Tellurium - Modified Surface States of GaAs(001) and InAs(001)

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We investigate the stability and electronic structure of 1×2 and 2×2 GaAs(001):Te and InAs(001):Te surfaces with different degrees of tellurium coverage ($\theta_{Te} = \frac{1}{4}, \frac{1}{2}, \frac{3}{4}, 1$), by means of first-principles pseudopotential calculations within density-functional theory. The adsorption stability decreases as the tellurium coverage increases. The adsorption on InAs(001) is more stable than on GaAs(001). As-Ga (or As-In) bonds for the uppermost As atoms are s^2p^2-like (nearly planar), while the Te bonds at the surfaces are sp^3-like. The hetero-dimers in $\theta_{Te} = \frac{1}{2}$ modify the character of GaAs(001):Te and InAs(001):Te surfaces resulting in a semiconductor structure.

I Introduction

There are observation [1] of the surfactant action of Te in the heteroepitaxial growth of large mismatch systems such as InAs/GaAs by addition of Te over GaAs(001). In ref. [2] the authors propose that the 2D growth is stabilized by half a monolayer of Te atoms that remain on the interface. This model is supported by the experimental indication that only the excess of half a monolayer of Te atoms floats at the InAs surface [3] and by a total energy calculation showing a reduction of the GaAs/InAs interface strain energy by a Te interlayer [4]. Our previous theoretical calculations with adsorbed atoms at bridge positions [5, 6] determined a pattern of atomic relaxation with dimerization in (-110) direction in agreement with experimental results [7], indicating that the GaAs(001):Te-2 × 2 ($\theta_{Te} = 1$) surface has two dimers geometries at the lowest configuration. Also, for the concentration ($\theta_{Te} = \frac{1}{2}$) Te atoms prefers to be adsorbed on the sites off-chain, indicating a monoatomic adsorption. We report an investigation of stability and electronic structure of 1 × 2 and 2 × 2 GaAs(001):Te, Ga terminated, and InAs(001):Te, In terminated surfaces, covered by Te and As atoms with concentration $\theta_{Te} = \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$ and 1.

II Calculation

Our calculations to simulate the systems are based on density-functional theory within the local-density approximation (DFT-LDA). We consider an artificial periodic slab geometry along the (001) direction. The unit cell includes an atomic slab with six atomic GaAs(001), or InAs (001) layers for Ga (or In) terminated surfaces, covered by Te or As adlayer and a vacuum region equivalent in thickness to a six layers. The dangling bonds on the back-side of the slab (As surface) were satured H atoms. The tree uppermost layers and surface are allowed to relax. The eletric field resulting from the inequivalence of the two surfaces is corrected by a dipole calculated self-consistently [8]. The electron-ion interaction is treated by using fully separable, norm-conserving pseudopotentials [9]. For the electron-electron interaction we employ the exchange correlation potential of Ceperlay-Alder [10] as parameterized by Perdew and Zunger [11]. Single particle orbitals are expanded into plane waves up to a cutoff energy of 12 Ry. $\vec{k}$-space integrations are replaced by a sum over eight (1 × 2 cells) or four (2 × 2 cells) special points in the irreducible part of the surface Brillouin zone. The minimum of the total-energy functional

with respect to both the electronic and atomic degrees of freedom is found by means of a molecular-dynamical approach [12].

III   Results and discussion

The stability of the Te and As adsorption on GaAs(001) e InAs(001) surfaces are investigated for 1×2 and 2×2 cells. To analyze the stability we consider the formation energies (grand canonical potentials) defined as [13]:

$$E^{form} = \frac{E^{tot} - E^{Ga(In)} - n_{As}\mu_{As}}{n_{Te}} - \mu_{Te}, \quad (1)$$

where E^{tot} is the total energy of relaxed structure, $E^{Ga(In)}$ is the total energy for full relaxed clean surface GaAs(InAs), n_{Te} and n_{As} are the number of adsorbed tellurium and arsenic atoms at the surface, and μ_{Te} and μ_{As} the chemical potentials. This a relative formation energy and we can take it as a function of the tellurium chemical potential, fixing μ_{As} from the As bulk value. The maximum value for μ_{Te} corresponds to the Te bulk elemental phase and the lower limit was taken as the chemical potencial of Te atoms adsorbed on GaAs(001) or InAs(001) surface, $\mu_{Te}^{Ga(In)As(001)}$:

$$\mu_{Te}^{Ga(In)As(001)} \leq \mu_{Te} \leq \mu_{Te}^{bulk}. \quad (2)$$

Our calculated value for the chemical potencial of Te atoms adsorbed on the surfaces, relative to μ_{Te}^{bulk}, is $-1.40 eV/atom$ for GaAs(001), and $-1.49 eV/atom$ for the InAs(001). These values define the range for the different coverages at the surfaces. Fig. 1 shows the formation energies with $\theta_{Te} = \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$ and 1 for (a)GaAs(001):Te and (b)InAs(001):Te. The formation energies in units eV/1x1 surface, for the adsorptions on GaAs(001) are $E^{form} = -3.75 - \mu_{Te}$ for $\theta_{Te} = \frac{1}{4}$, $E^{form} = -2.34 - \mu_{Te}$ for $\theta_{Te} = \frac{1}{2}$, $E^{form} = -1.72 - \mu_{Te}$ for $\theta_{Te} = \frac{3}{4}$ and $E^{form} = -1.40 - \mu_{Te}$ for a full coverage of Te ($\theta_{Te} = 1$). We also have considered three possible geometries for the $\theta_{Te} = \frac{1}{2}$ in a 2×2 cell with Te-Te, Te-As and As-As dimers at the surface. As their surface energies differ by less than 0.05 eV/cell, the 1×2 reconstruction with hetero dimers at the surface should be the more stable structure, in agreement with STM observations [7]. The Te fully coverage has the same formation energy for 1×2 and 2×2 reconstructions. For adsorption on InAs(001) surfaces, we have obtained the formation energies in units eV/1x1 surface as: $E^{form} = -4.16 - \mu_{Te}$ for $\theta_{Te} = \frac{1}{4}$,

$E^{form} = -2.56 - \mu_{Te}$ for $\theta_{Te} = \frac{1}{2}$, $E^{form} = -1.86 - \mu_{Te}$ for $\theta_{Te} = \frac{3}{4}$ and $E^{form} = -1.49 - \mu_{Te}$ for a Te fully coverage ($\theta_{Te} = 1$). Also here we have the same formation energy for 1×2 or 2×2 systems. As found for GaAs, the three geometries with $\theta_{Te} = \frac{1}{2}$ present the more stable structure with a 1×2 reconstruction. In Fig. 1, we can observe that the stability decrease as the tellurium concentration increase at the coverage, and the adsorption on InAs(001) (Fig. 1b) is more stable than on GaAs(001) (Fig. 1a).

We verified that As-Ga (or As-In) bonds for the uppermost As atoms are $s^2 p^2$-like (nearly planar) while the Te-Ga (or Te-In) at the surfaces are sp^3-like for every coverage and reconstruction. The surface band structure presents a semi-metalic character for every coverages with $\theta_{Te} \neq \frac{1}{2}$, at the GaAs(001) or InAs(001). For the $\theta_{Te} = \frac{1}{2}$ concentration we verified a 1×2 reconstruction, with the hetero dimers modifying the structure to a semiconductor character.

In Fig. 2 we present the electronic band structure of the 1×2 semiconductor surface: (a)GaAs(001):Te and (b)InAs(001):Te. These systems have five surface states at the hetero dimers. The surface states charge densities are plotted in Fig. 3 for GaAs that have the same behavior for InAs. The first unoccupied state C1 (Fig. 2 and 3-a) is about 0.6 eV below the conduction band along the $\bar{K} - \bar{J}' - \bar{} , \bar{} - \bar{K}$ directions for GaAs and 0.8eV for InAs. This state are σ^* like. The V1 and V2 surface states (Fig. 2 and 3-b, 3-c) are antibonding π^* - combinations of p_z orbitals localized at As and Te surface atoms. The V2 state is well localized around the $\bar{K}$ point and 0.44 eV above the valence band for GaAs and 0.4 eV for InAs. For GaAs(001):Te, V1 has a dispersion of 0.82 eV along $\bar{J} - \bar{K} - \bar{J}' - \bar{} , \bar{}$, while InAs(001):Te has a dispersion of 0.71 eV at the same directions. The surface state V3 (Fig. 2 and 3-d) corresponds to the interaction between the second layer, the surface, and the third layer atoms. At the internal gap, we verify the surface state V4 with s-state combinations localized at the As surface atoms. Finally, the V5 state at the botton of the valence band are σ - like, with combinations of Te and As s-orbitals at the surface. This V5 state is well localized around the $\bar{K}$ point at the surface Brillouin zone for GaAs and spread along $\bar{J} - \bar{K} - \bar{J}'$ for InAs with a maximum dispersion of 0.6eV.

IV   Conclusion

We observed that the adsorption stability decreases as the tellurium coverage increases. The formation energies indicate that the tellurium adsorption on InAs(001) is more stable than on GaAs(001). The uppermost As atoms have s^2p^2-like bonds while the Te at the surfaces have sp^3-like bonds. The surface states at the fundamental gap are antibonding π^*-combinations of p_z or-

bitals localized at the surface atoms (Te or As) and π-bonding combinations of As-As, Te-Te dimers and As-Te hetero-dimers. The GaAs(001):Te and InAs(001):Te surfaces with $\theta_{Te} = \frac{1}{2}$ exibit a σ-type surface state below the valence band localized at the As-Te hetero-dimer. The hetero-dimers in $\theta_{Te} = \frac{1}{2}$ modify the character of GaAs(001):Te and InAs(001):Te surfaces resulting in a semiconductor structure.
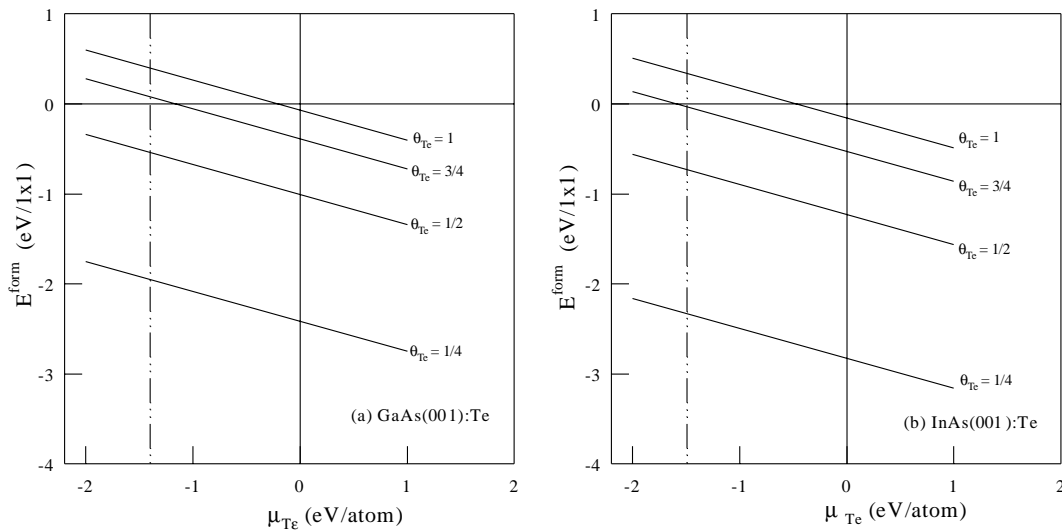

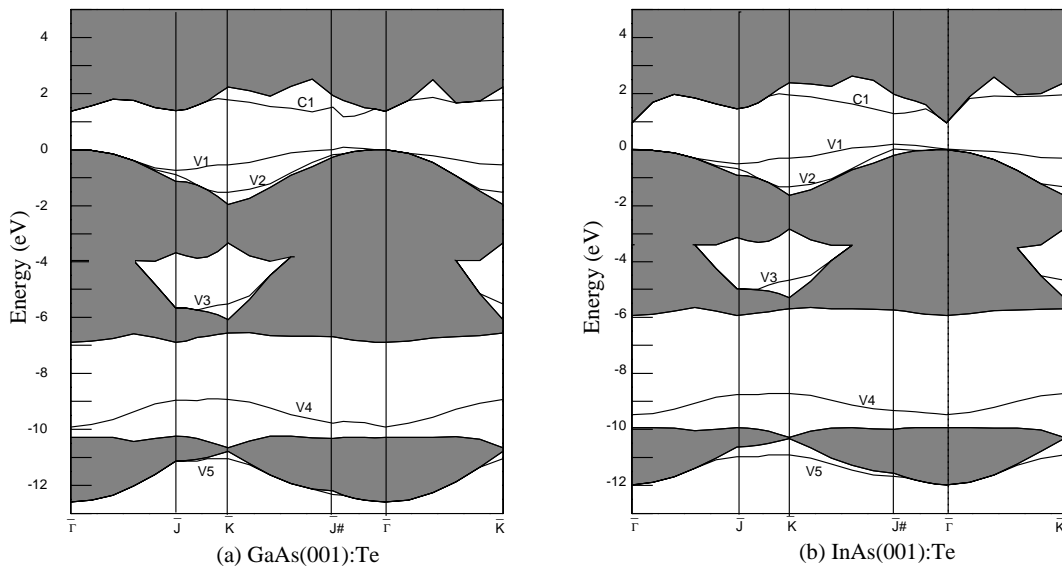Figure 1. Formation energies for (a) GaAs(001):Te; and (b) InAs(001):Te.

Figure 2. Electronic band structure for (a) GaAs(001):Te-(1×2); and (b) InAs(001):Te-(1×2) with $\theta_{Te} = \frac{1}{2}$.
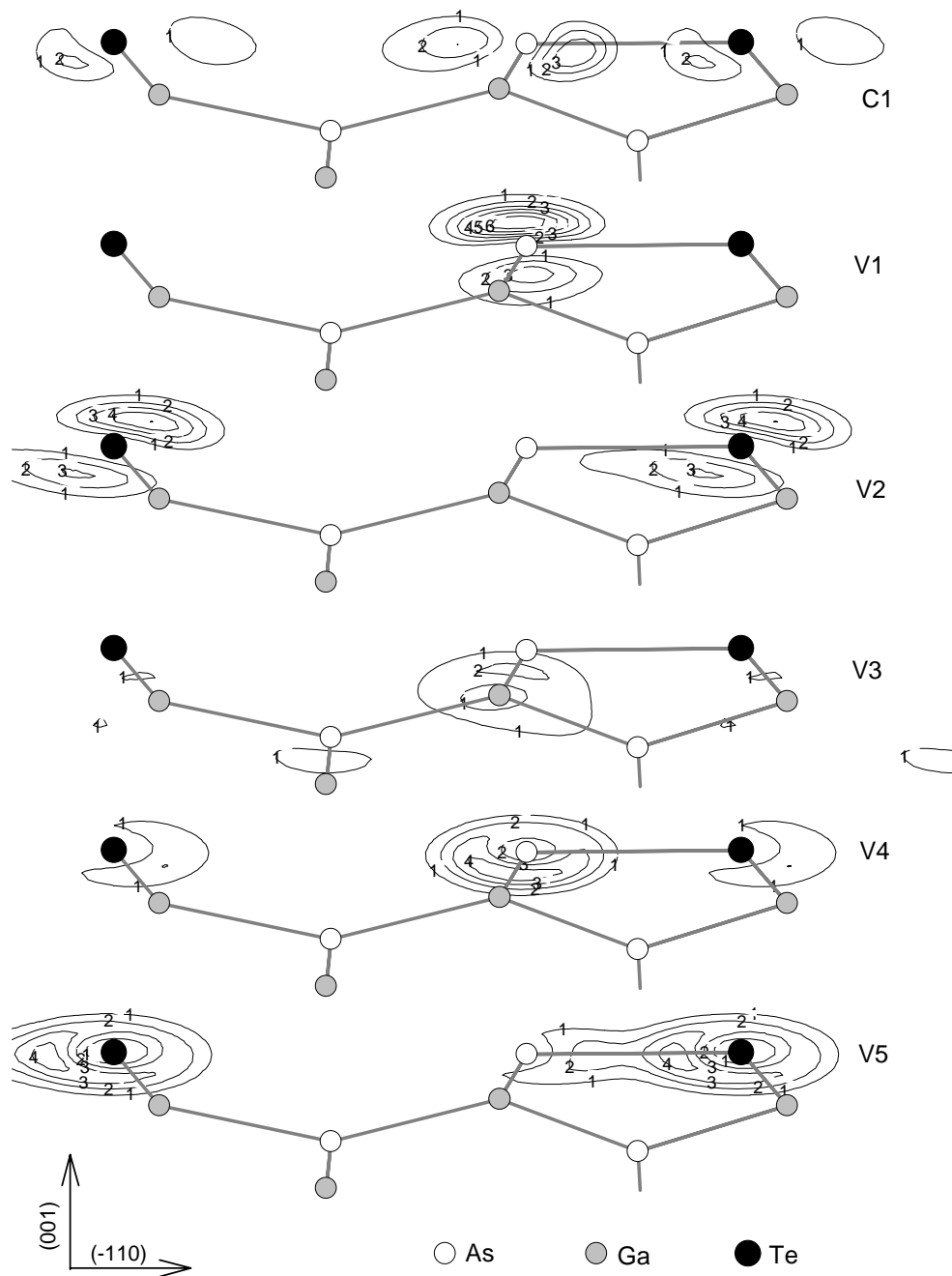
Figure 3. Energy-resolved charge density contour plots for the GaAs(001):Te-(1×2) with $\theta_{Te} = \frac{1}{2}$.

Acknowledgments

References

[1] N. Grandjean, J. Massies and V. H. Etgens, Phys. Rev. Lett. **64**, 799 (1992).

[2] N. Grandjean and J. Massies, Phys. Rev. B **53**, 13231 (1996).

[3] W. N. Rodrigues, V. H. Etgens, M. Sauvage-Simkin, G. Rossi, F. Sirotti, R. Pinchaux and F. Rochet, Sol.

State. Comm. **95**, 873 (1995).

[4] R. H. Miwa, A. C. Ferraz, W. N. Rodrigues and H. Chacham, Surf. Sci. **415**, 20 (1998).

[5] A. C. Ferraz and R. Claudino da Silva, Surf. Sci. **352-354**, 379 (1996).

[6] R. Claudino da Silva and A. C. Ferraz, Braz. J. Phys. **27/A**, 234 (1997).

[7] D. K. Biegelsen, R. D. Bringans, J. E. Northrup and L. E. Swartz, Phys. Rev. B **41**, 5701 (1990).

[8] J. Neugebauer and M. Scheffler, Phys. Rev. B**46**, 16067 (1992).

[9] X. Gonze, R. Stumpf and M. Scheffler, Phys. Rev. B **44**, 8503 (1991).

[10] P. M. Ceperlay and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[11] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[12] R. Carr and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[13] A. Kley and J. Neugbauer, Phys. Rev. B **50**, 8616 (1994).