Comparative Study of Si and Ge Nanoparticles with Exotic Core Phases for Solar Energy Conversion

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Abstract — Third generation photovoltaic cells promise to overcome the Shockley–Queisser limit of solar cell energy conversion. In the Multiple Exciton Generation (MEG) pathway quantum confined highly energetic electron-hole pairs relax by emitting additional electron-hole pairs. The overall utility of this process is undermined, however, by the very fact that quantum confinement pushes the gap of nanoparticles (NPs) out of the solar spectrum. Here we propose that Si and Ge NPs with core structures made out of exotic high-pressure phases of bulk Si and Ge have lower gaps, more intense absorption and higher MEG rates than those of made out of the cubic diamond phase. Some of these exotic phases have already been proven to exist in colloidal NPs or on laser treated surfaces, therefore, our findings may open the door for promising solar applications of such exotic nanoparticle systems.

Index Terms — photovoltaic cells, third generation, multiple exciton, nanoparticles.

I. INTRODUCTION

Third generation solar cell designs aspire to transcend the Shockley–Queisser limit of 33.7% for the efficiency of solar energy conversion by employing path breaking new paradigms. Multiple exciton generation (MEG) is one of these new paradigms, where an incoming photon generates a high energy exciton, which then decays into multiple excitons. While the efficiency of MEG in bulk semiconductors is small, in 2002 Nozik suggested that in nanoparticles (NPs) the effective Coulomb interaction is enhanced by quantum confinement and the electronic screening decreased, driving the efficiency of MEG to promisingly high values \cite{1}. In 2004–2006, the Klimov group demonstrated that a strong MEG may indeed be obtained in semiconducting NPs (e.g., Ref. [2]), triggering intense theoretical and experimental interest \cite{3–11}. While the efficiency enhancement reported in Ref. [2] was later reanalyzed \cite{3}, the presence of MEG was eventually verified in colloidal NPs, albeit with a reduced magnitude \cite{6}. Recently, Semionin et al. demonstrated that the excess electrons generated by the MEG can be efficiently extracted from the NPs to the electrodes of a functioning PbSe NP solar cell; the MEG enhanced the external quantum efficiency above 100% within a region of the solar spectrum \cite{12}.

The remaining challenges include the high-energy threshold required to activate the MEG, estimated theoretically to be twice the optical gap but found experimentally around thrice the gap. Therefore, the solar photons can be best captured by multiple exciton generation in materials with gaps in the 0.5–1.0 eV range \cite{13}. For concentrated solar cells with a concentration factor of 500, the optimal gap has been shown to be as low as 0.1 eV \cite{14}.

However, while the quantum confinement enhances the Coulomb interaction, thereby enhancing MEG \cite{1}, it also increases the gap. The increase of the gap with decreasing NP radius can swiftly shift the MEG threshold energy outside the solar spectrum, rendering NP systems irrelevant for solar applications. Trying to control this problem by increasing the NP radius is problematic, however, because it reduces quantum confinement, thus the effective Coulomb interaction and the MEG efficiency. Therefore, the NP size and composition needs to be identified that optimizes these two competing requirements simultaneously: (i) quantum confinement should increase the excitation gap with respect to the bulk only moderately, but (ii) quantum confinement should increase the efficiency of MEG. Since in its simplest form (i) requires increasing the radius, while (ii) requires decreasing it, these two design criteria are obviously competing.

In this paper we explore whether these seemingly contradictory optimization criteria can be resolved by expanding the search space to nanoparticles with exotic core phases. We demonstrate our approach by studying Si and Ge NPs, preferred primarily because of their non-toxicity and abundance.

We carried out density functional theory (DFT) and many body perturbation theory (MBPT) calculations of the electronic, optical, and impact ionization properties of hydrogenated Si NPs and Ge NPs with exotic core structures resembling those of high-pressure phases. We showed that these nanoparticles, especially those with the BC8 and ST12 structures, exhibit simultaneously (i) low optical absorption thresholds and (ii) enhanced MEG rates even on absolute
energy scales. Hence we propose that these systems are promising candidates for deployment as the absorbers of MEG based solar cells.

To put our work into context, we recall that bulk Si retains its cubic diamond (Si-I or cd) structure upon compression up to 11.7 GPa, while its optical gap is reduced. Above 11.7 GPa, Si-I transforms to the metallic β-tin phase (Si-II) which, upon pressure release does not revert back to Si-I, but transforms into a series of metastable high-density phases with distorted tetrahedral bonding [15]. Under slow pressure release, the Si-XII/R8 phase is detected at ~8 GPa, followed by a transition to the Si-III/BC8 phase. Subsequent annealing at moderate temperatures leads to the formation of hexagonal diamond (Si-IV/hd) [15,16]. If β-tin is decompressed rapidly (<100 ms), two additional phases may be observed, Si-VIII and Si-IX, for which only incomplete structural information is available. It has been recently proposed that Si-IX has the Ibam structure [17]. Finally, two other Si polymorphs were predicted theoretically but not yet observed experimentally, ST12 [18] and body-centered tetragonal (bct) [19].

In 2006, Arguirov et al. reported the formation of BC8 Si NPs within amorphous Si in a-Si/SiO2 multilayer stacks [20]. In addition, Smith et al. [21] showed that R8 and BC8 NPs were formed when “black silicon” was produced by irradiating highly doped Si surfaces with femtosecond laser pulses. The authors argued that pressure waves generated by the fs pulses first amorphized regions of the sample and then induced the nucleation of R8 and BC8 NPs within these regions. Importantly, in the regions of the sample where BC8 NPs were detected, the absorption was substantially enhanced, especially at subgap energies, and then decreased upon annealing of the NPs. This suggests that BC8 particles played an active role in enhancing the low energy absorption.

These experiments suggest that Si NPs with core structures based on high-pressure Si phases are promising candidates to exhibit a lower gap than Si-I NPs and low energy optical absorption. This is especially true for the BC8 phase, which is gapless in the bulk. Therefore, we have selected these phases as the subjects for our study to analyze whether the strength of the Coulomb interaction is preserved in these phases so that the efficiency of MEG is preserved in such Si NPs.

Besides Si, Ge is another material to be explored for potential application for forming MEG-based NP solar cells. [22-25] The stable form of germanium at ambient conditions is the cubic diamond (CD) structure (Ge I phase). Upon applying a pressure of about 10 GPa, the structure of Ge transforms to the metallic β-tin phase (Ge II). After the release of pressure, one can end up with a variety of phases at room temperature and ambient conditions, depending on the kinetics of the transition. Slow decompression leads preferentially to the ST12 phase (Ge III) while faster transition to the BC8 phase (Ge IV). Interestingly, the electronic structure of ST12 germanium has not yet been experimentally explored. It can be expected though to have a gap larger than the CD phase. A value of ~1.4 eV is suggested by empirical pseudopotential calculations. More importantly, ab-initio calculations suggested that flat states lie around band edges yielding an enhancement in the density of states compared to the CD diamond phase [25], which is favorable for increasing the probability of the formation of multiple excitons. [26] The BC8 phase is known to be metallic. Recent reports confirmed the existence of other phases in germanium, such as the R8 phase, [27] or the hexagonal diamond one (Ge V) [28] but these have not yet been fully characterized. Contrary to the BC8 and ST12 phases of silicon, where the BC8 is metastable and ST12 is probably unstable; the ST12 phase of bulk germanium is metastable while the BC8 is unstable. The BC8 phase is only observable for a few hours before it transforms to the hexagonal diamond structure. We note that, with the exception of β-tin, all phases have Ge atoms forming four covalent bonds in tetrahedral directions.

Upon nanostructuring it is expected that gaps become larger than the bulk counterpart due to quantum confinement. [29,30] In case of BC8 nanoparticles for example, a small gap should open. Synthesizing Ge in the nanoparticle form has a long history and several different approaches were outlined in the literature, both “bottom-up” [31] and “top-down” methods were shown to produce germanium nanoparticles with cubic diamond core phase. [32] A recent work showed that microwave assisted heating proved to be a very efficient preparation method of diamond Ge NPs in solution. [33] Theoretical calculations suggested that ST12 nanoparticles were less stable than diamond ones given the formation under equilibrium conditions. However, kinetic trapping may stabilize one phase over the other. [34] This can be done for example through quenching of the initially amorphous NP. [34] Similar kinetic trapping may have happened in the case of a very recent study of Kim et al., where the successful colloidal synthesis of Ge NPs in the ST12 phase [35] was reported. Cluster-beam evaporated Ge NPs also showed signatures of ST12 core structure. [36]

II. METHODS

To explore the possible advantages of Si and Ge NPs with exotic high-pressure core structures, we carried out electronic structure calculations within Density Functional Theory (DFT) and Many Body Perturbation Theory (MBPT). We used the local density approximation (LDA) and norm-conserving pseudopotentials with an energy cutoff of 35 Ry. We relied heavily on the QUANTUM ESPRESSO package [37]. Quasiparticle energies were obtained within the GW scheme employing the approach of Nguyen et al., which avoids the explicit calculation of empty electronic states and the inversion of large dielectric matrices [38]. Optical absorption spectra were calculated within time-dependent density
functional theory (TDDFT), using the LDA and random phase approximation (RPA) and the Liouville-Lanczos approach [38]. Based on the results of our previous study [26], we assumed that the major contribution to MEG came from impact ionization (II) processes and we approximated MEG rates with II rates. We used the Fermi golden rule to obtain the decay rate of excitons to biexcitons. The initial exciton and final biexciton states were approximated as singly and doubly excited Slater determinants, built up from DFT orbitals in the generalized gradient approximation. To account for the dielectric screening within our GW and II calculations we computed the dielectric matrix within the RPA using iterative techniques.

The core geometry of the Si NPs was built by isolating a sphere of a given radius from the structure of the respective Si bulk phases. The radius and center of this sphere were chosen so as to obtain NPs with no more than two dangling bonds per surface atom. All dangling bonds were saturated with hydrogen atoms. The whole structure was then allowed to relax to the nearest local energy minimum.

### III. Results and Conclusions

The electronic gap of Si NPs with various core structures as a function of NP diameter is shown in Fig. 1. Sizes are given as twice the average radial distance of the NP surface atoms to the center, with size error bars representing the corresponding standard deviation. The BC8 NPs have significantly smaller gaps than all the other nanoparticles. For example, at the LDA level the gap of a BC8 NP of diameter 2.5 nm is 1 eV lower than that of Si-I NPs of the same size. This substantial difference is consistent with the fact that BC8 is a semimetal in the bulk. In fact, recent quasiparticle calculations for bulk BC8 predicted a 0.44 eV direct overlap of the bands at the H point, while measurements suggested an indirect overlap of 0.3 eV.

![Graph showing size dependence of gap for various exotic core structures](image)

**Fig. 1.** The size dependence of the gap as a function of the Si nanoparticle diameter for various exotic core structure Si NPs.

Fig. 2 illustrates the electronic gap of Ge NPs with various core structures as a function of NP size. BC8 nanoparticles have the smallest gap in the entire energy range. Interestingly, contrary to expectations, the gaps of ST12 nanoparticles are smaller than that of diamond ones and there is a crossover at a diameter of about 2.5 nm. This finding may imply that ST12 nanoparticles below a certain diameter might perform better than diamond ones for photovoltaic applications.

![Graph showing size dependence of gap for various exotic core structures](image)

**Fig. 2.** The size dependence of the gap as a function of the Ge nanoparticle diameter for various exotic core structure Ge NPs.

To sum up our findings, first we have calculated the electronic and optical properties and the impact ionization rates of Si nanoparticles with core structures based on high-pressure Si bulk phases. We used several levels of theory including DFT-LDA, TDDFT-RPA, and MBPT at the GW level. We found that BC8-like NPs exhibited significantly lower electronic gaps and a redshifted optical absorption compared to diamond-like ones. Importantly, they also showed an enhanced MEG efficiency, contrary to the expectation that lowering the gap may lead to reduced MEG efficiency because of the reduced effective Coulomb interaction. Several additional factors were explored that can further lower the NP’s gap and further enhance the efficiency of MEG, including surface reconstruction, residual compressive stress from matrix embedding, and chemical shifts caused by chalcogens at the NP-matrix interface. An optical gap lower than in diamond-like particles is a highly desirable feature not only for MEG-based solar cells but also for long wavelength absorber layers in all-Si NP tandem cells. Tantalizingly, recent experiments have shown that it is possible to form Si NPs with BC8 core structures in amorphous Si samples under high compressive strain conditions.

Turning to germanium, we computed the properties of Ge NPs with exotic core structures made out of high-pressure phases of bulk germanium. We found that ST12 nanoparticles have lower Kohn-Sham gaps than diamond NPs for nanoparticles with diameter of < 2.5 nm. BC8 NPs have smaller gaps than
the other two considered phases in the entire size regime. The low gaps translate to higher absorption only in case of BC8 nanoparticles, while ST12 nanoparticles absorb light comparable to diamond ones. Investigations of the impact ionization probabilities lead us to the conclusion that both BC8 and ST12 have higher probability of generating double electron-hole pairs at a given NP size.

Our findings imply that Si and Ge nanoparticles with exotic core structures made out of the high-pressure phase of their bulk counterparts may perform better for photovoltaic purposes than those with diamond cores and may offer a way of utilizing the multiple exciton generation phenomenon most efficiently.

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