$ of 5 mV is applied. The arrows indicate the onset of current conduction though the valley antibonding state, which corresponds to the bright upper line for $V_{BG} > 0$ in Fig. 2(b). The second dip (without arrows) is caused by the onset of current conduction through the other (front-gate) side channel. (b) The doubly differentiated drain current with respect to $V_{FG}$. The axes are adjusted to fit the diagonal line on the threshold of current conduction taking into account the size of the BG and FG capacitance. For a positive $V_{BG}$ value, the onset of conduction appears as a bright diagonal line that deviates slightly from the expected line because of an artifact caused by taking the second derivative. Another bright line, which corresponds to the arrows in Fig. 2(a), for a positive $V_{BG}$ value arises from the level coincidence between the source Fermi surface and the antibonding state.

**Figure 3** | Transport measurements and EL spectra under bipolar operation. (a) The first derivative of current through n- and p-type contacts with respect to $V_{FG}$ for $t_{SOI} = 6$ nm. Constant diode bias for n- and p-type contacts of $V_{Sn} = -1.5$ V and $V_{Sp} = 2.5$ V are applied, respectively. Carrier density and valley splitting are adjusted by using the front and back gates. The broken red and solid purple lines indicate the current minima and provide an eye guide for the antibonding state of the valley coupled states, respectively. (b) Injection current through n- and p-type contacts, $I_{pn}$, as a function of front-gate voltage $V_{FG}$ at $V_{BG} = 40$ V. Simultaneously obtained EL spectra are also shown on the right, where the integration time of each spectrum is 10 s. (c) EL spectra given by the bias conditions slightly shifted from the broken red line in Fig. 3(a). The energy differences between the NP and TO peaks at a given $V_{BG}$ value are consistent with the TO phonon energy in silicon ($\sim 58$ meV).
where $E_F$ is the energy difference between the $\Gamma_{15}$ and $\Gamma_{15}^{\ast}$ states, $k_0$ is a wavevector for conduction minima, and $\xi_{el}(z)$ is an electron envelope function. This equation well reproduces the valley splitting observed in standard MOSFETs and its linear dependence on the electric field (Supplementary Information Sec. II-D). If we use eq. (1) for a silicon standard MOSFETs and its linear dependence on the electric field, the large valley splitting is also proportional to the electric field.

The second part of eq. (2) extracts the $k_0$ component of the Fourier coefficient for a multiple product of electron and hole envelope functions and is a function of the gate field. This part is closely related to the valley splitting described by eq. (1) because it extracts its $2k_0$ component as the squared product of the electron envelope function. In a usual envelope function (without singularity), the amplitude of the $k_0$ component in regard to the Fourier coefficient follows that of $2k_0$. Accordingly, if the QW is sufficiently thin, eq. (2) correlates closely with eq. (1). Therefore, we can expect that the NP transition increases according to the increase in the valley splitting.

The intensity of an indirect TO phonon mediated transition ($I_{TO}$) is proportional to the square of the overlap integral of the electron and hole envelope functions $\left| \int dz \xi_{hh}(z) \xi_{el}(z) \right|^2$. Therefore, the intensity ratio $I_{NP}/I_{TO}$ is given by

$$I_{NP}/I_{TO} \propto \left| \int dz e^{-ik_0z} \xi_{hh}(z) \xi_{el}(z) \right|^2 \left| \int dz \xi_{hh}(z) \xi_{el}(z) \right|^2$$

The field dependence of eq. (3) is plotted as a line in Fig. 5(b), where we subtract a constant offset to compensate for the enlarged zero-field valley splitting (residual product that appears due to the introduction of the proportional factor in eq.(2), see also Supplementary Information Sec. II-D). Although our 2DES model might be rather phenomenological due to a lack of the identification in regard to the large valley coupling, the tendency of $I_{NP}/I_{TO}$ agrees reasonably well with the experiment. Further application of the field finally results in a decrease in the $I_{NP}/I_{TO}$ ratio due to the separation of the envelope functions but it might be possible to overcome this by using much thinner QWs (Supplementary Information Fig. S6).

**Discussion**

We discuss here another possible origin of the observed strong NP transition such as quantum dots (QDs) formed by the interface roughness and interface states.
First we deduced the QD model as a cause of strong NP transitions. The roughness of the BOX/Si interface is much higher than that for FOX/Si, whose potential variation could localize electrons and thereby form QDs at the BOX/Si interface for positive V_{BG} values. These QDs may cause strong NP transitions owing to the carrier confinement. In this case, however, a strong NP transition should also be observed for negative V_{BG} values because the holes can also be localized by potential variations, the absence of such behaviour in the experiment suggests a low probability for this cause.

Electrons trapped at the interface states represent another possible origin, where the strong light emission is attributed to the interface states\(^5\). The reported emission energy is approximately 1.6 eV and is not similar to our case. Though in our case the interface states, whose energy is similar to that of the confined electron state in the QW, may play a role because the emission energies follow the quantum confined Stark shift. Further study will be needed to address the cause of strong NP transitions at the BOX/Si interface using other methods such as C-V measurement\(^6\).

If our conductive-electron model is correct, the question is what causes the large valley coupling. It is not clear as noted before, but it would be reasonable to speculate that atomic-scale scattering centers located at the interface, which may be formed by interface imperfection or strain, are the cause. Their rapidly varying potential significantly changes the electron wavefunction and causes the large valley splitting.

We have shown the enhancement of a NP optical transition by using strong valley coupling and shown its electric field dependence in silicon. The NP direct optical transition intensity can be electrically tuned to make it three orders of magnitude greater than under a bulk condition. A simple model based on the effective-mass theory can explain the results qualitatively, and the model highlights the bulk condition. A simple model based on the effective-mass theory can explain the results qualitatively, and the model highlights the strong correlation between the valley coupling and the direct optical transition. Further study will be needed to address the cause of strong NP transitions at the BOX/Si interface using other methods such as C-V measurement\(^6\).

### Methods

**Device fabrication.** The SOI-MOSFETs used in the experiments were fabricated on SIMOX (separation by implantation of oxygen) (001) wafer\(^7\) annealed at 1350°C for 40 hours to minimize the influence of interfacial roughness at the Si and buried oxide (BOX) interface\(^8\). The SOI layer was then thinned by using thermal oxidation and etching with dilute hydrofluoric acid solution. This was followed by dry gate oxidation at 700°C and etching to define the device geometry. Two SOI thicknesses (t_{SOI}, namely 4.3 and 6 nm (measured by ellipsometry), were prepared. Front poly-Si gates were then formed to define the channel width and length. Then heavily doped n- and p-type contacts were formed by phosphorous and boron implantation. Finally, the devices were annealed in a hydrogen atmosphere to activate the dopants. The nominal thicknesses of the front-gate oxide (t_{ox}) and the buried oxide (t_{BOX}) were approximately 20 and 400 nm, respectively.

1. Canham, L. T. Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers. Appl. Phys. Lett. 57, 1046–1048 (1990).
2. Cullis, A. G. & Canham, L. T. Visible light emission due to quantum size effects in highly porous crystalline silicon. Nature 353, 335–338 (1991).
3. Wilson, W. L., Szaif, P. F. & Brus, L. E. Quantum confinement in size-selected surface-oxidized silicon nanocrystals. Science 262, 1242–1244 (1993).
4. Lu, Z. H., Lockwood, D. J. & Baribeau, J.-M. Quantum confinement and light emission in SiO_{2}/Si superlattices. Nature 378, 258–260 (1995).
5. Pavesi, L. et al. Optical gain in silicon nanocrystals. Nature 408, 440–444 (2000).
6. Takeoka, S., Fujii, M. & Hayashi, S. Size-dependent photoluminescence from surface-oxidized Si nanocrystals in a weak confinement regime. Phys. Rev. B 62, 16802 (2000).
7. Liu, J. et al. Ge-on-Si laser operating at room temperature. Optics Lett. 35, 679–681 (2010).
8. Zheng, B. et al. Room-temperature sharp line electroluminescence at $\lambda = 1.54 \mu m$ from an erbium-doped silicon light-emitting diode. Appl. Phys. Lett. 86, 2842–2844 (2005).
9. Peng, X.-H. et al. Strain-engineered photoluminescence of SiGe nanoclusters. Phys. Rev. B 74, 035339 (2006).
10. Weber, J. & Alonso, M. I. Near-band-gap photoluminescence of Si-Ge alloys. Phys. Rev. B 40, 5683 (1989).
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Author contributions

J.N. designed and planned the experiments, fabricated the devices, and collected and analyzed the data. K.N. supported the device fabrication. A.F. planned and supervised the study. J.N. and A.F. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Additional information

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