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Atomistic modelling of the interface structure of Si nanocrystals in silica

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Abstract.
Silicon as the basis of the conventional microelectronics industry is expected to be able to integrate both optical and electronic functionalities, leading to optics on silicon chips. Nevertheless, the long radiative lifetimes have until now obstructed efficient light amplification in this material. A novel nano-crystalline approach has disclosed a new prospect for silicon in the laser application field. The observed superior light emitting properties (compared to regular and porous silicon) of silicon nanocrystals (Si-nc’s) embedded into amorphous silica (a-SiO$_2$) are associated with more stable Si/SiO$_2$ interfaces in the new structures. However, the mechanism of this phenomenon still remains unclear, in part since the atomic structure of the Si-nanocrystal interface has not been known. In the present work, by means of molecular dynamics atomistic models, small Si-nc’s embedded into defect-free a-SiO$_2$ are constructed using two different classical interatomic potentials. After series of annealing runs, the interface structure and defects were carefully analyzed. The results show a thin suboxide layer, along with mostly undercoordinated defects at the interface region.

1. Introduction
Due to the inefficient capability of light emission, related to the indirect bandgap, the optical properties of silicon were never utilized in the conventional microelectronic industry. However, the idea of using low-cost silicon chips for light beam control in electronic devices has always been extremely fascinating. Pavesi et al. [1] recently demonstrated that light amplification can be achieved in small Si-nc’s embedded into a-SiO$_2$. Later on Kriachtchev et al. [2] also showed that the amplified pulses in the new systems can be very short, which is very important for fast operation of the optical devices. These first observations have stimulated a new generation of research activities in this field. The main interest is concentrated on the physical explanation of this phenomenon, in order to control the optical properties and increase the optical gain in the new structures. Within this novel nanocrystalline approach, the possibilities of maximization of the free carrier confinement and significantly decreasing the radiative lifetime have been firmly established. The wavelength of emitted light appeared to depend strongly on the size of the Si-nc, the smaller nanocrystals emitting shorter light waves with stronger intensity. The nature of luminescence in Si-nc is, however, still unclear. At the same time, the Si/SiO$_2$ interface is believed to play an active role in determining the optical properties of these structures [3] as a source of coordination defects which may serve as radiative recombination centers. Therefore, a clear understanding of the nature of the interface defects may help in elucidating the luminescence phenomenon in Si-nc.
Previous theoretical studies, mostly using DFT optimization of the system, have dealt with a very limited number of atoms due to the heavy computational cost of the method [4, 5]. There are also theoretical studies which were carried out for the flat Si/SiO$_2$ interfaces, where only one crystal plane of Si can interact with the silica substrate [6]. In the present work, we utilize computationally efficient classical interatomic potentials and molecular dynamics simulations (MD) to approach the experimental conditions by creating realistic-sized atomistic model of the Si-nc’s embedded into an amorphous silica matrix. In this approach it is possible to carry out high-temperature annealings to optimize the interface structure, without any built-in assumptions of the bonding or matrix structures.

2. Methods
In the present work by means of the MD parcas code [7] the insertion of Si-nc into amorphous silica matrix has been simulated. The size of the Si-nc was chosen to be 329 atoms, which corresponds to a sphere of $\sim$ 2.5 nm in diameter (almost exactly the same as in the in as in experiments [1]). A realistic structure of $a$-SiO$_2$ was constructed in two steps. At first, the Monte Carlo code bomc [8] based on the Wooten, Winer and Weaire (WWW) method [9] was used. This approach creates a structure free of coordination defects by simulating a continuous random network evolving with bond-switch Monte Carlo moves and a Keating potential [8]. During the second step, the structure was relaxed by MD to room temperature and zero pressure for 75 ps using both the Ohta [10] and Watanabe [11] potentials. These potentials have the advantage that they can describe in addition to the ideal bonding environment also coordination defects. In this way, we obtained two cubic cells of $\sim$80 nm$^3$ size (5184 atoms) with periodic boundary conditions. Both potentials were used during the insertion process of Si-nc’s into the $a$-SiO$_2$. For this purpose, holes of the same radius as the Si-nc were cut in the middle of silica cells. In order to avoid the formation of unreasonably short bonds at the initial stages of the MD run, the Si-nc was compressed evenly over the volume for about 3 Å before the insertion.

The preparation of the Si-nc/$a$-SiO$_2$ structure was performed as a series of annealing runs combined with pressure monitoring. A statistical variation was provided by random shifts of the insertion position of the nc, i.e. the same spherically cut nc surface facing different parts of the silica matrix, forming different interfaces.

The first pressure monitoring run aimed to release the compressive stress of the nc. Subsequently, a series of annealing runs were applied between the temperatures 1100 K and 300
K, with decreasing maximum temperatures, in order to find a reasonably low-energy interface structure. A last pressure control run carried out at a constant temperature of 300 K was used to release the strain due to temperature ramping procedures. One of the final structures constructed in this way is depicted in Fig. 1. All the processes have been monitored by the value of the average total energy per atom. The difference of this quantity in the final structures for different interfaces never exceeded 0.02 eV for either potential. This might be due to the relatively big difference in the numbers of the interface atoms and the atoms of the entire system, even though the sizes of the nanocrystal and surrounding matrix are comparable. Apparently, the actual number of defects in the interface region is fairly small and can not significantly affect the macroscale parameters.

3. Results and discussion
We have analyzed about 20 structures with different interfaces for both the Ohta and Watanabe potentials. Fig. 2 shows the radial distribution of the total energy per atom for one of the structures with the lowest average total energy. All the defects are clearly located in the narrow area around the interface. We conclude that, at least in the absence of long-time scale diffusion processes, the defective region is never wider than 5-6 Å. The coordination defects for the same structure are shown in Fig. 3. Having compared plots like Fig. 2 and 3 for all structures, we visually determined the width of the interface region. This comparison also elucidates the nature of the defects. The most favorable coordination defects formed at the interface are undercoordinated defects with one dangling bond; this result is very close in absolute values for both potentials. This conclusion is in very good agreement with DFT studies of flat interfaces (for example Ref. [6]). A difference appears for the overcoordinated defects, which seem to be formed easier with the Watanabe potential.

![Figure 2](image1.png)  
**Figure 2.** Scatter plot of the radial distribution of the total energy per atom for the Si-nc/a-SiO$_2$ obtained with the Ohta potential. The Si atoms of Si-nc ($\square$) are shown differently from Si of a-SiO$_2$ ($\diamond$). $\triangle$ is used to represent O atoms.

![Figure 3](image2.png)  
**Figure 3.** Scatter plot of the radial distribution of coordination defects in the same structure as in Fig. 1. The same markers are used for the same types of atoms. Note that the $r$-scale is focused on the interface region.

The presence of a suboxide layer (SiO$_x$, i.e. structures where Si has 4 bonds in total, but some of these are to Si and not to O as in ideal silica) was analyzed using bonding neighbourhood analysis. Since in a suboxide all the bonds are saturated, the corresponding atoms are not visible
in Fig. 3. However, they are associated with a difference in the total energy. This is visible as a much larger number of dots in the interface ‘cloud’ in Fig. 2 (potential energy) than in Fig. 3 (coordination defects).

The complete information of the nature of interface defects is summarized in Table 1. All the numbers are obtained as the percent fraction of the undercoordinated and overcoordinated defects, as well as the suboxide atoms, relative to the entire number of interface atoms for both potentials. The average thickness of the interface region is also given in the last column of the table.

Table 1. Si-nc/a-SiO$_2$ interface defects as the percentage of the total amount of interface atoms. The last column represents the mean width of the interface for both potentials. The error bars are the standard error of the mean.

| Potential     | Undercoord. | Overcoord. | Suboxide atoms | $\Delta r_{\text{Interface}}$[Å] |
|---------------|-------------|------------|----------------|----------------------------------|
| Ohta [10]     | 14.29% ± 0.6% | 3.8% ± 0.2% | 11.0% ± 0.5%   | 6.4 ± 1.5                       |
| Watanabe [11] | 10.5% ± 0.4% | 1.6% ± 0.1% | 12.8% 0.6%      | 6.8 ± 0.3                       |

These data show that the interface region is rather thin (< 7 Å) and not very damaged, since the total amount of coordination defects never exceeds 20 % of the entire number of interface atoms. Certainly, some destruction of crystal perfection in the interface region is observed (Fig. 1), but this might also relate to stretched bonds, which are not easy to analyse due to the amorphous structure which we have employed in the present simulations. At the same time, the number of overcoordinated defects is negligible in comparison with the undercoordinated ones.

4. Conclusion

By means of MD methods atomistic models of Si nanocrystals (∼2.5 nm) embedded into a-SiO$_2$ (∼4.3 nm) with periodic boundary conditions has been constructed. The results show that the interface region between the nanocrystal and silica is thin (< 7 Å) and that less than 1/5 of the atoms in it have defective bonding environments. Undercoordinated atoms clearly dominate over overcoordinated ones.

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