

## Optical response of $\pi$ -conjugated molecular monolayer adsorbed on the semiconductor Si(001) surface: A first-principles study

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The modification of the semiconductor-surface optical response is investigated for the prototypical system of 9,10-phenanthrenequinone adsorbed on Si(001). By means of *first-principles* calculations we reproduce and explain recently measured reflectance-anisotropy data. The detailed analysis of the optical signal shows that intramolecular  $\pi$ - $\pi^*$  transitions as well as adsorption-modified Si bulk states contribute to the surface spectrum. The calculations illustrate the sensitivity of optical spectroscopy to molecular adsorption, but demonstrate clearly that a naive interpretation of the spectrum in terms of gas-phase molecular data fails.

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The organic functionalization of semiconductor surfaces has become important for developing new semiconductor-based devices.<sup>1</sup> Organic chemistry offers a vast variety of selectively bonding molecules that form self-terminating, ordered monolayers for applications such as organic sensors or molecular-electronic circuits. The adsorption of those molecules on semiconductor substrates allows, on the one hand, for the formation of covalent, adsorbate-substrate bonds (i.e., strongly bonded and robust overlayers) and on the other hand, for the coupling of surface electronic signals into common semiconductor-based electronic devices.

Experimentally, mainly scanning tunneling microscopy, core-level and infrared spectroscopy, as well as electron diffraction, are used to study the adsorption of organic molecules on semiconductors.<sup>2</sup> The optical spectroscopies such as reflectance anisotropy (or difference) spectroscopy (RAS or RDS) are highly successful for semiconductor-surface exploration and real-time monitoring of the epitaxial growth and oxidation processes.<sup>3–6</sup> They are nondestructive, do not depend on ultrahigh vacuum conditions, and are compatible with truly challenging preparation conditions such as surfaces under liquids. However, measurements of the optical properties of thin organic layers (e.g., Refs. 7–9) are still scarce. Likewise, most computational studies focus on the energetics and electronic properties of thin organic layers<sup>10–13</sup> rather than on their optical spectra.<sup>14–16</sup> Therefore, the contribution of organic thin films to the semiconductor-surface optical response is essentially unknown, hindering the use of optical spectroscopies for organic-layer characterization.

Recently, Hacker and Hamers<sup>9</sup> studied the optical anisotropy of 9,10-phenanthrenequinone (PQ or C<sub>14</sub>O<sub>2</sub>H<sub>8</sub>) adsorbed on Si(001) as a prototype for a  $\pi$ -conjugated overlayer system. Such  $\pi$ -conjugated systems are of special interest for electronic and optical applications due to their relatively small band gap. PQ has two highly reactive carbonyl groups likely to bond to the surface (“bonding group”) and a delocalized  $\pi$ -electron system (“functional group”), and it forms a large variety of derivatives. The  $\pi$  conjugation, likely to remain intact upon adsorption, should allow for the direct observation of intramolecular as well as interface- and substrate-related transitions in the experimentally accessible

photon-energy range.<sup>17</sup> Indeed, a pronounced RAS feature was measured for photon energies of about 5.2 eV and assigned to such intramolecular  $\pi$ - $\pi^*$  transitions.

Here we use the prototypical example of PQ adsorption to analyze in detail the optical response of an organic monolayer adsorbed on Si(001). It is shown that significant optical anisotropies arise upon organic-molecule adsorption. However, a naive interpretation of these features in terms of intramolecular transitions fails completely. Rather, the electronic structure of the gas-phase molecule as well as the semiconductor-bulk wave functions are strongly modified by the adsorption process and give rise to new optical fingerprints.

Our calculations are based on density functional theory in generalized gradient approximation (DFT-GGA),<sup>18</sup> as implemented in the VASP package.<sup>19</sup> Periodically repeated  $p(4 \times 2)$  supercells model the surface. The computational details are similar to those in Refs. 13 and 16. The reflectance anisotropy is calculated according to the scheme devised by Del Sole.<sup>20</sup> The slab polarizability is obtained within independent-particle approximation from the all-electron wave functions obtained using the projector-augmented wave (PAW) method.<sup>21,22</sup> We apply a rigid energy shift of 0.5 eV to the conduction bands<sup>23</sup> in order to account for the DFT band-gap underestimation. This value leads to a good agreement between the calculated and measured bulk critical-point energies of Si. Fortunately, it is nearly appropriate also for gas-phase PQ, as verified by occupation constraint ( $\Delta$  self-consistent-field (SCF)) calculations of the transition energies.

X-ray photoemission spectroscopy<sup>24</sup> shows that PQ bonds to Si(001) via the dicarbonyl groups, while infrared data demonstrate that the  $\pi$  conjugation is preserved and indicate hydrogen co-adsorption. The scanning tunneling microscopy images and cluster calculations<sup>24</sup> are interpreted in terms of a heteroatomic Diels-Alder reaction leading to the structure shown in Fig. 1(a).

Based on the experimental findings we considered a large number ( $>20$ ) of conceivable bonding configurations where PQ bonds via the dicarbonyl group to Si surface atoms and stands upright on the surface. The two most relevant structures are shown in Fig. 1: the top dimer (TD) model, where PQ sits atop the Si dimer, forming the proposed [4+2]-

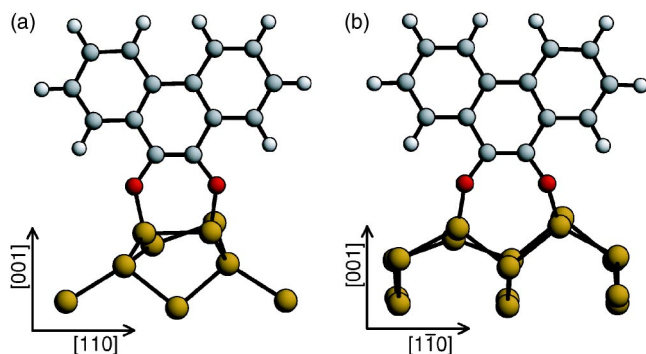


FIG. 1. (Color online) Structural models for PQ adsorption on Si(001): TD geometry (a) and CD geometry (b). Large (dark and red, gray, light) circles denote Si (O, C, H) atoms, respectively.

cycloaddition product,<sup>24</sup> and the cross dimer (CD) structure, where PQ bridges two adjacent dimers within one dimer row. Mind that PQ in a CD structure is rotated by 90° with respect to TD. We account for the possible presence of additional hydrogen by allowing for the co-adsorption of H atoms. A surface coverage of 0.5 monolayer (ML) (i.e., one molecule per two surface dimers) in a staggered TD geometry, where the molecules form zigzag chains perpendicular to the dimer rows, is energetically most favored. The hydrogen co-adsorption at the remaining Si dimers is favored for a wide range of the hydrogen chemical potential. The second most favored structure is a 0.5 ML coverage in a CD geometry. In order to saturate all Si dangling bonds, the PQ molecules either form pairs bridging two dimers or, in case of hydrogen co-adsorption, they arrange in zigzag chains along the dimer rows.

The RAS spectra calculated for the CD and TD geometries are compared with the measured data<sup>9</sup> in Fig. 2. The signal of the clean surface has been subtracted. Experiment shows a broad, positive feature around 3 eV that is most likely step related<sup>25,26</sup> and does not occur in the spectra calculated for flat surfaces. The measured RAS shows significant positive and negative peaks near the Si bulk critical points  $E_1$  and  $E_2$  at 3.5 eV and 4.3 eV, respectively. In the high-energy region the two features  $B_1$  and  $B_2$  at 5.2 eV and 5.7 eV, respectively, and a positive anisotropy  $T_+$  above 6 eV are identified. These features appear almost unchanged for a wide range of exposures (data for 0.1 and 1.3L are shown in Fig. 2), indicating the self-terminating nature of the adsorption process. While the  $E_1$  and  $E_2$  features indicate the modification of Si bulk states, the  $B_1$  feature was earlier assigned to the  $\pi$ - $\pi^*$  transitions of the PQ molecules.<sup>9</sup> This interpretation rests on the absence of the 5.2 eV feature in the RAS spectra of 1,2-cyclohexanedione-covered Si(001) surfaces.<sup>9</sup> Cyclohexanedione presumably bonds to Si(001) in a similar way as PQ does. It does not possess, however, a  $\pi$ -conjugated electron system.

Turning to the calculated spectra, the positive and negative peaks at the Si bulk critical-point energies are reproduced by both the TD and CD geometries and are even enhanced by the co-adsorption of hydrogen. The high-energy features  $B_1$  and  $B_2$  are clearly reproduced by the TD model, irrespective of the H co-adsorption, whereas in the CD case

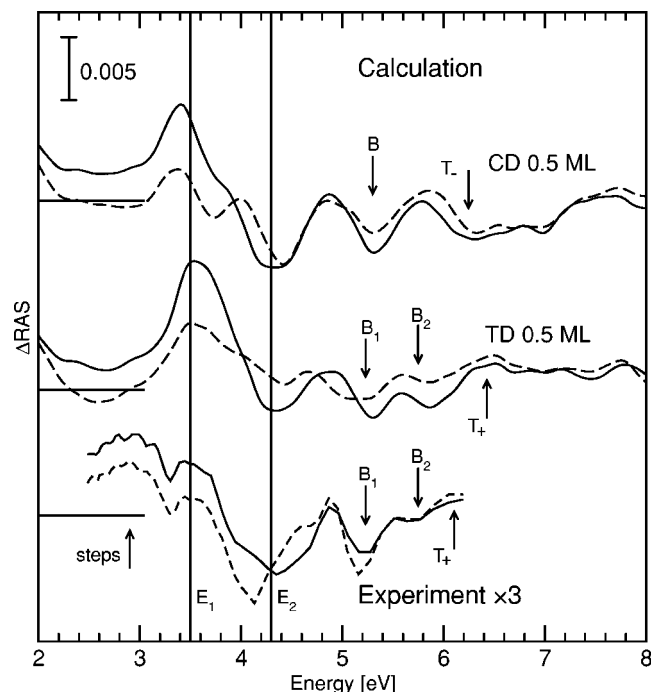


FIG. 2. RAS spectra  $\Delta r/r = \text{Re}\{(r_{110} - r_{1\bar{1}0}) / \langle r \rangle\}$  calculated for the structures shown in Fig. 1 in comparison with the experiment in Ref. 9. The signal of the clean Si(001) $c(4 \times 2)$  surface is subtracted. Calculations: The dashed (solid) lines denote PQ adsorption in the CD and TD geometries (with H co-adsorption). Experiment: The solid (dashed) lines represent the data for 0.1L (1.3L) exposure.

only one feature  $B$  is observed. The assignment of  $B_1$  (or  $B$ , respectively) to the  $\pi$ - $\pi^*$  intramolecular transitions as proposed by Hacker and Hamers<sup>9</sup> appears questionable, since this would imply a change of polarity for the CD geometry, where the molecules are rotated by 90°, as compared to TD. A sign reversal, expected for the features due to intramolecular transitions, occurs only for photon energies between 6 eV and 7.5 eV. The measured positive anisotropy  $T_+$  at high energies is reproduced by the TD geometry only.

Summarizing, we find that the TD geometry accounts for the measured data. However, the differences with respect to the CD geometry, where the molecules are rotated by 90°, are comparatively small. In order to understand the similarity of the TD and CD spectra we analyze in the following the origin of the optical anisotropies. The valence orbitals are classified with respect to their localizations either below or above the Si surface. This decomposition allows for the separation of the substrate- and organic-layer contributions to the total optical signal. The respective RAS spectra for the energetically most relevant TD 0.5 ML+H structure are shown by the fourth, fifth, and sixth curves in Fig. 3. It can be seen that the RAS features at the  $E_1$  and  $E_2$  bulk-critical points, as well as the  $B_1$  and  $B_2$  features, arise from transitions involving Si bulk states. In addition, the total signal is modified by molecular transitions denoted as  $M_1$ ,  $M_2$ , and  $M_3$ . The contribution of these features to the overall optical anisotropy is comparatively weak. This explains the small influence of the molecule orientation on surface-optical anisotropy.

What is the origin of the features  $M_1$ - $M_3$ ? To answer this

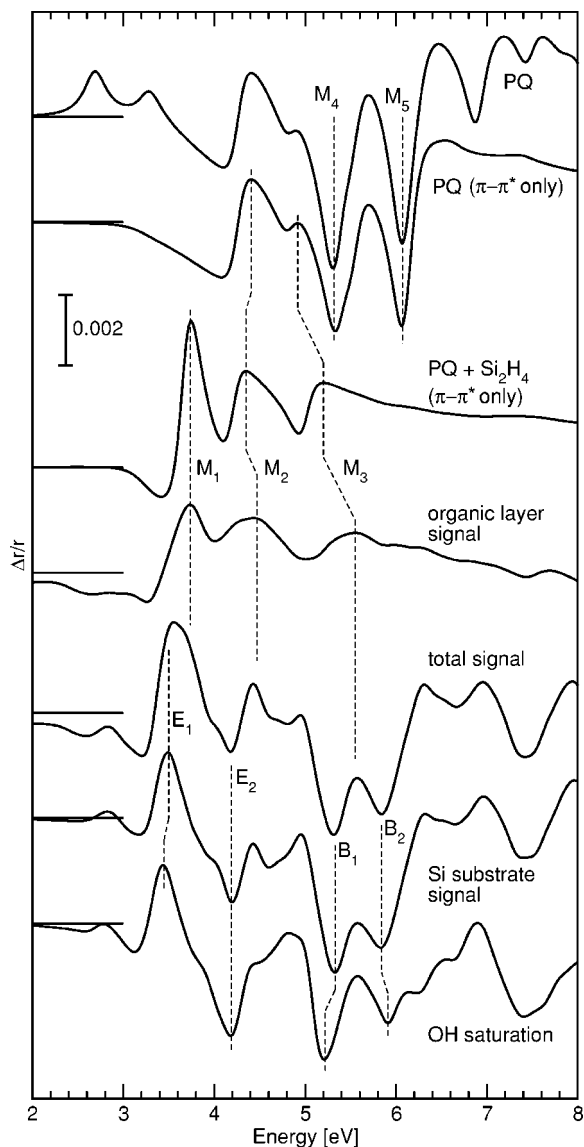


FIG. 3. RAS spectrum calculated for the TD 0.5 ML with co-adsorbed hydrogen and its decomposition, using three-layer model calculations with different constituents (see text).

question we perform model calculations where we use the dielectric function of gas-phase molecules or clusters instead of the full-slab polarizability to calculate the surface-reflectance anisotropy. Specifically, we employ a three-layer model for the surface region: isotropic bulk Si, anisotropic, organic thin film, and vacuum. The topmost RAS curve in Fig. 3 is obtained from the PQ gas-phase absorption spectrum. Interestingly, it shows pronounced  $\pi$ - $\pi^*$  transition-related  $M_4$  and  $M_5$  features that nearly coincide in energy with the measured  $B_1$  and  $B_2$  peaks. However, the RAS obtained from the gas-phase PQ molecules clearly fails to reproduce the calculated organic-layer contribution to the total signal. This can be expected; the carbonyl group-related transitions will vanish or at least be shifted to much higher energies upon bonding with the substrate. Therefore, in a second step, we calculate the RAS as above, but restrict the optical response to the  $\pi$ - $\pi^*$  transitions of the gas-phase

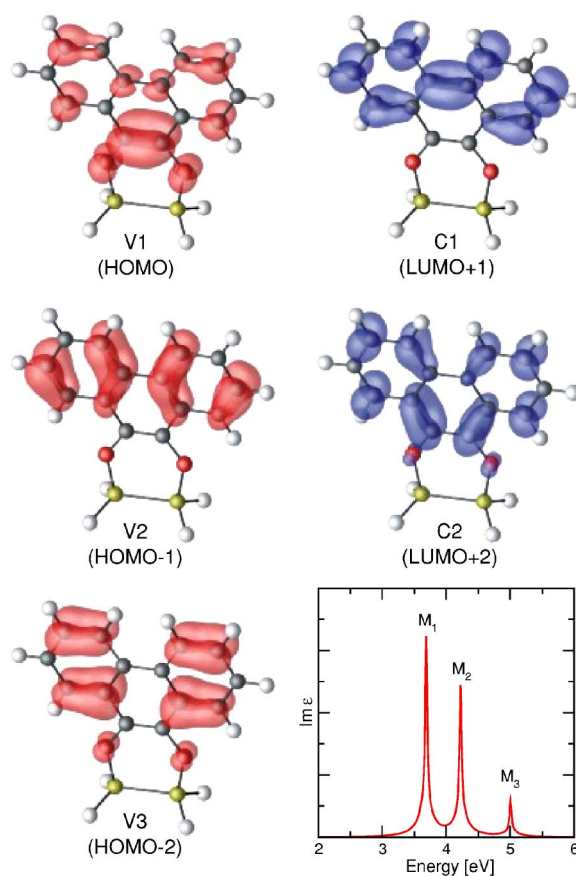


FIG. 4. (Color online) Relevant molecular orbitals of the PQ +  $\text{Si}_2\text{H}_4$  cluster discussed in the text. The inset shows the absorption spectrum due to transitions between these states.

molecule. The resulting second curve in Fig. 3, however, agrees only slightly better with the organic-layer contribution to the total RAS. To model the bonding with the Si substrate we therefore construct in a third step an artificial PQ +  $\text{Si}_2\text{H}_4$  cluster (see Fig. 4), using the relaxed coordinates from the TD model. The Si—O bonding leads to a charge redistribution in the molecule and also to the formation of a new C=C double bond (V1 in Fig. 4) between the carbonyl group C atoms, which correspond now to the highest occupied molecular orbital (HOMO). By restricting the calculation to the transitions between the three highest occupied  $\pi$  orbitals and the two lowest unoccupied  $\pi^*$  orbitals, one obtains the third curve of Fig. 3. Obviously, the line shape and peak positions of the organic-layer signal are well described by such a model for the constituents of the organic film. Thus, the essential parts of the molecular contributions to the RAS can be traced back to a few  $\pi$ - $\pi^*$  transitions within the PQ molecule. However, the bonding to the substrate must be taken into account. The feature  $M_1$  arises solely from the transitions involving the C=C double bond, which forms as a result of the [4+2] Diels-Alder reaction with the Si=Si dimer. At the same time, the formerly pronounced  $M_4$  and  $M_5$  features are strongly reduced in amplitude and shifted in energy, due to the substrate-bonding related changes of the respective molecular orbitals. Whereas  $M_2$ 's energetic position remains mainly unchanged upon bonding to the sub-

strate, the feature  $M_3$  in the organic-layer signal is shifted by about 0.6 eV towards higher energy with respect to its position in the gas-phase spectrum (cf. Fig. 3). This is due to a relative lowering of the contributing valence orbital  $V_3$  with respect to the HOMO energy level. Figure 4 shows the molecular states responsible for the RAS features related to the organic overlayer;  $M_1$ ,  $M_2$ , and  $M_3$  stem from  $V_1$ - $C_2$ ,  $V_2$ - $C_1$ , and  $V_3$ - $C_1$  transitions, respectively.

A similar strategy as applied above is used to verify the Si-substrate contributions to the total RAS signal: The PQ molecules are simply replaced by two OH groups each. By keeping the slab geometry (including the O atoms) fixed, the RAS contribution of the strained and rebonded substrate can be calculated. The obtained spectrum (bottommost curve in Fig. 3) reproduces all main features of the Si-substrate signal, i.e., the  $E_1/E_2$  features as well as  $B_1$  and  $B_2$ . Evidently,  $B_1$  and  $B_2$  do not arise from molecular transitions, but are clearly due to the adsorption-induced distortions of the substrate. The calculations for a H-terminated substrate (not shown here) demonstrate, however, that dangling-bond passivation (by hydrogen) in combination with strain are not sufficient to reproduce features similar to  $B_1$  and  $B_2$ . Both the adsorption-induced strain in the silicon lattice and the formation of Si—O bonds contribute to these anisotropies. These computational findings are consistent with our earlier result that the anisotropy at 5.2 eV does not change its sign upon

rotating the molecules by  $90^\circ$  (see the CD and TD curves in Fig. 2) as well as the absence of a negative peak at 5.2 eV in the organic-layer signal (cf. the third and fourth curves in Fig. 3).

In conclusion, the influence of organic layers on the optical properties of semiconductor surfaces has been calculated from *first principles*, using the adsorption of 9,10-phenanthrenequinone on Si(001) as a model case. It is shown that the optical anisotropy of the substrate is significantly altered. The calculations are in good agreement with experiment. The detailed analysis of the spectrum shows that a simplified interpretation of the spectra in terms of the anisotropic molecular transitions fails; the molecule-substrate bonding leads to strong modifications of the intramolecular transitions, even for molecules where bonding and functional groups are seemingly decoupled. Specific  $\pi$ - $\pi^*$  transitions were identified as the main sources of the organic-layer anisotropy signals. However, the total spectrum is dominated by contributions from the adsorption-modified Si bulk states.

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