



Search for potential precursors for Si-atomic layer deposition – A quantum chemical study

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ABSTRACT

Thin film of silicon is an interesting material for many technological applications in electronic industry and in energy harvesting technologies, but requires a method for controlled growth of thin films. The purpose of this study is to screen a wide variety of Si content precursors for Si atomic layer deposition (ALD) reactions using state-of-the-art density-functional calculations. Among the studied 85 Si content precursors we found that $C_7H_{12}OSi$ -Methoxy-trivinyl-silane and C_7H_9NSi -Benzyliminosilane show positive indications for ALD reactivity for Si deposition. We believe that this finding will be helpful to develop low-cost, high-energy efficiency thin-film solar cells for future scale up implementation in photovoltaics.

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1. Introduction

One of the key technologies with the great scope of reducing greenhouse gas emissions is the solar cell, photovoltaics (PV). Critical factors for bringing PV even stronger into the market are the reduced cost and the increased energy efficiency. The current PV market is based on 300 μm thick silicon wafers cut from large ingots. The current trend is to further reduce the thickness, and hence the cost, of the material. However, due to the finite size of the cutting tools, the proportion of material wasted in the cutting process is increasing to substantial amounts ($\sim 50\%$). Alternative methods to produce thin layers of silicon are therefore sought. One concept is to reduce the silicon thickness down to 10–20 μm , which would also enable new designs such as flexible solar cells. Furthermore, the deposited Si would enter as a nucleation or capping layer enabling deposition on inexpensive supports (like steel, glass, etc) in production for PV devices. The development of low cost, high efficiency processes for deposition of Si in solar cells is a key to future scale up of PV [1]. Materials of such 10–20 μm thickness cannot be made with the current top-down approach but require the deposition of the materials on a support. Silicon can be deposited in numerous alternative manners such as physical and metal-organic chemical vapor deposition processes (PVD and MOCVD, respectively) providing suitable growth rates.

Nanoparticles of silicon can also be deposited through wet chemical methods forming a basis for radically new design of solar cells. However, in order to achieve the required properties, such as adherence and conformal coating, it is necessary to use a support which is reactive towards silicon.

Atomic layer deposition (ALD) has emerged as an important technique for depositing thin films for a variety of applications. Miniaturization in the semiconductor industry has led to the requirement for atomic level control of the thin film deposition. Miniaturization has produced very high aspect structures that need to be conformally coated. Any other thin film technique can approach the conformality achieved by ALD on high aspect structures. The ALD of single-element semiconductors such as Si and Ge can also be deposited using hydrogen radical-enhanced ALD. Studies of Si ALD using SiH_2Cl_2 and H radicals have demonstrated the self-limiting nature of Si ALD growth versus both SiH_2Cl_2 and hydrogen radical exposures [2,3]. The surface chemistry for Si ALD is based on the desorption kinetics for H_2 , HCl, and SiCl_2 from silicon surfaces. H_2 desorbs at 535 °C [4,5], HCl desorbs at 575 °C [4], and SiCl_2 desorbs at 725 °C [4,6] from silicon surfaces. A Si ALD growth per cycle of $\sim 1.6 \text{ \AA}$ was also observed between 550 and 610 °C. But, this temperature is too high for the fabrication of new devices/materials and novel structures such as Si-Ge hetero-junctions or super-lattices, because of the inter-diffusion of Si and Ge. At lower temperatures, the Si ALD growth per cycle decreases as a result of incomplete surface reactions. Si is very reactive and easily reacts with oxygen, forming silicides from oxide substrates (like SiO_2) or metallic substrates. Consequently, the

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nucleation of Si ALD is very difficult. The nucleation problems have limited the surface chemistry for Si ALD. The purpose of this study is to find a potential candidate for Si ALD using state-of-the-art density-functional calculations.

2. Computational details

All calculations have been performed using the atomic orbital density-functional theory (DFT) method as implemented in the DMol³ (MaterialStudio6.0) [7,8] Double numerical polarized (DNP) basis set that includes all occupied atomic orbitals plus a second set of valence atomic orbitals and polarized *d*-valence orbitals was employed. For exchange and correlation we applied the gradient corrected approach using the generalized gradient approximation (GGA) functional following the approach suggested by Perdew-Burke-Ernzerhof (PBE) [9,10]. It was shown by Delley [11] that the PBE functional with the efficient DNP numerical basis set gives enthalpies of formation for a large set of tested compounds and molecules from the NIST database closer to the experimental values. The estimated error was found to be lower than that obtained with the hybrid B3LYP/6-31G** functional. Self-consistent-field convergence criterion was set to the root-mean-square change in the electronic density to be less than 1×10^{-6} electron/Å³. The convergence criteria applied during geometry optimization were 2.72×10^{-4} eV for energy, 0.054 eV/Å for force and 0.005 Å for displacement. For all the optimized molecular structures we performed frequency analysis to check whether the obtained structure was a true minimum and only the ground state structures are analysed in this paper. In general, quantum simulations of surface reactions, such as those of ALD on the growing surface, can be performed using either a finite cluster or periodically extended supercell model of the reacting surface site. Here, for each Si system, we have used in first place a finite cluster approach. If the reactivity computed on the cluster was found to be positive, the extended model (periodic) was applied to simulate the Si ALD surface reactions.

For the surface calculations, a (100)-slab has been cut from the bulk crystal (FCC Si) structure, previously optimized with respect

to stress and strain. On the so-obtained slabs, all atoms have been allowed to relax minimizing the forces acting on them. A thick vacuum region was included to prevent slab-to-slab interaction along the normal direction to the surface. We found that a thickness of 12 Å was sufficient to achieve the energy convergence below the 1 meV/atom threshold. In order to obtain the asymmetric dimer reconstruction at the Si (100) surface we have used large atomic displacement factor for the surface atoms. Once the reconstructed Si (100) was obtained the OH groups are added to the surface dimers and the system was fully relaxed. For consistency of the computed values we have used similar computational parameters for the bulk and the cluster calculations in the DMol³ program. It should be noted that all the formation energies reported in this manuscript (both in the cluster model and in the periodic surface model) are at zero Kelvin. In order to compare the reaction energy between the cluster model and the surface 2D model at 300 K, the phonon contribution to the total energy for the 2D model is needed. This is a challenging task due to the huge computational effort involved. However we observed that the thermal contribution (zero-point energy) to the reaction energy in the cluster model calculation is less than 15 kJ/mol (at T = 300 K). Given that the energies per formula units are very close in the cluster and 2D model we expect the phonon correction to be negligible with respect to the zero-point energy. We therefore speculate that the picture of the relative reactivity for the analyzed precursors should not change significantly when the effect of the temperature is taken into account.

3. Results and discussion

In order to identify the potential precursor for Si ALD reactions we have considered 85 Si content precursors for our initial screening process (see Table 1). Since there is no unique criteria for the selection of the precursor molecule for the screening, the aforementioned molecules are chosen randomly among the precursors in the Chemspider database [12] with the lowest molecular formula (less than 40 atoms in the precursor). The precursors correspond to the lowest energy structure of the given molecular

Table 1
List of Si content precursors used in the screening process. The Chemspider ID is given in the parenthesis. Precursors are grouped according to the molecular formula. All the precursors contain either H or C and H. In addition one or more elements from Group V, Group VI and Group VII might be present.

H	H, C	H, C, Group V	H, C, Group VI	H, C, Group VII
H ₄ Si (22393), H ₆ Si ₂ (66736), H ₈ Si ₃ (122661)	C ₄ H ₁₂ Si (6156), C ₅ H ₁₀ Si (59499), C ₆ H ₁₄ Si (63007), C ₆ H ₁₈ Si ₂ (66675), C ₈ H ₁₈ Si ₂ (76286), C ₈ H ₂₀ Si (11919), C ₉ H ₁₄ Si (63045), C ₁₀ H ₁₀ Si (9227120), C ₁₀ H ₁₆ Si (63058), C ₁₀ H ₁₆ Si (263289), C ₁₂ H ₁₂ Si (63083), C ₁₄ H ₁₄ Si (123064), C ₁₅ H ₁₅ Si (4887719), C ₁₅ H ₁₅ Si (9404894), C ₁₆ H ₁₆ Si (9520373), C ₁₆ H ₁₆ Si (228965), C ₁₇ H ₁₆ Si (502323), C ₁₈ H ₁₆ Si (63117)	C ₄ H ₉ NSi (74110), C ₅ H ₁₄ SiN (14072949), C ₅ H ₁₅ SiN (67521), C ₆ H ₁₂ N ₂ Si (26905), C ₆ H ₁₉ N ₃ Si (76493), C ₇ H ₉ NSi (25933522), C ₇ H ₁₉ NSi (63633), C ₈ H ₂₂ N ₂ Si (10654667), C ₈ H ₂₄ N ₄ Si (66803), C ₁₀ H ₂₁ N ₂ Si (4909829), C ₁₀ H ₂₂ N ₂ Si (9140753)	C ₅ H ₁₂ O ₃ Si (68503), C ₅ H ₁₄ O ₃ Si (17017), C ₆ H ₁₆ O ₃ SSi (19280), C ₆ H ₁₈ O ₃ Si ₂ (23150), C ₇ H ₁₂ O ₃ Si (13806759), C ₈ H ₂₀ O ₄ Si (6270), C ₉ H ₁₄ O ₃ Si (17131), C ₉ H ₁₈ O ₃ Si (73227), C ₁₂ H ₁₂ O ₂ Si (13100), C ₁₄ H ₁₆ O ₂ Si (73339), C ₁₈ H ₁₆ O ₃ Si (63119) C ₆ H ₁₁ N ₃ Si (511524), C ₉ H ₂₃ NO ₃ Si (12933), C ₁₃ H ₂₃ NO ₃ Si (313782)	ClH ₃ Si (55530), Cl ₂ H ₂ Si (55266), Cl ₃ H ₃ Si (23196), Cl ₄ Si (23201), Cl ₆ Si ₂ (75334), FH ₃ Si (10328917), F ₂ H ₂ Si (109934), F ₃ H ₃ Si (122985), F ₄ Si (22962), F ₆ Si ₂ (123131), BrH ₃ Si (55529), Br ₂ H ₂ Si (123104), Br ₃ H ₃ Si (74222), Br ₄ Si (74225), Br ₆ Si ₂ (13783143), IH ₃ Si (10328917), I ₂ H ₂ Si (122989), I ₃ H ₃ Si (122986), I ₄ Si (75335), I ₆ Si ₂ (13783159), CH ₂ Cl ₄ Si (14523), CH ₃ Cl ₃ Si (6159), C ₂ H ₆ Cl ₂ Si (6158), C ₃ H ₆ Cl ₂ Si (29039), C ₃ H ₉ ClSi (6157), C ₃ H ₉ ISi (76879), C ₃ H ₉ BrSi (68599), C ₄ H ₉ F ₃ Si (480635), C ₄ H ₁₁ ClSi (67897), C ₆ H ₁₅ ClSi (13221), C ₆ H ₁₅ ClSi (26908), C ₈ H ₁₁ ClSi (12487), C ₁₂ H ₁₀ Cl ₂ Si (6375), C ₁₄ H ₁₄ ClSi (9308756), C ₁₆ H ₁₅ F ₂ N ₃ Si (66326), C ₁₈ H ₁₄ ClSi (4905153), C ₁₈ H ₁₅ ClSi (6216) C ₄ H ₉ F ₃ O ₃ SSi (58839), C ₇ H ₁₅ F ₃ O ₃ SSi (110158)

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