

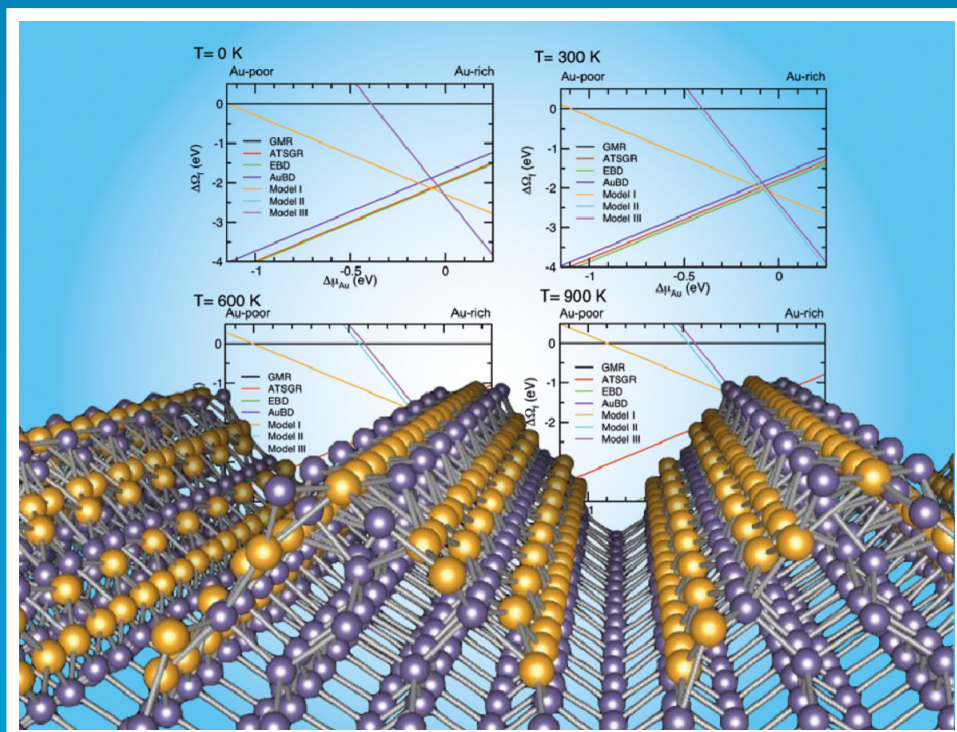
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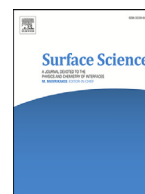


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Temperature stabilizes rough Au/Ge(001) surface reconstructions



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ABSTRACT

The temperature-dependent energetics of self-assembled Au nanowires on Ge(001) surfaces is studied with the help of density-functional theory (DFT) calculations: By calculating the surface phonon modes within harmonic approximation the surface vibrational free energy is obtained to complement the zero-temperature DFT total energies. We consider several previously suggested structural models for a Au coverage between 0.75 and 1.75 monolayer and investigate a temperature range between 0 and 900 K. The stability of the investigated surface models is found to depend clearly on temperature. We find that the extended Ge bridge dimer model previously predicted to be most stable for a large range of preparation conditions is less prominent in the phase diagrams for finite temperatures. On the other hand, a model derived previously from the giant missing row structure with a higher Au coverage gets stabilized by temperature. These findings explain, at least partially, the discrepancies between experimental data and previous theoretical investigations neglecting temperature effects.

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Self-assembled metallic nanowires on semiconductor surfaces are popular model systems to explore the peculiarities of low-dimensional physics [1–7]. The Au-induced nanowires on Ge(001) surfaces have attracted particular attention as they have been proposed to host a Tomonaga-Luttinger liquid [3]. Therefore, the precise electronic properties of Au/Ge(001) are intensively studied. Some data are interpreted in terms of an one-dimensional (1D) electronic structure [3,8–12] while other studies indicate that the electronic properties of Au/Ge(001) are not well described by a 1D system [13–17].

The controversy on the Au/Ge(001) electronic properties is fueled by the difficulty to clarify the exact Au coverage and the details of the atomic structure. The range of the gold coverage reported in experimental studies ranges from 0.25 [18], 0.50 [8] or 0.75 [12,16,19] to about one monolayers (ML) or even higher coverages [14,20,21]. Scanning tunneling microscopy (STM) studies [3,8,10,11,16,18,19,22–25] show that the Au-induced nanowires on Ge(001) are perfectly straight and have a regular width and an interwire spacing of about 1.6 nm. Numerous attempts were made to establish structural models for the Au/Ge(001) surface. They can be roughly classified into four categories [26,27]: (i) simple linear or zigzag gold chains on top or between Ge dimer rows of the clean Ge(001) surface [8], (ii) dimer-row models [23,26,28,29], (iii) bridged dimer-row models [26], and (iv) so-called giant missing row (GMR) models [18].

Some structure models (cf. Fig. 1) out of the large number of structural variants proposed for various Au coverages are particularly

relevant: STM simulations by Sauer et al. [26] for the giant missing row (GMR) model were able to explain some measured features [10,11,16,22]. Also, a recent spot-profile analysis low energy electron diffraction (SPA-LEED) study [21] supports the GMR model. However, the GMR surface formation energy is high. The Au-trimer stabilized Ge ridge (ATSGR) model derived from the GMR model is energetically more favorable, but its simulated STM images exhibit almost linear features and cannot explain the measurements.

Seino and Bechstedt [30,31] studied various modifications of the GMR model characterized by a higher Au coverage (Models I, II, and III in Fig. 1). These models partially account for the experimental STM data, in particular, for the VW patterns [10,11,16,22]. However, they are energetically stable only for an extremely narrow range of very Au-rich preparation conditions. In contrast, the extended Ge bridge dimer (EBD) model originally proposed by Sauer et al. [26] is energetically favored for a broad range of preparation conditions. It does not account, however, for the STM data. This holds as well for the Au bridge dimer (AuBD) model [26].

Summarizing so far, despite the many structural models that have been proposed over the years, none could be established that is both energetically favorable and consistent with the experimental data. This problem might be related to the neglect of temperature in the previous calculations [26,28–31]. Temperature effects are instrumental for the formation of the Au/Ge(001) nanowires [19,24,25] and show up as well in the measured properties. For example, the Au nanowires are formed upon deposition of Au on substrates held at 650 or 770 K [12,16] or

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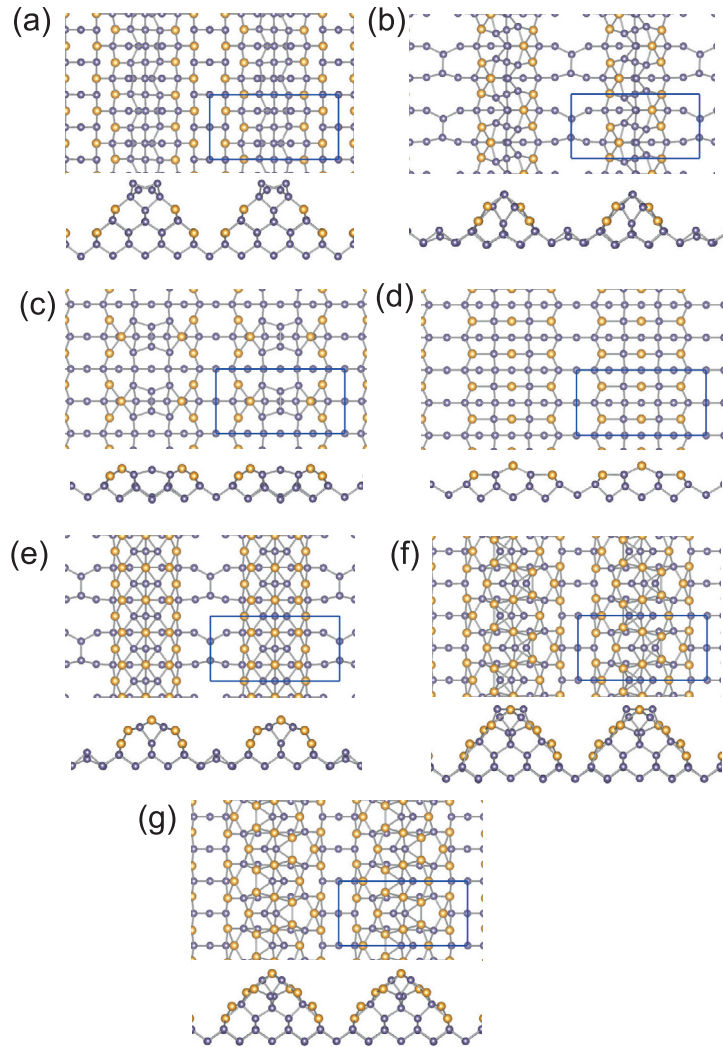


Fig. 1. Scheme of the most relevant Au/Ge(001) surface models: (a) GMR, (b) ATSGR, (c) EBD, (d) AuBD, and modified GMR models I (e), II (f) and III (g) (see text). Purple and gold balls indicate Ge and Au, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

result from annealing the samples at 650 K [17]. In the present work it is investigated to what extent the thermal phonon occupation modifies the Au/Ge(001) surface energetics and whether it helps to explain the discrepancies between experiment and previous theory.

The present density-functional (DFT) calculations are performed using the Vienna Ab-initio Simulation Package (VASP) code [32] within the generalized-gradient approximation (GGA) [33]. The electron-ion interaction is described by the projector-augmented wave (PAW) technique [34]. Thereby Ge 3d, 4s and 4p as well as Au 5d, 6s and 6p electrons are treated as valence electrons. The electronic wave functions are expanded into plane waves up to a cutoff energy of 400 eV. The Au/Ge(001) surfaces are modeled by periodically repeated slabs containing eight Ge layers, surface Au atoms and a vacuum region of 16–20 Å. The bottom layer of the slab is hydrogen saturated. Surface unit cells with $p(4 \times 2)$ surface translational symmetries are employed. All calculations are performed using the Ge equilibrium lattice constant of $a_0 = 5.78$ Å. An uniform $2 \times 4 \times 1$ Monkhorst-Pack grid was used for the Brillouin zone sampling. The hydrogen atoms as well the atoms of the bottom three Ge layers were frozen while all other atoms are relaxed until the Hellmann–Feynman forces are below 10 meV/Å.

In order to determine the temperature influence on the surface energetics we follow Refs. [35,36]. The thermodynamic grand canonical potential Ω in dependence on the chemical potentials μ_i of the surface constituents is used to compare energetically surface structures with dif-

ferent stoichiometry. It is given as

$$\Omega(T, V, \mu_i) = F(T, V) - \mu_{\text{Ge}} N_{\text{Ge}} - \mu_{\text{Au}} N_{\text{Au}}, \quad (1)$$

where T is the temperature, V is the substrate crystal volume and the free energy F can be written within adiabatic approximation as

$$F(V, T) = F_{\text{el}}(V, T) + F_{\text{vib}}(V, T). \quad (2)$$

The electronic entropy contributes far less to the surface energetics than the vibrational contributions [35]. We therefore approximate $F_{\text{el}}(V, T) = E_{\text{tot}} - TS_{\text{el}}$ by the zero-temperature DFT total energy E_{tot} . The harmonic approximation is used to determine the vibrational free energy

$$F_{\text{vib}}(T) = \frac{\Omega'}{8\pi^2} \int d^3k \sum_i \left(\frac{1}{2} \hbar \omega_i(\mathbf{k}) + k_{\text{B}} T \ln[1 - e^{-(\hbar \omega_i(\mathbf{k})/k_{\text{B}} T)}] \right), \quad (3)$$

where k_{B} is the Boltzmann constant, Ω' represents the volume of the supercell and $\omega(\mathbf{k})$ are the wave-vector dependent phonon frequencies. The latter are calculated using the frozen phonon approach [37]. Many vibrational states are folded onto the Brillouin zone center in case of a large surface unit cell as considered here. Therefore we restrict the Brillouin zone sampling in Eq. (3) to the Γ point, which leads to an error bar of few percent for the relative energy differences [35,36]. The temperature-dependent chemical potentials μ_{Ge} and μ_{Au} that correspond to the Gibbs free energy per particle are similarly obtained from

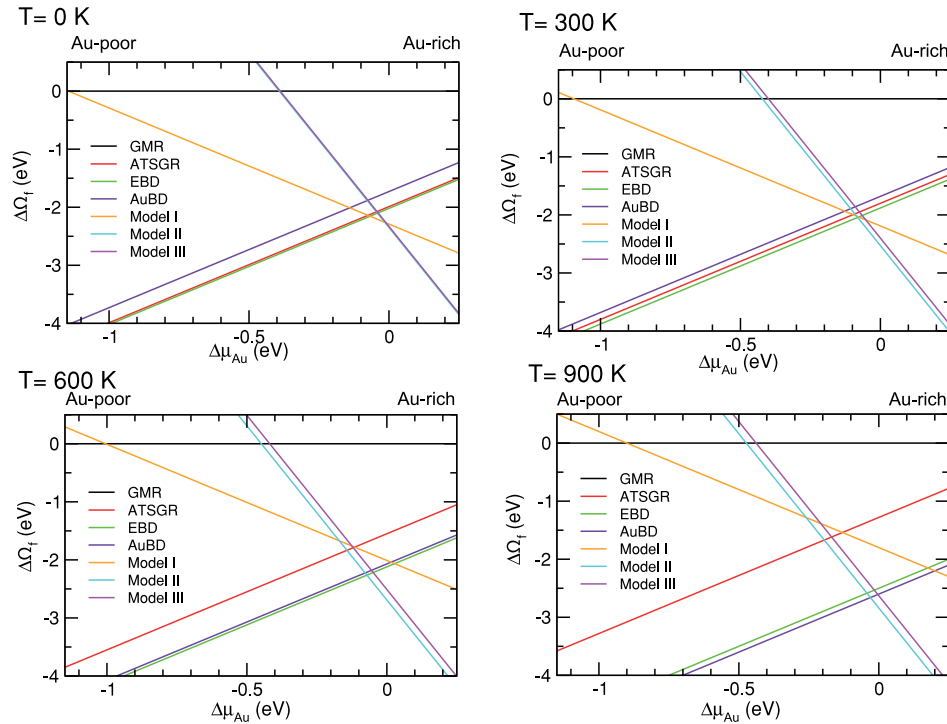


Fig. 2. Relative formation energies in eV/($p(4 \times 2)$ unit cell for Au/Ge(001) surface models in dependence on the Au chemical potential deviation from its bulk value, $\Delta\mu_{\text{Au}}$, calculated for 0, 300, 600, and 900 K.

Table 1

Au and Ge coverages Θ_{Au} and Θ_{Ge} in ML and calculated surface formation energies (in eV/($p(4 \times 2)$ unit cell, relative to the GMR model) of the structure models shown in Fig. 1 for various temperature between 0 and 900 K assuming that the Au chemical potential equals its bulk value, i.e., $\Delta\mu_{\text{Au}} = 0$. The value of $\Theta_{\text{Ge}} = 0$ is defined by the clean Ge(001) surface and the negative values of Θ_{Ge} indicate the reduction in Ge atoms in the surface.

	Θ_{Au}	Θ_{Ge}	0 K	300 K	600 K	900 K
GMR	1.00	1.50	0.00	0.00	0.00	0.00
ATSGR	0.75	2.00	-1.99	-1.80	-1.55	-1.28
EBD	0.75	-0.25	-2.02	-1.88	-2.12	-2.50
AuBD	0.75	-0.50	-1.73	-1.68	-2.07	-2.60
Model I	1.25	1.75	-2.29	-2.19	-2.01	-1.80
Model II	1.75	1.00	-2.35	-2.53	-2.69	-2.84
Model III	1.75	0.75	-2.33	-2.40	-2.51	-2.63

the zero-temperature DFT total energy corrected with the vibrational free energy in harmonic approximation.

Table 1 the relative formation energies for the Au/Ge(001) structure models shown in Fig. 1 are compiled. The giant Ge zigzag chain structure recently proposed by Tsay [28] is not included here, as we find it more than 3 eV less stable than the iso-stoichiometric Models I, II, and III. It can be seen in Table 1 that the relative surface energies change by up to 0.3 eV already at room temperature. This has clear implications for the stability of the various surface reconstructions as shown by the temperature-dependent phase diagrams in Fig. 2. In the phase diagram we vary the Au chemical potential in a relatively broad range from more than one eV below its bulk value to values in excess of the Au bulk chemical potential. The experimentally relevant range of the Au chemical potential can be expected to be substantially smaller: González et al. [38] estimate a reduction of the metal chemical potential with respect to the bulk value by 0.3–0.5 eV from the ratio of the effusion cell aperture to the sample area. This appears as a meaningful estimate also in the present case. The Ge chemical potential is assumed to equal its bulk value in the calculation of the phase diagrams.

The ATSGR and the EBD models are nearly degenerate at zero temperature and energetically favored for a broad range of preparation conditions. This degeneracy is lifted with rising temperature and, depending on its value, the EBD and AuBD models represent the surface ground state. Model I, stable for a small window of the Au chemical potential at 0 K, completely disappears from the range of stable models for finite temperatures. The Model II, on the other hand, nearly degenerate with Model III for 0 K, gets clearly stabilized by temperature. On the one hand, its energy is lowered with respect to Model III. On the other hand, its stability range extends towards less Au-rich preparation conditions on expense of the Model I and the EBD model.

The accuracy of the temperature-dependent surface formation energies calculated here is limited by physical approximations as well as numerical limitations. So it is known that the Au/Ge(001) surface energetics depends sensitively on the choice of the exchange-correlation functional [26] and an harmonic effects will certainly be important for temperature at or above room temperature. However, some error cancellation can be expected when comparing different models. The trend found here that relatively flat surface structures such as the EBD model are less favored at elevated temperature than comparatively rough surfaces such as represented by Model II corresponds to the expectation that structures with a large number of under-coordinated surface atoms are particularly susceptible to temperature-dependent changes of the vibrational free energy.

In summary, density-functional theory calculations that account for the vibrational free energy show that (i) the ground state geometry of the Au/Ge(001) surface depends sensitively on the temperature and (ii) that surface structures containing a large number of under-coordinated atoms – that in fact seem to be more compatibly with the available experimental data than flat surfaces – increase their stability range with rising temperature. These findings seem suitable to explain partially the difficulties of previous DFT calculations to account for the experimentally observed surface structures and may help to derive more realistic models.

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