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Comment on

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"Cycloaddition chemistry at Semiconductor Surfaces...", by J.S. Hovis, et al.

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Hovis et al. report on an IR spectroscopy study of cyclopentene on C(001) where they conclude that, although with a low sticking coefficient, the adsorption process does take place and occurs on surface dimers. In order to observe adsorption features on diamond they found it necessary to expose the surface to quite large amounts cyclopentene, no less than 5000 L (though, what is actually present, is an IR spectrum upon exposure of C(001)-2x1 to 10000 L), which I found too large, not to be suspicious. The analysis of the IR spectrum obtained afterwards is, then, quite persuading in itself. The shift of an alkene-like =C-H vibrational band from 3040 to 2953 cm⁻¹, considered typical of reacted alkenes on (001) surfaces (Si, Ge and C surfaces), is observed and the overall spectrum is compared to condensed cyclopentene on the C(001) surface, which is, as could be expected, different. Such an argument, however, proves that cyclopentene is adsorbed on the diamond surface, but it does not say where the reaction has taken place, in particular, it does not prove that the dimers are involved. The high exposure required in this sense is quite suspicious and may either indicate (as the authors hypothesize) an extremely low sticking coefficient or an adsorption on totally different sites, i.e. on defects. I find that with the only aid of IR spectroscopy it is not possible to single out the adsorption site and claim that the adsorption has taken place on the dimers. The analogy with similarly oriented and reconstructed surfaces induces to think that a similar adsorption occurs on diamond, but this is not a proof. An example of a misleading adsorption on defects is the one of oxygen on Si(100)2x1 that occurs preferentially (if not only) on defects. There are, at least, two types of experiments which showed it (from mine as well as from a different research group). We performed Valence Band (VB) photoemission experiments of oxygen on Si(100)2x1 (1) and, indeed, we found the appearance of a typical band at 7eV, which is usually considered the fingerprint of the dissociative oxygen adsorption on silicon surfaces (2). Without any further check we would have fallen in the trap of assuming the oxygen adsorption dissociative and involving the surface dimers, since it is the most logical assumption on such a surface. VB photoemission, however, provides a check on the reaction sites through the surface bands related to the silicon dimers and those bands were not at all affected by the adsorption process in spite of the appearance of an 'unambiguous' band at 7 eV. Therefore, we had to conclude that oxygen adsorption did take place on Si(100)2x1, but not on the dimers. A partial quenching of the surface states, indeed occurs also in the case of oxygen on Si(100)2x1 for large exposures, a fact which does not allow us, at this point, to claim a reactivity of the dimers. A second type of experiment on the same system was performed by STM by Avouris and Cahill (3) and they also came to the conclusion that oxygen adsorbs on defects consisting in a dimer vacancy in which two adjacent Si atoms along the <110> direction appear to be missing. Such defects are characterized by a high density of states near the Fermi level which should enhance the reactivity towards oxygen. Therefore, I found reasonable to wonder how, without any check of the surface sites, with the only aid of a molecular band, after an exposure to a very large amount of cyclopentene, Hovis et al. are so sure that the adsorption on C(001)2x1 took place on the dimers.

- (1) M. Carbone, K. Bobrov, G. Comtet, G. Dujardin, L. Hellner, Surf. Sci. submitted.
- (2) G. Dujardin, G. Comtet, L. Hellner, T. Hyrayama, M. Rose, L. Philippe, M.-J. Besnard-Ramage, *Phys. Rev. Lett.* 1994 73 1727.
- (3) Ph. Avouris, D. Cahill, *Ultramicroscopy* 1992, 42, 838

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