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Dopant Gas Effect on Silicon Chemical Vapor Depositions

A Surface Potential Model

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A surface potential model is proposed to consistently explain the known dopant gas effects on silicon chemical vapor deposition. This model predicts that the effects of the same dopant gases on the diamond deposition rate using methane and carbon tetrachloride should be opposite and similar to those of silane, respectively. Available data is in agreement with this prediction.

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Chemical vapor deposition (CVD) has been widely used for thin film depositions. This technique is especially applicable to thin film silicon solar cells. Deposition rate of a few microns per minute can be easily obtained, and p-n junction can be made by mixing silicon chemical vapors (CV), such as silane and silicon tetrachloride, with depant gases, like diborane and phosphine. In general CVD of silicon is carried out at a substrate temperature around 1000 to 1200°C, and single crystal silicon wafer is used for an epitaxial growth of thin films. However, for an economic thin film solar cell, non-crystalline, and oftentimes non-silicon substrates, are required. Furthermore, interaction between the substrate chosen and the silicon thin film deposited should be kept minimal. For example, at a substrate temperature around 1200°C, silicon thin films deposited on graphite show a significant diffusion of silicon and carbon and the formation of silicon carbide[1]. Much less diffusion is noted, however, when the substrate temperature is below 800°C[2]. Similar high temperature interaction between the silicon films deposited and other types of substrate has also been reported[3]. Preferably, one should use the lowest possible substrate temperatures to minimize such interactions and diffusions.

At low substrate temperatures, however, other problems arise. First, silicon film deposited is polycrystalline with small grain sizes[4]. Second, much lower deposition rate than that at high substrate temperature is obtained using the CVD technique[5]. Small grain size means a shortening of lifetime for the charge carriers due to trapping by the grain boundaries[6]; low deposition rate makes CVD a non-economic technique for depositions. To solve the former problem the author has developed a technique to increase the silicon crystallinity at low substrate temperatures[7]. An enhancement of two to four orders of magnitude is obtained for the silicon films deposited on quartz and graphite at 600°C substrate temperature[7,2]. Our next goal is to increase the deposition rate of low temperature CVD. As part of our effort toward this goal we describe in this paper a conceptual model which could lead to a better understanding of the existing information on the variation of CVD deposition rates. This model is shown to consistently explain the known dopant gas effects on the deposition rates of silicon chemical vapors and correctly predicts for those on carbon chemical vapors. The implications and application of this model to other studies are also discussed.

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It has been known that silicon deposition rate using silane, SiH_4, and silicon tetrachloride, $SiCl_4$, is increased by diborane, B_2H_6, and decreased by phosphine, PH_3, and arsine, AsH_3[8]. Existing theories considering active site blocking[8b] and strong bonding between the CV molecules and dopant gas molecules[8c] have not been advanced enough to explain the known effects in a consistent way, nor can they be used to predict the dopant gas effect on other CV molecules. In our approach we make use of the fact that diborane, a p-type dopant gas for silicon, gives an opposite effect on the deposition rate of silicon chemical vapors from those by phosphine and arsine both of which being n-type dopant gases. This implies a possible correlation between the electronic structure of the dopant atoms with the observed effects cited. The mechanism involved in the CVD process is first analyzed, in order to see how this property can be incorporated into the deposition process.

Chemical vapor deposition can be viewed as a two-step process: adsorption of the CV molecule on the substrate surface followed by its thermal decomposition. As an example, deposition of silane follows

$$SiH_4 \text{ (gas)} \rightarrow SiH_4 \text{ (adsorbed)} \xrightarrow{heat} Si + 2H_2 .$$

The thermal decomposition part involves a transfer of thermal energy from the substrate to the CV molecule needed for its decomposition. At a fixed substrate temperature, the maximal amount of thermal energy which can be acquired by the CV molecule is constant. The efficiency of this energy transfer, however, depends on the residence times of the CV molecule on the substrate surface. In other words, for an effective decomposition of the CV molecule to take place on the surface, a sufficient amount of thermal energy necessary for such decomposition should be transferred to the CV molecule before it desorbs from the surface. Therefore, at a fixed substrate temperature, decomposition of the CV molecule will be determined by the adsorption efficiency of this molecule on the substrate surface. This argument is in agreement with the work of Farrow who found that silane adsorption is the rate limiting step for the decomposition of this molecule[8b]. Accordingly, at a given substrate temperature, any factors which enhance the adsorption rate of the CV molecule should also enhance its decomposition and therefore its deposition rate. Our problem

is thus simplified to that of the effect of dopant gas on the adsorption of silicon chemical vapor molecules.

From the chemical point of view, silane has the partially ionic Si^+ -H^- bonds[9]. Being tetrahedral, such a molecule possesses no net dipole moment[10]. However, the ionic character mentioned would make silane a molecule with four negatively charged hydrogen atoms surrounding a positively charged silicon atom in the center. Such a molecule would be attracted by a surface with positive surface potential and be repelled from one with negative surface potential. In other words, making the surface potential more positive would ... ... lane better and enhance its adsorption rate. The same argument applies ... ...licon tetrachloride which has Si^+-Cl^- ionic bonds, similar to those in ...ane.

Next, we study the effect of dopant gas on the surface potential of a substrate. Diborane, arsine and phosphine thermally decompose to release boron, arsenic and phosphorus atoms, respectively. These atoms then adsorb on the surface and become doped into the silicon film deposited. As mentioned earlier, the observed deposition rate dependence of silane and silicon tetrachloride showed possible correlation with the electronic structure of the dopant atoms. Furthermore, during silicon CVD, there is always a silicon surface with freshly adsorbed silicon and dopant atoms[11]. Our problem is therefore similar to the study of the effect of dopant atoms on the ... ce potential of a silicon surface. Supporting this approach is the experimental observation that when the substrate is covered with a monolayer of boron atoms, the deposition rate of silane is the highest among the depositions using the silane-diborane mixtures[8c].

First, we define a reference surface to be a silicon surface with only adsorbed silicon atoms. This is the case when pure silicon chemical vapor is used. A boron adso.bed silicon surface can be seen to be different from the reference one. Boron, being a p-type dopant and electron deficient relative to silicon, should, relative to the reference surface, lower the local electron density on the surface silicon atoms around th: adsorption site. This would increase the electron affinity of the silicon surface onto which boron is

adsorbed[12]. The effect on the surface potential is seen from the relation defining this property[12].

$$(E_F - E_I)_S = (E_V - E_i) + (\Phi - \phi)$$

Here E_F, E_I, E_V are the energies for the Fermi level, intrinsic level and top of the valence band, respectively, S stands for surface, Φ and ϕ are photo-electric threshold and work function, respectively. Furthermore, $\Phi = X + E_G$, X is the electron affinity, and E_G, the band gap between the bottom of the conduction band and the top of the valence band. An increase in electron affinity, on the surface is seen to make the surface potential more positive than the reference surface defined above[13]. Such a surface would then attract molecules like silane and silicon tetrachloride. This should enhance the adsorption and therefore the deposition rate of these molecules. On the other hand, phosphorus and arsenic, which are n-type dopants and electron-excessive relative to silicon, would make the surface potential more negative than the reference one. Accordingly, the deposition rate of silane and silicon tetrachloride should be lowered when they are mixed with phosphine and arsine. The observed dopant gas effect on the deposition rates of silicon chemical vapors is thus satisfactorily explained. These results are summarized in Table I.

An immediate test of the proposed model is to choose some CV molecule of different bonding character from that of SiH_4 and $SiCl_4$. Different dopant gas effect on the deposition rate of this chosen CV molecule should then be expected. One such molecule is methane, CH_4. Methane is also tetrahedral but has the $C^- - H^+$ type of ionic bonds. The hydrogen atoms are partially positively charged in methane, opposite to that for silane. The dopant gas effect on the deposition rate of methane should then be just the opposite of that for silane. When one goes to another carbon CV molecule, carbon tetrachloride, CCl_4, however, the dopant gas effect should be similar to that for silane. This is because of the $C^+ - Cl^-$ ionic bonding character of this molecule. The predicted dopant gas effect for methane and carbon tetrachloride are also listed   Table I. For a meaningful test of our model to carbon CVD, data on t.   position should be used. Diamond film has the similar st   film, and differs from the layer structure of a graphite
     The   literature data on the dopant gas effect on diamond

Table I. Predicted and observed dopant gas effects on the deposition rates of silicon and carbon chemical vapors[*]

Bonding Characters	SiH_4 $Si^+ - H^-$	$SiCl_4$ $Si^+ - Cl^-$	CH_4 $C^- - H^+$	CCl_4 $C^+ - Cl^-$
B_2H_6	I	I	D	I
	I[a]	I[a]	D[b]	
PH_3	D	D	I	D
	D[a]			
AsH_3	D	D	I	D
	D[a]			

[*] I and D indicate an increase and decrease, respectively, in deposition rate. The first row for each dopant gas is for the predicted effects, the second row for the observed effects.

a. Ref. 9.
b. Ref. 14.

deposition concerns the methane-diborane system[14]. The results clearly show from that observed using only methane. This is just the effect predicted by our model.

Although limited by the existing information for a full test of our model, agreement with the available data is encouraging. It is therefore worthwhile to point out some useful works, both experimental and theoretical, that are necessary for a better understanding of the CVD process. (1) Experiments for the lacking information listed in Table I should be carried out for a complete

test of our model. (2) Our model descrives the dopant gas effect through the dopant atom effect on the surface potential. This can therefore be tested by applying a bias voltage to the substrate and observe its effect on the deposition rate of pure CV molecules. Similarly, an electric field can be applied to the surface and tested for its effect on the deposition rate of each CV molecule. (3) Surface properties for silicon and diamond should be studied in the presence of adsorbed boron, arsenic and phosphorus atoms. This includes surface properties such as the surface states and work function. Such study would allow a direct understanding of the adsorbed dopant atom effect on the surface properties and is essential to our final understanding of the problem discussed in this paper. (4) Theoretical calculation on the interactions between an adsorbed dopant atom and another adsorbed CV molecule is also very important. Such interactions could be long ranged and involve coupling with the surface[15]. Calculations of the interactions described in this paper could be very difficult at the moment[16] but certainly are necessary for a better understanding of the adsorption mechanism.

Once the suggested experiments are shown to support our model proposed here, 't will then be possible to increase the deposition rate of CVD at low temperatures. By adjusting the surface potential according to the principles described in this paper one should be able to increase the deposition rate beyond the current limit. One can also choose the right combination of CV molecule and dopant gas that allows the maximal increase in deposition rate. Examples from Table I are $SiH_4-B_2H_6$, CH_4-PH_3, $CCl_4-B_2H_6$, etc. The remaining limiting factor will then be the amount of thermal energy available at low temperatures. One needs then to find a compromise between the maximal thermal energy needed and the minimal interaction and diffusion allowed between the deposited thin film and the substrate chosen. All these principles should also be applicable to the CVD of other types of thin films, such as those for Si_3N_4, SiC, W, etc.

Finally, since our model is concerned mainly with the effect of one adsorbed species on the adsorption of another molecule, this work should also be useful to surface catalysis studies. In surface catalysis molecular adsorption plays an essential role before decomposition or chemical reaction takes

place. By varying the surface potential as described in this paper one should observe changes of the chemical reaction rates between adsorbed molecules. This should allow a better understanding and control of the chemical reactions under study. In addition, vrrying the magnitude and sign of the surface potential should provide impo: tant information on the formation and strength of the chemisorptive bonds between the adsorbed molecule and the surface. Again, more experimental and theoretical work along this line are needed to further advance our idea to surface catalysis.

Acknowledgement

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