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Surface-state dependent optical properties of OH-, F-, and H-terminated 4H-SiC quantum dots[†]

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Density functional calculations are performed for OH-, F- and H-terminated 4H-SiC 10-20 Å diameter clusters to investigate the effect of surface species upon the optical absorption properties. H-termination results in a pronounced size-dependent quantum-confinement in the absorption, whereas F- and OH-terminations exhibit much reduced size dependent absorption due to surface states. Our findings are in good agreement with recent experimental studies, and are able to explain the little explored dual-feature photoluminescence spectra of SiC quantum dots. We propose that along with controlling the size, suitable surface termination is the key for optimizing optical properties of 4H-SiC quantum structures, such as might be exploited in optoelectronics, photovoltaics and biological applications.

1 Introduction

Spatial confinement of electrons and holes allows the optical properties of quantum dots (QDs) to be significantly changed, with quantum confinement dramatically increasing the energy gap with decreasing dot diameter¹. In recent years, quantum confinement has enabled tuning of absorption and emission properties of different materials over a wide range of the electromagnetic spectrum²⁻¹⁰. Compound semiconductors such as PbS, PbSe, PbTe, ZnO, CdS, CdSe, and CdTe have been widely investigated due to their tunability from infrared to ultraviolet, for use in applications in optoelectronics, photovoltaics, and biology¹¹⁻¹⁶. Whilst QDs hold great potential, their surfaces often introduce undesired electronic states, and given the very high surface-to-volume ratio, these make exploitation of the QDs problematic¹⁷. Control and modification of QD-surfaces is therefore of great importance in order to preserve quantum confinement⁹, and there is some evidence that optical absorption can be significantly enhanced by suitable terminating species^{18,19}. Although both IV-VI and II-VI QDs have shown promising results, their cytotoxicity is a major concern²⁰, and their optical properties have been found to be severely affected by the oxidation²¹.

Because of its wide band-gap, thermal stability, oxidation resilience, chemical inertness and biocompatibility, SiC is a promising QD-material across the range of applications²²⁻²⁴. There

has been significant progress in controlled SiC-QD synthesis, with etching-based methods developed to synthesize QDs from 3C-SiC^{10,25-27}. The most commonly used methods involve anodic electrochemical etching of bulk SiC in an HF/ethanol solution^{25,28} and high temperature etching of SiC powder in HF/HNO₃²³. Both methods yield porous SiC, which is subsequently ultrasonicated in an appropriate solvent (e.g. water or ethanol), and centrifuged to isolate the QDs. The reported diameter of nearly spherical 3C-SiC-QDs thus obtained lies between 10 and 60 Å, with evidence of mixed surface terminations^{25,29,30}. These methods have also been applied to the more commercially relevant 4H- and 6H-polytypes^{28,31}.

SiC-QDs have shown bright photoluminescence (PL), with an impressive quantum yield of ~17%, comparable to that of many direct-band-gap materials²⁴. PL spectra commonly feature peaks over a range of wavelengths, with different peaks depending upon the excitation wavelength^{28,32,33}. High-energy peaks consistently appear at fixed emission wavelengths, independent of excitation wavelength. However, where the excitation wavelength is systematically increased, quantum-confinement renders the optical gap of the smallest SiC-QDs too large for excitation to occur, and with increasing wavelength, SiC-QDs with decreasing size cease to be excited. Thus, the experimental observation of a red-shift in the absorption spectrum with increasing excitation wavelength is taken as evidence of quantum-confinement. Although the reported excitation wavelength at which the confinement effect becomes evident varies, to our knowledge all studies agree on the general appearance of the PL spectra^{28,30,32,34}. In this paper, for brevity, we refer to the existence of two distinct optical signatures as *dual-feature*.

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Additionally, photoluminescence excitation spectroscopy indicates multiple electronic states participating in the optical transitions^{28,30,32,33}. It is also noted that size-dependent quantum-confinement is seen to depend upon the solvents used in the SiC-QD preparation, supporting the view that the surface termination is likely to be important^{29,31,33}.

Density functional theory (DFT) based studies have provided some deep insights into how surface composition and termination play a dominant role in the optical properties of SiC nanostructures (clusters and nanowires)^{35–43}. It was reported that H-terminated SiC-QDs with reconstructions containing Si-Si dimers affects the onset and shape of the absorption spectra for QDs smaller than 30 Å³⁶. Additionally, double bonded oxygen adsorbates tend to lower the energy gap due to highly localized states⁴². There has also been a suggestion that in small tetrahedral H-terminated 3C-SiC clusters, quantum confinement is less important in the lowest unoccupied molecular orbital (LUMO) than the highest occupied molecular orbital (HOMO)⁴⁰.

Oxygen containing species have been examined for 3C-SiC-QDs. For individual carboxylic and anhydride species, DFT suggests the introduction of gap states, so that when present, these groups will be important in SiC-QD PL spectra³⁷. Hydroxyl surface groups have also been studied for 3C-SiC nano-particles and wires, where it is concluded that they reduce the energy gap in comparison to H termination^{38,39}.

Fluorine termination of SiC nanowires has also been analyzed⁴³. This is also predicted to reduce the band-gap relative to hydrogen termination, the effect being ascribed to a difference in electronegativities in the two terminating species.

Of particular note in this study, the interplay between quantum confinement and surface states affecting the resultant energy gap and PL has been reported for porous Si and Si QDs⁴⁴, where a combination of size and termination were found to dictate the recombination mechanism, and this might be expected to be the case for SiC-QDs.

Previous DFT based surface studies have mainly focused on 3C-SiC and have not provided an explicit relationship with the dual-feature PL found in experiments. Here, we present a DFT study into the differences in optical properties predicted for differing chemical terminations that may result during sample preparation.

2 Computational method

Density-functional theory calculations, as implemented within the AIMPRO code^{45,46}, are performed for quasi-spherical SiC-QDs with core diameters varying from 10 to 20 Å. Atoms are modeled using norm-conserving pseudo potentials⁴⁷. Kohn-Sham orbitals are expanded using sets of independent real-space, atom-centered Gaussian basis-sets⁴⁸: for C, O, F, and Si we used sets with four different widths, whereas for H three widths are used. In addition, *d*-Gaussians of 1, 2, 2, and 4 widths are included to account for polarization for O, C, Si and F, respectively.

To construct the SiC-QDs, atoms within some chosen distance of either a Si or C atom in bulk SiC are selected (Si or C centered), and the atoms at the surface saturated by either a H atom, a F atom, or an OH group. This construction generally produces surface Si and C atoms requiring two or three terminating groups. In

the case that three are required, this means that there is a single Si-C bond linking the surface atom to the SiC core, and the surface atom is removed. Where there are two unsaturated bonds, two cases have been examined. The first is where two terminating atoms are added generating, for example, SiH₂ and CH₂ surface groups. Where these surface sites neighbor each other, this saturation results in significant steric repulsion between the terminating species. Therefore where pairs of two-fold bonded surface sites neighbor each other, an alternative is to first form C-C or Si-Si reconstructions, and only saturate the remaining sites. Both full saturation and reconstruction have been examined in this study. For F- and OH-terminated SiC-QDs, where terminating species would be placed within a covalent bond-length, we have also evaluated structures with a small fraction of H-terminating groups to reduce unrealistic steric repulsion.

To take advantage of the accuracy afforded by representation of the charge density in reciprocal space using a plane-wave expansion (Fourier transform), the SiC-QDs are modeled using periodic boundary conditions⁴⁶, with the cut-off in energy is sufficient to converge the energies to within 10 meV. This means that the SiC-QDs are placed in a periodic boundary condition. The lattice constant is chosen to be equal to four times the nominal core diameter to allow for both the surface groups and sufficient vacuum between SiC-QDs to minimize interactions. Once the core has been prepared and the surface groups added, the SiC-QDs are geometrically optimized until atomic forces are smaller than 0.06 eV/Å.

The dielectric function is evaluated from matrix elements of the Kohn-Sham wave functions and energy levels^{49,50} with a polynomial broadening of 0.1 eV, from which the absorption cross-sections (ACS) are obtained. The electronic density of states (DoS) are similarly calculated and aligned to the Fermi energy at zero.

Although underestimation of the energy gap in DFT calculations is well known, the aim of this study is to establish the systematic differences between different surface termination. DFT calculations are well placed to predict these trends^{41,51,52}.

3 Results

3.1 QD structures

We first present data relating to the optimized structures of the SiC-QDs. In this study, the QD size varies between 10–20 Å, the range that exhibits quantum confinement effects⁴¹, since the exciton Bohr radius in 4H-SiC is 12–18 Å^{25,28}. The composition of QDs are included in the electronic supplementary information. Figure 1 shows the 20 Å SiC-QDs, with different centering and surface treatments. The average Si-C, O-H, Si-X, C-X (X=H, O and F in each case), Si-Si and C-C bond lengths in Å are calculated to be 1.87, 1.00, (1.50, 1.64, and 1.59), (1.10, 1.46, and 1.42), 2.39, and 1.60, respectively, all of which lie within the anticipated range for Si and C based single bonds^{42,53}. This provides evidence that the optimized structures have reasonable geometries to represent the near spherical SiC-QDs observed in experiments. We note the calculated bond-lengths vary only very slightly with QD-size.

Fig. 1 Optimized 20 Å SiC-QDs. (a) and (b) are Si-centered, H-terminated SiC-QDs with and without surface reconstructions, respectively. (c) and (d) are C-centered, H-terminated SiC-QDs with and without surface reconstructions, respectively. (e) and (f) are Si-centered SiC-QDs (with surface reconstructions) terminated with OH- and F-groups, respectively. White, red, yellow, gray, and green atoms are H, O, Si, C and F, respectively. The regions indicated by the red and blue ellipses highlight surface sites where the choice of reconstruction or two surface groups varies.

3.2 Effect of surface reconstruction and surface composition

In order to distinguish the effect of surface reconstructions from surface termination, we compare two groups of Si centered H-terminated QDs for the 10 to 20 Å size, where one group includes surface reconstruction.

(a)

(b)

Fig. 2 ACSs for H-terminated Si centered 4H-SiC QDs as a function of core diameter for surfaces that are (a) reconstructed, and (b) not reconstructed. The contours indicate 10^{-7} a.u.² to 10^{-3} a.u.², in factors of 10.

Figure 2 shows the ACS for H-terminated Si centered QDs with and without surface reconstruction. The overall appearance and variation with core diameter is similar, although the onsets, where they differ, are at lower energies where reconstructions are present: the steeper slope (contour) found in reconstructed QDs relative to non-reconstructed for sizes less than 14 Å indicate that surface reconstructions cause greater energy-gap narrowing for small QDs. Additionally, ACS magnitudes near the onsets are larger for the reconstructed QDs.

The ACS show the trends with core diameter, but to understand the origin of the differences it is instructive to examine the DoS. The data for the 20 Å QD is shown in Fig. 3. Of note, the recon-

Fig. 3 Density of states for reconstructed and unreconstructed 20 Å diameter Si centered, H-terminated QD.

structed surface leads to a larger DoS near the HOMO, and this is the origin of the larger ACS. The HOMO of the unreconstructed QD is around 0.2 eV lower in energy, and the LUMO around 0.2 eV higher than the reconstructed case, which explains the lower energy onset in the case of the reconstructed surface.

(a)

(b)

(c)

(d)

Fig. 4 Wave function iso-surfaces for Si centered, H-terminated, 20 Å SiC-QDs. (a) and (c) are HOMOs, and (b) and (d) LUMOs, with (a) and (b) showing the reconstructed surface, and (c) and (d) the non-reconstructed surface. Yellow, gray, and white atoms are Si, C, and H, respectively. The green and blue iso-surfaces show the molecular orbitals of positive and negative phase, with amplitude of $0.04 \text{ a.u.}^{-3/2}$. The clusters are shown with the *c*-axis of the underlying 4H-SiC vertical.

The wave functions for the two surface reconstructions are shown in Fig. 4. The HOMO where reconstruction has occurred (Fig. 4(a)) indicates some localization around the reconstructions, with even more significant localization in the LUMO (Fig. 4(b)). In contrast, the HOMO (Fig. 4(c)) and LUMO (Fig. 4(d)) for the unreconstructed case are distributed throughout the core. This suggests that the homo-nuclear dimers present in reconstructions lead to surface states, narrowing the energy gap. Energy gap narrowing and an increase in absorption due to Si-Si dimers has

been reported previously⁴², with similar conclusions drawn as in the current study. Despite the impact reconstruction has upon the ACS, it is important to note that quantum size effects are observed across the sizes examined in this study irrespective of the reconstruction.

(a)

(b)

Fig. 5 ACSs for H-terminated C-centered 4H-SiC QDs as a function of diameter for surfaces that are (a) reconstructed, and (b) not reconstructed. The contours indicate 10^{-7} a.u.² to 10^{-3} a.u.², in factors of 10.

Previous reports^{39,40} suggested that energy-gap changes relate to a shifting HOMO while the LUMO remains constant with different surface terminations. However, the influence of dimers in the structures were not investigated in Ref. 39 while in Ref. 40 the LUMO pinning ascribed to nearest-neighbor π and σ^* orbitals may be related to the tetrahedral structures studies, in contrast with our pseudo-spherical models.

Another choice made at the point of construction of the QDs is the species upon which the cluster is centered. Figure 5 show the ACS for C-centered SiC-QDs. The relatively small differences between the Si and C centered structures are most likely a consequence of the differing mixtures of C-H and Si-H bonds at the surface^{40,41}, as previous studies report QDs with Si-H surface bonds

exhibit smaller energy gaps compared to C-H surface^{35,36,42,54}. Although there are minor differences, the overall trends for C-centered SiC-QDs are very close to those of the Si-centered clusters shown in Fig. 2, and we conclude that so far as the optical properties are concerned there is no significant dependence upon the choice of center. Indeed, this is what one might expect since these clusters are of the order of the exciton Bohr radius, so that the states involved in the optical transitions involve all of the Si and C atoms.

However, the role of the hydrogen chosen to terminate the clusters and remove any dangling bonds remains to be analyzed. We now therefore turn to the effect of hydroxyl (OH) and fluorine (F) termination on the same cores as presented above for the hydrogen termination case.

(a)

(b)

Fig. 6 ACSs for (a) OH-terminated and (b) F-terminated, Si centered 4H-SiC QDs by QD diameter. The contours indicate 10^{-7} a.u.² to 10^{-3} a.u.², in factors of 10.

3.2.1 Effect of surface termination groups on optical absorption

Figure 6 shows the ACS for OH- and F-terminated QDs, where all clusters have been reconstructed and are Si centered, and can be compared directly with Fig. 2(a). The effect of OH- and F-termination upon the absorption onset is immediately evident: the differences between, for example, Figure 6(a) and Fig. 2(a) is much larger than the effects of reconstruction or whether the cluster is centered on the Si or C. In particular, the quantum confinement effect appears to increase from hydroxyl, to fluorine, to hydrogen termination, with H-termination showing the clearest size dependence. The absorption onset for the H-termination increases from 2.5 to 4.4 eV with reducing size, a net increase of ~ 2 eV in the 10–20 Å diameter range, whereas for F- and OH-termination, almost no size-dependent change is observed. As a result, for low core diameters there is a large difference in the onset energy as a function of termination, so that for example, in the case of 10 Å SiC-QDs, the difference in onset for the ACS for OH- and H-termination is nearly 2.5 eV.

3.2.2 Effect of surface termination on density of states and associated HOMO and LUMO wave functions

Figure 7 shows the DoS for Si-centered, surface-reconstructed, 20 Å-diameter SiC-QDs terminated by OH, F, and H, with zero energy aligned to the Fermi energy. The major effect of terminating species is variation in the HOMO: OH, F, and H have energies of -0.51 eV, -0.76 eV, and -1.23 eV, respectively. In contrast, the LUMO energies are relatively constant, lying in the 1.0–1.1 eV range.

Fig. 7 DoS of 20 Å, Si-centered QDs in the vicinity of the optical gap.

The difference in the energies of the HOMO is related to the degree of wave function localization at the surface. Figure 8(a) shows the OH-termination HOMO is strongly associated with surface C p -orbitals and oxygen lone-pairs. Similarly, HOMOs of F-terminated clusters are associated with F lone-pairs (Fig. 8(b)), whereas H-termination (Fig. 4(a)) show no such localization. Although the HOMOs are localized on one part of the SiC-QD surfaces in the figure, the surface states associated with the lone-pairs in fact form a band of orbitals that when taken together cover the surfaces. The lone-pair energies are not significantly af-

fected by the core diameter because they are localized on the surface, leading to the relatively weak size dependence in the ACS (Fig. 6). We conclude the insensitivity of optical absorption for OH- and F-terminated SiC-QDs is a reflection of surface states associated with the terminating species.

Fig. 8 HOMOs of the 20 Å, Si-centered SiC-QDs terminated by (a) OH and (b) F. The corresponding H-terminated molecular orbital is shown in Fig. 4(a). Choice of iso-surfaces, the atom colors, and orientation of the SiC-QDs are as indicated in Fig. 4.

3.3 Discussion

Where quantum confinement is present, energies can be predicted following a 'particle in a sphere model'¹, that predicts that they are discrete and scale with the QD diameter, d , as d^{-2} . Figure 9(a) summarises the energy gap of the QDs as a function of the size and terminating species. H-termination results in a large size dependence, whereas F- and OH-termination do not. Figure 9(b) allows for comparison of H-terminated clusters with different compositions, and surface reconstructions, encapsulating the conclusions above that reconstruction and choice of cluster center have no significant impact upon the energy gap relative to the effect of the termination. The energy-gap as a function of size for H-terminated QDs agrees quantitatively with previous DFT results⁴¹, whereas those obtained using tight-binding are systematically larger³⁹, but exhibit the same trend.

However, to understand the size-dependence of SiC-QDs, we need to include all possible configurations of surface states. In a simple model, we consider two factors. The states associated with

Fig. 9 (a) Energy gap versus QD size with different surface termination groups and (b) energy gap of -H terminated QD versus QD size by surface reconstruction and surface composition.

the SiC core exhibiting quantum confinement will result in a narrowing of the optical gap as the core diameter increases. This is represented schematically by the solid lines in Figs. 10(a) and (b). The second component arises from two surface effects. The first is the introduction of states due to homo-nuclear bonds arising from reconstruction. In the case of H-termination, this introduces an unoccupied state below that of the core, as represented by the higher of the dashed lines in Fig. 10(a). This state is relatively independent of core diameter, as it is essentially a surface effect. For a large enough cluster, this surface state is expected to lie outside the core gap, *i.e.* reconstructions impact the optical properties of relatively small SiC-QDs. However, as noted above, at a quantitative level the impact of the reconstruction is relatively modest. For F- and OH-termination (Fig. 10(b)) the lone-pair orbitals mean that there are both occupied and empty surface-states within the gap arising from the core. Therefore we can divide the predicted optical properties of F- and OH-terminated SiC-QDs into two regions. In region A, the HOMO and LUMO are associated with surface states and the energy gap is approximately constant. In region B, the HOMO and LUMO originate from core states, so that quantum confinement effects become significant.

The dual-feature PL spectra of SiC-QDs observed experimentally is represented schematically in Fig. 10(c). In a QD ensemble

Fig. 10 Illustration of core and surface states related HOMO and LUMO as a function of size in surface reconstructed 4H-SiC QD for (a) H-termination and (b) OH- or F-termination. (c) Shows a simplified dual-feature photoluminescence spectrum of SiC QDs.

containing a range of core sizes, short wavelengths excite all QDs^{28,32,33}, whereas longer wavelengths excite only large QDs. However, 10–60 Å SiC-QDs yield PL peaks which are largely insensitive to excitation wavelength up to around 320 nm. The dual feature of the PL spectra has been discussed in terms of quantum confinement effects only being responsible for the observed size-dependence of emission in larger SiC QDs^{28,30,33}, but to-date a clear explanation regarding the size-independent features has not yet been fully established. However, it can be explained if the emission (and excitation) is not purely a core property, but rather has a contribution from surface states (Figs. 10(a) and (b)). Red-shifts for excitation wavelengths above around 360 nm show the onset of quantum-confinement effects, as only those SiC-QDs large enough to be in region B in Fig. 10 are excited.

Fig. 11 Change in energy of core related and surface related JDOS versus inverse square of diameter for (a) OH termination and (b) F termination.

In a previous investigation on SiC quantum ring⁵⁵, quantum size effect is absent when the excitation wavelengths are smaller than 350 nm and spectral shifts due to quantum confinement is noted for excitation wavelengths larger than 350 nm. Experimental findings indeed validate the argument that the complex interplay between surface reconstructions and terminating species is critical below the threshold diameter of $< 30 \text{ Å}$. In the present context, we could define the threshold size in a similar fashion, when the QD core related joint density of states (JDOS) start to dominate over those that are surface related (Figs. 2(a)).

To illustrate the relative roles of the surface and core states as simulated in this study, we have plotted the JDOS contours related to absorption onsets, and at 10^3 eV^{-1} representative of the core (Fig. 11). Core atoms related JDOS shows a linear correlation with diameter⁻² for both OH and F terminating groups, consistent with the particle in a sphere model^{1,56}. However, the surface-state related JDOS do not increase. The particle in a sphere model imposes a boundary condition for the wavefunction to be zero at the QD edge resulting in the confinement energy scaling as diameter⁻², analogous to the energy of the free electron in a one dimensional infinite square well potential. Since the core-related JDOS originate from electron wavefunctions that are spatially delocalised to the QD core, this boundary condition is satisfied re-

sulting in energy scaling with diameter⁻². On the other hand, surface-related JDOS with wavefunctions localised to the QD edge do not conform to the model's boundary condition resulting in a constant or size-independent trend. Based on the trend, we predict the surface related states will define the emission up to between 25 and 27 Å diameter for F- and OH-terminations (the intersections of the lines in Fig. 11). For other surface groups, the intersection is expected to differ from these values, but the general feature of a dual-feature optical spectrum for systems involving main-group lone-pairs is expected.

4 Summary

In summary, we have investigated 10–20 Å diameter SiC-QDs with OH-, F-, and H-termination. By examining the electronic structures of a wide range of compositions and surface treatments, we conclude that the dual-feature PL spectra observed experimentally is best explained by considering the interplay of core and surface states, where surface states dominate at small scales (smaller than around 25 Å) and core states dominate at for larger SiC-QDs.

We find that the chemical nature of the surface termination groups is a critical factor in controlling the quantum confinement of 4H-SiC QDs, and hence the optical properties. It is also noted that although surface reconstructions have an impact, it is generally much smaller than that arising from the choice of termination.

An important conclusion follows. If it is desirable to have a wide range of absorption energies, one might best realize this by using a suitable range of the sizes of the optically absorbing cluster. Surface states must then be avoided, and from our analysis, H-termination is favorable. We find that for SiC-QDs smaller than $\sim 30 \text{ Å}$, surface termination with hydrogen is a highly effective, although experimentally challenging, route^{57,58} to tune the optical properties for a wide spectral range since it significantly suppresses the influence of surface states.

However, one might wish the SiC-QDs to absorb and/or emit with wavelengths only weakly dependent upon the particle size, and then one might exploit the commonality of the energies arising from the terminating species. We predict that over a relatively wide range of core diameters, OH- and F-terminated SiC-QDs show weak quantum confinement due to wavefunction localisation to surface atoms introducing surface states within the energy gap. Indeed, we project a threshold size after which surface states lose their influence to be around 26 Å for both surface species.

Finally, we note that SiC-QDs are fabricated using the wet etching methods employing HF, ethanol and water, which will naturally lead to a range of chemical termination of the surfaces. It is therefore critical to understand the chemical nature of the surface termination, since control of surface states will be essential in either exploiting or eliminating the size-dependent optical characteristics.

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