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# Ab initio study on localization and finite size effects in the structural, electronic, and optical properties of hydrogenated amorphous silicon

Philippe Czaja[a], Massimo Celino[b], Simone Giusepponi[b], Michele Gusso[c], Urs Aeberhard[a,*]

[a] IEK-5 Photovoltaik, Forschungszentrum Jülich, 52425 Jülich, Germany
[b] ENEA, C. R. Casaccia, Via Anguillarese 301, 00123 Rome, Italy
[c] ENEA, C. R. Brindisi, 72100 Brindisi, Italy

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ABSTRACT

We present a first-principles study of the structural, electronic, and optical properties of hydrogenated amorphous silicon (a-Si:H). To this end, atomic configurations of a-Si:H with 72 and 576 atoms respectively are generated using ab initio molecular dynamics, where the larger structures are defect free, closely matching the experimental situation and enabling the comparison of the electronic and optical properties with experimental results. Density functional theory calculations are applied to both configurations in order to obtain the electronic wave functions. These are analyzed and characterized with respect to their localization and their contribution to the density of states, and are used for calculating ab initio absorption spectra of a-Si:H. The results show that both the size and the defect structure of the configurations modify the electronic and optical properties and in particular the value of the band gap. This value could be improved by calculating quasi-particle (QP) corrections to the single-particle spectra using the $G_0W_0$ method. We find that the QP corrections can be described by a set of scissors shift parameters, which can also be used in calculations of larger structures. The analysis of individual contributions to the absorption by evaluating the optical matrix elements indicates that strong localization enhances the optical coupling, but has little effect on the average transition probability $\langle |v_{cv}|^2 \rangle$, for which we find a dependence $E^2$ + const on the photon energy $E$, irrespective of the nature of the initial or final state.

## 1. Introduction

Hydrogenated amorphous silicon (a-Si:H) has been used as a cheap and efficient absorber material in silicon thin-film solar cells for more than 40 years [1], and has lately found another application in photovoltaics as a passivation layer in silicon-heterojunction cells. Understanding its microscopic structure in order to optimize its macroscopic properties for the application in photovoltaics has motivated several ab initio studies of a-Si:H throughout the years [2–8]. Two principle challenges are thereby met. First, a model atomic structure has to be generated that correctly reproduces certain experimental features of a-Si:H, such as the defect density, the radial pair correlation function, or the vibrational properties. Second, the electronic structure has to be calculated on a level that allows for the extraction of physically meaningful macroscopic properties. From the viewpoint of photovoltaics, special interest lies on the description of the optical properties and on the identification and characterization of localized defect states, which have a crucial impact on the device performance due to their role as recombination centers in non-radiative recombination [9].

While the generation of defective a-Si:H configurations, i.e., configurations containing dangling bonds, is instructive for studying the origin and the nature of localized defect states, these configurations are not well suited for obtaining realistic macroscopic properties, due to an overestimation of the defect density. In fact, structures containing one defect need to have a size of at least $10^6$ atoms to yield realistic defect densities [10], which is out of the range of current studies dealing with structure sizes of the order of 1000 atoms. The generation of defect-free configurations is therefore an important step towards a full ab initio description of a-Si:H. However, for a long time defect-free configurations of a-Si and a-Si:H could be generated only with model approaches such as the Wooten-Winer-Weaire algorithm [11], the Bethe-lattice approach [2] or the Reverse Monte-Carlo approach [12]. Only recently, large-scale (~500 atoms) atomistic simulations of a-Si:H using a quench-from-a-melt approach [7,13] combining both classical and ab initio molecular dynamics (MD) have been reported to yield configurations of low defect density [8]. The same approach was used to generate low-defect and even defect-free a-Si:H configurations of 72 atoms within ab initio MD [6]. Following this approach, we present

* Corresponding author.
*E-mail address:* u.aeberhard@fz-juelich.de (U. Aeberhard).

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atomistic ab initio MD simulations on a-Si:H, resulting in defective and defect-free configurations of 72 and 576 atoms, respectively.

The calculation and analysis of the electronic structure and the optical properties of a-Si:H on the Density-Functional-Theory (DFT) level has been the subject of a number of recent works [4–8]. The focus of interest in these works has been mainly on the origin of mid-gap states and band tails, and on the effect of hydrogen concentration and structural features on the mobility gap and the optical gap respectively. Very little attention has however been paid to the effect of computational artifacts on the electronic and optical properties. In particular, two effects should be taken into account when trying to reproduce the experimental properties of a-Si:H, and are therefore investigated in this work: the effect of the super-cell size and the effect of many-body interactions. A recent work stated that finite size effects do not play any role for structures larger than 72 atoms [6], which however disagrees with our findings. The incomplete description of many-body effects on the other hand is a well-known problem of standard DFT [14], and is the reason why the optical and mobility gaps are severely underestimated in previous studies using the local density approximation (LDA) or the generalized gradient approximation (GGA). Good values for the gaps have however been achieved recently with hybrid functionals [8]. In this work we try to incorporate many-body interactions systematically by explicitly calculating the quasi-particle corrections [15] to the Kohn–Sham energies. These corrections are often described by a heuristic approach – termed *scissors shift* (SS) [16] – where the electron energies are simply shifted to fit the experimental band gap. Since a distinct experimental value of the band gap of a-Si:H does however not exist, a set of shifting parameters can only be determined from a GW calculation. Here we present the results of such a calculation.

## 2. Technical details

Born–Oppenheimer molecular dynamics (BOMD) simulations and electronic structure calculations are performed on the DFT [17,18] level, using a PBE-GGA exchange–correlation functional [19] and periodic boundary conditions (PBC), meant to mimic an infinitely extended system.

For the BOMD simulations of the small structure (72 atoms) the PWscf (Plane-Wave Self-Consistent Field) code of the Quantum ESPRESSO suite [20,21] is used with ultrasoft pseudopotentials, whereas for the large structure (576 atoms) the Quickstep code of the CP2K suite [22] is used with norm-conserving Goedecker-Tetter-Hutter pseudopotentials [23–25]. All MD simulations are restricted to the Γ-point, which is justified by the size of the super cell.

The electronic structure is calculated with the PWscf code of the Quantum ESPRESSO package using norm-conserving pseudopotentials. **k**-point summations are carried out on a $4 \times 4 \times 4$ grid for the small system, and on a $2 \times 2 \times 2$ grid for the large system. The plane-wave cut-off energy is set to 52 Ry. These parameters were chosen by checking the convergence of the total energy of the system.

Quasi-particle corrections to the Kohn–Sham energies for the small configuration are obtained by performing single-shot $G_0W_0$ calculations [26] with the BerkeleyGW code [27] within the generalized plasmon-pole (GPP) approximation [28–30] on a $2 \times 2 \times 2$ grid using 3000 bands and a kinetic energy cut-off of 10 Ry. These values were chosen by checking the convergence of the LUMO–HOMO gap with respect to all three parameters simultaneously. The Kohn–Sham wave functions are retained as they are assumed to differ very little from the quasi-particle wave functions [30]. The GPP approximation is chosen because it has the advantage of requiring the dielectric tensor $\epsilon(\omega)$ only in the static limit $\omega \to 0$, while still taking into account the effects of dynamical screening. This ensures an accuracy similar to a full-frequency calculation for many semiconductors, including c-Si [31,30].

The BerkeleyGW code is also used for calculating the optical properties within linear-response theory using the random phase approximation (RPA) [32]. Electron-hole interaction is disregarded as it is generally assumed to have no significant effect on the absorption spectra of amorphous semiconductors [10].

## 3. Generation of the atomic structure

The first step towards the ab initio description of a-Si:H is the generation of physically meaningful atomic configurations, i.e., configurations that reproduce the experimental properties of a-Si:H. Our method of choice to achieve this is a simulated-annealing quench-from-a-melt protocol [7,13,33]. With this method two configurations are generated, one consisting of 64 Si + 8 H atoms, which we will refer to as the small system, and one consisting of 512 Si + 64 H atoms, which we will refer to as the large system. Both structures are cubic with a size of $a = 11.06$ Å and $a = 22.12$ Å respectively, resulting in a density of 2.214 g/cm$^3$ that matches the experimental value [7]. A hydrogen concentration of about 11% is chosen as this is the nominal concentration set in experimental materials optimized for photovoltaic performance [34].

The small structure is generated by randomly inserting H atoms in a crystalline Si cell, avoiding placing atoms too near to each other to minimize the energy of the system. A long (≈ 50ps) BOMD simulation is then performed on the system at constant volume and temperature $T = 2000$ K, controlled by an Andersen thermostat [35]. This simulation assures that any remaining crystalline symmetry in the atomic configuration is destroyed. During the high temperature simulation, atoms cover a distance of about 2 nm, which ensures that the final configuration retains no memory of the initial geometry. Afterwards the temperature is lowered to $T = 1200$ K within 5 ps and held constant for another 5 ps, as an intermediate step prior to the final quench to $T = 300$ K. This quench takes another 5 ps, which results in a high quench rate of $\sim 10^{14}$ K/s. The quenched configuration is then used as a starting point for a final BOMD simulation at room temperature to fully thermalize the amorphous system. After 30 ps of simulation another 5 ps are used to compute average physical quantities and to characterize the system with respect to structural and electronic properties. The final configuration at the end of the simulation is shown in Fig. 1.

The starting configuration for the large system is produced by replicating the small system in all directions. Since a high temperature annealing was already performed for the small system, a low temperature annealing in order to minimize the spurious defects at the internal interfaces is sufficient. For that purpose BOMD simulations are performed for 80 ps in time steps of 20 a.u. at constant volume. The temperature is controlled by a Nosé thermostat [36]. Within the first 60 ps the temperature is modified from 300 K to 600 K and back to 300 K in steps of 100 K. Afterwards, an additional simulation run at $T = 300$ K is performed for 20 ps. Fig. 2 shows the final configuration at the end of the simulations.

## 4. Structural properties

In order to characterize the system and estimate its quality in terms

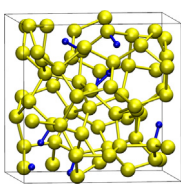

**Fig. 1.** Small a-Si:H configuration in the simulation box. The super cell consists of 64 Si atoms (yellow) and 8 H atoms (blue). Periodic boundary conditions are used in all three directions. The configuration is obtained by quenching from 2000 K to 300 K at a rate of $\sim 10^{14}$ K/s and subsequent thermalization at 300 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)