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MECHANISMS AND RATE DETERMINING STEPS IN PLASMA INDUCED HIGH RATE CVD OF SILICON AND GERMANIUM: SIMILARITIES AND DIFFERENCES

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ABSTRACT The recent progress in the understanding of the reaction mechanism of plasma induced CVD of silicon from silane and the identification of the rate determining steps enabled us to significantly increase the deposition rate of device quality a-Si, μ c-Si and epi-Si. The mechanism is similar to that found for thermal CVD. The first step is the fragmentation of monosilane into SiH_2 and H_2 followed by fast insertion and formation of disilane and trisilane. The higher silanes represent the reactive intermediates for the silicon deposition because their reactive sticking coefficients are orders of magnitude larger than that of monosilane. All these features of the mechanism are well documented by experimental data from our and several other laboratories and by theoretical calculations which will be summarized here.

The understanding of plasma CVD of germanium from monogermane is less complete. Our recent data show that there are at least two different kinetic regimes with a different reaction mechanism. The data show that, unlike in the case of silicon, higher germanes are probably not involved in the process. A very preliminary interpretation of the data suggests that divalent fragments and possibly other radical species are the dominant precursors for the deposition of germanium. Significant differences between silicon and germanium are found also regarding the amorphous-to-crystalline transition.

1. INTRODUCTION

The effort to understand the reaction mechanism and the rate limiting steps in the plasma induced CVD (P CVD) of silicon and germanium is motivated by the need to increase the deposition rate of device quality materials. So far, the P CVD was the only method which allowed one to prepare high quality a-Si for solar cells and other devices [1,2]. Nanocrystalline silicon (nc-Si, frequently called also "microcrystalline, μ c-Si") with a typical crystallite size of 3 to 20 nm emerged recently as a novel material for a number of device applications [3]. It can be prepared by

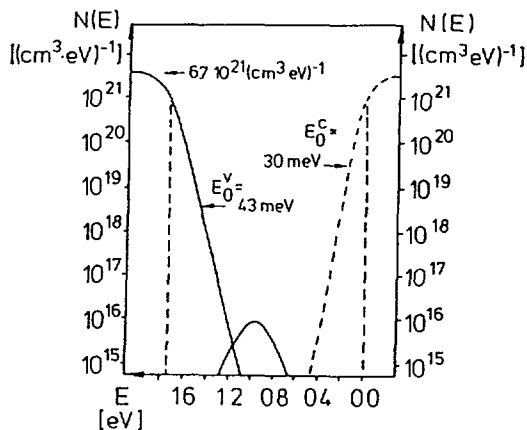
P CVD from silane diluted with hydrogen or by chemical transport at temperatures between about 60 and 500°C [3]. At higher temperatures, polycrystalline silicon with crystallite size of ≥ 100 nm is grown [4,5].

In all these cases the application of glow discharge plasma helps one to increase the deposition rate and to improve the material quality. A similar improvement is expected also for the epitaxial growth at temperatures below about 600°C, where the thermal CVD and molecular beam epitaxy yield only very low growth rates of less than 0.1 nm/s. Using the P CVD we could reach significantly higher rates, but much work has to be done regarding the quality of the deposited epi-films.

The typical deposition rate of device quality a-Si which is achieved in the laboratory and in the industrial production is about 0.1 to 0.2 nm/s. This means that for the deposition of a 500 nm thick layer of intrinsic, photosensitive a-Si in the solar cells, the deposition time ranges between about 80 and 40 min: Increasing the rate to 1.7 nm/s reduces the deposition time to less than 5 min which results in a significant reduction of the production costs.

Such an increase of the deposition rate resulted in the past in a strong deterioration of the material quality. Only Curtins et al. succeeded to reach empirically comparable rates and good material quality by the use of 80 MHz excitation frequency [6]. However, only the recent progress in the understanding of the reaction mechanism and the rate limiting steps allowed us to reach even higher rates for device quality material, and to provide the basis for scaling towards large industrial reactors [7-10].

Figure 1 shows an example of the defect density distribution within the mobility gap of a-Si prepared at a deposition rate of 1.64 nm/s. The density of dangling bonds of about $< 3 \cdot 10^{15}$ cm $^{-3}$ and Urbach edge of about 43 meV are among the lowest values ever reported in the literature for a-Si samples which were, however, deposited at much lower rates [2].



$$j = 72 \text{ mA/cm}^2, T_{\text{dep}} = 260^\circ\text{C}, r_{\text{dep}} = 16.4 \text{ \AA/s}, d = 38 \mu\text{m}$$

Fig.1: Density of defect states within the mobility gap of a-Si (measured by the constant photocurrent method, CPM) deposited at high rate of 1.64 nm/s [11]. Total pressure 0.2 mbar, $T_{\text{dep}} = 260^\circ\text{C}$, discharge current density 7.2 mA/cm^2 .

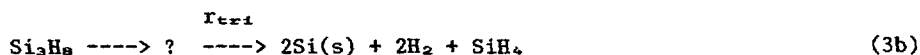
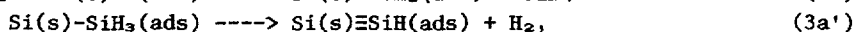
Very little is known about the kinetics and mechanism of P CVD of germanium. Various observations indicate that there seem to be significant differences in the conditions for the preparation of device quality a-Si and a-Ge. For example, strong dilution of germane with hydrogen, intense discharge and ion bombardment of the gro-

wing film are necessary to obtain good quality a-Ge [12-14], whereas such conditions yield a-Si of a poor quality. The chemical and physical explanation of the empirical finding regarding the optimum conditions for the a-Ge deposition are lacking.

This paper represents an attempt to bring more insight into the kinetics and possible mechanisms of the a-Ge deposition. The emphasis will be on the differences of the kinetics and mechanisms in $\text{GeH}_4/\text{H}_2/\text{Ge}$ and $\text{SiH}_4/\text{H}_2/\text{Si}$ -systems under plasma conditions. Because of the limited space available here we shall restrict ourselves to a brief summary of the results available in our recent papers regarding the mechanism of a-Si and c-Si deposition and compare them with new data on the kinetics of the decomposition of germane and deposition of a-Ge and c-Ge.

2. THE REACTION MECHANISM AND RATE DETERMINING STEPS IN a-Si DEPOSITION

The mechanism of a composite reaction cannot be proved with certainty because the kinetic data can very often be explained in terms of different mechanisms. In that sense, the most likely mechanism of the P CVD of a-Si is summarized in equations (1-3) [7-9]. Here, r_{a1} and r_{t1} are the overall reactive sticking coefficients of di- and trisilane.



The basic kinetic data and theoretical analysis of that mechanism have been published recently [7-9]. More recent work of Kulkarni et al. suggested that, at a temperature of $\leq 400^\circ\text{C}$ where the surface is covered with chemisorbed hydrogen, only one silicon atom is deposited from one molecule of disilane (eq. 3a) due to the insertion of the SiH_2 into a surface Si-H -bond [15,16]. The actual mechanism of the surface reactions is rather complex and depends on the surface temperature and the related coverage with chemisorbed hydrogen.

No data regarding the detailed mechanism of trisilane decomposition are available. Thus we assume in analogy with the disilane a stoichiometry indicated in reaction (3b). The numerical modeling of the kinetic data based on the overall mechanism is sensitive to the exact number of Si atoms deposited from di- and trisilane in the sense that the calculated reactive sticking coefficients of these species depend on that number. A fairly good fit of the calculated and measured values of the time dependent concentrations of mono- di- and trisilane and of the deposition rate can be obtained regardless of the details of reactions (3a,b) [17].

A decisive check of the mechanism provides the measured correlation of the di- and trisilane concentrations because reaction (2b) is the only way that trisilane can be formed in that system because the numerically feasible reaction (4) is endothermic and therefore slow [8].



Thus, using only the reactions (2b), (3a) and (3b), which yield three independent linear algebraic equations for the three unknown quantities $[\text{SiH}_2]$, r_{d_1} and r_{t_1} , one can unambiguously calculate these quantities for various dwell times of the species in the plasma. In a recent paper [8] this has been done under the assumption that two and three Si atoms are deposited from di- and trisilane, respectively. More recent recalculations have shown that the calculated value of the SiH_2 -concentration of about 10^{10} cm^{-3} does not change significantly if the stoichiometries of eq. (3a) and (3b) are used.

This straightforward calculation does not use any assumption regarding reactions (1) and (2a). The calculated concentration of SiH_2 can now be used to calculate the disilane concentration according to reaction (2) and to verify in this way the self-consistency of the mechanism. Figure 2 shows that the agreement between the measured and calculated data is very good.

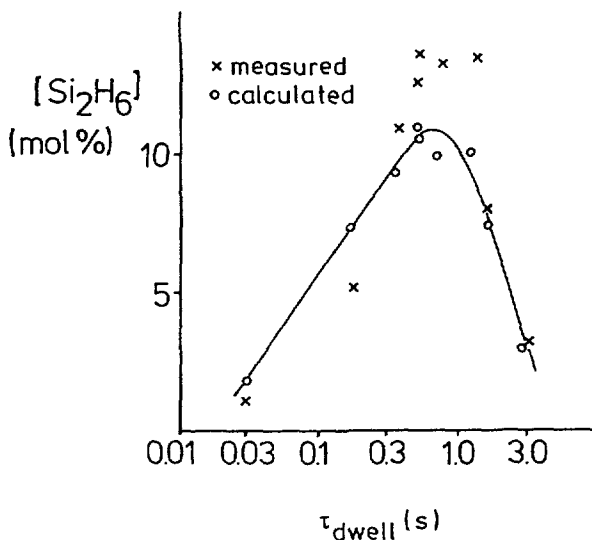


Fig.2: Comparison of the measured and calculated (eq. (2a)) concentration of disilane vs. dwell time of monosilane in the discharge. Total pressure 0.2 mbar, pure monosilane admitted, discharge current density 0.06 mA/cm² [8].

As stated at the beginning of this section, even such a good agreement cannot be taken as a proof of the unambiguity of that mechanism. A critical researcher has to ask whether another mechanism could explain the measured data. This has been done for the frequently discussed model of SiH_3 assuming (without any experimental evidence) that disilane is formed from two SiH_3 radicals according to equation (5) with a rate constant equal to that of reaction (2a).



These assumptions strongly favour the SiH_3 model (the rate constant k_5 is smaller than k_{2a} and the reaction of two silyl radicals yields disilane in an excited state which decomposes with a high probability into SiH_2 and SiH_4 at the low pressure used in the experiments). In spite of that, the calculated SiH_3 concentration of 10^{13} cm^{-3} which would be necessary to explain the experimental data in Fig.2 is at least two to three orders of magnitude larger than the reported one (see [8] for the references). More recent data and calculations confirm these conclusions.

tion between the deposition rate and the concentration of digermane shows that the latter is not the precursor for the deposition. The deposition of germanium proceeds evidently via GeH_x fragments. The cross section data for electron impact excitation of various states of GeH_4 [12a] and the pronounced tendency of germanium towards divalency suggest that GeH_2 is the most likely precursor for the deposition. This is in contrary to the case of silicon (see reactions 1-3).

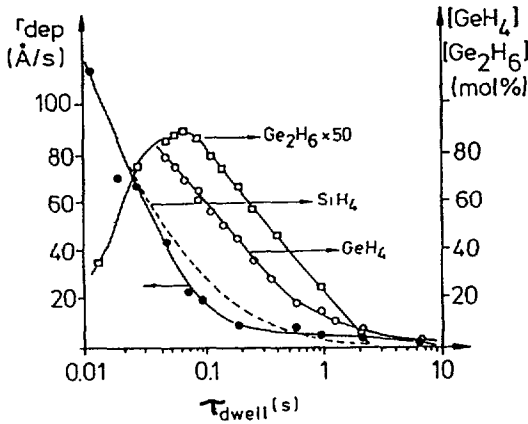


Fig.4: Dependence of the deposition rate and of the concentration of mono- and digermane on the dwell time of the germane in the discharge. Total pressure 0.2 mbar, $T_{\text{substrate}} 150^\circ\text{C}$, discharge current density 3.6 mA/cm^2 . The decomposition of silane under the same plasma conditions is shown for comparison.

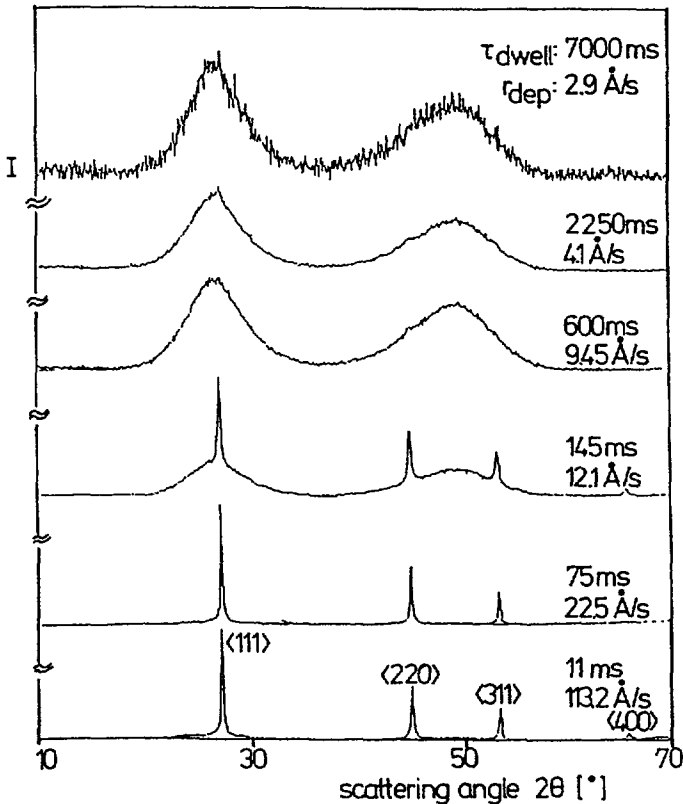


Fig.5: X-Ray scattering from a-Ge and c-Ge films deposited under conditions of Fig. 4 and various dwell times as indicated. The deposition rates are given as well.

Both silane and germane are thermodynamically unstable but germane is less stable due to its higher positive free enthalpy of formation of 21.7 kcal/mol as compared to silane 8.2 kcal/mol. Also the temperature of the onset of thermal decomposition of germane (about 285°C) is significantly lower than that of silane (about 550°C). In spite of that, germane decomposition in the discharge is, under the same conditions, significantly slower [26]. This lower reactivity of germane is well known from many other systems and related to different polarity of the Ge-H bond as compared to Si-H bond which has negative partial charge on hydrogen.

Another significant difference between silicon and germanium is found in the a-c transition. As mentioned above, in the case of silicon c-Si is formed at low silane concentrations and deposition rates whereas a-Si requires deposition to occur at a high silane concentration far away from the partial chemical equilibrium. Figure 5 illustrates that the opposite behaviour is found during the deposition of germanium. Crystalline germanium is obtained under conditions of high germane concentration and deposition rates up to 12 nm/s ! Only when the deposition rate decreases below 1 nm/s a-Ge is formed. This difference is probably related to a structural instability of a-Ge which has been occasionally observed by other researchers as well [27].

For lack of space available here we cannot discuss these results in more detail. Also the regime of even lower deposition rates where another a-c transition occurs has to be left out. We refer to the coming paper for further details [26].

4. CONCLUSIONS

The reaction mechanism and the rate limiting steps of the deposition of a-Si and c-Si are relatively well understood and described in terms of the composite model summarized in eq. (1-3). A careful check for the selfconsistency strongly supports this mechanism.

The SiH₃ model cannot explain the experimental data for the high rate deposition of good quality material.

The plasma CVD of germanium proceeds via GeH_x fragments. Germylene, GeH₂ is the most likely candidate for the deposition at high rates.

There are significant differences between silicon and germanium deposition regarding the reaction mechanism, decomposition rates of SiH₄ and GeH₄, and of the crystalline-to-amorphous transition. Several hypothesis which can explain these differences have been suggested.

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