Incomplete melting of the Si(100) surface from molecular-dynamics simulations using the Effective-Medium Tight-Binding model.

K. Stokbro,1,2,3 K. W. Jacobsen,3 J. K. Nørskov,3 D. M. Deaven,4 C. Z. Wang,4 and K. M. Ho4

1Mikroelektronik Centret, Danmarks Tekniske Universitet, Bygning 345ø, DK-2800 Lyngby, Denmark.

2 Scuola Internazionale Superiore di Studi Avanzati, via Beirut 4, I-34014 Trieste, Italy.

3Center for Atomic-scale Materials Physics and Physics Department, Danmarks Tekniske Universitet, DK 2800 Lyngby, Denmark

4 Ames Laboratory, Ames, Iowa 50011

Abstract

We present molecular-dynamics simulations of the Si(100) surface in the temperature range 1100-1750K. To describe the total energy and forces we use the Effective-Medium Tight-Binding model. The defect-free surface is found to melt at the bulk melting point, which we determine to be 1650 K, but for a surface with dimer vacancies we find a pre-melting of the first two layers 100 K below the melting point. We show that these findings can rationalize recent experimental studies of the high temperature Si(100) surface.
I. INTRODUCTION

Most work on the Si(100) surface has focussed on the behaviour at low and intermediate temperatures, while to our knowledge there have to date only been two experimental studies \[1,2\] of the atomic structure at temperatures near the bulk melting point. Both of these studies indicate that the surface undergoes a phase transition at a temperature below the bulk melting point, however, there is no consistent picture of the nature of the transition, the exact transition temperature, and the atomic structure beyond the phase transition.

Metois and Wolf \[1\] studied the structure of the Si(100) surface with Reflection-Electron Microscopy (REM). In the temperature interval 1400-1455K the experiment shows a sudden increase in the number of holes on the surface, and at 1455K the surface structure cannot be resolved any longer and it is suggested that the surface at this temperature becomes rough at the atomic scale. In the experimental study by Fraxedas et. al \[2\] the surface order of Si(100) was studied as a function of the surface temperature by means of X-ray Photo-electron Diffraction (XPD). At 1400 K the order suddenly decreases, and this is attributed to a phase transition where the two first surface layers melt and form a liquid layer. For the Si(100) surface molecular-dynamics simulations based on the Stillinger-Weber potential have been used to study the solid-liquid interface \[4\], but there are no studies of the surface melting. To our knowledge, the only first principles molecular-dynamics study of the melting of a semiconductor surface is by Takeuchi et. al. \[3\]. They study a Ge(111) surface at a temperature close to the melting point and find evidence for the existence of an incomplete melted phase.

The experiment by Metois and Wolf shows that the Si(100) surface has an increasing concentration of vacancies as a function of the temperature. Since the vacancy formation takes place on a time scale of seconds, it is not possible to study the vacancy formation in a molecular dynamics simulations, however, given a certain vacancy concentration we can study what is the surface structure attained within a time scale of \(\approx 10 - 100\) ps.

In this report we present a molecular-dynamics study of the Si(100) surface with and
without vacancies for a number of temperatures in the range 1100-1750K. To describe the bonding of Si we have used the Effective-Medium Tight-Binding (EMTB) model [5]. We show that this approximate total energy method describes the melting point and the properties of liquid Si very accurately. Using the computational efficiency of the method to simulate a slab with a unit cell containing 188 atoms for up to 35 ns at a number of different temperatures and surfaces with and without defects, we show that while the defect-free surface shows no sign of premelting, a surface with 25% of dimer vacancies shows melting of the first layer 100 K below the melting point. We show that the results of the simulation can be used to understand the experimental observations for this system.

II. TECHNICAL DETAILS

The Effective-Medium Tight-Binding (EMTB) model [5] is based on Effective-Medium Theory [6,7] in which the total energy calculations are simplified by comparisons to a reference system (the effective medium). The so-called one-electron energy sum is calculated using an LMTO tight-binding model [8]. The main approximations in the model is the use of a first-order LMTO tight-binding model and a non-self-consistent electron density [9] and potential [10]. In previous studies we have demonstrated the ability of the model to describe the low temperature structure of the Si(100) surface, [5] and generally we have found the accuracy for the total energy and atomic structure of solid Si systems to be correct within 10-20 percent, which is comparable to plane-wave calculations with a cutoff of 8 Ry. However, the EMTB method is in computational efficiency comparable to empirical tight-binding methods and for the system sizes treated here something like three orders of magnitude faster than plane-wave calculations. It is therefore very well suited for large scale molecular-dynamics simulations.

The super-cell for the calculation is a 12 layer thick slab with 16 atoms in each layer except for the upper layer in which we have introduced a vacancy concentration of 25 percent by removing four atoms; thus a total of 188 atoms. Since all atoms are free to move we obtain
information of a clean surface and a surface with vacancies in the same simulation run. The classical equations of motion for the nuclei are integrated using the Verlet algorithm with a time step of 1.08 fs and we control the temperature by using Langevin dynamics [11] with a friction coefficient of 2 ps\(^{-1}\). The lattice constant is determined by scaling the EMTB (T=0K) value (10.167\(a_0\)) using the experimental thermal-expansion coefficient.

### III. RESULTS

Initially, the atomic structure of the bottom surface consists of two dimer rows with each 4 dimers, while the vacancies are introduced on the upper surface by removing a dimer from each row. Starting from the c(2x4) reconstruction we first increase the temperature of the thermostat to 1100K. After thermalization this system is followed over 3ps. The final configuration is used as input for four other simulation temperatures: 1450K, 1550K, 1650K, and 1750K, which are followed over 29ps, 35ps, 33ps and 18ps, respectively.

We first summarize the calculations by showing in Fig. 1 the average structure factor parallel to the dimer rows, \(|S_{-11}|^2\), as a function of the simulation temperature. The structure factor is projected onto 3 intervals of the z axis corresponding to the position of layers 1-2, 3-4, and 5-6 on both the vacancy covered and the clean surface. The structure factor is averaged over the atomic configurations of the last 2ps, 15ps, 15ps, 15ps and 5 ps for each of the five simulations temperatures, respectively. The calculated variances in the structure factors show that except for the 1650K calculation, the simulations seem to have obtained an equilibrium state. In Fig. 2 we show the corresponding average atomic density perpendicular to the surfaces, and for the 1550K calculation a snapshot of the atomic-structure is shown in Fig. 3.

The observed atomic structures obtained in the simulations are the following: At 1100K the two surfaces show no tendency to break up the dimer rows; each dimer stays in a buckling mode moving up and down with a frequency of \(\approx 3\) THz, and the buckling angle reverses independently of the configurations of the other dimers. For the clean surface we find this to
be the picture up to 1750K where the entire slab melts, and Fig. 1b shows that the structure factor for this surface is constant up to the melting transition.

The vacancy surface shows a much more complex behaviour. At 1450K we observe diffusion of one of the vacancies within the simulation time. After the diffusion the dimers remain intact and the structure factor shown in Fig. 1a is only slightly affected. At 1550K the two first layers of the vacancy surface lose all their order and form a disordered state, see Fig. 3, and there is a strong interaction with the third layer which forms an interface between the bulk structure and the disordered surface. From Fig. 1a we see that now the structure factor has vanished for the two outermost layers, while the structure factor of the third layer is slightly decreased due to the interaction with the disordered state. At 1650K the first four layers disorders (cf. Fig. 1a and Fig. 2). At 1750 K all the layers melt after a short transient period, and Fig. 2 shows a constant atomic density \( n = 2.54 g/cm^3 \) in the range \(-10a_0 < z < 10a_0\). This is an increase of 6 percent compared to the crystalline density, and in good agreement with the experimental atomic density \( n = 2.51 g/cm^3 \) for liquid silicon at 1750K.

We first extract from the simulations the Si bulk melting point, \( T_m \), predicted by the EMTB model. At 1750K the whole slab melts, without a partially-melted transient period, and we therefore have \( T_m < 1750K \). At 1550K there are two phases present in the calculation with a large interaction between the two. Since Fig. 1a shows that there are only small fluctuations in the structure factor of the layers, this strongly suggests that the simulation has obtained an equilibrium state. Furthermore, if the melting temperature was close to 1550K, the temperature in the 1650K simulation would be well above the melting point and the slab should readily melt since a melted phase is already present in the calculation. From these considerations we estimate a melting temperature of \( T_m \approx 1650\pm100K \), in good agreement with the experimental melting point of 1685K.

The rather large error bar in the melting temperature comes from finite size effects leading to large fluctuations in the temperature. On top of this there may be a systematic overestimate of the melting temperature in the simulation because of the fixed super-cell
size parallel to the slab. However, the possibility of the system to respond with volume changes perpendicular to the slab reduces this problem considerably. The presence of the surface thus allows the liquid to acquire the correct density as noted above.

In the simulation with the thermostat set at 1650K the temperature fluctuates around the melting point, and we may have a coexistence of solid and liquid phases at this temperature. This suggests that the melting of the two additional layers in the 1650K simulation is rather due to large fluctuations of the temperature around the melting point than the existence of a surface phase transition where four layers disorders. Note also the large fluctuations observed in the structure factor of layer 5-6 at this temperature, shown in Fig. 1a, which makes it questionable whether an equilibrium state has been obtained within the simulation time.

The temperature in the 1550K simulation, on the other hand, is well below the bulk melting point and the atomic structure in this case must be due to a surface phase transition taking place at a temperature \( T_F < 1550 \). From simulations of metal surfaces it is known \(^{14}\) that just at the surface melting temperature the defects become mobile, and we therefore estimate \( T_F = 1450 \pm 100K \). Since we have \( T_F < 1550 < T_M \) we can expect to have obtained equilibrium within our simulation time for this temperature. We now consider the 1550K simulation in more detail.

In Fig. 4 we show the radial distribution function averaged over the atoms in layer 2 and layer 6-7. For comparison we also show similar averages obtained for the 1750K simulation in which case the whole slab has become liquid. The figure clearly shows that the two outermost layers in the 1550K simulation have formed a liquid state, with an average coordination very different from the bulk state, but almost identical to that of liquid Si. It is worth noting that the radial distribution function obtained for the liquid Si is in good agreement with experiment \(^{12}\) and that obtained by Stich et al. \(^{13}\) in a Car-Parrinello calculation (the position of the first maximum is \( 4.67a_0(4.65a_0) \) and integration up to \( 5.90a_0 \) gives an average coordination of \( 6.55(6.5) \), where the values obtained in Ref. \(^{13}\) are given in parenthesis). The formation of a liquid surface bilayer in the 1550K simulation is further illustrated by
Fig. 5, where we from the lateral mean-square displacement of the surface atoms deduce a two dimensional diffusion constant of $D = 2.1 \times 10^{-5}$ cm$^2$/s. We also observe a jump in the average potential energy during melting at 1550K from which we deduce a latent heat of melting the surface atoms of $\Delta E \approx 3$eV. This must be compensated by an increase in the entropy $\Delta E = Nk_B T \Delta S$ (where $N$ is the number of atoms taking part in the phase transition), which when attributed to the atoms in the two first layers ($N = 28$), gives an increase in the entropy of $\Delta S \approx 0.8$.

We now relate our simulations for the Si(100) to those of Ref. [3] for the Ge(111) surface. The outermost layer of the Ge(111) surface consists of fourth a monolayer Ge adatoms, which gives this surface a more open structure than the Si(100) surface. The Ge(111) surface has more resemblance with the vacancy covered Si(100) surface, and there are indications that the adatoms on the Ge(111) surface and the vacancies on the Si(100) surface play similar roles in the surface melting process. Similar to the vacancy diffusion we found in the 1450 K simulation, Takeuchi et. al. found a metastable state in the first part of their simulation where only the adatoms diffuse. Afterwards the Ge(111) surface undergoes a phase transition where the two first layers become liquid, and the increase in entropy and the diffusion constant are very similar to the values we have found for the vacancy covered Si(100) surface. (For Ge(111) the values are $D_{Ge} = 3.5 \times 10^{-5}$ cm$^2$/s, $\Delta S_{Ge} \approx 1.0$).

For the Ge(111) surface it was also found that the electronic structure of the melted layers was metallic, and lately this has been supported by an electron energy loss spectroscopy (EELS) study of the surface conductivity of Ge(111) [15]. However, we only find a weak metallic behaviour for the incomplete melted Si(100) surface. This is illustrated in Fig. 6, which shows the Projected Density of States(PDOS) of the atoms in the two first layers of the vacancy surface(solid line) and the clean surface(dotted line), and we see that the number of states in the gap is only slightly increased for the incomplete melted vacancy surface compared to the non-melted clean surface. We therefore expect that the surface melting of Si(100) will be difficult to detect with EELS.
IV. COMPARISON WITH EXPERIMENTS

We now compare our findings to the experimental results of Ref. [1,2]. One of our results is that the phase transition only takes place when a high concentration of vacancies is present on the surface, and the question arises what are the vacancy concentrations in the experiments. STM studies yield estimates that the surface at room temperature has a vacancy concentration of 5-10 percent. When the surface is heated up one may observe atoms evaporating, and since they leave a vacancy behind this process may increase the vacancy concentration. Metois and Wolf found that at temperatures below 1400K the sublimation process proceeds slowly enough, that the sublimation holes are filled with atoms diffusing from step edges and the vacancy concentration is relatively stable up to this temperature. In the temperature interval 1400-1455K the number of holes increases drastically and at 1455K the surface structure cannot be resolved any longer.

The experiment by Metois and Wolf is in a non-equilibrium state and they relate the observed behaviour to kinetic surface roughening. The kinetic roughening is caused by the larger activation energy for sublimation compared to the activation energy for diffusion, which means that the sublimation rate will increase faster with temperature than the diffusion rate, and at some temperature the sublimation rate will become too fast for the vacancies to be filled with atoms diffusing from step edges. However, we note that the observed behaviour is not necessarily due to kinetic roughening but can alternatively be due to the existence of a roughening phase transition. Both kinetic roughening and a roughening phase transition will give rise to an increased vacancy concentration as a function of the temperature, and the vacancy concentration in the experiments of Ref. [1,2] at 1450K will therefore be well above the 5-10 percent concentration at room temperature. From the available data we cannot determine the exact vacancy concentration in the two experiments, and probably they will not have the same concentrations, since it will depend on experimental details, such as base pressure and the crystal miscut angle.

It is not possible to use molecular dynamics simulations to determine the (equilibrium or
non-equilibrium) concentrations of vacancies since the simulation time scales are too short. However, for a given vacancy concentration molecular dynamics can be used to study the attained surface structure within a time scale of \( \approx 10 - 100 \) ps, which is long compared to fundamental surface vibration frequencies. In the simulation we have studied a vacancy concentration of 25 percent, where we find a phase transition at 1550 K to an incomplete melted state with two melted layers. We expect the same phenomena to take place for higher or slightly lower vacancy concentrations. However, the results cannot be generalized to low vacancy concentrations, since in this case the time scale of the formation of an incomplete melted phase may become comparable to the time scale of the processes that alter the vacancy concentration. For instance, on the time scale of desorption of Si dimers (seconds) the simulation for the clean surface will show incomplete melting, since the desorption of Si dimers will give rise to an increased vacancy concentration on the surface. In a real experiment there will also be adatoms diffusing of step edges and adsorption of atoms from the gas phase, and these processes will lower the vacancy concentration.

We now make quantitative comparisons with the experimental study of Ref. \[2\], where the XPD anisotropy \( A_{(hkl)}(T) \) is measured along the (100) and (111) directions as a function of temperature. The anisotropy in a given direction is defined as \( A_{(hkl)}(T) = (I_{max}(T) - I_{min}(T))/(I_{max}(300K) - I_{min}(300K)) \), where \( I_{max} \) (\( I_{min} \)) stands for the maximum (minimum) intensity for a given peak. We have simulated the XPD intensity peaks using Single-Scattering Cluster (SSC) calculations \[17\], with the same SSC parameters as quoted in Ref. \[18\]. For the electron mean-free path the value is 25Å (corresponding to the energy of the 2s photo electrons), in spite of the generally accepted rule of using half of its nominal value. \[19\] The anisotropy along the (111) direction is extremely sensitive to the actual choice of mean-free path, and we have therefore chosen only to make comparison with the anisotropy along the (100) direction, which we have found to be rather insensitive to the value of the mean-free path.

For each simulation temperature we have calculated the anisotropy along the (100) direction for 20 different configurations and Fig. 7 shows the corresponding averages. We
have performed calculations using both a mean-free path of 12.5 Å and 25 Å. In each case the anisotropies have been scaled such that at 1100K the anisotropy of the clean surface fits the experimental measurements, and Fig. 7 shows that the relative anisotropies are quite insensitive to the choice of mean-free path. We may therefore relate our calculations directly to the experimental measurements. First of all we see that vacancies lead to a drop in the anisotropy, and the observed increase in the vacancy concentration of Ref. [1] should therefore be measurable by XPD. We find that an increase in the vacancy concentration by 10 percent would be consistent with the small decrease in the experimental anisotropy observed in the temperature range $\approx 1390 - 1425 K$. Since we must expect [16] that the surface already has a vacancy concentration around 10 percent at 1390K, the vacancy concentration will be 20 percent at 1425K, very similar to the concentration in our simulation.

An increase in the vacancy concentration, however, can hardly describe the overall drop in the anisotropy observed in the range 1390-1500K. Fig. 7 indicates strongly that the decrease in the anisotropy after 1425K is related to the defect-induced disordering we have described above. This picture is in accordance with Ref. [18], where they found that the experimentally observed drop in anisotropy could be explained by assuming a disordered bilayer at the surface. The experiment also shows that the thickness of the melted layer is constant up to the bulk melting point, again indicating that the melting of the two additional layers in the 1650K simulation is related to bulk melting rather than surface melting.

V. SUMMARY

In summary, we have performed molecular-dynamics simulations for the Si(100) surface using the EMTB model. We find that in the presence of a vacancy concentration of 25 percent the surface undergoes a phase transition at 1550K, where the two first layers melt and form a liquid state. The incompletely melted state shows several similarities to the incomplete melting of Ge(111) [3], except that the electronic surface structure shows a much weaker metallic behaviour. We have also shown that the simulation results are in both
quantitative and qualitative agreement with experimental studies of the surface structure.

ACKNOWLEDGMENTS

We thank C. Fadley for providing us the program for the SSC calculations and J. Fraxedas for instructions on how to use the program. Many discussions with P. Stoltze and E. Tosatti are gratefully acknowledged. The Center for Atomic-scale Materials Physics is sponsored by the Danish National Research Foundation. Kurt Stokbro acknowledges eec contract ERBCHBGCT 920180 and contract ERBCHRXCT 930342 and CNR project Supaltemp.
REFERENCES

[1] J. Metois and D. Wolf, Surf. Sci. 298, 71 (93).

[2] J. Fraxedas, S. Ferrer, and F. Comin, Europhys. Lett. 25, 119 (1994).

[3] N. Takeuchi, A. Selloni, and E. Tosatti, Phys. Rev. Lett. 72, 2227 (1994).

[4] U. Landman, W. D. Luedtke, R. N. Barnett, C. L. Cleveland, M. W. Ribarsky, E. Arnold, S. Ramesh, H. Baumgart, A. Martinez, and B. Kahn, Phys. Rev. Lett. 56, 155 (1986).

[5] K. Stokbro, N. Chetty, K. Jacobsen, and J. Nørskov, Phys. Rev. B 50, 10727 (1994).

[6] J. Nørskov and N. Lang, Phys. Rev. B 21, 2131 (1980).

[7] K. Jacobsen, J. Nørskov, and M. Puska, Phys. Rev. B 35, 7423 (1987).

[8] O. Andersen and O. Jepsen, Phys. Rev. Lett. 53, 2571 (1984).

[9] N. Chetty, K. Jacobsen, and J. Nørskov, Lett. J. Phys. Condens. Matter 3, 5437 (1991).

[10] K. Stokbro, N. Chetty, K. Jacobsen, and J. Nørskov, J. Phys. Condens. Matter 6, 5415 (1994).

[11] D. Heermann, Computer Simulation Methods in Theoretical Physics (Springer-Verlag, Berlin, Heidelberg, 1986).

[12] Y. Waseda and K. Suzuki, Z. Phys. B. 20, 339 (1975); P. Gabathuler and S. Steeb, Z. Naturforsch. Teil A 34, 1314 (1979).

[13] I. Stich, R. Car, and M. Parrinello, Phys. Rev. Lett. 60, 204 (1988).

[14] P. Stoltze, J.K. Nørskov, and U. Landman, Phys. Rev. Lett. 61, 440 (1988).

[15] S. Modesti, et. al., Phys. Rev. Lett. 73, 1951 (1994).

[16] R. Hamers, R. Tromp, and J. Demuth, Phys. Rev. B 34, 5343 (1986).
[17] C. Fadley, Prog. in Surf. Sci. 16, 275 (1984).

[18] J. Fraxedas, S. Ferrer, and F. Comin, Surf. Sci. 307-309, 775 (1994).

[19] D. Naumovic et al., Phys. Rev. B 47, 7462 (1993).
FIGURES

FIG. 1. The equilibrium average structure factor parallel to the dimer rows, $|S_{-11}|^2$, as a function of the simulation temperature. The structure factor is projected onto 3 intervals of the $z$ axis corresponding to the position of layer 1-2, 3-4, and 5-6, for a) The vacancy covered surface, and b) the clean surface.

FIG. 2. The equilibrium average atomic density perpendicular to the surfaces for each simulation temperature.

FIG. 3. A snapshot of the atomic structure in the 1550K simulation at $t = 30$ps. The supercell is repeated twice in the horizontal direction.

FIG. 4. The radial distribution function projected onto layer 2 and layer 6-7 for the 1550K simulation (solid line) and the 1750K simulation (dashed line).

FIG. 5. The atomic displacement in the surface plane projected onto layer 1-2, 3-4, and 5-6, as a function of time for the 1550K simulation. The 2-dimensional diffusion constant, $D$, for layer 1-2 is defined by $< r^2 >= 4Dt$.

FIG. 6. The PDOS of layer 1-2 of the vacancy surface (solid line) and the clean surface (dotted line) in the 1550K simulation. The average is taken over the last 15 ps of the simulation.

FIG. 7. The XPD anisotropy as obtained from SSC calculations with an electron mean-free path of 12.5Å (solid line) and 25 Å (dashed line) as a function of the simulation temperature. The experimental measurements are from Ref. [2].
The diagram shows the radial distribution function $g(r)$ as a function of distance $r$ in units of $a_0$ for two temperatures, 1550K and 1750K. The graph highlights two different layers: Layer 6–7 and Layer 2. The peak of the distribution function is more pronounced for the higher temperature, indicating a greater density or interaction in the 1750K region compared to 1550K.
\( (x-x_0)^2 + (y-y_0)^2 \) [\( a_0^2 \)]

\[ D = 2.1 \times 10^{-5} \text{ cm}^2/\text{s} \]

Layers:
- Layer 1–2
- Layer 3–4
- Layer 5–6
Surface PDOS [states/(eV atom)]

- Vacancy surface
- Clean surface

$\varepsilon - \varepsilon_f$ [eV]
Temperature [K]

Anisotropy along (100)

- $\lambda_E = 12.5 \, \text{Å}$
- $\lambda_E = 25.0 \, \text{Å}$

Clean surface
Vacancy surface

$\Delta$ Experimental measurements