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Reply to ''Comment on 'Surface silicon-deuterium bond energy from gas-phase equilibration' ''

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The free energy of binding of deuterium to a surface silicon atom is obtained directly from our previously reported experiment. However, comparison with first-principles calculations of the surface Si-D bond energy requires an estimation of the contribution to the free energy from the vibrational entropy S_{vib}. Herring and Van de Walle determine a value of 2.99 eV for the bond energy at 800 °C from our data, using a harmonic oscillator model to estimate S_{vib}. Our method of estimating S_{vib} from solubility measurements gives a lower Si-D bond energy of 2.49 eV. These values are both lower than the bond energy from Van de Walle's first-principles calculation. Uncertainties involved in comparing theory with experiment are discussed.
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Herring and Van de Walle argue that the measure of binding most directly following from our experiment is the free energy at 800 °C of a deuterium atom bonded to a surface silicon atom, relative to that of a silicon surface at 800 °C with a dangling bond and a free deuterium atom at rest far from the surface. From our observations[1] and known properties of deuterium gas (enthalpy, entropy, and molecular dissociation energy)[2] they determine that the free energy of the bound state lies 3.29 eV below that of the unbound state. On this point we agree with them.

A second objective of their comment is to compare our experiment with the first-principles theoretical calculation of Van de Walle.[3] We disagree with some of their arguments relating to this issue. Van de Walle's calculation gave a value of E_B=3.65 eV for the ground-state bond energy of surface Si-D. The bond energy differs from the free energy of binding discussed above due to the difference (S_{vib}) between nonconfigurational or vibrational entropies of the bound and unbound states. The relation between the bond energy and the free energy of binding (G_B) given above can be expressed as

$$E_B - E_{\mathrm{vib}} + TS_{\mathrm{vib}} = -G_B = 3.29 \text{ eV/atom}, \tag{1}$$

where E_B is the ground-state bond energy and E_{vib} is a temperature-dependent contribution to the bond energy due to vibrational motion of the bound hydrogen. An estimation of the bond energy from the experimentally determined free energy requires assumptions about S_{vib}. Herring and Van de Walle propose a method which gives a significantly different value for S_{vib}, and hence for E_B, than the method we used.

We determined[1] a value for the bond energy ($E_B - E_{\mathrm{vib}}$) at 800 °C by assuming that the vibrational entropy of D bound to a surface Si atom (S_{vib}) is the same as the vibrational entropy of a D atom at a solution site $(S_{\mathrm{vib}})_{\mathrm{sol}}$ which can be evaluated from solubility measurements. In particular,

$$S_{\mathrm{vib}} = (S_{\mathrm{vib}})_{\mathrm{sol}} = 8.68k, \tag{2}$$

since

$$(S_{\mathrm{vib}})_{\mathrm{sol}} - S_{\mathrm{gas}} = k \ln(C_0) = -2.34k, \tag{3}$$

$S_{\mathrm{gas}} = 11.02k$ is the entropy of deuterium gas at 800 °C (Ref. 2) and $C_0 = 0.096$ D/Si bar$^{-1/2}$ is the solubility prefactor.[4] With Eq. (1) this gives

$$(E_B - E_{\mathrm{vib}}) = 2.49 \text{ eV} \tag{4}$$

for the surface Si-D bond energy at 800 °C. This value is about 1 eV lower than the value predicted by Van de Walle's first-principles calculation.[3] Our original analysis[1] neglected the temperature dependence of the deuterium molecular dissociation energy and hence gave the slightly higher value of 2.67 eV for Si-D binding energy at 800 °C, as Herring and Van de Walle correctly point out.

Herring and Van de Walle propose an alternative approach to evaluate S_{vib} in which surface Si-D is modeled as a harmonic oscillator with one stretch mode and two bending modes, and which assumes there are no contributions to S_{vib} from changes in the configuration or vibrational modes of the surface silicon atoms. Using vibrational frequencies of 1520 and 507 cm^{-1} for the Si-D stretch and bend modes, respectively, this model gives $(S_{\mathrm{vib}})_{\mathrm{HO}} = 3.28k$ and $(E_{\mathrm{vib}})_{\mathrm{HO}}$=0.16 eV at 800 °C. From this and our measured free energy (equation 1 above) it follows that the surface Si-D bond energy is

$$(E_B - E_{\mathrm{vib}})_{\mathrm{HO}} = 2.99 \text{ eV}, \tag{5}$$

at 800 °C, and

$$(E_B)_{\mathrm{HO}} = 3.15 \text{ eV} \tag{6}$$

at absolute zero. It is important to note that the difference of 0.50 eV between the surface Si-D binding energy at 800 °C obtained by our method using the solubility prefactor [Eq. (4)] and that of Herring and Van de Walle using a harmonic-oscillator model [Eq. (5)] is entirely due to the difference of $(S_{\mathrm{vib}})_{\mathrm{sol}} - (S_{\mathrm{vib}})_{\mathrm{HO}} = 5.4k$ in the Si-D vibrational entropies which these two methods use.

We do not agree with the statements of Herring and Van de Walle, that our method of estimating S_{vib} is a poor approximation, untrustworthy, and qualitatively implausible. Although the local environments of surface Si-H and H at a bond-center solution site are different, the vibrational frequencies have been reported to be nearly the same[3,5] for these two cases. Thus, if one applied the same harmonic-oscillator model to both cases, one obtains almost the same values for vibrational energy and entropy, which supports our approach. Herring and Van de Walle argue that the potential for H in solution in silicon might be flat over a large volume about its equilibrium site, and that this might qualitatively explain why the vibrational entropy inferred from the measured solubility prefactor is larger than the value expected for a harmonic potential. However, such an environment at solution sites has not been experimentally verified. The nonconfigurational entropy of adsorption may also differ from values predicted by the harmonic-oscillator model due to H-induced changes in vibrational modes of the surface silicon atoms which may not be negligible as Herring and Van de Walle assume. The assumptions and approximations made by Herring and Van de Walle, and those made by us, each have uncertainties which translate into uncertainty in the inferred value of the surface Si-D bond energy.

The ground state Si-D bond energy from Van de Walle's first-principles calculation is 0.5 eV higher than the experimental value obtained from our data using the harmonic-oscillator model [Eq. (6)]. Herring and Van de Walle argue that the measured bond energy includes a contribution of 0.3 eV due to reconstruction of the surface from a 1×1 to a 7×7 structure, in which case the discrepancy between theory and experiment becomes 0.2 eV. However, there is no experimental evidence indicating that the (111) facets of the cavities undergo the 7×7 reconstruction, and it may be that the small size of the facets hinders their reconstruction. The average cavity diameter is 15 nm. Furthermore, extended (111) surfaces transform from the 7×7 to a 1×1 structure above 830 °C,[6] which shows that the difference in free energy between these structures at the 800 °C temperature of our experiment must be very small. Finally, in their discussion of the influence of surface reconstruction on the energetics of hydrogen adsorption, they consider the change in bond energy but ignore the change in entropy which should also be important if reconstruction does occur.

Herring and Van de Walle question whether the surface Si-D bond energy might be different for differently oriented facets of the internal cavities. This question is discussed in detail in our paper.[1] Infrared-absorption spectroscopy studies of D on internal cavity surfaces indicate that the surface Si-D bond energy is essentially the same for the (100) and (111) facets.[7]

Comparison between experimental and theoretical values for the surface Si-D binding energy should include an assessment of the uncertainty in the theoretical value. One way to estimate this uncertainty is to compare the first-principles calculation with experiment for the case of hydrogen in solution in silicon where measurements have been made[4,8] over a temperature range sufficiently wide to enable independent determination of both the ethalpy and entropy terms to the free energy of solution. Solubility measurements give a value of 1.80 eV for the enthalpy of solution.[4,8] The value reported by Van de Walle for the ground-state energy of H at the bond-center solution site in silicon from his first-principles calculation is 1.19 eV above the molecular ground state.[2,3] Allowing for the temperature dependencies of the gas enthalpy (H_g) and the enthalpy of the solution site $(E_{\mathrm{vib}})_{\mathrm{sol}}$ (assuming a harmonic-oscillator model), the enthalpy of solution predicted by the calculation is about 1.2 eV at the temperature where the solubility measurements were made.

Van de Walle's first-principles calculation thus gives a value for the enthalpy of solution which is 0.6 eV lower than the experimental value, and a value for the surface Si-D bond energy which is 0.5–1 eV higher than the experimental value. Their discussions of the charge state of H in solution, which is a controversial topic,[9] and the idea of H rattling around the equilibrium solution site do not reconcile these differences. These considerations might influence the entropy of solution, but should have little or no effect on the surface Si-D bond energy.

The present degree of uncertainty in the experimental value of the surface Si-D bond energy and in the first-principles calculation does not support the level of agreement between theory and experiment of ''one or two tenths of an eV'' claimed by Herring and Van de Walle. Additional experiments over a range of temperatures might allow the Si-D bond energy to be determined from an activation energy rather than from the free energy at a single temperature. This would reduce the uncertainty arising from the vibrational entropy. Additional calculations with improved theoretical treatments of local vibrational modes might also help to resolve the differences between theoretical and experimental values for the surface Si-H bond energy and for the energy of H in solution in silicon.

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