Accademia Nazionale di Scienze Lettere e Arti di Modena
(fondata nel 1683)

ATTI E MEMORIE

MEMORIE

SCIENTIFICHE, GIURIDICHE, LETTERARIE

SERIE IX – VOL. I – FASC. I, 2017

Accademia Nazionale di Scienze Lettere e Arti di Modena

Modena 2017

Acc. Naz. Sci. Lett. Arti di Modena
Memorie Scientifiche, Giuridiche, Letterarie (a.a. 2017)
Ser. IX, v. I (2017), fasc. I

Stefano Ossicini, Ivan Marri*

TEACHING SILICON NEW POSSIBILITIES

RIASSUNTO

Anche se il silicio rappresenta di gran lunga il materiale maggiormente utilizzato in microelettronica, fotonica e fotovoltaico, negli ultimi anni, diverse problematiche sono sorte rispetto all'evoluzione di questi settori, legate ad aspetti fondamentali sia riguardo gli aspetti materiali che di processo. Ne sono esempi le limitazioni alla velocità operativa dei dispositivi microelettronici, dovute ai problemi di interconnessione, la mancanza di proprietà ottiche non lineari di secondo ordine nel silicio di volume, la necessità di aumentare l'efficienza nelle celle solari. Esiste una forte spinta alla creazione di sistemi basati sul silicio dotati di nuove funzionalità capaci di risolvere questi e altri problemi. Negli ultimi anni, il nostro gruppo ha sviluppato nuovi strumenti teorici per lo studio delle proprietà strutturali, elettroniche e ottiche dei sistemi basati sul silicio, in particolare nano strutture di silicio. Le nostre indagini hanno permesso di predire nuove proprietà del silicio, aprendo così nuovi orizzonti possibili alla applicazione di questo materiale in diversi ambiti tecnologici. In questo articolo ricapitoliamo i nostri risultati più significativi.

1. *Introduction*

Silicon (Si) is cheap, easy to handle and fairly simple to manufacture moreover it shows optimal thermal and good mechanical properties. Si is today the electronic material per excellence. This environmental friendly material is the most used semiconductor for photovoltaic applications and its role in the optoelectronic industry is becoming more and more important. Nevertheless the increasing demand for new, innovative and more efficient devices has forced scientists to explore new functionalities of Si-based materials. In photonics the main interest lies on the possibility to merge electronics and photonics on the same chip, We

* Dipartimento di Scienze e Metodi dell'Ingegneria, Università di Modena e Reggio Emilia and CNR - Istituto di Nanoscienze S3, Modena.

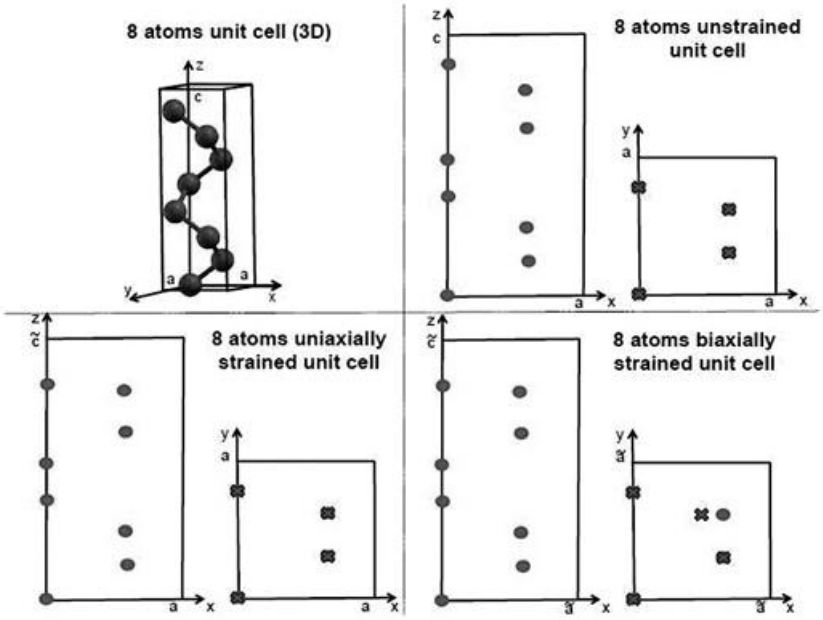

Figure 1: (Color online) Panel a) unstrained 8 atoms Si bulk unit cell in three dimensions (3D); panel b) unstrained 8 atoms Si bulk unit cell projected onto the x-z plane (red circle) and onto the x-y plane (red circle and black cross); panel c) uniaxially strained 8 atoms Si bulk unit cell; panel d) biaxially strained 8 atoms Si bulk unit cell.

have therefore to render Si a good light emitter, improving for instance its nonlinear optical properties.[1] For photovoltaic applications we have to add to Si new features in order to maximize solar radiation harvesting and to minimize occurrence of loss thermalization processes.[2] All these points are object of increasing interest by researchers and industries and can be realized by exploring Si new properties. Noticeably, nanoscience and nanotechnologies have opened new possibilities to tune material properties by size reduction to the nanoscale and through manipulation of matter at the atomistic level.

The ability to design novel materials with new functionalities and to engineering original devices for specific applications in different tech-

[1] N. DALDOSSO, L. PAVESI, "Laser & Photon. Rev." 3 (2009), pp. 508-534.
[2] F. PRIOLO, F. GREGORKIEWICZ, M. GALLI, T.F. KRAUSS, "Nature Nanotechnol." 1 (2014), pp. 19-32.

nological fields heavily depends on our capacity of describing optical excitations and of predicting electronic response to external perturbations. In this context theory plays a crucial role, not only from the point of view of the fundamental research, but also because a precise knowledge of the structural, electronic, and optical properties of materials represents a fundamental step towards the design and fabrication of innovative devices and nanodevices. In these last twenty years we have realized, using the Density Functional Theory (DFT) formalism,[3] theoretical tools for the prediction and the study of novel behaviors in Si-based systems in order to identify new Si-based materials and device architectures with improved performance for applications in microelectronics, photonics and photovoltaics. In the next sections we will review our most important results.

2. *New properties in silicon based systems*

2.1. *Nonlinear optical properties*

In these last years, silicon photonics is looking at the nonlinear optics to generate new light sources, starting from one or more pump beams.[4,5] The interest towards the development of a CMOS-compatible, micro-sized optical conversion system is justified both by the possible development of an all-optical, all-Si photonic circuit, and by the demonstration of new light-conversion mechanisms. Additionally, important applications emerge in the field of the all-optical-signal-processing when optical nonlinearities are exploited.[6] Some groups demonstrated optical-parametric oscillators by employing ring and disk micro- resonators composed by SiO_2[7] or Si_3N_4.[8] Other groups proposed parametric generation schemes in Si waveguides[9] and micro-resonators[10] as well as they

[3] G. ONIDA, L. REINING, A. RUBIO, "Rev. Mod. Phys." 74 (2002), pp. 601-659.
[4] H. RONG, R. JONES, A. LIU, O. COHEN, A. FANG, M. PANICCIA, "Nature" 433 (2005), pp. 725-728.
[5] M.A. FOSTER, A.C. TURNER, J.E. SHARPING, B.S. SCHMIDT, M. LIPSON, A.L. GAETA, "Nature" 441 (2006), pp. 960-962.
[6] C. LANGROCK, S. KUMAR, J.E. MCGEEHAN, A.E. WILLNER, M.M. FEIER, J. LIGHTW. "Technol." 24 (2006), pp. 2579-2592.
[7] L. RAZZARI, D. DUCHESNE, M. FERRERA, R. MORANDOTTI, S. CHU, B.E. LITTLE, D.J. MOSS, "Nature Phot." 4 (2010), pp. 41-45.
[8] J.S. LEVY, A. GONDARENKO, M.A. FOSTER, A.C. TURNER-FOSTER, A.L. GAETA, M. LIPSON, "Nature Phot." 4 (2010), pp. 37-40.
[9] Q. LIN, J. ZHANG, P.M. FAUCHET, G. P. AGRAWAL, "Optics Expr." 14 (2006), pp. 4786-4799.
[10] S.F. PREBLE, Q. XU, M. LIPSON, "Nature Phot. " 1 (2007), pp. 2093-2096.

experimentally demonstrated wavelength generation via four-wave-mixing at threshold powers lower than few hundreds of microwatts.[11]

The working principle of all these devices is related to the existence of a nonzero third order nonlinear electrical susceptibility [χ^3]. On one side, this leads to the demonstration of efficient optical parametric generation in Si, SiO_2 and Si_3N_4 micro-resonators, but on the other side it has an inherent limitation, since χ^3 nonlinear optical effects are less efficient, for constant incident power, than χ^2 related effects. Until now, the nonlinear conversion of light into silicon devices has been based on χ^3 effects, this is because Si itself in its bulk crystalline form (because of its centrosymmetry) has a χ^2 tensor equals to zero. Obviously a χ^2 related nonlinear light conversion in Si will be much more efficient.

In 2006, the observation of nonlinear electro-optical phase modulation in a slow-wave Si based Mach-Zender interferometer suggested a route to induce a second-order nonlinear effect in crystalline Si.[12,13] In this work the lack of inversion symmetry in Si were obtained by applying an external mechanical strain field. In this situation a significant χ^2 is induced allowing a phase-modulation of the incident light. In 2012 in a theoretical-experimental collaboration we performed second-harmonic-generation (SHG) experiments and first-principle DFT calculations (see Fig. 1 for a model of strained Si bulk) proving, for the first time, that large values of the second-order nonlinear susceptibility χ^2, up to 40 pmV^{-1} at 2300 nm, can be induced in strained Si bulk. As a consequence nonlinear strained Si could provide a competing platform for a new class of integrated light sources spanning the near-to mid-infrared spectrum. By developing new first principles numerical tools, we applied ab initio techniques to study new non-linear optical properties of a medium, with an accuracy that complement experimental observations.[14,15,16,17] Remarkably, until then, ab initio procedures were developed and used to investigate only linear optical response effects and not nonlinear optical properties of a medium. By extending theoretical

[11] A. C. Turner, M. A. Foster, A. L. Gaeta, M. Lipson, Optics Expr. 16 (2008) 4881-4887.
[12] R. S. Jacobsen, K. N. Andersen, P. I. Borel, J. Fage-Pedersen, L. H. Frandsen, O. Hansen, M. Kristensen, A. V. Lavrinenko, G. Moulin, H. Ou, C. Peucheret, B. Zsigri, A. Bjarklev, Nature 441 (2006) 199-202.
[13] M. Cazzanelli, F. Bianco, E. Borga, G. Pucker, M. Ghulinyan, E. Degoli, E. Luppi, V. Véniard, S. Ossicini, D. Modotto, S. Wabnitz, R. Pierobon, L. Pavesi, Nature Materials 11 (2012) 148-154.
[14] E. Luppi, E. Degoli, M. Bertocchi, S. Ossicini, V. Véniard, Phys. Rev. B 92 (2015) 075204.
[15] M. Bertocchi, E. Luppi, E. Degoli, V. Véniard, S. Ossicini, Phys. Rev. B 86 (2012) 035309.
[16] M. Bertocchi, E. Luppi, E. Degoli, V. Véniard, S. Ossicini, J. Chem. Phys. 140 (2014) 214705.
[17] M. Bertocchi, E. Degoli, S. Ossicini, V. Véniard, E. Luppi, Nanosci. Nanotech. Lett. 9 (2017) 1102-1107.

spectroscopy ab initio procedures to the study of nonlinear optical processes, we predicted that different strains in bulk Si are able to enhance the χ^2 signal in different energy regions spanning from the infrared to the visible (see Fig. 2).

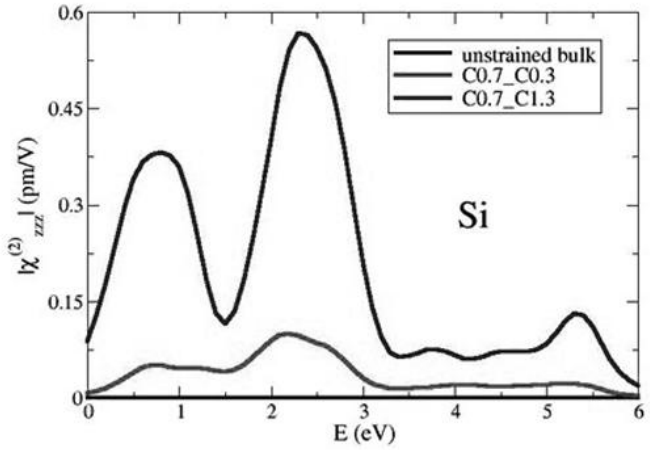

Figure 2: (Color online) Calculated SHG spectra for the Si unstrained and strained systems. Turning on the internal strain of Si from unstrained bulk (black line) up to the C0.7_C0.3 (red/light gray line) and C0.7_C1.3 (blue/dark gray line) compressive systems (structures with Si-Si bond compressed of 0.7% and 0,3%, or of 0.7% and 1.3%, respectively) the intensity of the second order response function is enhanced at particular energy regions. Reprinted with permission from ref.[14]

2.2. *Doping in Si nanostructures*

Doping of semiconductors represents the key developing route of the current solid-state electronic industry. The possibility of tailoring the electronic and transport properties of semiconductors by simple incorporating additive atoms has offered the chance of engineering materials according to the specific needs. Currently the scaling down of devices size to achieve technological improvements in electronics, photonics and photovoltaics requires a full understanding of the nature of doping process at nanoscale.[18,19,20] Impurities in nanostructures, such as nano-

[18] M. AMATO, M. PALUMMO, R. RURALI, S. OSSICINI, "Chem. Rev." 114 (2014), pp. 1371-1412.

crystals (NCs) and nanowires (NWs), can lead to novel and unexpected properties, that can be very different from those of the corresponding bulk materials. It is well known that the intentional adding of impurities has the general purpose of increasing the number of free charges into the semiconductor, hence the current ow when a voltage bias is applied. In Si bulk this goal is fulfilled by incorporating very small amounts of selected additives, usually B or P atoms, to them, generally no more than a few parts per million. These impurities increase the number of electrons or holes and therefore the mobility of the material. For instance, in the case of n-type doping, when a P atom is added to a Si bulk, it gives rise up to an extra energy level into the band gap. Because of the strong dielectric screening of the host semiconductor this energy level is very shallow and the impurity requires little energy, typically around the thermal energy or less to ionize.

On the other hand when we attempt to study doping at nanoscale, in particular for Si NCs and NWs, we have to look at three main phenomena, potentially undermining the doping efficiency: the quantum confinement effect, that enhances the band gap and that can influence the position of impurity energy level into the band gap; the surface segregation, that can affect electrical properties of the doped nanostructures; and the dielectric mismatch, related to the presence, in a nanostructures, of an embedding medium with a lower dielectric constant if compared to the bulk precursor. This property reduces the screening of the impurity potential strongly increasing the ionization energy of the dopant. All these effects have, in different ways, an influence on the efficiency of impurities activation Si nanostructures, compromising the doping process with respect to bulk case.[21,22] During these last years we have performed several DFT based investigations in order to show how this dopant deactivation in Si NCs and NWs can be circumvented using the concept of impurity compensation and of selective doping.

Photoluminescence (PL) experiments on doped Si NCs show that the PL intensity is quenched by the introduction of the impurities.[23] It has, however, been shown that this quenching can be avoided when the Si NCs

[19] E. ARDUCA, M. PEREGO, "Materials Science in Semiconductor Processing" 62 (2017), pp. 156-170.
[20] I. MARRI, E. DEGOLI, S. OSSICINI, "Progress in Surface Science" 92 (2017), pp. 375-40.
[21] M.T. BJÖRK, H. SCHMID, J. KNOCH, H. RIEL, W. RIESS, "Nature Nanotechnol." 4 (2008), pp. 103-107.
[22] F. IORI, E. DEGOLI, R. MAGRI, I. MARRI, G. CANTELE, D. NINNO, F. TRANI, O. PULCI, S. OSSICINI, "Phys. Rev." B 76 (2007), p. 085302.
[23] M. FUJII, K. TOSHIKIYO, Y. TAKASE, Y. YAMAGUCHI, S. HAYASHI, "J. Appl. Phys." 94 (2003), pp. 1990-1995.

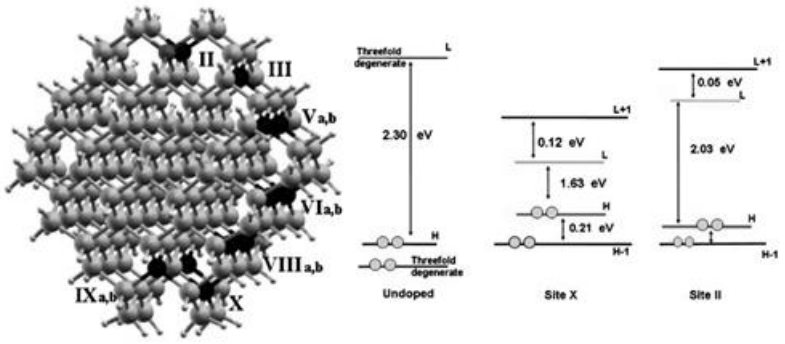

Figure 3: (Color online) Left: phosphorus impurity path in a $Si_{145}BPH_{100}$ NC (diameter 1.9 nm). The B atom (magenta, dark grey) position is kept fixed, while the P atom (black) is moved to explore several substitutional sites, labeled by Roman numbers. The position II corresponds to the minimum distance between the dopants (D = 0.368 nm), whereas the position X is related to the maximum distance (D = 1.329 nm). Right: calculated energy levels of the undoped $Si_{147}H_{100}$ NC and the codoped $Si_{145}BPH_{100}$ NC with two different impurity-impurity distances. H stands for HOMO and L for LUMO. Reprinted with permission from ref.[22]

are simultaneously doped and compensated with both B and P impurities.[24] These codoped Si NCs exhibit PL energies red-shifted with respect to those of the corresponding undoped Si NCs, moreover these energies can range from the visible to below the band gap energy of the bulk Si. Through a systematic study of the structural, electronic and optical properties of B and P simultaneously doped Si NCs, using ab-initio DFT calculations,[22,25] we have shown that B and P codoped com-

[24] T. KANNO, H. SUGIMOTO, A. FUCIKOVA, J. VALENTA, M. FUJII, "J. Appl. Phys." 12 (2016), p. 164307.

[25] G. CANTELE, E. DEGOLI, E. LUPPI, R. MAGRI, D. NINNO, G. IADONISI, S. OSSICINI, "Phys. Rev." B 72 (2005), 114531; S. OSSICINI, E. DEGOLI, F. IORI, R. MAGRI, G. CANTELE, F. TRANI, D. NINNO, "Appl. Phys. Lett." 87 (2005), p. 173120; S. OSSICINI, F. IORI, E. DEGOLI, E. LUPPI, R. MAGRI, G. CANTELE, F. TRANI, D. NINNO, "IEEE J. Sel. Top. Quantum El." 12 (2006), pp. 1585-1591; F. IORI, E. DEGOLI, E. LUPPI, R. MAGRI, I. MARRI, G. CANTELE, F. TRANI, S. OSSICINI, "J. Lum." 121 (2006), pp. 335-339; S. OSSICINI, E. DEGOLI, F. IORI, O. PULCI, G. CANTELE, R. MAGRI, O. BISI, F. TRANI, D. NINNO, "Surface Sci." 601 (2007), pp. 2724-2729; F. IORI, S. OSSICINI, E. DEGOLI, E. LUPPI, R. POLI, R. MAGRI, G. CANTELE, F. TRANI, D. NINNO, "Phys. Status Solidi A" 204 (2007), pp. 1312-1317; R. MAGRI, E. DEGOLI, F. IORI, E. LUPPI, O. PULCI, S. OSSICINI, G. CANTELE, F. TRANI, D. NINNO, "J, Comput. Meth. Sci. Eng." 7 (2007), pp. 219-232; L.E. RAMOS, E. DEGOLI, G. CANTELE, S. OSSICINI, D. NINNO, J. FURTHMÜLLER, F. BECHSTEDT, "Phys. Rev." B 78 (2008), p. 235310; F. IORI, E. DEGOLI, M. PALUMMO, S. OSSICINI, "Superl. Microstr." 44 (2008), pp. 337-347; S. OSSICINI, O. BISI, E. DEGOLI, I. MARRI, F. IORI, E. LUPPI, R. MAGRI, R. POLI, G. CANTELE, D. NINNO, F. TRANI, M. MARSILI, O. PULCI, V. OLEVANO, M. GATTI, K. GAAL-NAGY, A. INCZE, G. ONIDA, "J. Nanosci, Nano-

pensated Si NCs exhibit properties that strongly differ from the ones of the undoped and single doped Si NCs. In particular we showed that, if carriers are perfectly compensated, the Si NCs undergo a minor structural distortion around the impurities inducing a significant decrease of the impurities formation energies with respect to the single doped case. Moreover we proved that codoping can be exploited to tune the electronic and optical properties of Si NCs, in a highly controllable way (see Fig.3). In particular we demonstrated that NC's energy gap can be tuned by changing the reciprocal impurity separation, thus confirming the possibility of exploiting Si NCs for photonic applications, in full agreement with later experimental observation.[26]

Concerning Si NWs the dopant deactivation can be rode out in core-shell silicon-germanium NWs (SiGe NWs),[18,27,28] playing on the particular energy band alignment that comes out at the Si/Ge interface. When two semiconductors form an interface, like in the case of core-shell SiGe NWs, they can exhibit a band offset. Its origin is related to the band bending at the interface, that results from the difference in band gaps of the two materials and to the consequent charge transfer. Valence and conduction band offset (VBO and CBO) magnitudes determine the ability of electrons or holes to pass from one side of the hetero-junction to the other one. It has been demonstrated that the band offset of Si/Ge systems, like superlattices, bulk hetero-junctions and SiGe NWs has a type II character, that means that the Valence Band Maximum (VBM) and the Conduction Band Minimum (CBM) of the system are located on different sides of the junction. In particular the VBM is always on the Ge part, while the CBM is on the Si one.[18]

Taking advantage of this type II band offset, by means of ab-initio DFT based theoretical calculations, we demonstrated the possibility of creating, through a selective doping of core or shell, an one-dimensional (1-D) electron or hole gas, which has not to be thermally activated and which can furnish carriers also at very low temperatures.[27,29,30,31]

---

tech." 8 (2008), pp. 479-492; F. IORI, S. OSSICINI, "Physica" E 41 (2009), pp. 939-946; R. GUERRA, S. OSSICINI, "J. Am. Chem. Soc." 36 (2014), pp. 4404-4409; N. GARCIA-CASTELLO, S. ILLERA, J.D. PRADES, S. OSSICINI, A. CIRERA, R. GUERRA, "Nanoscale" 7 (2015), pp. 12564-12571; I. MARRI, E. DEGOLI, S. OSSICINI, "Phys. Status Solidi" A (2017), p. 1700414.

[26] O. ASHKENAZI, D. AZULAY, I. BALBERG, S. KANO, H. SUGIMOTO, M. FUJII, O. MILLO, "Nanoscale" 9 (2017), pp. 17884-17892.

[27] M. AMATO, S. OSSICINI, R. RURALI, "Nano Lett." 11 (2011), pp. 594-598.

[28] L.J. LAUHON, M.S. GUDIKSEN, D. WANG, C.M. LIEBER, "Nature" 420 (2002), pp. 57-60.

[29] M. AMATO, R. RURALI, S. OSSICINI, "J. Comput. Electron" 11 (2012), pp. 272-279.

[30] M. AMATO, M. PALUMMO, R. RURALI, S. OSSICINI, "J. Appl. Phys." 112 (2012), p. 114323.

[31] M. AMATO, M. PALUMMO, R. RURALI, S. OSSICINI, "J. Phys. D: Appl. Phys." 47 (2014), p. 394013.

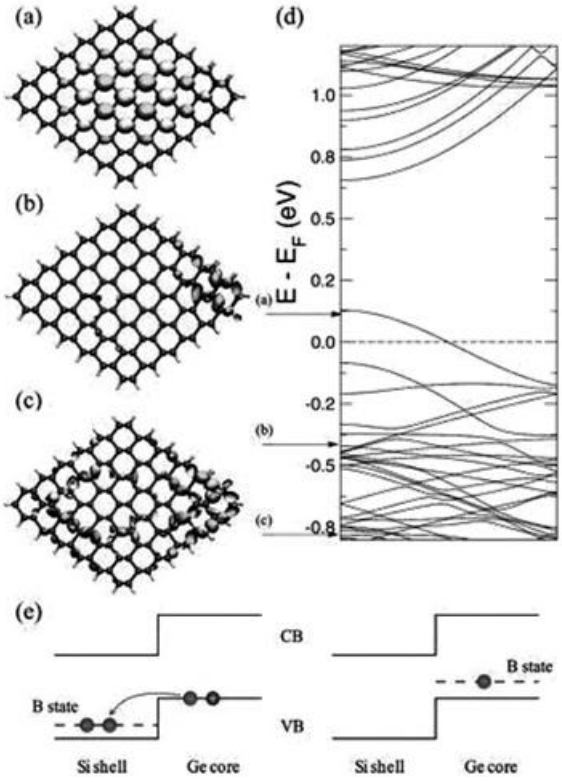

Figure 4: (Color online) Band structure of a Ge-core/Si-shell NW with B doping in the Si shell (d); labeled arrows indicate the states whose real-space distribution is shown in the side panels (a-c). Lateral panels show the core character of the top of the valence band (a), the impurity state, 0.46 eV below the band edge (b) and the highest energy Si-shell state (c). A qualitative model of the band offset (not in scale) for B-doping of a Ge-core/Si-shell NW is shown below (e). Doping of the Si-shell yields a hole at the top of the valence band localized in the Ge-core (left-hand side), whereas doping of the Ge-core is similar to the case of a pure Ge NW (right-hand side). Reprinted with permission from ref.[27]

We describe here, p-type doping in core-shell NWs, choosing Ge-core/Si-shell NWs as example (see Fig. 4). Similar discussions can be made for the other possible selective n- and p-type doping combinations in the Ge-core/Si-shell or Si-core/Ge shell NWs.[27,28,29] We start by considering B substitution of a Ge atom of the core. The band offset at the Si/Ge interface suggests that no enhancement of the doping effi-

ciency should be observed. Looking at the wave function localization and band structure (see Fig. 4, right panel) we can say that the level due to the dopant atom is above the top of the valence band due to Ge-core; nevertheless the gap between the dopant level and the adjacent band is too high to be activated by thermal excitation. Hence this configuration presents the same limit of adding B impurities in a pure NW. Then we put a B atom into the Si-shell (see Fig. 4, left panel) and we find that the top of the valence band is still located on Ge-core, while the dopant energy level falls down into the valence band creating a hole at its top. Electrons will flow from the top of the valence band attracted by the ionized dopant potential, and a 1-D hole gas will be created. There will be no need of thermal energy to activate charge carriers. It is worth to note that our results have been validated by a recent experimental work in which the existence of hole accumulation in intrinsic Ge-core/p-type Si-shell NWs has been demonstrated.[32] Since core-shell NWs are attracting a lot of interest as promising building blocks for next generation electronics,[33] photovoltaics thermoelectrics,[34,35] and optoelectronics,[36] our findings can give a crucial contribution to the development of such devices and more in general to the understanding of the doping process at nanoscale.

2.3. *Multiple Exciton Generation in Si nanocrystals*

Being source of clean and renewable energy, the possibility of converting solar radiation into electric current with high efficiency is one of the most important topic of modern scientific research. One of the hardest tasks is finding a suitable route to reduce in influence of loss factors, like for instance the phonon-assisted carrier relaxation mechanisms. In this context, Multiple Exciton Generation (MEG) or Carri-

[32] N. FUKATA, Y. MINGKE, W. JEVASUWAN, T. TAKEI, Y. BANDO, W. WU, Z. L. WANG, "ACS Nano" 9 (2015), pp. 12182-12188.
[33] J. XIANG, W. LU, Y. HU, Y. WU, H. YAN, C.M. LIEBER, "Nature" 441 (2006), pp. 489-493; S. OSSICINI, M. AMATO, R. GUERRA, M. PALUMMO, O. PULCI, "Nanoscale Res. Lett." 98 (2010), pp. 1637-1649.
[34] G. JOSHI, H. LEE, Y. LAN, X. WANG, G. ZHU, D. WANG, R. W. GOULD, D.C. CU , M.Y. TANG, M.S. DRESSELHAUS, G. CHEN, Z. REN, "Nanolett." 8 (2008), pp. 4670-4674.
[35] *M. Amato, M. Palummo, S. Ossicini, R. Rurali, SiGe Nanowires for Thermoelectrics Applications*, in *Nanoscale Thermoelectrics* ed. by X. Wang , and Z. M. Wang, Springer, Berlin, 2014, pp. 497-515.
[36] M.S. GUDIKSEN, L.J. LAUHON, J. WANG, D.C. SMITH, C.M. LIEBER, "Nature" 415 (2002), pp. 617-620.

er Multiplication (CM), that is the counterpart of the Auger recombination,[37,38] is currently promising. This effect leads to the generation of multiple electron-hole (e-h) pairs (excitons) after absorption of a single high.energy photon, with energy at least twice the energy gap of the system. By reducing the occurrence of high-energy dissipative processes and by increasing the number of carriers generated after photon absorption, CM is expected to increase solar cell efficiency. CM has been recorded in a large variety of NCs like for instance PbSe, PbS, CdSe, CdT, PbTe, InAs,[39] Ge[40] and Si[41] NCs. Effects induced on CM dynamics by energy transfer quantum cutting processes were observed[42,43,44] in Si NCs organized in a dense array. This effect, called space separated quantum cutting (SSQC), differs from the standard CM (one-site CM), because the generation of two e-h pairs after absorption of a single photon occurs in two different (space separated) NCs. CM via SSQC stems from the NC-NC interaction and represents one of the most suitable routes for solar cell loss factor minimization.

Recently our group has developed a new full ab-initio code in order to calculate, within first order perturbation theory, CM and Auger recombination lifetimes in both k-dispersive and low dimensional systems.[37,38,45] The computation of these physical quantities for a realistic system (several hundreds of atoms) requires massive parallel solution of mathematical problems that has been obtained by implementing efficient linear algebra algorithms. Our methodology has been applied to calculate CM lifetimes in both isolated (one-site) and interacting (two-site) Si NCs.

---

[37] M. GOVONI, I. MARRI, S. OSSICINI, "Phys. Rev." B 84 (2011), p. 075215.
[38] M. GOVONI, I. MARRI, S. OSSICINI, "Nature Photon." 6 (2012), pp. 672-679.
[39] A.P. LAZARO, J.T. STEWART, R.L. SANDBERG, W.K. BAE, W-K. KOH, J.M. PIETRYGA, V.I. KLIMOV, "Acc. Chem. Research" 46 (2013), pp. 1261-1269.
[40] S. SAEED, P. STALLINGA, F.C. SPOOR, A.J. HOUTEPEN, L.D. SIEBBELES, T. GREGORKIEWICZ, "Light: Sci. and Appl." 4 (2015), p. e251.
[41] M.C. BEARD, K.P. KNUTSEN, P. YU, J.M. LUTHER, Q. SONG, W.K. METZGER, R.J. ELLINGSON, A.J. NOZIK, "Nano Lett." 7 (2007), pp. 2506-2512.
[42] D. TIMMERMANN, L. IZEDDIN, P. STALLINGA, I.N. YASSEVICH, T. GREGORKIEWICZ, "Nature Photon." 2 (2008), pp. 105-109.
[43] D. TIMMERMAN, J. VALENTA, K. DOHNALOVA, W.D.A.M. DE BOER, T. GREGORKIEWICZ, "Nature Nano" 6 (2011), pp. 710-713.
[44] M.T. TRINH, R. LIMPENS, W.D.A.M. DE BOER, J.M. SCHINS, L.D.A. SIEBBELES, T. GREGORKIEWICZ, "Nature Photon." 6 (2012), pp. 316-321.
[45] I. MARRI, M. GOVONI, S. OSSICINI, "Beilstein J. Nanotech." 6 (2015), pp. 343-352; I. MARRI, M. GOVONI, S. OSSICINI, "J. Am. Chem. Soc." 136 (2014), pp. 13257-13266; I. MARRI, M. GOVONI, S. OSSICINI, "Solar Energy Materials & Solar Cells" 145 (2016), pp. 162-169; I. MARRI, M. GOVONI, S. OSSICINI, "Phys. Status Solidi" C (2017), p. 1700198.

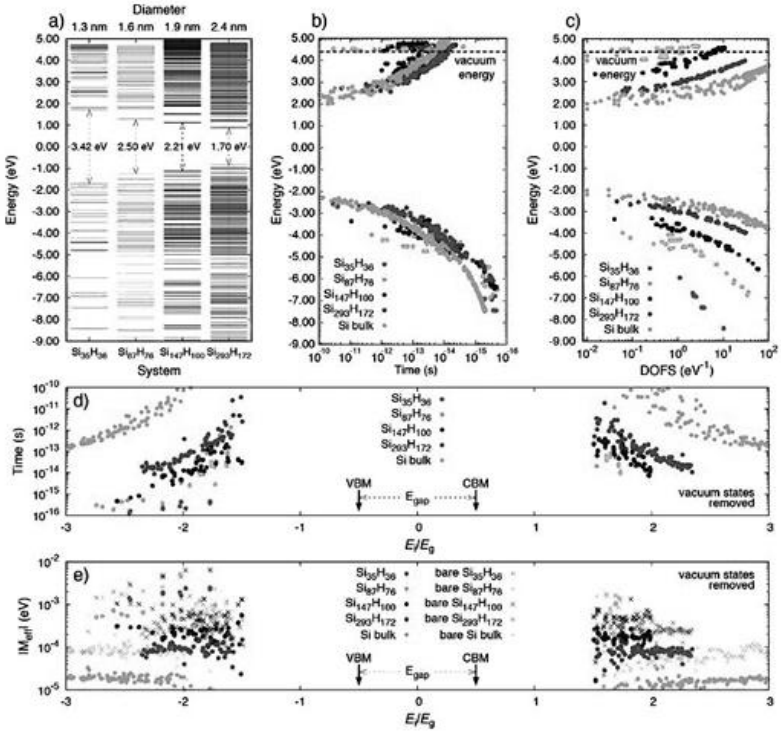

Figure 5: (Color online) Electronic structures of $Si_{35}H_{36}$, $Si_{87}H_{76}$, $Si_{147}H_{100}$ and $Si_{293}H_{172}$ NCs are reported in (a). One-site CM lifetimes calculated for the considered Si NCs and for the Si bulk are reported in (b) and (d). Both mechanisms which are ignited by electron relaxation (positive energy) and hole relaxation (negative energy) are considered. In (b), CM lifetimes are given as a function of the energy of the initial carrier, E_i. In (d) CM lifetimes are expressed in terms of the ratio E_i/E_g . The zero of the energy scale is set at the half band gap for each NC system. Dashed horizontal lines in (b) and (c) denote the vacuum energy level. In our calculations, we omit vacuum states, that is, conduction band states with an energy higher than the vacuum energy. The calculated density of final states are reported in (c). The results were obtained considering a broadening of 5 meV. The effective Coulomb matrix elements are given in (e). The filled circle data points represent results obtained by including both bare and screened terms in our equations and colored crosses represent only the bare terms. Reprinted with permission from ref.[45]

By considering spherical and H-terminated Si NCs ($Si_{35}H_{36}$, $Si_{87}H_{76}$, $Si_{147}H_{100}$, $Si_{293}H_{172}$, with diameter and energy gap ranging from 1.3 nm to 2.4 nm and from 3.42 eV to 1.70 eV, respectively) we have demonstrated that one-site CM can benefits from size reduction via quantum

confinement.[38,45] CM lifetimes calculated for the isolated Si NCs are reported in Fig. 5 as a function of both the energy of the initial carrier E_i (panel (b) absolute energy scale) and the ratio between the energy of the initial carrier and the energy gap of the system (E_i/E_g, panel (d), relative energy scale). In both cases, CM lifetimes are obtained by omitting vacuum states, which are conduction levels above the vacuum energy. The calculated CM lifetimes for Si NCs are then compared with those obtained for Si bulk. Looking a panel (d), where the energy scale adopted is the most appropriate for predicting possible photovoltaic applications of CM, we see that one-site CM lifetimes are faster in Si NCs than in Si bulk. In this range of energies, CM is sufficiently fast to compete with concurrent non-CM processes and, playing a fundamental role in the determination of the excited carrier dynamics, can be exploited to improve solar cell performance.[38]

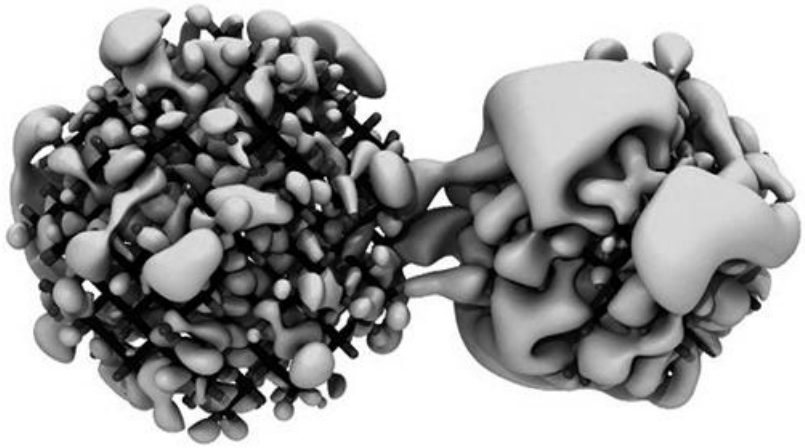

Figure 6: (Color online) Wave function localization for a couple of closely spaced and interacting Si NCs. The wave function sharing regime is evident.

Moreover we demonstrated, by calculating the properties of two Si NCs located at different distances,[38,45] that, for interacting NCs (two-site CM), the efficiency of SSQC processes is strongly affected by wave functions delocalization (see Fig. 6). This effect can boots CM dynamics when NC-NC interaction is not negligible, highlighting the impact of NC-NC interaction on CM dynamics. It is clear that only a

full quantum picture of the system, considered as a whole, properly describes the CM dynamics of two interacting nanocrystals in the considered range of separations. Thus, thanks to the ability of generating long-lived single e-h pairs distributed on different interacting nanostructures, SSQC is expected to have a great impact on solar cell devices based on Si NCs as long as the NCs are arranged in dense arrays. By tailoring CM by means of NCs proximity, NC-NC interaction can therefore be used to overcome the current solar cell limitations, opening a new route to the establishment of third-generation photovoltaics.

3. *Conclusions*

Within the DFT formalism we have developed, in these last years, advances theoretical tools for the calculation of microscopic properties of realistic systems to foster the realization of new Si-based materials and devices with desired and well-defined properties and functionalities. Regarding the optical excitations we have developed a new formalism for the calculation of nonlinear optical properties, valid for any kind of crystals and nanosystems, reaching a comprehensive understanding of the nonlinear microscopic physical mechanisms in the second-order response and the corresponding macroscopic relation with physical measurable quantities. We proved the possibility of exploiting the strain to overcome the inability of bulk Si to produce a significant second harmonic generation signal. Concerning doping we have considered the case of B and P co-doped Si NCs showing that, if carriers are perfectly compensated, the Si NCs undergo a minor structural distortion around the impurities inducing a significant decrease of the formation energies with respect to the single doped case. Due to co-doping additional peaks are introduced in the absorption spectra giving rise to a size-dependent red shift of the absorption spectra. This renders possible to tune the band gap of Si NCS, also below the Si bulk band gap in the infrared region. We showed, also, that efficient n- and p-type doping can be achieved in SiGe core-shell NWs, taking advantage of the band offset at the Si/Ge interface. An one-dimensional hole or electron gas is created at the band edge and the carrier density is uniquely controlled by the impurity concentration with no need of thermal activation. Additionally, SiGe core-shell NWs provide naturally the separation between the different types of carriers, electron and holes, and are ideally suited for photovoltaic applications. Regarding MEG, we presented DFT cal-

culations of CM lifetimes for isolated and strongly coupled Si NCs. Our results suggest that CM is more efficient in Si NCs than in Si bulk and that NC-NC interaction can be exploited to influence CM energy threshold and CM dynamics, especially when NCs are placed in close proximity. The new predicted effects can be exploited to improve solar cell performance.

Acknowledgements

The authors thank the Super-Computing Interuniversity Consortium CINECA for support and high-performance computing resources under the Italian Super-Computing Resource Allocation (ISCRA) initiative, PRACE for awarding us access to resource FERMI IBM BGQ, and MARCONI HPC cluster based in Italy at CINECA. Ivan Marri acknowledges support/funding from European Union H2020-EINFRA-2015-1 programme under grant agreement No. 676598 project MaX materials at the exascale.

ABSTRACT

Although silicon is the most widely used material in microelectronics, photonics and photovoltaics, in recent years concerns about the evolution of these sectors have been raised which seem related to fundamental materials and processing aspects. Example are the limitations of the operating speed of microelectronic devices due to the interconnect, the lack of optical second-order nonlinearities in bulk silicon, the necessity to improve the efficiency in solar cells. Silicon based systems with new functionalities able to solve these and other problems are highly desirable. In the last years, our group has developed new theoretical tools to study structural, electronic and optical properties of silicon based systems, in particular silicon nanostructures. Our analyses have permitted to predict new properties of silicon, thus opening new possibilities for applications of this material in different technological fields. Here we review our main results.