Materials Science in Semiconductor Processing 42 (2016) 147–149

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Double bubble secondary building units used as a structural motif for enhanced electron–hole separation in solids

M.R. Farrow, C.R.A. Catlow, A.A. Sokol, S.M. Woodley *

Department of Chemistry, Kathleen Lonsdale Materials Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom

ARTICLE INFO

Article history:
Received 1 May 2015
Accepted 11 August 2015
Available online 21 August 2015

Keywords:
Water splitting
Photovoltaics
Photocatalysis
Core–shell nanoparticles
Electron–hole separation

ABSTRACT

A structural motif designed for enhancing electron–hole separation in semiconducting composite materials, the so-called double bubble, is introduced. The addition of silicon carbide in the construction of heterogeneous double bubble systems, along with zinc oxide and gallium nitride, yields electronic structures that are favourable for electron–hole separation. The standard formation enthalpies of such systems are comparable with those of fullerenes, suggesting that these systems would be achievable and of direct benefit to photovoltaic and electrochemical applications such as water splitting; with the $(SiC)_{12}@(ZnO)_{48}$ proving to be the most promising building block for future functional composite materials.

1. Introduction

Harnessing solar energy to split water into hydrogen and oxygen is a path to create clean and renewable hydrogen for power generation. Traditional photocatalysts operating in the UV-light spectrum that have been developed for this purpose are wide band gap oxide semiconductors [1]. A variety of visible spectrum photocatalysts capable of water splitting have already been proposed [2,3]. Oxynitride materials that possess smaller band gaps have been investigated as a promising alternative to the semiconductor oxides [4] for water splitting and, recently, a promising photocatalyst has been proposed as a solid solution between ZnO and GaN [5]. We have previously reported a novel new structural motif for enhancing electron–hole separation, using so-called 'double bubble' secondary building units (SBU) of GaN and ZnO [6,7]. These motifs were constructed from previous computational simulations of nanoclusters that predicted bubble (or cage) architectures [8,9]. Such structures have been observed experimentally [10–12]; moreover, layered core–shell nanoparticles have been designed for quantum dots of ZnS and CdSe for a similar purpose of electron–hole separation [13] as well as a multitude of other applications from optical coatings to electronics to medical applications [14]. In this paper, we build on our previous work and investigate another promising material, SiC, as a moiety of the double bubble along with ZnO and GaN compounds. SiC is popular in many industrial applications due to its mechanical and chemical stability. Moreover, it readily forms composite materials, and importantly, supports well both electron and hole charge carriers [15].

2. Method

We construct our double bubble from the binary tetrahedral compounds of ZnO, GaN, and SiC that are predicted to have stable bubble structures. We focus on the family of high-symmetry structures with symmetry T_h due to their greater stability when compared to clusters of neighbouring sizes [8,16]. The systems are constructed by inserting a twenty-four atom bubble inside a ninety-six atom bubble, subject to aligning with the same direction of orthogonal axes, with overlapping centre of masses of each individual bubble, and minimising the interior cation (anion) to exterior anion (cation) distances – see Fig. 1. A good choice of software for the calculations is the density functional theory code FHI-aims [17] due to its high accuracy and computational efficiency. We chose the solids corrected Perdew–Burke–Ernezerhof (PBEsol) generalised gradient approximation (GGA) exchange-correlation (XC) functional for geometry optimisation of the systems. We then performed single-point energy calculations at the hybrid level of theory using the PBEsol0 XC functional that includes 25% Hartree–Fock electron exchange. The electronic structures were characterised by computing their Density of States (DOS) and partial DOS from the PBSsol0 calculations. We note that in test geometry optimisations using the PBEsol0 XC functional, we have found only minor changes in atomic configuration, therefore, we used the PBEsol optimised geometries. All our calculations were performed with settings for the atomic species basis sets at 'tight accuracy' (convergence better than 1 meV per atom for total energies) and with scalar ZORA relativistic treatment. The forces were converged to 0.001 eV/Å.

* Corresponding author.
E-mail address: scott.woodley@ucl.ac.uk (S.M. Woodley).

http://dx.doi.org/10.1016/j.mssp.2015.08.023

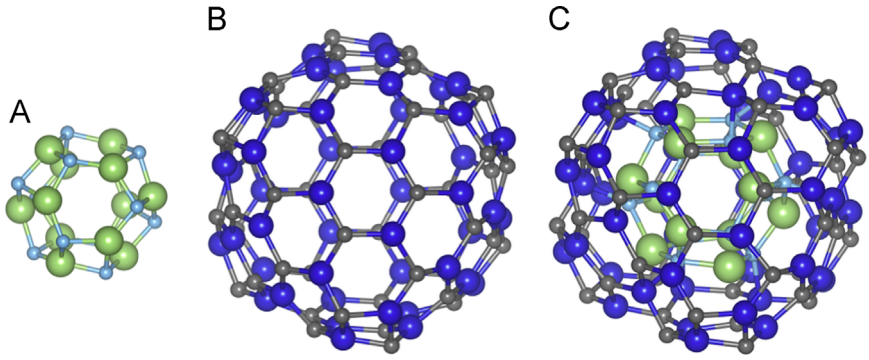

Fig. 1. Construction of an exemplar double bubble nanocluster of $(GaN)_{12}@(SiC)_{48}$: a GaN bubble of twenty-four atoms (A) is placed inside a larger, ninety-six atom SiC bubble (B) to form a double bubble nanocluster (C). Atom colours: green is Ga, sky blue for N, dark blue for Si and steel for C. Graphics generated using the VESTA package [18]. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this paper.)

3. Results and discussion

We propose that heterogenous double bubble systems are good candidates to achieve electron–hole separation and hence be of value for photovoltaic, electrochemical, and catalytic applications. Therefore, we have constructed and tested a variety of systems based on high-symmetry wide band-gap semiconducting compounds, results of which are reported below.

The calculated standard enthalpy of formation (H_f) for the single and double bubble systems is roughly comparable with that of fullerenes with respect to bulk carbon (*ca* 40 kJ mol^{-1}) [19] as can be seen in Table 1. We also show in Table 1 the calculated frontier electronic orbital energies, *i.e.* the level of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and their differences (E_g) for the double bubble systems as well as their moieties. There is a consistent change in E_g with compound for single bubble systems of the same size; ZnO having the largest values and GaN the smallest. For ZnO the expected behaviour of quantum confinement is found *i.e.* E_g decreases with nanocluster size, whereas the reverse is found for GaN (*cf.* ref. [8]), and there is no significant change for SiC. All mixed double bubble systems have lower values of E_g than the single bubble systems. Comparing our data with previous work [7], for each type of outer bubble E_g is lowest when the inner bubble is comprised of SiC and greatest when it is comprised of ZnO.

The Density Of electronic States (DOS) and contributions from each element, partial DOS (pDOS), for the systems are shown in Fig. 2. The lowest unoccupied states are localised on the cations, and the valence electrons are localised on the anions. Fig. 3 shows

Table 1
Electronic frontier orbital energies, E_{HOMO} and E_{LUMO}, their differences, E_g, and calculated standard enthalpies of formation per mole of atoms, H_f, from SiC, ZnO and GaN bulk for the investigated nanocluster systems.

System	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	H_f (kJ mol^{-1})
$(SiC)_{12}$	−6.67	−2.64	4.03	123.93
$(SiC)_{48}$	−6.50	−2.46	4.04	97.30
$(GaN)_{12}$	−6.85	−3.05	3.80	91.77
$(GaN)_{12}@(SiC)_{48}$	−6.49	−3.30	3.19	89.05
$(ZnO)_{12}@(SiC)_{48}$	−6.48	−3.01	3.47	81.69
$(SiC)_{12}@(GaN)_{48}$	−6.35	−3.02	3.33	73.73
$(GaN)_{48}$	−6.92	−2.90	4.02	61.11
$(ZnO)_{12}$	−7.47	−2.70	4.77	57.77
$(SiC)_{12}$ at $(ZnO)_{48}$	−6.45	−2.97	3.47	47.07
$(ZnO)_{48}$	−7.35	−3.04	4.31	40.10

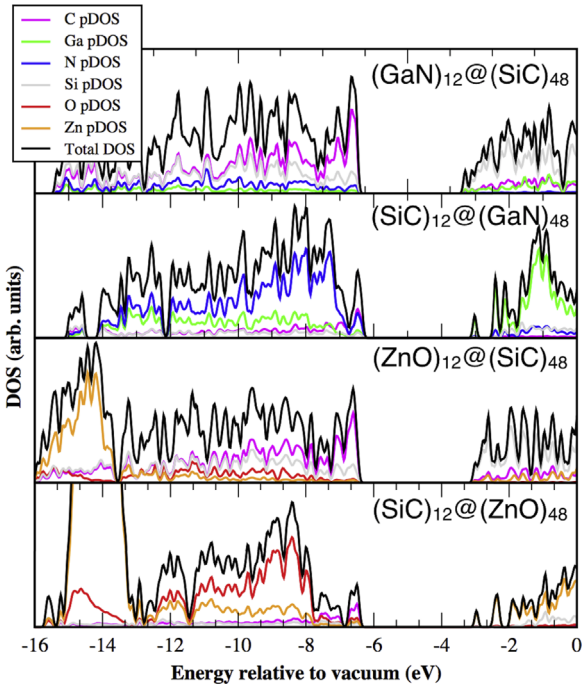

Fig. 2. Density of electronic states (DOS) and partial DOS (pDOS) of the double bubble nanoclusters as calculated using the FHI-aims code using a Gaussian broadening with a dispersion of 0.05 eV.

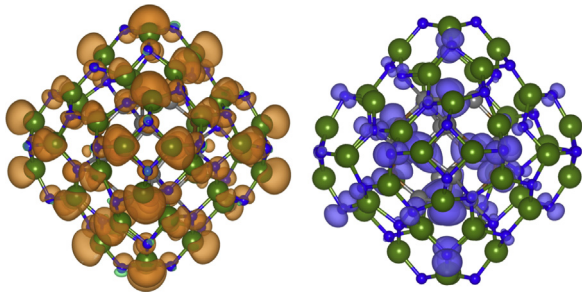

Fig. 3. Exemplar electron (left) and hole (right) spin-density isoplots for the $(SiC)_{12}@(GaN)_{48)}$ nanocluster system. The electron is predominantly localised on the outer bubble on the Ga atoms, whereas the hole is located on the inner bubble on the C atoms. *Colours*: Ga is shown in green, N in dark blue, Si in steel grey and C in brown. The semi-transparent orange and light blue surfaces show the electron isodensity and the hole isodensity, respectively. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this paper.)

the spin density obtained from singly ionised nanoclusters, $(SiC)_{12}@(GaN)_{48}$, that graphically illustrates the above observations. As expected, in the example shown, the excitation holes will localise on the inner SiC bubble with the electrons residing on the outer GaN bubble, which could be usefully exploited in continuous composite materials under investigation for both electronic properties and thermodynamic stability [20].

4. Conclusions

Silicon carbide is a cheap and robust material that readily supports holes. Our calculations show that a double bubble with a SiC interior and ZnO exterior has a much lower energy of formation that previous double bubbles considered with an energy lower than taking a weighted average of its moieties (56.87 kJ mol^{-1}). The addition of silicon carbide in the construction of novel semiconductor composite materials has proved to be of great value to the task of electron–hole separation, which would be of direct benefit to wide-ranging photovoltaic and catalytic applications. These materials have a comparable enthalpy of formation to fullerenes with respect to bulk carbon [19]. Reliable core–shell nanoparticles synthesis has already been established and therefore it is plausible that these double bubble compounds will be created in the near future.

Acknowledgements

The authors would like to thank John Buckeridge for useful discussions during the preparation of this manuscript. Volker Blum is gratefully acknowledged for his advise on optimisation of FHI-aims. This work was funded under the eCSE programme of the ARCHER UK national supercomputing service, and HPC time on ARCHER provided via our membership of the UK's HPC Materials Chemistry Consortium, which is funded by EPSRC (EP/L000202).

References

[1] A. Kudo, Y. Miseki, Heterogeneous photocatalyst materials for water splitting, Chem. Soc. Rev. 38 (1) (2009) 253–278, http://dx.doi.org/10.1039/B800489G.
[2] Y. Lee, H. Terashima, Y. Shimodaira, K. Teramura, M. Hara, H. Kobayashi, K. Domen, M. Yashima, Zinc germanium oxynitride as a photocatalyst for overall water splitting under visible light, J. Phys. Chem. C 111 (2) (2007) 1042–1048, http://dx.doi.org/10.1021/jp0656532.
[3] R. Asai, H. Nemoto, Q. Jia, K. Saito, A. Iwase, A. Kudo, A visible light responsive rhodium and antimony-codoped SrTiO3 powdered photocatalyst loaded with an IrO2 cocatalyst for solar water splitting, Chem. Commun. 50 (19) (2014) 2543–2546, http://dx.doi.org/10.1039/C3CC49279F.
[4] A. Fuertes, Chemistry and applications of oxynitride perovskites, J. Mater. Chem. 22 (8) (2012) 3293–3299, http://dx.doi.org/10.1039/C2JM13182J.
[5] K. Maeda, T. Takata, M. Hara, N. Saito, Y. Inoue, H. Kobayashi, K. Domen, GaN: ZnO solid solution as a photocatalyst for visible-light-driven overall water splitting, J. Am. Chem. Soc. 127 (23) (2005) 8286–8287, http://dx.doi.org/10.1021/ja0518777.
[6] M.R. Farrow, J. Buckeridge, C.R.A. Catlow, A.J. Logsdail, D.O. Scanlon, A.A. Sokol, S.M. Woodley, From stable ZnO and GaN clusters to novel double bubbles and frameworks, Inorganics 2 (2) (2014) 248–263, http://dx.doi.org/10.3390/inorganics2020248, URL: ⟨http://www.mdpi.com/2304-6740/2/2/248⟩.
[7] A.A. Sokol, M.R. Farrow, J. Buckeridge, A.J. Logsdail, C.R.A. Catlow, D.O. Scanlon, S.M. Woodley, Double bubbles: a new structural motif for enhanced electron–hole separation in solids, Phys. Chem. Chem. Phys. 16 (39) (2014) 21098, http://dx.doi.org/10.1039/c4cp01900h, URL: ⟨http://pubs.rsc.org/en/content/articlehtml/2014/cp/c4cp01900h⟩.
[8] S.A. Shevlin, Z.X. Guo, H.J.J. van Dam, P. Sherwood, C.R.A. Catlow, A.A. Sokol, S. M. Woodley, Structure, optical properties and defects in nitride (III–V) nanoscale cage clusters, Phys. Chem. Chem. Phys. 10 (14) (2008) 1944–1959, http://dx.doi.org/10.1039/B719838H.
[9] M.R. Farrow, Y. Chow, S.M. Woodley, Structure prediction of nanoclusters; a direct or a pre-screened search on the DFT energy landscape? Phys. Chem. Chem. Phys. 16 (39) (2014) 21119–21134, http://dx.doi.org/10.1039/c4cp01825g, URL: ⟨http://pubs.rsc.org/en/content/articlehtml/2014/cp/c4cp01825g⟩.
[10] D. Golberg, Y. Bando, O. Stephan, K. Kurashima, Octahedral boron nitride fullerenes formed by electron beam irradiation, Appl. Phys. Lett. 73 (17) (1998) 2441, http://dx.doi.org/10.1063/1.122475, URL: ⟨http://scitation.aip.org/content/aip/journal/apl/73/17/10.1063/1.122475⟩.
[11] A. Kasuya, R. Sivamohan, Y.A. Barnakov, I.M. Dmitruk, T. Nirasawa, V. R. Romanyuk, V. Kumar, S.V. Mamykin, K. Tohji, B. Jeyadevan, K. Shinoda, T. Kudo, O. Terasaki, Z. Liu, R.V. Belosludov, V. Sundararajan, Y. Kawazoe, Ultrastable nanoparticles of CdSe revealed from mass spectrometry, Nat. Mater. 3 (2) (2004) 99–102 , URL: ⟨http://dx.doi.org/10.1038/nmat1056⟩; ⟨http://www.nature.com/nmat/journal/v3/n2/suppinfo/nmat1056_S1.html⟩.
[12] A.N. Enyashin, S. Gemming, M. Bar-Sadan, R. Popovitz-Biro, S.Y. Hong, Y. Prior, R. Tenne, G. Seifert, Structure and stability of molybdenum sulfide fullerenes, Angew. Chem. Int. Ed. 46 (4) (2007) 623–627, http://dx.doi.org/10.1002/anie.200602136.
[13] B.O. Dabbousi, J. Rodriguez-Viejo, F.V. Mikulec, J.R. Heine, H. Mattoussi, R. Ober, K.F. Jensen, M.G. Bawendi, (CdSe)ZnS core–shell quantum dots: synthesis and characterization of a size series of highly luminescent nanocrystallites, J. Phys. Chem. B 101 (46) (1997) 9463–9475, http://dx.doi.org/10.1021/jp971091y.
[14] R. Ghosh Chaudhuri, S. Paria, Core/shell nanoparticles: classes, properties, synthesis, mechanisms, characterization and applications, Chem. Rev. 112 (4) (2012) 2373–2433, http://dx.doi.org/10.1021/cr100449n.
[15] A. Walsh, J. Buckeridge, C.R.A. Catlow, A.J. Jackson, T.W. Keal, M. Miskufova, P. Sherwood, S.A. Shevlin, M.B. Watkins, S.M. Woodley, A.A. Sokol, Limits to doping of wide band gap semiconductors, Chem. Mater. 25 (15) (2013) 2924–2926, http://dx.doi.org/10.1021/cm402237s arXiv:http://dx.doi.org/10.1021/cm402237s.
[16] M.B. Watkins, S.A. Shevlin, A.A. Sokol, B. Slater, C.R.A. Catlow, S.M. Woodley, Bubbles and microporous frameworks of silicon carbide, Phys. Chem. Chem. Phys. 11 (17) (2009) 3186–3200, http://dx.doi.org/10.1039/B902603G.
[17] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, M. Scheffler, Ab initio molecular simulations with numeric atom-centered orbitals, Comput. Phys. Commun. 180 (11) (2009) 2175–2196, http://dx.doi.org/10.1016/j.cpc.2009.06.022, URL: ⟨http://linkinghub.elsevier.com/retrieve/pii/S0010465509002033⟩.
[18] K. Momma, F. Izumi, *VESTA3* for three-dimensional visualization of crystal, volumetric and morphology data, J. Appl. Crystallogr. 44 (6) (2011) 1272–1276, http://dx.doi.org/10.1107/S0021889811038970.
[19] R.F. Curl, R.C. Haddon, On the formation of the fullerenes, Philos. Trans.: Phys. Sci. Eng. 343 (1667) (1993) 19–32, http://dx.doi.org/10.2307/54131 (and Discussion), URL: ⟨http://www.jstor.org/stable/54131⟩.
[20] J. Buckeridge, D. Scanlon, A. Walsh, C. Catlow, Automated procedure to determine the thermodynamic stability of a material and the range of chemical potentials necessary for its formation relative to competing phases and compounds, Comput. Phys. Commun. 185 (1) (2014) 330–338 http://dx.doi.org/10.1016/j.cpc.2013.08.026, URL: ⟨http://www.sciencedirect.com/science/article/pii/S0010465513002993⟩.