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Comment on "Sulfur-Induced Reconstruction of Ag(111) Surfaces Studied by DFT"

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Using DFT calculations, we have shown that S/Ag(111) with $\sqrt{7} \times \sqrt{7}$ R19° ordering has three Ag adatoms in addition to three S atoms in each supercell. The structure proposed by a recent paper is not energetically competitive.

Adsorption of sulfur on Ag(111) has been studied experimentally using STM and theoretically using DFT in our previously published article in this journal.¹ Aside from a novel dot-row structure, we have also studied extensively through DFT calculations the $(\sqrt{7} \times \sqrt{7})$ R19° ($\sqrt{7}$ in short) structure, which is the subject of the recent paper² by Alvarez Soria et al. Our work is not cited or discussed by these authors. Specifically, we have identified two structures that are labeled $\sqrt{7}$ -a and $\sqrt{7}$ -b in Figure 8 in ref 1. Both of these two structures have three Ag and three S atoms in the top layer, with a complete substrate underneath it. In comparison, the structure obtained by Soria et al. at 3/7 ML S coverage has a similar structure as our $\sqrt{7}$ -a structure in the top layer, but the second layer has three vacancies.

Both the $\sqrt{7}$ -a structure in ref 1 and the structure proposed by Alvarez Soria et al. have their origin in the model postulated by Schwaha et al.,³ and reproduced by Yu et al.⁴ The key difference is that in the $\sqrt{7}$ -a structure there are three extra Ag atoms in each $\sqrt{7}$ supercell on top of the clean surface, while in ref 2 no extra Ag atoms are introduced.

To determine which structure is more favorable thermodynamically, one needs to take into account the energy cost of introducing extra Ag atoms into the system. Using DFT calculations, this can be achieved through calculating the chemical potential of S for a Ag_mS_n complex on top of a clean surface, which at zero temperature is given by

$$\mu_{\text{S}} = [E_{\text{ad}}(\text{Ag}_m\text{S}_n, L) - E_{\text{clean}}(L) - m\mu_{\text{Ag}}]/n \quad (1)$$

where $E_{\text{ad}}(\text{Ag}_m\text{S}_n, L)$ is the total energy of system of a Ag_mS_n complex adsorbed on top of a slab of L layers, and $E_{\text{clean}}(L)$ is the energy of the clean slab. An important quantity in the above equation is the chemical potential of the Ag atom μ_{Ag} , which can be calculated from energies of clean systems with different slab thicknesses. Note that for $m = 0$ (i.e., no extra Ag atoms) this should give the same result as the adsorption energy per S atom through eq 1 in ref 2, aside from a constant that is independent of S coverage.

Figure 1 shows the top views of the three $\sqrt{7}$ structures in refs 1 and 2, together with values of the chemical potentials. These values are obtained by averaging results using slabs with thickness ranging from four to seven. It shows that the structure obtained in ref 2 is much less stable than either of the two $\sqrt{7}$ structures in ref 1. In addition, the structure in Figure 1(c) ($\sqrt{7}$ -b in ref 1) is the most stable of them all.

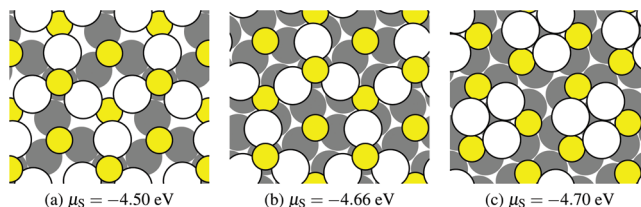


Figure 1. Top views and μ_{S} of various $\sqrt{7}$ structures. The small yellow circles are S atoms; open white circles are first-layer Ag atoms; and the darker circles are second-layer Ag atoms. (a) Structure obtained in ref 2, (b) $\sqrt{7}$ -a, and (c) $\sqrt{7}$ -b structure in ref 1.

The energy difference between $\sqrt{7}$ -a and $\sqrt{7}$ -b (0.04 eV per S atom) is small enough that one might not be able to choose $\sqrt{7}$ -b as the correct structure with complete confidence. However, the higher energy cost (>0.16 eV) for forming the structure in ref 2 from DFT calculations excludes it as a viable candidate for structures observed in experiments.

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