

Semiempirical Direct Dynamics Trajectory Study of the $\text{Si}^+ (^2\text{P}) + \text{H}_2 \rightarrow \text{SiH}^+ + \text{H}$ Reaction

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Abstract

Silicon chemical vapor deposition (CVD) is widely used in the microelectronic industry for the production of integrated circuits. For the underlying chemical reactions, the dynamical properties of the involved Si-H compounds are of fundamental interest. In this paper, we present a trajectory study of one of the most fundamental reactions necessary for the deposition technique $\text{Si}^+ (^2\text{P}) + \text{H}_2 \rightarrow \text{SiH}^+ + \text{H}$. Our interest in this reaction was triggered by the outstanding experimental work on this topic by Armentrout et al.[3]. In our simulation study, we performed classical trajectory calculations where we determined the necessary potentials "*on the fly*" using quantum chemistry [11]. We compare our theoretical results based on the semiempirical UHF/PM3 method with the experimental ones. Using a large range of impact kinetic energies, we calculated the cross section for the title reaction and find an excellent agreement with the experimental values.

1 Introduction

The interaction of atomic hydrogen with hydrogenated amorphous silicon (a-Si:H) has been widely investigated in order to understand the different bonding sites in the structure. This understanding might facilitate the optimization of the growth of poly-

morphous silicon films (pm-Si:H) which have good transport properties attributed to the incorporation of crystallites or "nanoparticles" in the film [6]. Indeed, the use of pm-Si:H as intrinsic layer in single junction p-i-n solar cells has resulted in efficiencies of 10 % in stable solar cells [7]. These electronic properties of the deposited film are strongly influenced by the hydrogen concentration in the film which can be controlled by our "Plasma Enhanced Chemical Vapor Deposition" (PECVD) conditions [9]. PECVD is a commonly used technique for the growth of such films. However, little is known about the detailed structure of these polymorphous films because of the small size of the incorporated silicon clusters produced in the gas phase; i.e. it is difficult to distinguish them from the amorphous phase. To address this question, a detailed understanding of the formation of clusters or crystallites and their contribution to the film deposition is essential.

Recently, there has been an intense interest in developing simple interatomic model potentials which permit direct calculation of the structural properties and energetics of complex semiconductors systems [16, 17].

In the present paper, we use classical trajectory calculation and we determine the necessary interatomic potentials "*on the fly*" using quantum chemistry. For sufficiently small Si-H systems, this approach turns out to be very efficient since it does not rely on any

"model" potentials nor fitting parameter.

2 Experimental

The experimental results have been published by Armentrout et al. [3]. They examined the reaction of ionic silicon with molecular hydrogen, $\text{Si}^+ (^2\text{P}) + \text{H}_2 \rightarrow \text{SiH}^+ + \text{H}$, by using a guided ion beam mass spectrometer. The total reaction cross section σ of this reaction has been measured as a function of relative reactant kinetic energy. It may be modelled using the general form $\sigma(E) = \sigma_0(E - E_0)^n/E^m$, where E is the relative translational energy, E_0 is the threshold energy, and σ_0 is an energy independent scaling factor [3]. This reaction proceeds without activation barriers, as it has been proved experimentally [4] and theoretically [13] for the same reaction with carbon. The experiments were performed at a temperature of 305 K. Consequently, Armentrout assumed for the hydrogen molecule that the average rotational energy was 0.027 eV and that the vibrational excitation was negligible at this temperature. Si^+ was produced in the ^2P ground state which has an electronic energy of 0.024 eV.

3 Simulation methodology

All trajectories are evaluated by solving Newton's equation of motion with a fifth order Gear algorithm [12]. We use the methods of molecular-dynamics simulations; i.e., we integrate the Newtonian equations of motion for all interacting particles yielding their phase space trajectories. The numerical integration stepsize is 0.001 fs which typically results in an energy deviation of less than 0.5 % along one trajectory of 200000 time steps. The maximum of the impact parameter b_{max} was determined to be 1.5 Å. We obtained this value by calculating many trajectories with different impact parameters and found that no reaction occurred when the impact parameter was larger than 1.5 Å.

Using a maximum impact parameter b_{max} , we can define the cross section as a function of the probability P of forming products

$$\sigma = \pi b_{max}^2 P$$

where the probability is simply the ratio of the sum of states in the product channel over the total sum of states for all channels. To study the dynamics of the considered chemical reaction, we used direct dynamics calculations. In this paper, the employed semiempirical molecular orbital method UHF/PM3 [11, 14, 15] has been successfully applied to the title reaction. This quantum mechanical method allows us to determine all interatomic potentials of our system "on the fly"; i.e. at each time step of the classical trajectory. Our criterion for obtaining a converged, self-consistent field is that the energy of two successive iteration steps differs by less than 10^{-6} Kcal/mol in order to obtain a very good energy conservation for the entire trajectory. At the end of each trajectory, a product analysis is performed to determine the vibrational and rotational energies, as well as the relative translational energies of the products based on their atomic coordinates and momenta.

4 Results and discussion

Figure 1 shows the cross section evolution as a function of reactant translational impact energy for H_2 molecules in their vibrational ground state and in a rotational state of $J = 1$.

The cross section rises to a maximum value of 1.69 Å² at 4 eV which is in a very good agreement with the maximum experimental value. Above 4.5 eV, the cross section decreases which can be attributed to product dissociation as $\text{Si}^+ (^2\text{P}) + \text{H}_2 \rightarrow \text{Si}^+ + \text{H} + \text{H}$.

The fact that even at the maximum not "all" reactants undergo the title reaction was interpreted as evidence that in many collisions, the system passes through configurations in which all three atoms interact strongly for times which are of the order of one rotational period [8, 10]. In other words, the non reactive scattering at these energies shows very unstable components. These complexes, such as SiH_2 , can then decompose into products or go back to the reactants via "loose" transition states. The employed

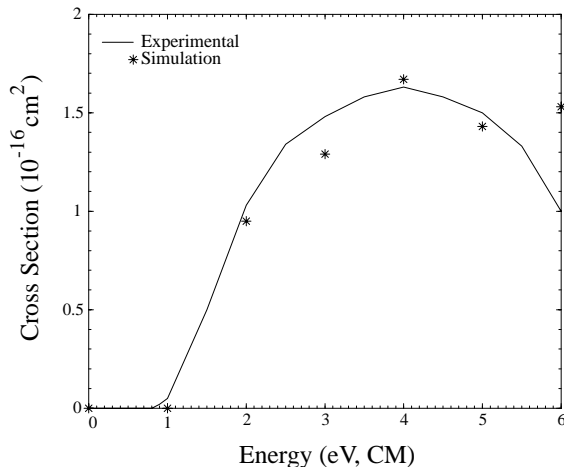


Figure 1: Cross section for the studied reaction as a function of translational impact energy.

semiempirical PM3 procedure gives completely satisfactory results for the studied reaction, as compared to the experiment, except for the very last point, all results are within the $\pm 20\%$ experimental uncertainty.

We like to point out that our calculational method does not only give excellent agreement with the experiments, but that it also avoids the use any fitting parameters and "model" potentials. Besides, this molecular orbital method is much faster than Hartree-Fock (HF) *ab initio* calculations [5]. This powerful, but less computationally expensive level of theory will allow us to use this simulation method for larger and more complex systems.

5 Conclusion

In this work, we used the semiempirical UHF/PM3 direct dynamics trajectories method to determine the cross section for the endothermic ion-molecule reaction of Si^+ with H_2 . This theory gives excellent agreement with experiments for the behavior of the cross section. Such an agreement is obtained without any fitting parameters nor any model potentials. It is instructive to alternatively calculate the cross

section by using MNDO [1] and AM1 [2] semiempirical approximations. In fact, first attempts show that the PM3 approach yields the best agreement with experiments.

In addition, the dependence of this reaction on the initial vibrational and rotational energy of the hydrogen molecule will be investigated. In conclusion, semiempirical theory promises to be very useful for the modelling of the dynamics of small SiH systems.

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