

Hydrogenated Silicene on Ag(111): a theoretical investigation through optical excitations

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SUMMARY - In this work we theoretically investigate the adsorption of silicene-based layers onto the Ag(111) surface, focusing onto the $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ phase for which we consider different H coverages, mainly half and full coverage (so-called silicane). Within the Density Functional Theory framework we derive the structural and electronic properties in the ground state, then we construct the optical response within the independent particle (IP) approximation. We therefore address the features observed both in the absorption and reflectance spectra, showing their tight connection with the electronic properties.

BACKGROUND - Extensive investigations carried onto the silicene monolayer point to its properties being altered by the substrate onto which it is synthesized [1]. These include the Ag(111) surface, which was one of the first historically considered, where the loss of the desired Dirac cone is due to the strength of the Si-Ag interaction affecting electronic and optical properties regardless of the specific silicene phase [2,3]. In order to decouple the Si atoms from the metal ones, one of the possible approaches is the passivation of Silicene through adsorption of H atoms [4]. In addition, in literature it has been discussed which phase of the adlayer is more likely to form, namely silicane or half-silicane [5,6].

OPTICAL EXCITATIONS AT THE INDEPENDENT PARTICLE LEVEL - The study of the excited states is a way to gather information from a different observation window of a system. Optical excitations experimentally require a relatively cheap and affordable equipment; moreover they can be less damaging for the sample. Theoretically, though, such states have been tackled with sufficient accuracy only recently, through the many-body perturbations formalism [7,8]. In this framework, the RPA-IP approach neglects any further interaction between the electrons; however it is sometimes a good enough approximation for metallic systems, with polarization parallel to the surface [8]. In such a case the dielectric function can be written as:

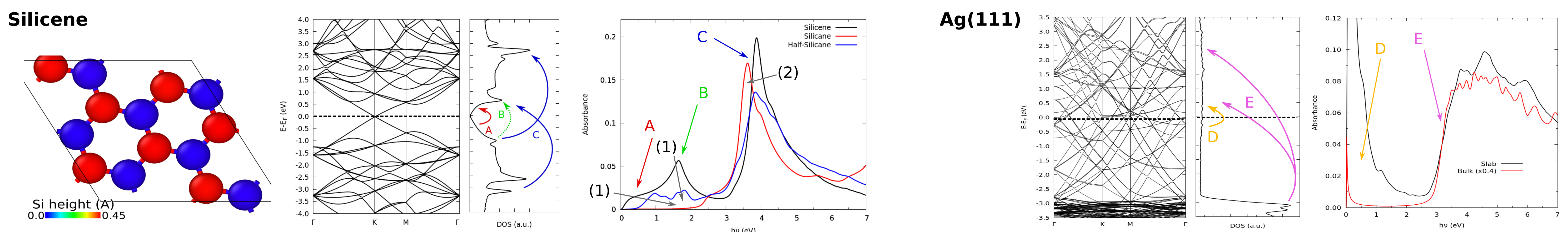
$$\epsilon_M^{-1} = 1 + \frac{\gamma}{V} \sum_n^{cond.} \sum_m^{val.} \sum_{\mathbf{k}} \frac{W_n W_m |\langle m, \mathbf{k} | \hat{\mathbf{p}} + [\hat{\mathbf{r}}, V^{NL}] | n, \mathbf{k} \rangle|^2}{(\epsilon_{m,\mathbf{k}} - \epsilon_{n,\mathbf{k}}) [(\omega + i\tau)^2 - (\epsilon_{m,\mathbf{k}} - \epsilon_{n,\mathbf{k}})^2]}$$

The absorbance spectrum for the slab is then constructed as: $A(\omega) = (\omega L/c) \text{Im} \epsilon_M(\omega)$

Finally, the reflectivity can be constructed through Snell's equations, however both experimentally and theoretically it is better to deal with the difference in reflectance between the clean surface and the surface with the adsorbate as $\Delta R/R$, called surface differential reflectivity spectrum (SDRS). To deal with a slab, a three-regions model (vacuum, slab, bulk) can be considered [8,9] to obtain:

$$\frac{R_{Ads.} - R_{Surf.}}{R} = \frac{4\omega L}{c} [F(\epsilon_{bulk}) \Delta \epsilon_{AS}^{Im} - F'(\epsilon_{bulk}) \Delta \epsilon_{AS}^{Re}] \quad \Delta \tilde{\epsilon}_{AS} = \tilde{\epsilon}_{Ads.} - \tilde{\epsilon}_{Surf.}$$

We performed the structural and electronic relaxations through Quantum ESPRESSO package, using PBE-NC pseudopotentials ($E_{cut}=86$ Ry), with an unshifted $6\times 6\times 1$ k-point mesh, increased to $17\times 17\times 1$ ($31\times 31\times 1$ for the free standing systems) for the density of states. The van der Waals interaction has been included in the form of the Grimme-D2 correction. The optical properties have been calculated through Yambo code, with the denser k-points mesh. We constructed the Ag slab with 5 layers, with the two topmost ones left free to relax, using a bulk lattice constant of 4.216 Å.



Two effects can be addressed due to the hydrogenation of silicene: (1) a progressive opening of a bandgap, which involves the loss of the bands related to the Dirac cone (A,B) and (2) a redshift of the deep valence-conduction transition peak (C). Clean Ag shows Drude-like intraband transitions with $\omega_D=8.9$ eV (D) and valence to conduction ones (E).

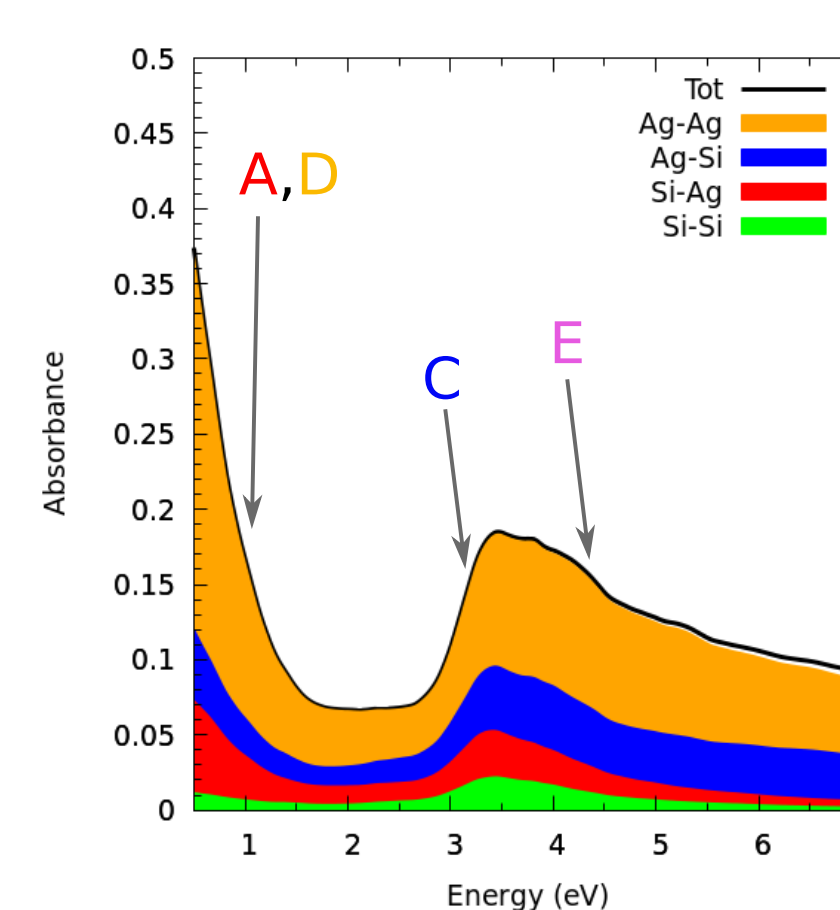
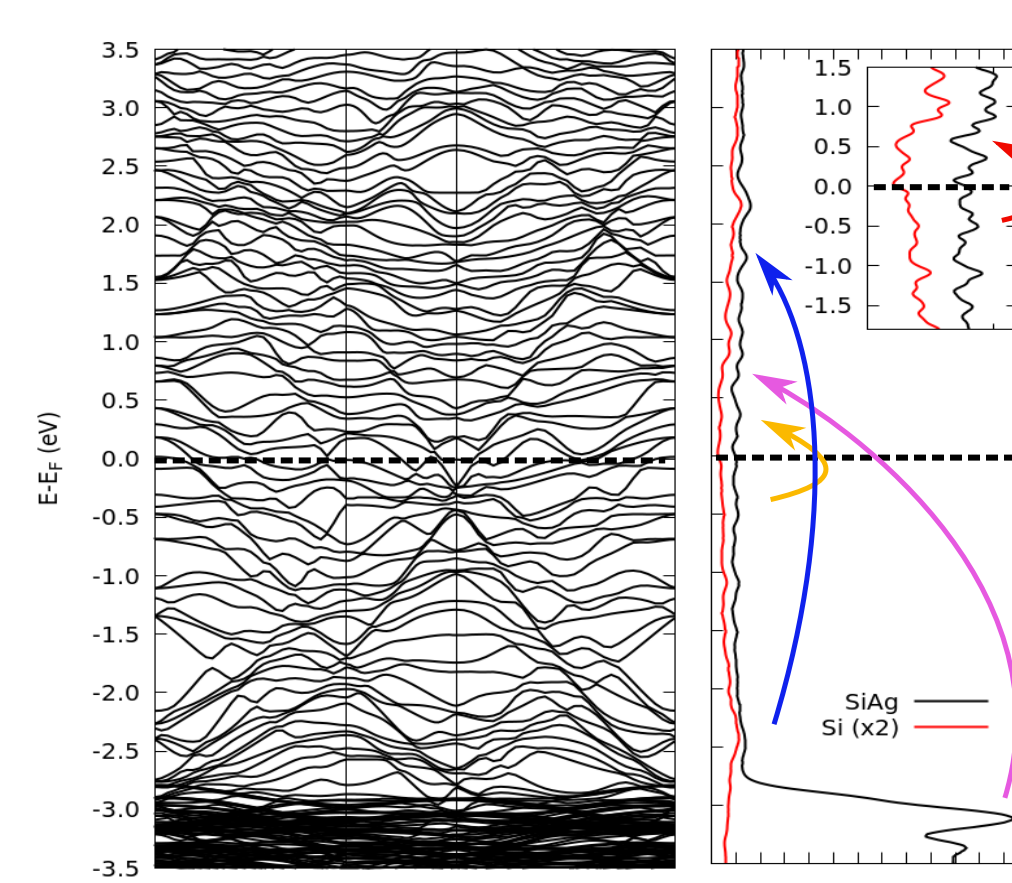
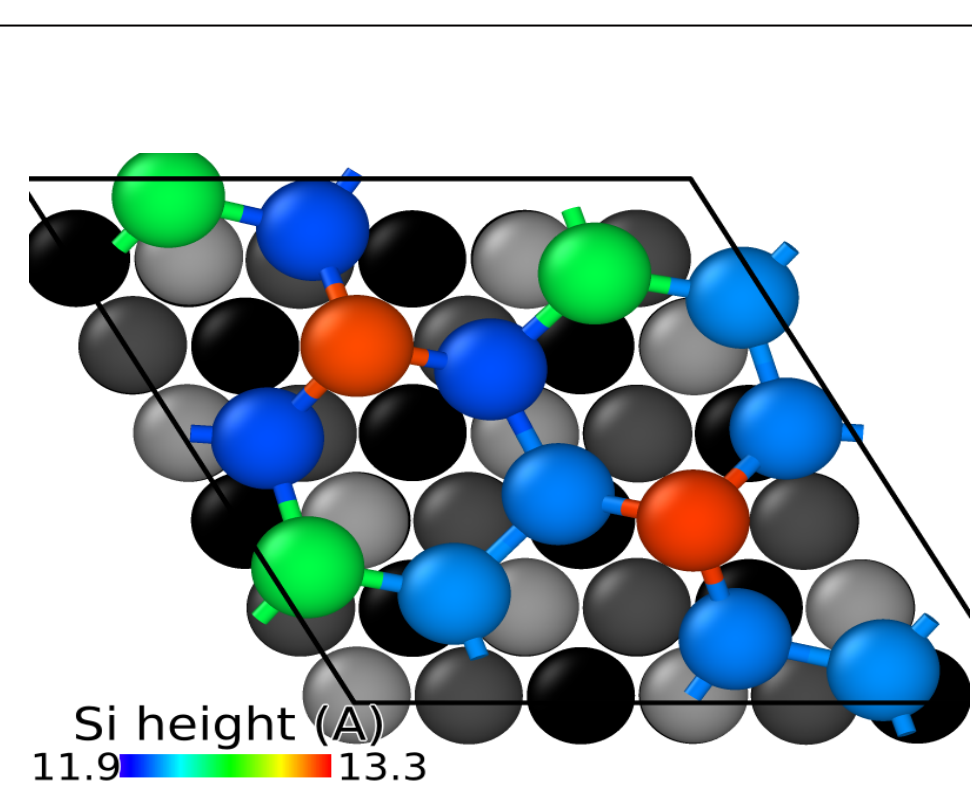
Silicene/Ag(111)

$$E_{ads} = -9.86 \text{ eV}$$

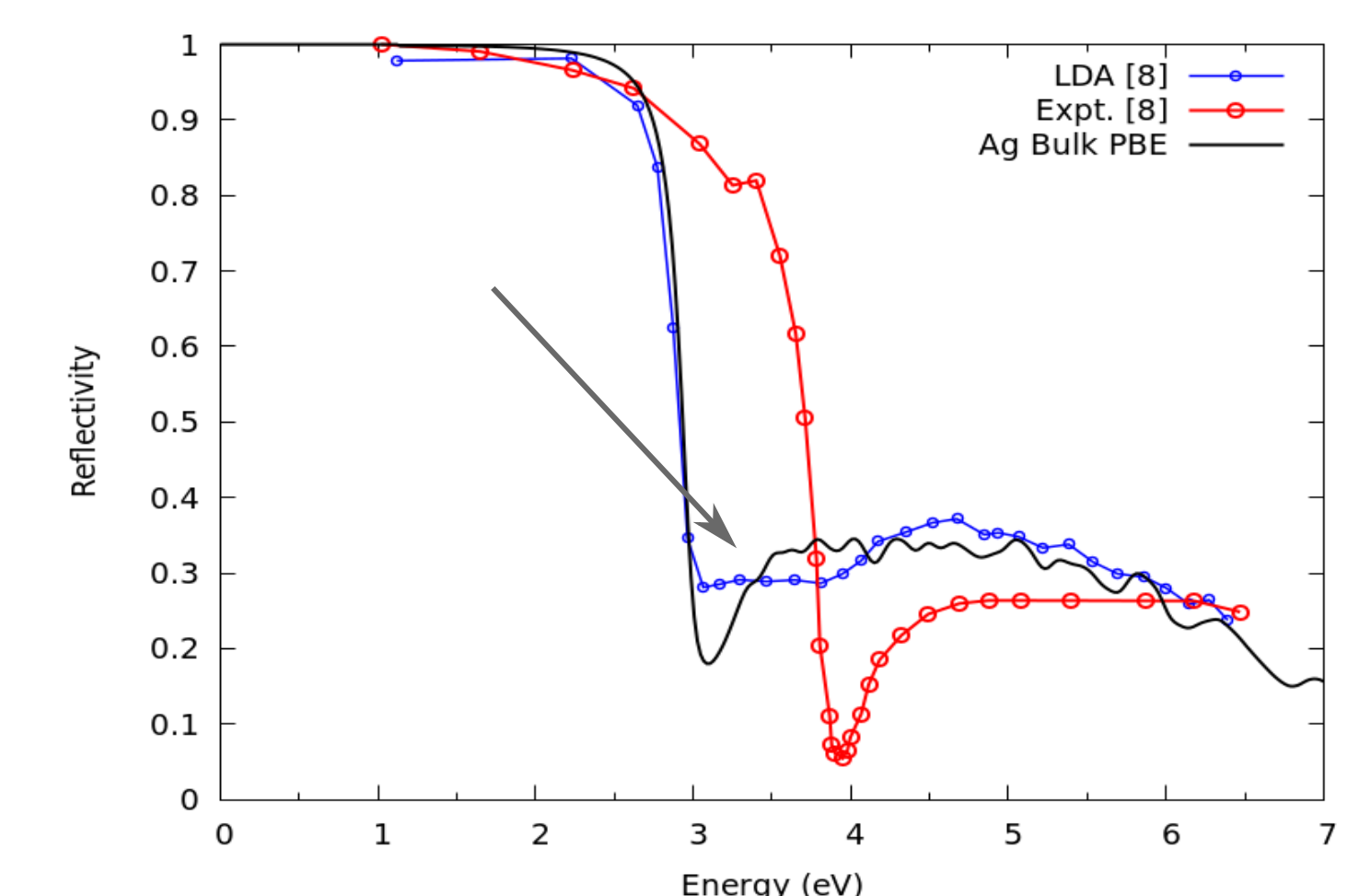
$$d_{Ag}^{Si} = 2.47 \text{ \AA}$$

$$\Delta e_{sil} = 0.41$$

$$E_{ads} = E(AgSiH_N) - E(Ag) - E(SiH_N)$$



SDRS spectra



Differences are due to the simpleness of the approach and the slab partially including the intraband transitions.

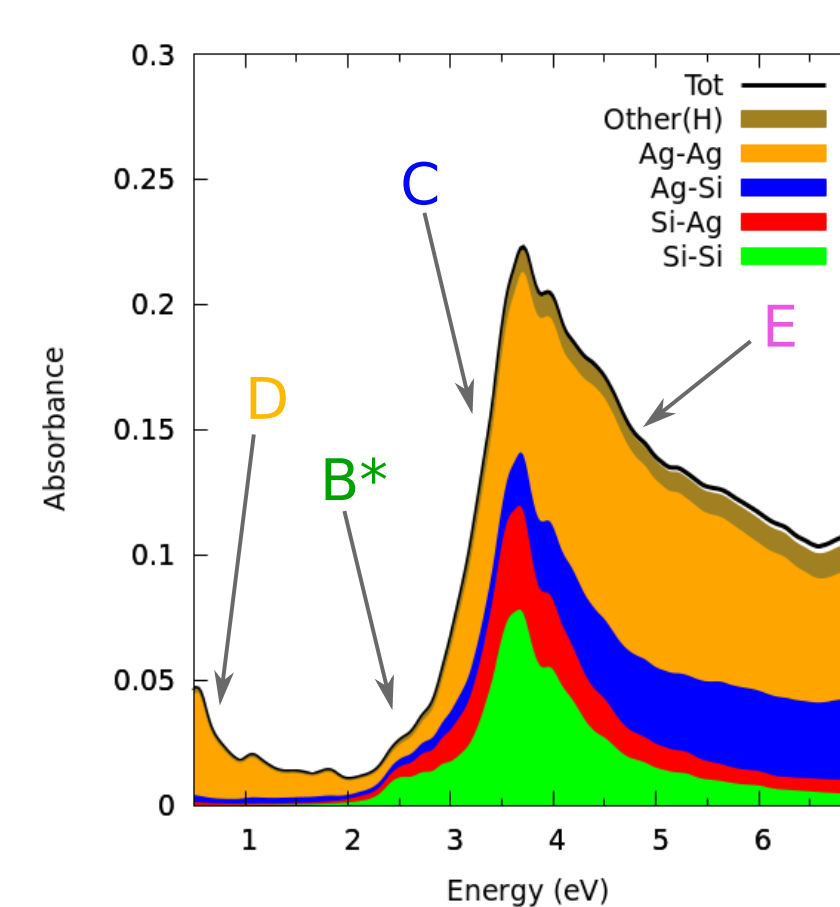
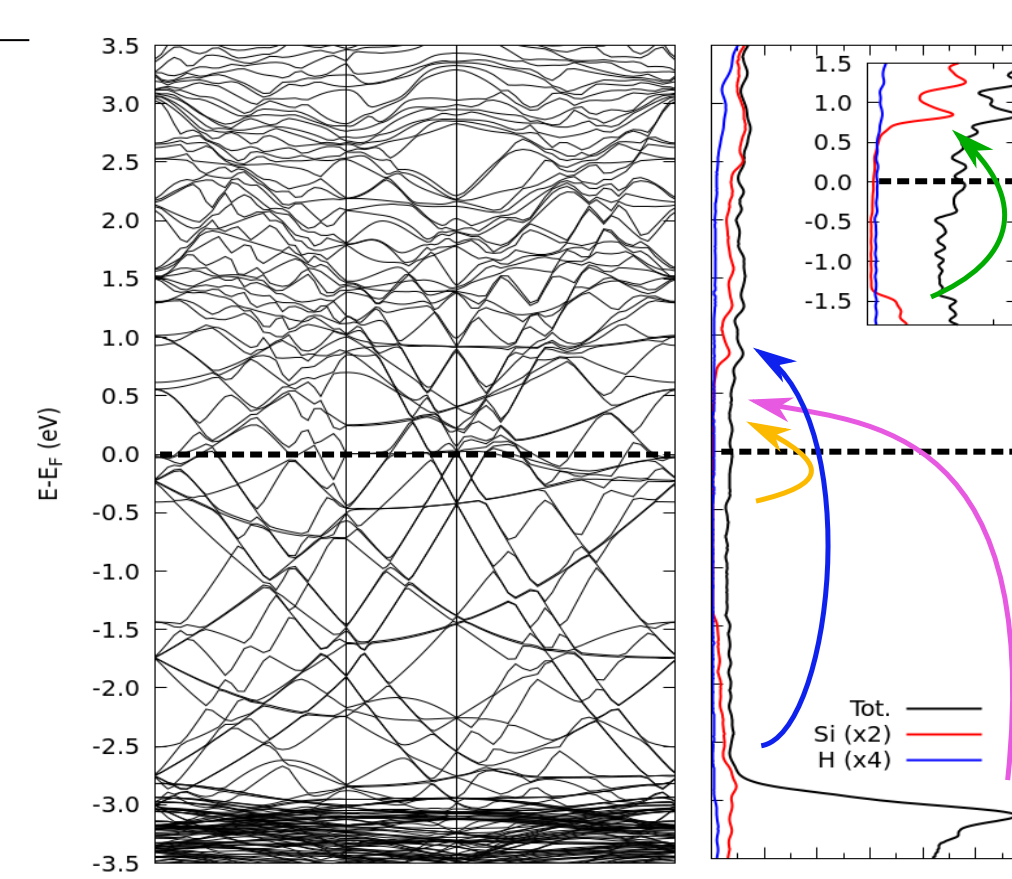
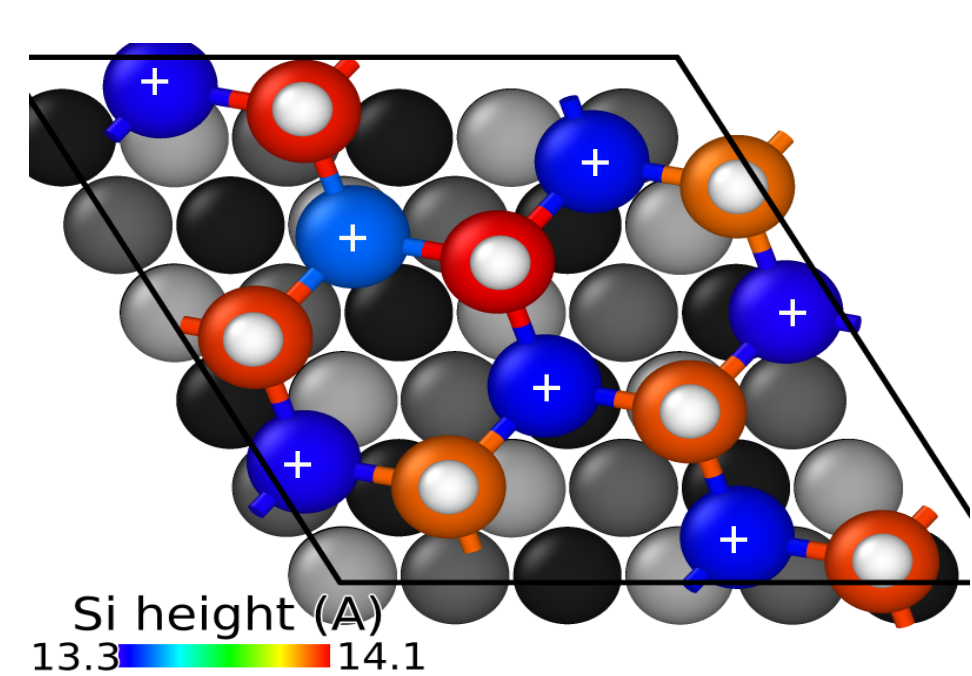
Silicane/Ag(111)

$$E_{ads} = -2.40 \text{ eV}, -2.36 \text{ eV/H}$$

$$d_{Ag}^H = 1.98 \text{ \AA}, d_{H}^{Si} = 1.51 \text{ \AA}$$

$$\Delta e_{sil} = 0.30, \Delta e_H = 0.30/H$$

$$E_{ads}/H = [E(AgSiH_N) - E(AgSi) - NE(H)]/N$$

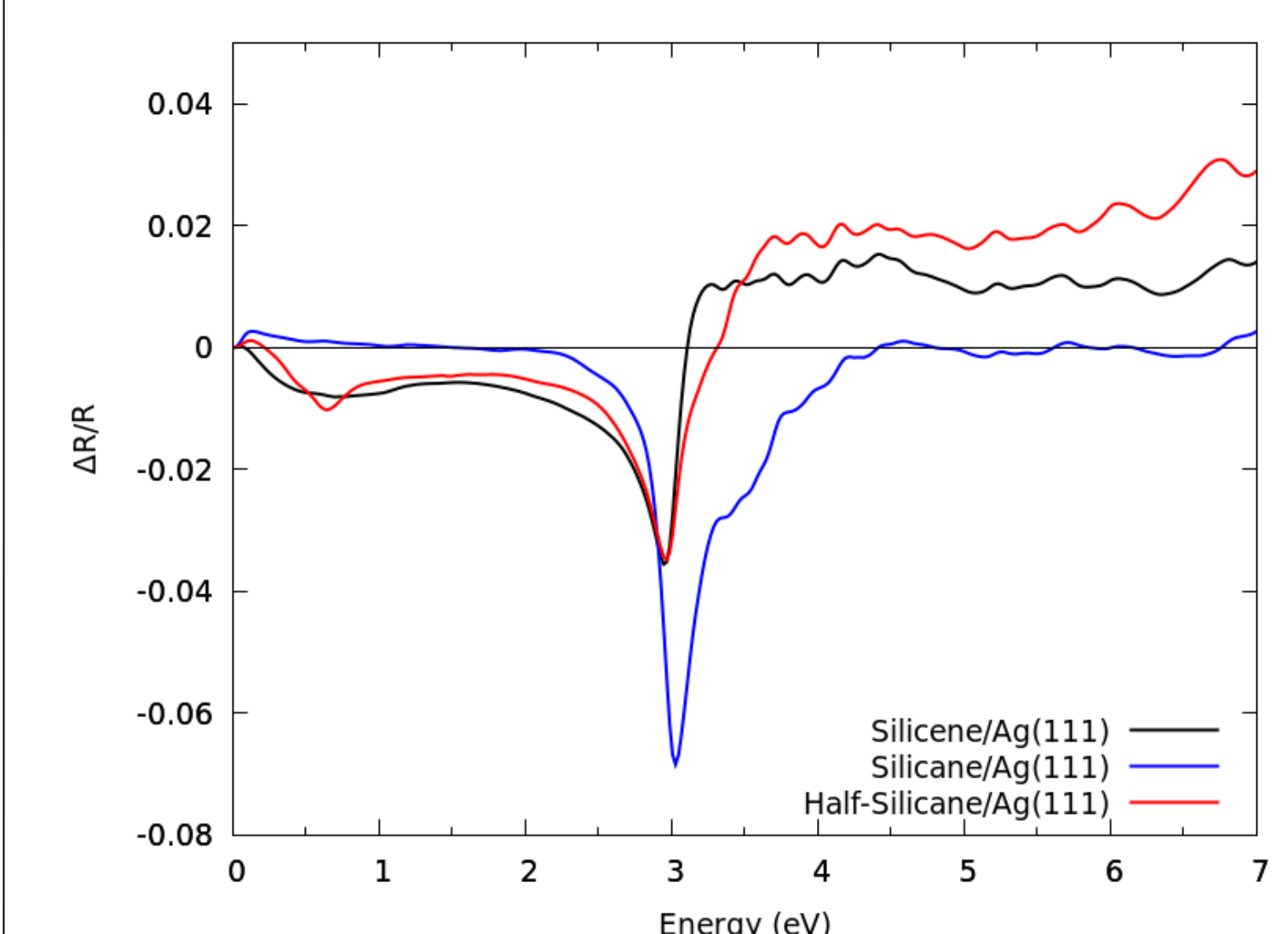
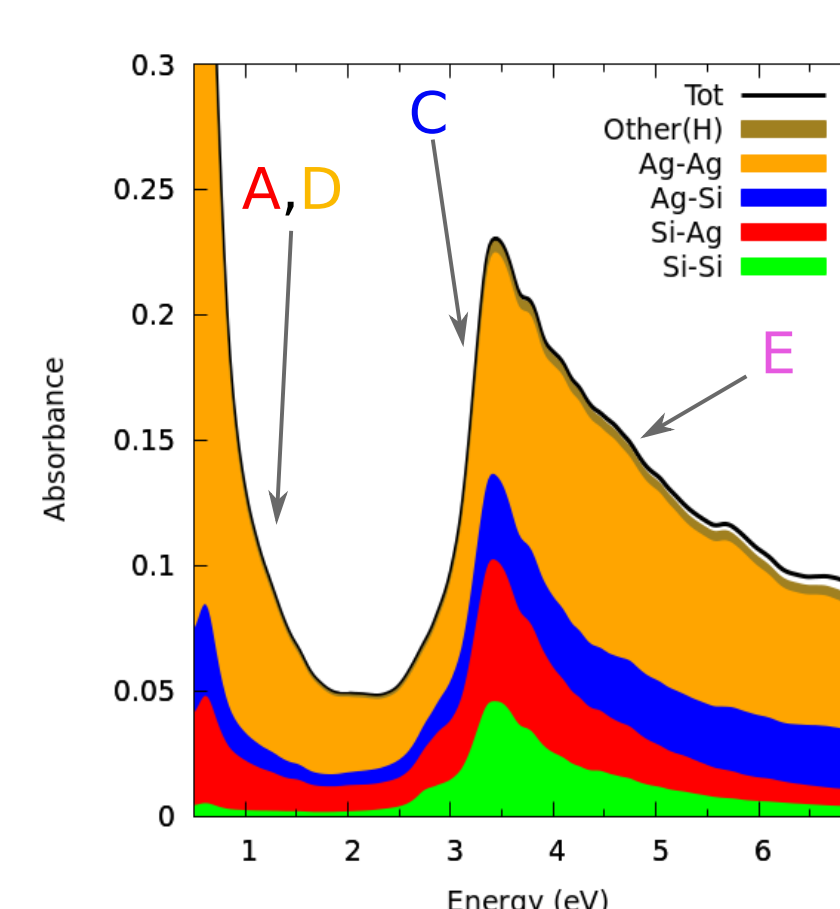
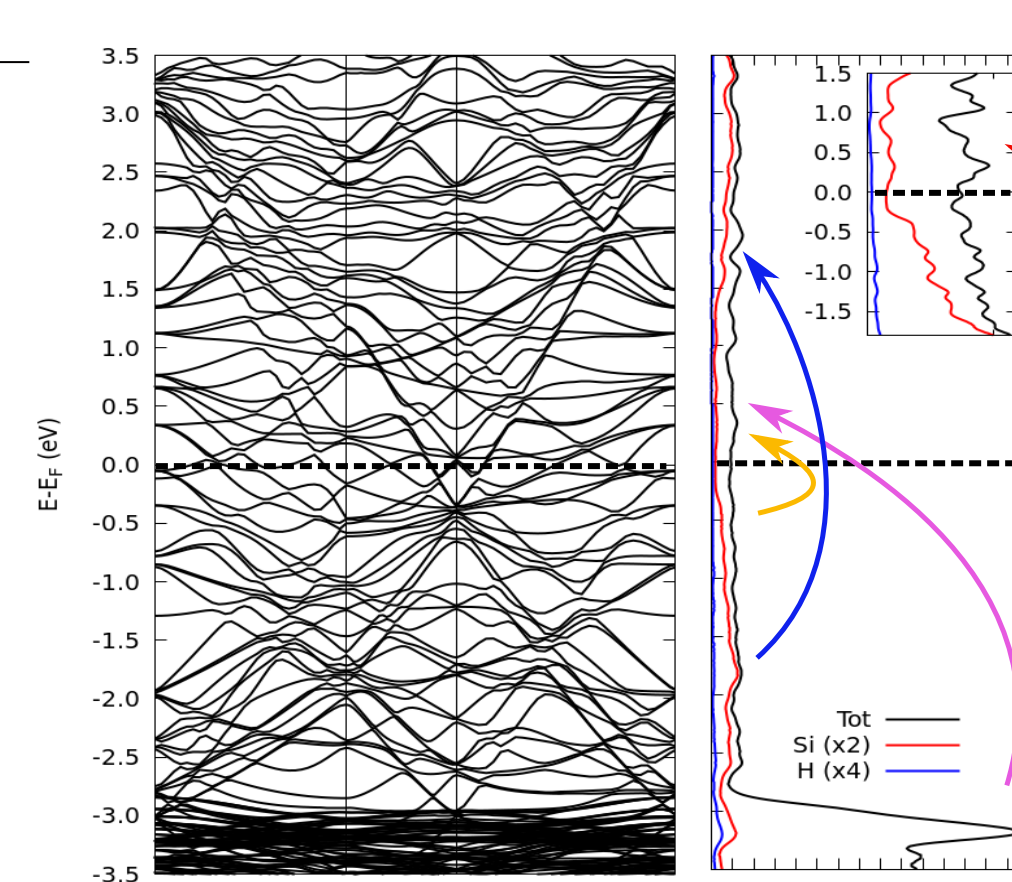
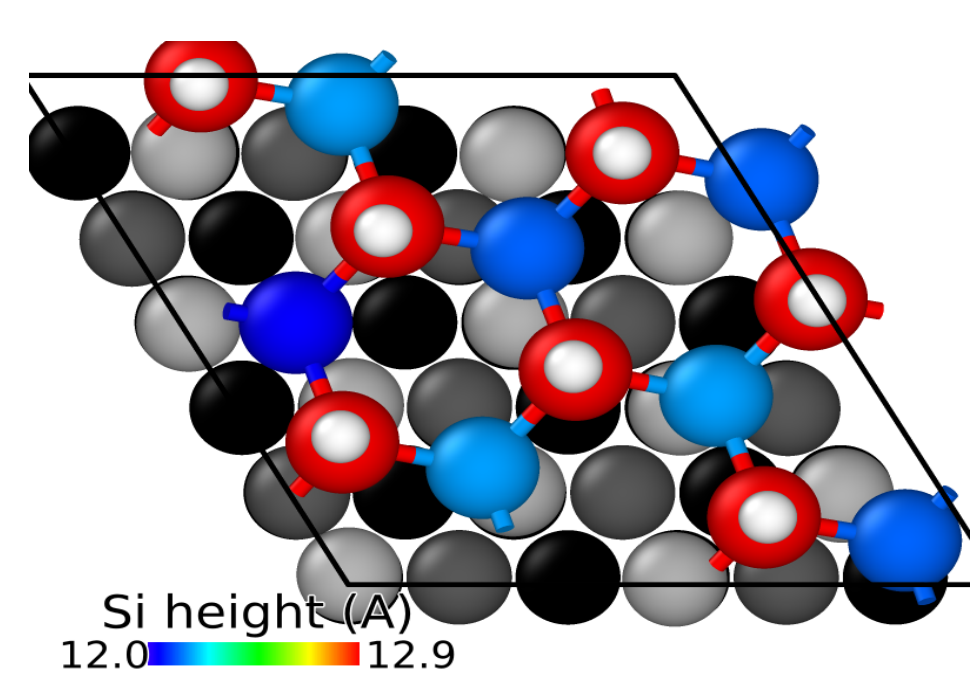


Half-Silicane/Ag(111)

$$E_{ads} = -11.11 \text{ eV}, -2.67 \text{ eV/H}$$

$$d_{Ag}^{Si} = 2.69 \text{ \AA}, d_{H}^{Si} = 1.51 \text{ \AA}$$

$$\Delta e_{sil} = 0.20, \Delta e_H = 0.03/H$$



Silicane shows a different spectrum, due to the weaker interaction with the substrate.

CONCLUSIONS - From the structural and electronic properties we calculated for H-passivated silicene adsorbed onto the Ag(111) surface we highlight the strong interaction of Si atoms with both Ag and H ones, leading to the loss of its characteristic Dirac cone. We can relate this effect to an enhanced sp^3 hybridization of Si orbitals, compared with the pristine case. Nonetheless we observe the footprint of the electronic structure in the optical excitation spectra, which we exploited to characterize the systems.

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