Local excitons in silicon induced by SiGe quantum huts

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Abstract

Embedment of suitable sized quantum dots into silicon matrix may be exploited to convert silicon to a direct bandgap semiconductor. The outstanding problem is the identification of local excitons, a signature of direct bandgap property and their comportment within the dots that can be utilized in engineering optoelectronic devices, quantum communications, etc. Here, we show that element specificity and surface sensitivity of the core-level photoemission spectroscopy (CoLePES) can be exploited to probe local excitons directly. We engineered self-protected inverted SiGe quantum huts (IQHs) embedded epitaxially in Si(001) matrix and discover NEW features in Ge 3d core level spectra at lower binding energy side of the main peak instead of usual observation of satellites at the higher binding energy side. Energy of these features depends on core hole screening by the excitons located at different parts of IQHs. To our knowledge, this is the first observation of core level features due to excitons. This discovery reveals two phenomena: IQHs contain local excitons necessary for type I photoluminescence and CoLePES is a direct probe of local excitons. We believe that these discoveries will help amalgamation of microelectronics and solid state photonics important for optoelectronic applications.
Silicon, an indirect bandgap semiconductor, is a poor optical material requiring phonon assistance for electronic transitions. Nanostructure embedding in Si is being exploited to engineer high-speed low-power optical output devices, lasers, electro-optic modulators, etc., where the photoluminescence yield is comparable to the direct bandgap quantum dots. Recent experiments show carrier multiplication efficiency of 190% in germanium nanocrystal of 5-6 nm size and quantum-confined exciton induced strong Stark effect in thin germanium quantum-well on silicon. However, the strain at the Si/Ge interface generally gives rise to type-II band alignment exhibiting power law dependence (exponent = 0.7 - 1.5) of photoluminescence energy making it an inefficient optical material. A density functional theoretical study shows signature of direct band gap in Ge quantum structure grown on Si(001) and Si(111) crystals, while the indirect bandgap survives for Si(110) substrate. Moreover, incorporation of Ge into Si matrix enhances hole mobility and photoluminescence emission near 1.5 µm region. Thus, SiGe quantum structures embedded in Si seems a promising candidate for optoelectronic applications.

In order to address the outstanding issue of the behaviour of excitons, we employed core level photoemission spectroscopy (CoLePES), where incident photons excite core electrons at a fast time scale (∼ attosecond range) revealing the element specific local electronic structure. Small escape depth of the photoelectrons makes the technique surface sensitive. We have exploited these features to build a platform for studying the behaviour of excitons located at different parts of the Si/Ge quantum structures. The sample, Ge quantum structures [13.3nm (base) × 6.6nm (depth)] were grown on a Si buffer layer deposited on Si(001) surface using molecular beam epitaxy. A wetting layer of 1.1nm thick Ge was grown on top as shown in the high resolution cross-sectional transmission electron microscopy (XTEM) image in Fig. (a) and Fig. (b). The quantum structures possess inverted hut shape (called inverted quantum huts, IQHs) and are self-protected without capping layer unlike conventional systems. The sample surface was prepared in the ultra-high vacuum via controlled sputtering with low energy Ar ions and annealed subsequently at 400 °C. The exposed surfaces studied are denoted by s10, s17, s42, s72 and s100 corresponding to the wetting later (depth = 0), base region (depth 1.1 nm), mid region (depth 2.7 nm), mid region (depth 4.7 nm) and tip of IQHs (depth 6.6 nm), respectively as shown in Fig. (b).

Si 2p and Ge 3d core level spectra exhibit significantly different peak positions in the
FIG. 1. (a) XTEM image of Si/Ge quantum structure; dark and grey colours represent Ge and Si atoms, respectively. (b) High resolution XTEM image of the boxed region in (a). The horizontal lines represent the exposed surface after sputter anneal cycle; ‘s10(WL)’ refers to 10 minutes sputtered surface revealing the wetting layer (WL). At s17, s42, s72 and s100, the exposed surfaces are the base region (depth 1.1 nm), mid region (depth 2.7 nm), mid region (depth 4.7 nm) and tip of IQHs (depth 6.6 nm), respectively. (c) Si 2\text{p} and (d) Ge 3\text{d} core level spectra. Ge 3\text{d} spectra reveal mysterious new features in energy range 21-28 eV. The inset shows the energy shift of the Ge 3d_{5/2} (open symbols) and Si 2p_{3/2} (solid symbols) peaks at different locations of the quantum huts relative to s10 peaks.

spectra from different locations as shown in Fig. 1. The energy shift in Si 2p spectra can be understood as follows. There are two types of Si - (i) Si(1) (no Ge neighbour) and (ii) Si(2) (Si in SiGe alloys of IQHs). The shift to lower binding energies (decrease in local potential due to hybridization with Ge [18, 20]) indicates contribution from Si(2). The shift to higher
binding energies at s17 and s100 indicates large contribution from Si(1) as expected after removal of wetting layer and the IQHs, respectively. The Ge 3d peak, however, shifts by 200 meV towards higher binding energies from s10 to s17 whereas Si 2p shifts by 50 meV. The shift in the same direction indicates Fermi level shift. Ge 3d peak position remains almost unchanged at higher depth. The enhancement of Si 2p-Ge 3d energy separation indicates charge transfer between them due to variation of the relative concentration of Si/Ge [15, 21].

In addition, we discover new features at the lower binding energy side (21-28 eV) of Ge 3d bulk peaks. The intensity of the features strongly depends on the location in the IQH structure and cannot be associated to impurities for the following reason. Bonding with carbon and/or oxygen (electronegative) leads to enhancement in binding energy as observed earlier; the Ge 3d peaks in GeOx appear at higher binding energies [22]. Our detailed characterization of the samples including elemental analysis does not show signature of impurity in the system. Photoemission spectroscopy being a highly surface sensitive technique, captures weak intensities due to adsorption of impurities on aging [23]. While weak intensity at 31.5 eV in Ge 3d spectrum of s10 show signature of some surface oxygen, no such peak is present in other spectra having intense new features.

We simulated the experimental spectra to find the constituent features using least square error method following the selection and conservation rules associated to photoemission process. Si 2p spectra could be simulated using two peaks representing spin-orbit split 2p3/2 and 2p1/2 signals with a spin-orbit splitting of 0.63±0.02 eV [24]; a typical result is shown in Fig. 2(a). Fitting results of selected Ge 3d core level spectra are shown in Fig. 2(b)-(d). Intense broad peak at 29 eV consists of Ge 3d5/2 and 3d3/2 signals (spin-orbit splitting of 0.58±0.02 eV) from bulk Ge [25].

The features in 21-28 eV energy range are denoted by A, B, C and D. All the features could be captured well considering peak pairs possessing characteristics of Ge 3d5/2 and 3d3/2 signals. The position and intensities of A, B, C and D of s42 spectrum relative to the bulk Ge 3d peak are shown in Fig. 2(e). A, B, C and D are away from the main peak by about 2.8 eV, 4.6 eV, 6.5 eV and 7.8 eV, respectively. The intensities of the features at different depths from the sample surface are shown in Fig. 2(f). A and D are intense in s10 spectrum (the base region of IQHs). The intensity of A (blue line) and D (black line) exhibit a weak decrease with the increase in depth; intensity of D increases slightly between s10 and s17. Thus, the peaks A and D are attributed to the final states having the origin related to the
FIG. 2. Spectral fitting results of (a) Si 2p of s10, and Ge 3d of (b) s10, (c) s42 & (d) s100 surfaces. Solid line over the data points (symbols) represent the fit and other lines represent the component peaks. Inset in (b) is the expanded view of the low binding energy region. (e) Relative peak positions and intensities of the final state features in Ge 3d spectrum of s42 surface with respect to the 3d signals from Ge bulk. (f) Changes in relative intensities of different Ge 3d low binding energy features with the variation of depth within IQH; colours represent same objects in (e) and (f).

surface and interface of the wetting layer with the Si layers, respectively. The spectra from mid IQH structures are dominated by the contributions from B & C.

The interaction of the Ge 3d hole and valence electrons, termed as core hole screening, leads to multiple features in core level spectrum; well screened feature appear at lower binding energy relative to the poorly screened ones. The well screened features related to Zhang-Rice signlet, where the electron screening the core hole has formed a bound state with a carrier at the neighbouring site appear at even lower binding energies in the CoLePES
FIG. 3. Schematic of the core hole screening process by excitons. Few atoms are shown in each unit cell for clear visualisation of the process. Green and violate colours represent Si atoms and Ge atoms respectively and glow around the atoms represent corresponding electron clouds. Elongated red coloured glows represent excitons in the system.

spectra due to additional stabilization \[26, 28\]. In the present case, core hole screening comes from the excitons \[15, 16\], which are bound electron-hole pair and hence, the final states are expected to be better stabilized. The scenario is demonstrated in Fig. 3 where Ge 3$d$ core hole (black dot) forms at \((0.25, 0.25, 0.25)\) and excitons \((X_0\): electron-hole bound pair) are shown by red glow. In Figs. 3(a), the exciton is not located at the photoemission site and hence the signal corresponds to the bulk feature. The exciton in 3(b) screens the core hole. It has been observed that excitons in Ge QDs have lower binding energy than the excitons in similarly shaped & sized Si QDs \[29\] due to the lower bandgap. Therefore, the excitons associated with more numbers of Si atoms will be more strongly bound and the core hole screened state will be better stabilized. Thus, the corresponding photoemission feature will appear at the lowest binding energy, which is feature D. It is clear that the binding energies of various photoemission final states would be related to the number of Ge/Si atoms bonded to the Ge at the photoemission site as shown in Figs. 3(c-f). The mid region of IQH can be represented by the arrangements of Fig. 3(c) and Fig. 3(d), providing the features 'C' and 'B', respectively. Ge wet layer has atomic arrangement of the type shown in Fig. 3(e) having more Ge neighbours and can be associated with the feature 'A' in Ge 3$d$ spectra.
The scenario of Fig. 3(f) is similar to bulk Ge and is less probable to find in our sample as supported by the observed compositional analysis of those IQHs [15]. These descriptions beautifully match with the experimental observations.

The discovery of the distinct features due to core hole screening by excitons takes the core level spectroscopy a leap forward, and the element specificity and surface sensitivity of CoLePES makes it a powerful direct probe for local excitons. The finding of local excitons in the inverted quantum huts embedded in Si-matrix are consistent with the type I photoluminescence [16] and establish their candidature to engineer devices for optoelectronic applications and quantum communications.

METHODS

We have grown Ge quantum structures on a Si buffer layer prepared on Si(001) surface using molecular beam epitaxy, where the Ge atoms diffuse into the Si buffer layer. Quantum dots are usually prepared employing Stranski-Krastanov (S-K) mode-based epitaxial growth of self-assembled nanostructures, where the three dimensional islands are formed at the surface/interface followed by two dimensional wetting layer (WL) growth for II-V, III-IV and IV-IV semiconductor materials. Instead, here, Ge atoms diffuse into the underneath Si buffer layer grown on the substrate at temperatures of about 430 °C and form special type of self-protected IQHs [15, 16]; IQHs of much bigger size (75nm base and 21nm height) are reported to form at lower growth temperatures [30]. The high resolution XTEM (cross sectional tunneling electron microscopy) image shown in Fig. 1(b) exhibits a dimension of 13.3 nm (base) × 6.6 nm (depth) with sharp boundary; the confined volume significantly smaller than the previously reported SiGe IQHs [15, 16, 30]. The irony of this system is the self-protection of the quantum structures; no capping layer is needed to protect the quantum structures from external environment unlike the conventional quantum dot systems [17].

The sample preparation procedure is as follows. Si (001) wafer was cleaned by removing the unwanted oxide layer, inorganic and organic contaminations following RCA cleaning method, which was followed by HF etching of top oxide layer on wafer. Immediately after the cleaning, the wafer was mounted in the load-lock chamber of molecular beam epitaxy (MBE) machine and shifted to preparation chamber where the base vacuum was maintained close to 1×10^{-11} Torr. In the preparation chamber, the wafer was kept at 900 °C for 20
hours to remove further oxide layer grown on it during sample transfer through load-lock system. Later it had been transferred to ultra-high vacuum (UHV) growth chamber (base pressure around $10^{-11}$ Torr) and heated up to 1100 °C with a continuous flow of liquid N$_2$ to maintain the pressure, which opened up the dangling bonds of the top surface silicon atoms and provided the platform for epitaxial growth of Si and Ge layers on the surface. Subsequently, we have grown 100nm thick Si buffer layer at 750 °C. This was followed by successive growth of 1.7nm Ge, 8nm Si and again 1.7nm Ge with deposition rate of 0.3 Å/sec at 430 °C. A wetting layer of 1.1nm thick Ge was deposited on top of the system. The high resolution XTEM image of the quantum structures prepared are shown in Fig. 1(a) and Fig. 1(b) exhibiting hut shape with their apex towards the substrate and hence, are called inverted quantum huts, (IQHs). Although Ge quantum dot growth are normally followed by Si capped layer to protect the nanostructures underneath, here no cap layer had been deposited as it had been observed that SiGe quantum nanostructures are grown inverted with their apex towards Si substrate under this typical growth parameters, which ensures that they are self-protected quantum structures.

Photoemission measurements were carried out using a Gammadata Scienta R4000 WAL analyzer and monochromatic Al Kα source at an energy resolution of 350 meV. All the measurements were carried out at temperature 20K achieved by using an open cycle helium cryostat from Advance Research Systems. We exposed different parts of the IQH structures using controlled sputtering and identified the exposed surface by XTEM, EDX (energy dispersive analysis of x-rays) and SIMS (secondary ion mass spectrometry). In Fig. 1(b), we show various surface terminations studied. For example, ‘s10(WL)’ refers to 10 minutes sputtered surface revealing the wetting layer (WL). At s17, the base region of the IQHs is exposed (depth 1.1 nm). s42 and s72 are the mid regions of the IQHs having depth of 2.7 nm and 4.7 nm, respectively; these two regions expose the SiGe alloy within IQHs and the side interfaces between Si and IQHs. At s100, the tip of IQHs (depth of 6.6 nm) becomes visible.

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[1] Saito, H., Nishi, K. & Sugou, S., Influence of GaAs capping on the optical properties of
InGaAs/GaAs surface quantum dots with 1.5 µm emission. *Appl. Phys. Lett.*, 73, 2742 (1998).

[2] Priolo, F., Gregorkiewicz, T., Galli, M. & Krauss, T. F., Silicon nanostructures for photonics and photovoltaics. *Nature nanotechnology*, 9(1), 19-32 (2014).

[3] Cho, H., Kapur, P. & Saraswat, K. C., Power comparison between high-speed electrical and optical interconnects for interchip communication. *Journal of Lightwave Technology*, 22(9), 2021 (2004).

[4] Rong, H., Liu, A., Jones, R. & Cohen, O., An all silicon Raman laser. *Nature* 433, 292-294 (2005).

[5] Xu, Q., Schmidt, B., Pradhan, S. & Lipson, M., Micrometer-scale silicon electro-optic modulator. *Nature* 435(7040), 325 (2005).

[6] Cao, L., Fan, P., Barnard, E. S., Brown, A. M. & Brongersma, M. L., Tuning the color of silicon nanostructures. *Nano letters*, 10(7), 2649-2654 (2010).

[7] Saeed, S. *et al.*, Carrier multiplication in germanium nanocrystals. *Light: Science and Applications*, 4(2), e251 (2015).

[8] Kuo, Y. H., Lee, Y. K., Ge, Y. & Shen, R., Strong quantum-confined Stark effect in germanium quantum-well structures on silicon. *Nature*, 437(7063), 1334 (2005).

[9] Kurdi, M. E., Sauvage, S., Fishman, G. & Boucaud, P., Band-edge alignment of SiGe/Si quantum wells and SiGe/Si self-assembled islands. *Phys. Rev. B*, 73(19), 195327 (2006).

[10] Kholod, A. N., Saúl, A., Fuhr, J. D., Borisenko, V. E. & d’Avitaya, F. A., Electronic properties of germanium quantum films. *Phys. Rev. B*, 62(19), 12949 (2000).

[11] Wang, P. J., Meyerson, B. S., Fang, F. F., Nocera, J. & Parker, B., High hole mobility in Si/Si_{1−x}Ge_{x}/Si p-type modulation-doped double heterostructures. *Appl. Phys. Lett.*, 55, 2333 (1989).

[12] Süess, M. J. *et al.*, Analysis of enhanced light emission from highly strained germanium microbridges. *Nature Photonics*, 7, 466-472 (2013).

[13] Koch, S. W., Kira, M., Khitrova, G. & Gibbs, H. M., Semiconductor excitons in new light. *Nature materials*, 5(7), 523 (2006).

[14] Maiti, K. *et al.*, Understanding the bulk electronic structure of Ca_{1−x}Sr_{x}VO_{3}. *Phys. Rev. B*, 73, 052508 (2006).

[15] Sharma, M., Sanyal, M. K., Satpati, B., Seeck, Oliver H. & Ray, Samit K. Anomalous x-ray
scattering study of the growth of inverted quantum hut structures in a Si-Ge superlattice emitting strong photoluminescence. Phys. Rev. B 89, 205304 (2014).

[16] Sharma M., Sanyal M. K., Katiyar A. & Ray S. K., Excitation power-independent photoluminescence of inverted quantum hut structures embedded in SiGe superlattice. Appl. Phys. A, 119, 55-60 (2015).

[17] Brunner, K., Si/Ge nanostructures. Reports on Progress in Physics, 65(1), 27 (2001).

[18] Evjen, H. M., On the stability of certain heteropolar crystals. Phys. Rev., 39(4), 675 (1932).

[19] Maiti, K., Mahadevan, P. & Sarma, D. D. Evolution of electronic structure with dimensionality in divalent nickelates. Phys. Rev. B 59, 12457 (1999).

[20] Maiti, K. et al., Doping dependence of the chemical potential and surface electronic structure in YBa2Cu3O6+x and La2−xSrxCuO4 using hard x-ray photoemission spectroscopy. Phys. Rev. B 80, 165132 (2009).

[21] Agarwal, A., Patterson, J. K., Greene, J. E. & Rockett, A., Ultraviolet ozone induced oxidation of epitaxial Si1−xGex(111). Appl. Phys. Lett., 63, 518 (1993).

[22] LeGoues, F. K., Rosenberg, R., Nguyen, T., Himpsel, F. & Meyerson, B. S., Oxidation studies of SiGe. J. Appl. Phys., 65(4), pp.1724-1728 (1989).

[23] Biswas, D., Thakur, S., Ali, K., Balakrishnan, G. & Maiti, K. Anomalies of a topologically ordered surface. Sci. Rep., 5, 10260 (2015).

[24] Schmeisser, D. et al., Surface oxidation states of germanium. Surface science, 172(2), 455-465 (1986).

[25] Hollinger, G. & Himpsel, F. J., Probing the transition layer at the SiO2/Si interface using core level photoemission. Appl. Phys. Lett., 44(1), 93-95 (1984).

[26] Zhang, F.C. & Rice, T.M., Effective Hamiltonian for the superconducting Cu oxides. Phys. Rev. B 37, 3759(R) (1988).

[27] van Veenendaal M. A., Eskes H., & Sawatzky G. A., Strong nonlocal contributions to Cu 2p photoelectron spectroscopy. Phys. Rev. B 47, 11462 (1993).

[28] Böské, T. et al., Cu-O network-dependent core-hole screening in low-dimensional cuprate systems: A high-resolution x-ray photoemission study. Phys. Rev. B 57, 138 (1998).

[29] Takagahara, T. & Takeda, K., Theory of the quantum confinement effect on excitons in quantum dots of indirect-gap materials. Physical Review B, 46,(23), p.15578 (1992).

[30] Soo, Y. L. et al., “Inverted hut structure of SiGe nanocrystals studied by extended x-ray
absorption fine structure method. Appl. Phys. Lett., 78(23), 3684-3686 (2001).

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AUTHOR CONTRIBUTIONS

K.M. and M.K.S. conceived the project. A.B.D. prepared the sample under the supervision of M.K.S. Photoemission measurements were carried out by A.B.D., S.P., K.A., D.B. and S.T. under the supervision of K.M. Data analysis and manuscript preparation were done by A.B.D. and K.M. All the authors read the manuscript and provided their comments.

COMPETING FINANCIAL INTERESTS

The authors declare no competing financial interests.