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A Density Functional Theory based Thermodynamic model of Hydrogen Coverage on the W(110) Surface

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Abstract

Tungsten will be used as a plasma facing material in the next generation of fusion reactors. To aid in understanding atomic scale H-W interactions, we investigated hydrogen coverage on the tungsten (110) surface via periodic density-functional theory, providing the most stable configurations that hydrogen forms on the surface at coverage ratios of interval 0.25, step-wise, up to a full mono-layer of hydrogen. We then calculate the Gibbs free energy for the stable configurations in the presence of hydrogen gas at specified temperature and pressure. It follows that the configuration, and corresponding coverage ratio, which yields the lowest Gibbs free energy is used to estimate the macroscopic surface state. Our findings based on the model compare well to low energy electron diffraction (LEED) measurements, primarily the presence of well-ordered phases with coverage ratios 0.5, 0.75, and 1.0, respectively, and that no ordered phases are expected as temperature increases and surface depletion occurs.

1. Introduction

In our previous work, we showed via density functional theory (DFT) and comparison with low energy ion scattering (LIES) direct recoil spectroscopy (DRS) experiments that saturation of hydrogen on the W(110) surface is expected at a coverage of 1.0 [1]. Low energy electron diffraction (LEED) and Thermal Desorption Spectroscopy (TDS) experiments on single crystalline W(110) also find a saturation ratio of 1.0 under vacuum pressure and room temperature conditions[2–4]. Of course, with increasing temperature, due to entropic effects which favor the gas phase, the surface coverage will lower and eventually deplete. We herein estimate the expected coverage with specific temperature and pressure conditions by comparing the Gibbs free energy of a set of experimentally observed adsorption patterns corresponding to coverage ratios from the bare surface up to 1.0.

Due to the high melting point, high thermal conductivity, high sputtering threshold, and low tritium solubility of Tungsten (W), it has been chosen as the divertor material for the JET, WEST, and ITER tokamak fusions reactors[5–7]. Thus it is of high important to understand hydrogen-tungsten surface interactions at a fundamental level. Several experimental studies have been conducted on single crystalline samples of tungsten including TDS [8–10], LIES, DRS [11], LEED [3,4,12,13], and surface reflectance spectroscopy[14] measurements. Of these techniques, LEED and LIES/DRS are best able to probe atomic-scale phenomena on the surface.

Of note is the presence of well-ordered adsorption patterns seen in LEED measurements on the W(110) surface; more specifically, Gonchar et. al.[4], Estrup[3] and Altman et. al.[13] all observed diffraction patterns of $p(2\times 1)$, $p(2\times 2)$, which correspond precisely to coverages of 0.5, 0.75, respectively and vary in intensity depending upon the overall coverage. Upon further adsorption

of hydrogen up to the experimental saturation limit, the characteristic diffraction patterns disappear, suggesting a $p(1 \times 1)$ adsorption pattern at a mono-layer of coverage (with coverage ratio 1.0) that matches the symmetric pattern of the underlying surface. If the surface is prepared first at the saturated mono-layer coverage, and the temperature of the system is increased, intensity associated with the lower coverage symmetry patterns increases as a result of the desorption[4]. There is no sign of a unique ordered pattern corresponding to a coverage below 0.5 where the basic unit has a $p(2 \times 1)$ pattern[4].

While pure DFT models can provide an atomic-scale description on ideal single crystalline surfaces, they do not include temperature dependent effects. To better understand the changing state of the surface with ambient conditions, we constructed a free energy model that reflects the relative stability between the known symmetric patterns probed by LEED experiments in equilibrium with hydrogen gas at fixed temperature and pressure. The model provides a simple first estimate of the macroscopic surface coverage as a function of temperature and pressure based on a minimal atomic-scale picture using discrete coverages with fixed adsorption patterns.

2. Methodology

2.1 – Density functional theory calculations

To model hydrogen adsorbed to the W(110) surface we built a periodic DFT slab model consisting of 6 layers of tungsten and a 20 Å vacuum. A top-view schematic representation is provided in **figure 1**. The slab allows us to investigate surface coverage ratios of interval 0.25 ($\Theta_{W_{110}} = \frac{\# \text{ of adsorbed H}}{4}$). The surface model is able to represent $p(2 \times 1)$ $\Theta = 0.5$, $p(2 \times 2)$ $\Theta = 0.75$, and $p(1 \times 1)$ $\Theta = 1.0$ patterns predicted by LEED measurements[4,14].

We use the PBE functional[15] and Vanderbilt ultra-soft scalar-relativistic pseudo-potentials[16] for both tungsten and hydrogen atoms. The unit-cell is sampled with a grid of $11 \times 11 \times 1$ k-points.

More details on the DFT calculations can be found in our previous works[1,17,18]. In ref. 17 it is shown that with 6 layers of tungsten and a 20 Å vacuum the surface energy of W(110) is converged to 10 meV/Å². Vibrational properties of the adsorbed hydrogen atoms were calculated via Density Functional Perturbation Theory (DFT-PT)[19]. All DFT and DFT-PT calculations were carried out using Quantum Espresso[20].

Figure 1. Top-view schematic representations of the W(110) surface-slab used in this work. Light grey circles represent tungsten surface atoms, white circles represent the layer beneath.

2.2 - Gibbs energy calculations

We consider a system of $\frac{n_{tot}}{2}$ hydrogen molecules in the gas phase in contact with a W(110) surface, where n_{tot} can be an arbitrarily number, subject to the constraint that it must be greater than the saturation limit of adsorbed hydrogen atoms in the DFT working cell (taken as $n_{tot} = 6$ in the present work). For a given adsorption state there are $\frac{n_{tot}-n_{ads}}{2}$ hydrogen molecules remaining in the gas phase and n_{ads} atomic hydrogen particles adsorbed to the surface. The Gibbs free energy $G(T, p)$ of the system i.e. $\frac{(n_{tot}-n_{ads})}{2}H_2 + W_{110}H_{n_{ads}}$ is given in **equation 1**:

$$G(T, p) = g_{W_{110}H_{n_{ads.}}}(T) + \frac{(n_{tot} - n_{ads.})}{2} g_{H_2}(T, p) \quad (1)$$

where $g_{W_{110}H_{n_{ads.}}}$ is the contribution to the Gibbs energy of the adsorbed hydrogen and the surface, g_{H_2} is the per-particle Gibbs energy of a hydrogen molecule (i.e. the chemical potential of an H_2 as a function of P and T). g_{H_2} is calculated with **equation 2** via substitution of **equations 3** and **4**:

$$g_{H_2}(T, P) = h_{H_2}(T) - T \cdot s_{H_2}(T, P) \quad (2)$$

$$h_{H_2}(T) = e_{H_2}^{DFT} + e_{H_2}^{vib}(T) + e_{H_2}^{rot}(T) + e_{H_2}^{trans}(T) + k_B T \quad (3)$$

$$s_{H_2}(T, P) = s_{H_2}^{vib}(T) + s_{H_2}^{rot}(T) + s_{H_2}^{trans}(T, p) \quad (4)$$

The per unit-cell Gibbs energy of an adsorbed state, $g_{W_{110}H_{n_{ads.}}}$, is calculates as:

$$g_{W_{110}H_{n_{ads}}}(T) = \left(e_{W_{110}H_{n_{ads}}}^{DFT} + e_{W_{110}H_{n_{ads}}}^{vib}(T) \right) - T \cdot s_{W_{110}H_{n_{ads}}}^{vib}(T) \quad (5)$$

Mathematical details for the individual vibrational, rotational, and translational terms in the above expressions can be found in elsewhere [21].

The reference in energy E_{ref} was taken as the sum of the electronic energy of the bare W(110) surface $e_{W_{110}}^{DFT}$ plus the zero-point energy corrected value $e_{H_2}^{DFT}$ of the $\frac{n_{tot}}{2}$ molecules of hydrogen. By subtracting E_{ref} from $G(T, p)$, we obtain a Gibbs free energy of reaction $\Delta G(T, p)$ according to:

$$\Delta G(T, p) = G(T, p) - (e_{W_{110}}^{DFT} + \frac{n_{tot}}{2} e_{H_2}^{DFT}) \quad (6)$$

The state yielding the minimal Gibbs free energy of reaction $\Delta G(T, p)$ for a system in equilibrium under constant temperature and pressure with a fixed total number of particles corresponds to the most stable state, thus comparing $\Delta G(T, p)$ for each configuration in a set of well-chosen states provides a means to estimate the macroscopic coverage for the system.

3. Results

3.1 – DFT results

3.1a – stable adsorption patterns

Experimental [3,4,13,14] and theoretical evidence[1] suggests that at room temperature, and low pressure conditions, the W(110) surface saturates at a mono-layer of hydrogen, corresponding to a coverage ratio of $\Theta = 1.0$. In all published DFT works, the so-called “three-fold” (TF) site is found to be the most stable[1,22] for a single hydrogen adsorbing on the surface. LEED studies suggest that from below 30 K to beyond 400 K various well-ordered patterns emerge[3,4,13,14]. Accordingly, we found the most-stable TF adsorption patterns accessible in our unit-cell for each coverage ratio up to $\Theta = 1.0$, shown schematically in **Table 1** along with the corresponding per-hydrogen adsorption energy calculated according to:

$$E_{ads,\Theta} = \left(e_{W_{110}H_{n_{ads}}}^{DFT} - e_{W_{110}}^{DFT} - \frac{n_{ads}}{2} e_{H_2}^{DFT} \right) / n_{ads} \quad (7)$$

For a more detailed analysis of the stationary configurations that hydrogen can form up to and beyond $\Theta = 1.0$, the interested reader is referred to our previous work[1].

Table 1 Top-view schematics representations of the most-stable TF configurations at intervals of 0.25 up to one mono-layer. Light grey circles represent tungsten surface atoms, white circles represent the layer beneath. Adsorbed hydrogens are represented in dark grey. Each configuration is a unit repeated periodically in space. Per-particle hydrogen adsorption energies are provided (E_{ads}) in units of eV.

top-down schematic
Θ	0.25	0.5	0.75	1.0
Symm.	$p(2 \times 2)$	$p(2 \times 1)$	$p(2 \times 2)$	$p(1 \times 1)$
$E_{ads,\Theta}$ (eV)	-0.684	-0.692	-0.678	-0.656

3.1b –energy trends

Figures 2a and **2b** present the trend in surface energy and adsorption energy (per adsorbed hydrogen atom) vs. increasing coverage. The surface energy is calculated as:

$$SE_{\Theta} = \frac{1}{2A} \left(e_{W_{110}H_{n_{ads}}}^{DFT} - n_W e_{W_{bulk}} - \frac{n_{ads}}{2} e_{H_2}^{DFT} \right) \quad (8)$$

Where A is the surface area of our slab model ($30.47 \text{ \AA}^2$), n_W is the total number of tungsten in the slab (in our case $n_W = 24$), and $e_{W_{bulk}}$ is the energy per tungsten atom in the bulk as calculated by DFT. All other symbols were previously defined.

The steady decrease of surface energy with increasing coverage means that the overall system becomes more and more stable upon continued adsorption of hydrogen up to $\Theta = 1.0$ at 0 K. The adsorption energy per hydrogen drops from $\Theta = 0.25$ to $\Theta = 0.5$, where the minimum is found, then increases up to $\Theta = 1.0$.

In the LEED measurements of Gonchar *et al.*, after annealing at $T=120\text{-}200$ K and cooling to $T = 5$ K locally ordered patterns consistent with the $p(2 \times 1)$ structure are seen on W(110) at coverages as low as $\Theta \approx 0.3$ [4]. This is consistent with the $E_{ads,\Theta}$ minimum when $\Theta = 0.5$. Since the $\Theta = 0.5$ $p(2 \times 1)$ pattern is the most stable-configuration on a per-hydrogen basis, when molecular adsorption takes place on a bare surface, an adsorbed H_2 molecule would most favorably form the $p(2 \times 1)$ pattern locally as opposed to a more dispersed pattern such as the $\Theta = 0.25$ $p(2 \times 2)$ pattern, even when $\Theta < 0.5$.

Considering coverage $\Theta \geq 0.75$, the local electronic potential near a TF site is effectively different than that of a less-saturated surface as is seen by the increase in $E_{ads,\Theta}$ corresponding to a loss in stability per hydrogen atom at 0 K. The same trend continues at $\Theta = 1.0$ where there is a full mono-layer of hydrogen and the saturation coverage has been reached according to single crystalline LEED[3,4], LIES [1], and TDS experiments[2].

Figure 2. Energy trends of hydrogen adsorbed on the W(110) surface. **(a)** the surface energy (SE_{θ}) for the most-stable adsorption patterns by coverage. **(b)** The adsorption energy per hydrogen atom ($E_{ads,\theta}$) for the W(110) surface by coverage given in eV per adsorbed hydrogen.

3.2– Thermodynamic results

By fixing the total number of hydrogen atoms in the system n_{tot} and calculating $\Delta G(T, p)$ for each adsorption configuration according to **equation 6**, we can arrive at an estimate of the experimental surface state. Since the Gibbs free energy of the system is minimal at equilibrium under constant temperature and pressure with a fixed total number of particles, the corresponding adsorption configuration ($\theta = 0.0$, $\theta = 0.25$ $p(2 \times 2)$, $\theta = 0.5$ $p(2 \times 1)$, $\theta = 0.75$ $p(2 \times 2)$, or $\theta = 1.0$ $p(1 \times 1)$) with the lowest $\Delta G(T, p)$ serves as an estimate of the macroscopic adsorption state.

Figure 3a provides a set of plots of $\Delta G(T, p)$ vs. θ at different temperatures, all with $P = 5.5 \times 10^{-5}$ Pa. This pressure was chosen since it is within the range of surface analysis experiments[3,11]. Focusing on the minimum value of $\Delta G(T, p)$ with respect to the various isotherms shown in **Figure 3a**, we can see how the model yields the expected coverages plotted in **Figure 3b**. Mono-layer coverage $\theta = 1.0$ $p(1 \times 1)$ is predicted as more stable than the $\theta = 0.75$ $p(2 \times 2)$ configuration up to around 400 K (light grey with triangle markers). The surface coverage then drops somewhat quickly with respect to temperature; at 450 K (black with diamond markers)

$\Theta = 0.5$ $p(2 \times 1)$ is most stable relative to the other adsorption patterns. By 500 K the bare surface $\Theta = 0.0$ is expected.

3.2a – Comparison with LEED measurements

In the LEED measurements of Gonchar et. al. [4], the relative intensity of two electron diffraction peaks, corresponding to the $\Theta = 0.75$ $p(2 \times 2)$ and $\Theta = 0.5$ $p(2 \times 1)$ patterns, were measured with increasing temperature after a complete mono-layer ($\Theta = 1.0$ $p(1 \times 1)$) was first adsorbed to the surface at 77 K. The present model predicts the $\Theta = 0.75$ $p(2 \times 2)$ as the most stable adsorption pattern near 400 K and $P = 5.5 \times 10^{-5}$ Pa (**Figure 3b**); this agrees well with Gonchar et. al.'s measurements where the LEED peak corresponding to the $p(2 \times 2)$ pattern has its maximum intensity near 400 K. The LEED peak in Gonchar et. al. corresponding to the $p(2 \times 1)$ $\Theta = 0.5$ pattern has maximum intensity around 450 K, again in close agreement with the prediction of our model where near 450 K the $p(2 \times 1)$ $\Theta = 0.5$ pattern is most stable.

Interestingly, $\Theta = 0.25$ $p(2 \times 2)$ is never predicted as a stable phase in the Gibbs model, nor does a LEED pattern consistent with $\Theta = 0.25$ $p(2 \times 2)$ show up in Gonchar's measurements. Since there is no temperature having a $p(2 \times 2)$ $\Theta = 0.25$ phase with minimum $\Delta G(T, p)$ (**Figure 3b**); we can hypothesize that the system should deplete to bare coverage primarily via H_2 recombination of nearest neighboring adsorbed hydrogen atoms in the $p(2 \times 1)$ $\Theta = 0.5$, leaving behind localized patches of $p(2 \times 1)$ pattern at $\Theta < 0.5$. Again, this is consistent with the finding of local $p(2 \times 1)$ order in LEED measurements even below coverage 0.5 after annealing [4], however the present method is not directly capable to model such adsorption patterns.

In Gonchar's measurements, by 500 K, the intensity of the diffraction peaks corresponding to both the $\Theta = 0.75$ $p(2 \times 2)$ and $\Theta = 0.5$ $p(2 \times 1)$ patterns are reduced to zero, suggesting that the surface is either fully or nearly depleted of hydrogen. This is in strong agreements with our model, where

the surface is predicted to be bare at 500 K unless the background pressure of molecular hydrogen is on the order of $\sim 10^{-3}$ Pa or greater.

Figure 3. Temperature dependent coverage on the W(110) surface at $P = 5.5 \times 10^{-5}$ Pa. **(a)** Gibbs free energy of reaction (eq. 6) for each Θ at various temperatures. Connecting lines between different values of Θ at the same temperature are to aid the eye and do not represent calculated values. **(b)** Predicted coverage (Θ) vs. temperature.

4. Conclusions and Perspectives

Herein, we calculated the most stable three-fold (TF) adsorption patterns of hydrogen on the W(110) via DFT at coverages $\Theta = 0.25, 0.5, 0.75, \& 1.0$. The ordered TF patterns at $\Theta = 0.5, 0.75, \& 1.0$ correspond directly to the $p(2 \times 1)$, $p(2 \times 2)$, and $p(1 \times 1)$ patterns measured in low-energy electron diffraction (LEED) experiments from the literature; at $\Theta = 0.25$, ordered TF adsorption corresponds to a $p(2 \times 2)$ pattern not seen directly in LEED measurements. A temperature and pressure dependent free energy model was built to investigate the relative stability of the ordered patterns under experimental conditions. Our model successfully estimates characteristics of the coverage state seen in LEED experiments as a function of the temperature under vacuum pressure, particularly the onset of hydrogen depletion around 375 K, complete depletion (a bare surface) near 500 K, and that no ordered $\Theta = 0.25$ $p(2 \times 2)$ pattern is predicted at any temperature.

While the current model captures the aforementioned experimental features, it estimates the coverage at discrete intervals associated with the ideal adsorption patterns experimentally measured on clean W(110) surfaces; however, intermediate coverage ratios are indeed seen experimentally rather than discrete phase changes. The intermediate coverage patterns are expected to be composed primarily of patch-like combinations of the $p(2 \times 2)$ $\Theta = 0.75$ and $p(2 \times 1)$ $\Theta = 0.5$ patterns. In an upcoming study we construct and analyze a model that describes the surface state via a full partition function which includes the effect of higher energy adsorption configurations and allows for intermediate coverage ratios.

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