Lawrence Berkeley National Laboratory
Recent Work

Title
ON THE ENHANCEMENT OF SILICON CHEMICAL VAPOR DEPOSITION RATES AT LOW TEMPERATURES

Permalink
https://escholarship.org/uc/item/9pp8142m

Author
Chang, Chin-An.

Publication Date
1976-08-01

eScholarship.org Powered by the California Digital Library
University of California

0 0 0 0 4 3 0 5 6 6 9

Published in Journal of Electrochemical Society, Vol. 123, No. 8, 1245 - 1247 (August 1976)

UC-63
LBL-3938 Rev.
Preprint c.1

ON THE ENHANCEMENT OF SILICON CHEMICAL VAPOR DEPOSITION RATES AT LOW TEMPERATURES

Chin-An Chang

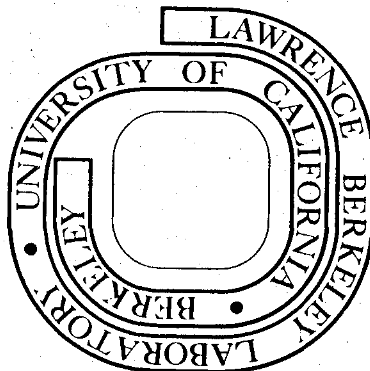
RECEIVED
LAWRENCE
BERKELEY LABORATORY
AUG 3 1977
LIBRARY AND
DOCUMENTS SECTION

August 1976

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room



LBL-3938 Rev. c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

0 0 0 0 4 3 0 5 6 7 0 LBL-3938 Rev.

Reprinted from JOURNAL OF THE ELECTROCHEMICAL SOCIETY
Vol. 123, No. 8, August 1976
Printed in U.S.A.
Copyright 1976

LAWRENCE BERKELEY LABORATORY
REPRINT NUMBER
1976 3 6 8-I
UNIVERSITY OF CALIFORNIA

Reproduced by permission of the Publisher, The Electrochemical Society, Inc.

On the Enhancement of Silicon Chemical Vapor Deposition Rates at Low Temperatures

Chin-An Chang[1]

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

Chemical vapor deposition (CVD) has been a widely used technique for thin film device fabrication. It is especially applicable to thin film silicon solar cells. A deposition rate of a few microns per minute can be easily obtained, and a p-n junction can be made by mixing silicon chemical vapors, such as silane and silicon tetrachloride, with dopant gases, like diborane and phosphine. In general, CVD of silicon is carried out at a substrate temperature *ca.* 1000°-1200°C, and a single crystal silicon wafer is used for an epitaxial growth of thin films. However, to make economic thin film solar cells for terrestrial photovoltaic applications, noncrystalline and often nonsilicon substrates are required. Furthermore, interaction between the substrate thus chosen and the silicon thin film deposited should be kept minimal. For example, at a substrate temperature *ca.* 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 diffusion.

At low substrate temperatures, however, other problems arise. First, silicon film thus deposited is polycrystalline with small grain size (4). Second, a 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 at the grain boundaries (6); low deposition rate makes CVD a noneconomic technique for deposition. To solve the former problem, this author has developed a technique to increase the silicon crystallinity at low substrate temperatures. An enhancement of two to four orders of magnitude is obtained for the silicon films deposited on quartz and graphite at a 600°C substrate temperature (2, 7). The next goal is to increase the deposition rate of low temperature CVD. In doing so we make use of the observations that certain dopant gases enhance the silicon CVD rate and others hinder it (8). An understanding of these facts will obviously be useful to the enhancement of the silicon CVD rate at low temperatures. However, as pointed out later, these dopant gas effects cannot yet be consistently accounted for by the existing theories. Therefore, this paper presents a conceptual model which consistently explains the known dopant gas effects on the rate of silicon CVD. We believe that this work will not only lead to an enhancement of the low temperature silicon CVD rate needed for economic solar cells, but also be useful to guide experimentalists in carrying out the CVD process more effectively and to stimulating interest among theorists about the problems related to this topic. The proposed model is further tested for its predicted dopant gas effects on different CVD systems and other relevant work which needs to be done is also discussed.

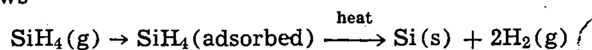
It is well known that the silicon deposition rate using silane and silicon tetrachloride is increased by diborane and boron tribromide, and decreased by phosphine and arsine (8). Existing theories considering either active site blocking (8b) or strong bonding between the chemical vapor molecules and both types of dopant gas molecules (8c) have not been advanced

[1] Present address: IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598.

Key words: silicon, CVD, enhanced rates, dopant effects, surface model.

enough to explain the known effects in a consistent way, nor can they be used to predict the dopant gas effect on other CVD systems. In this work we make use of the fact that diborane and boron tribromide, both p-type dopant gases for silicon, have an opposite effect on the deposition rate of silicon chemical vapor from that of phosphine and arsine which are 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, therefore, first analyzed, in order to see whether and how this property can be incorporated into the deposition process.

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



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

The thermal decomposition involves a transfer of thermal energy from the substrate to the chemical vapor molecule needed for its decomposition. At a fixed substrate temperature, the maximal amount of thermal energy which can be acquired by the molecule is constant. The efficiency of this energy transfer, however, depends on the residence time of the molecule on the substrate surface. In other words, for an effective decomposition of the molecule to take place on the surface, a sufficient amount of thermal energy for such decomposition should be transferred to the molecule before it desorbs from the surface. Therefore, at a fixed substrate temperature, adsorption of the molecule determines its decomposition rate. 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 (8c). Accordingly, at a given substrate temperature, any factors which favor the adsorption of the molecule on the substrate surface 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.

Diborane, phosphine, and arsine all readily decompose on a hot surface into the dopant atoms and hydrogen. Boron tribromide also readily releases its boron upon reduction by hydrogen at high temperatures. Diborane and boron tribromide have quite different structures and polarities and such differences could have profound effect on their interactions with the silicon surface (9). The fact that both diborane and boron tribromide enhance the silicon CVD rate and that they both easily produce boron at high temperatures makes it reasonable to assume the dominant role of boron adatoms in determining the observed boron dopant gas effects. The same assumption is applied to the n-type dopant gases, *i.e.*, phosphine and arsine. The available data on diborane and arsine further show that, upon thermal decomposition, both boron and arsenic atoms strongly adsorb on the silicon surface (8c). In addition, complete coverage of the silicon surface with boron gives the highest silane deposition rate among all the experiments using various silane-diborane mixtures (8c). Some correlation with the boron adatom concentration is also noted. For a rigorous treatment of the dopant gas effects, the contribution from the adsorbed undecomposed dopant gas molecules, if any, should also be taken into account. However, this cannot yet be done due to the lack of knowledge on the surface lifetimes of these molecules on a hot silicon surface. Therefore, only the dopant adatom effect is considered here which is justified by the experimental facts cited above.

From a chemical point of view, silane has the partially ionic Si^+-H^- bonds (10). Being tetrahedral, such a molecule possesses no net dipole moment (11). 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. A molecule of such polarity 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 enhance silane adsorption on the surface. The same argument applies to silicon tetrachloride which has Si^+-Cl^- ionic bonds, similar to those in silane.

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-adsorbed 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 the adsorption site. This would increase the electron affinity of the local silicon surface around the adsorbed boron (12). According to Allen and Gobeli, an increase in surface electron affinity increases the positive surface potential (12). This has been observed on both Si and Ge (9, 12). A boron-adsorbed silicon surface would thus attract molecules like silane and silicon tetrachloride better than the reference surface. 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 vapor is thus satisfactorily and consistently explained. These results are summarized in Table I.

One further support to our model is the agreement between the predicted and observed deposition rate dependence on the dopant atom concentration. This can be better understood if we describe our model using the surface-state concept (13). Compared with a reference surface defined earlier, adsorbed boron atoms decrease the surface-state electron density, whereas phosphorus and arsenic atoms increase it. The induced local surface dipoles have their positive and negative ends, respectively, pointed toward the vacuum. Interaction with silane is, therefore, more attractive in the former case and more repulsive in the latter than in that of the reference surface. Both types of interaction increase with increasing coverage of the dopant adatoms on the surface. As the adatom concentration reaches *ca.* 10^{12} atom/cm^2, the induced surface dipoles emerge into a continuum (13). Furthermore, it is reasonable to assume the dominance of short-range interactions between the chemical vapor

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

	SiH_4	$SiCl_4$	CH_4	CCl_4
Bonding characters	$Si^+ - H^-$	$Si^+ - Cl^-$	$C^- - H^+$	$C^+ - Cl^-$
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. (8).
[b] Ref. (17).

molecule and the surface (8c). One, therefore, expects appreciable dopant adatom effect beyond the concentration of 10^{12} atom/cm^2 on the adsorption of silicon molecules. The observed onset of significant changes in the deposition rate of silane and silicon tetrachloride at the above dopant adatom concentration (8) is thus consistent with the theory.

A quantitative treatment of this problem involves calculation of the interaction between an adsorbed chemical vapor molecule and a differently dopant-atom adsorbed silicon surface. To date, such calculations are extremely difficult, if not impossible (14, 15). Therefore, only a qualitative test is given here. Some semiquantitative work is in progress to estimate the dopant adatom effect on the local surface electron densities.

To test our model qualitatively, we chose a CV molecule of opposite polarity to that of SiH_4 and $SiCl_4$. The dopant gas effect on the deposition rate of this chosen molecule should then be opposite to that for SiH_4 and $SiCl_4$. One possible molecule is methane. Methane is also tetrahedral but has the C^--H^+ type of ionic bond. The polarity of methane is, therefore, opposite to that of silane. When carbon tetrachloride is used as a chemical vapor gas, its dopant gas effect should be similar to that of silane due to the C^+-Cl^- polarity of this molecule. The predicted dopant gas effects for methane and carbon tetrachloride are also listed in Table I. For a meaningful test of our model in carbon CVD, data on diamond deposition should be used. This is because the structure of diamond is similar to silicon, whereas the layer structure of graphite would complicate the deposition mechanism (16). The available literature data on the dopant gas effect on diamond deposition concern the methane-diborane system (17). The results clearly show that mixing methane with diborane lowers the diamond deposition rate from that observed using only methane. This is exactly the effect predicted by our model.

Although limited by the available information for a full qualitative test of our model, agreement with the existing data is encouraging. It is, therefore, worthwhile to point out some useful work that will be necessary to a better understanding of the CVD process. (*i*) Experiments for the lacking information listed in Table I should be carried out for a complete test of our model. Also, doping with other p- and n-elements, such as aluminum, should provide further testing of the model. (*ii*) As a test of the dopant adatom effect on the surface potential, a bias voltage of the proper polarity should be applied to the substrate and observation made of its effect on the deposition rate of pure chemical vapor molecules. A similar test should be made by the application of an electric field to the surface. (*iii*) Surface properties for silicon and diamond should be studied in the presence of adsorbed boron, arsenic, phosphorus, and other dopant atoms. Such properties include the surface states and work function, and surface lifetimes of adsorbed chemical vapor molecules. This 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.

Once the suggested experiments are shown to support our model proposed above, it will then be possible to increase the deposition rate of silicon CVD at low temperatures. For example, by applying a suitable bias voltage which matches favorably with the polarity of the chemical vapor molecule, the substrate surface potential can be adjusted to increase the deposition rate beyond the current limit. It is also obvious that the right combination of molecule and dopant gas to allow the maximal increase in deposition rate must be chosen. 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 be the amount of thermal energy available at low substrate temperatures. One needs then to find a compromise between the maximal thermal energy available 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, varying the magnitude and sign of the surface potential should provide important 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 is needed to further advance our idea to surface catalysis.

Acknowledgment

This work was supported by the U.S. Energy Research and Development Administration.

Manuscript submitted Jan. 26, 1976; revised manuscript received April 7, 1976.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1977 JOURNAL. All discussions for the June 1977 Discussion Section should be submitted by Feb. 1, 1977.

Publication costs of this article were assisted by the Lawrence Berkeley Laboratory.

REFERENCES

1. C.-A. Chang and W. J. Siekhaus, *J. Appl. Phys.*, **46**, 3402 (1975).
2. C.-A. Chang and W. J. Siekhaus, *Appl. Phys. Lett.*, **29**, 208 (1976).
3. T. L. Chu, J. C. Lien, H. C. Mollenkopf, S. C. Chu, K. W. Heizer, F. W. Voltmer, and G. F. Wakefield, *Solar Energy*, **17**, 229 (1975).
4. (a) C.-A. Chang, Unpublished results. (b) A. Emmanuel and H. M.-Pollack, *This Journal*, **120**, 1586 (1973).
5. (a) H. C. Theuerer, *ibid.*, **108**, 649 (1961); F. C. Everstegn and G. H. Put, *ibid.*, **120**, 106 (1973); L. H. Hall and K. M. Koliwad, *ibid.*, **120**, 1438 (1973). (b) R. G. Frieser, *ibid.*, **115**, 401 (1968). (c) A. Emmanuel and H. M.-Pollack, *ibid.*, **120**, 1586 (1973).
6. T. I. Kamins, *J. Appl. Phys.*, **42**, 4357 (1971); Y. Matukura, *Japan. J. Appl. Phys.*, **2**, 91 (1963).
7. C.-A. Chang, W. J. Siekhaus, T. Kaminska, and D. T. Huo, *Appl. Phys. Letters*, **26**, 178 (1975).
8. (a) See Ref. (5a). (b) P. Rai-Choudhury and P. L. Hower, *ibid.*, **120**, 1761 (1973). (c) R. F. C. Farrow, *ibid.*, **121**, 899 (1974).
9. W. H. Brattain and J. Bardeen, *Bell System Tech. J.*, **32**, 1 (1953); H. C. Montgomery and W. L. Brown, *Phys. Rev.*, **103**, 865 (1956).
10. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," p. 466, John Wiley & Sons, New York (1966).
11. A. L. McCellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Company, San Francisco (1963).
12. F. G. Allen and G. W. Gobeli, *Phys. Rev.*, **127**, 150 (1962).
13. J. Bardeen, *ibid.*, **71**, 717 (1947).
14. T. B. Grimley, *Proc. Phys. Soc.*, **90**, 751 (1967); see also R. Gomer, *Accounts Chem. Res.*, **8**, 420 (1975) and references therein.
15. J .R. Schrieffer, Private communication.
16. See, for example, S. Marinkovic, C. Suznjevic, and I. Dezarov, *Carbon*, **7**, 185 (1969); *ibid.*, **11**, 219 (1973).
17. D. J. Poferl, N. C. Gardner, and J. C. Angus, *J. Appl. Phys.*, **44**, 1428 (1973).

0 0 0 0 4 3 0 5 6 7 1

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720