Role of angular orientation of dipoles on work function during Caesium deposition on a metal surface - a Phenomenological Model

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Motivation

• Simple classical model based on point dipole model explains the experimental curve up to 0.5 coverage.
• QM Density Functional Theory able to explain complete experimental curve.
• Can improved classical model explain the whole curve?
• Angular rotation of point dipoles during higher coverage may have the answer.

[Taylor & Langmuir (1930) Experimental Data]
Adsorption

- **Physisorption:**
  - Heat of adsorption is low as weak Vander Wall’s forces of attraction are involved.
  - **Multilayer adsorption.**
  - Weakly bounded

- **Chemisorption:**
  - High heat of adsorption as chemical bonds are formed.
  - **Monolayer adsorption.**
  - Stronger bond.
Work Function Change during Caseation

- Cs atom is approximately **twice as big as tungsten atom**.
- Cs deposition on tungsten is a **strong chemisorption process**.
- Cs adatoms forms an **electric double layer** (charge) with net positive charge outward.
- Cs adsorption on tungsten is an exothermic process.
- Cs adsorption **affects both work function** and **heat of adsorption** of bare substrate.

Surface dipoles (electric double layer) that lowers the work function

[Sharon Chou poster (2012)]

Possible distortion of electron cloud of Cs atom [M. Prutton, Introduction to Surface physics.]

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Classical point dipole model

\[ \Delta \phi = 4\pi e\sigma_1 \theta \frac{M_0}{[1 + k]} \]

Where,

• **\( \Delta \phi \)** is the change in substrate work function
• **\( \sigma_1 \)** is the number of adatoms per unit area in one complete monolayer
• **\( \Theta \)** is the fractional monolayer coverage
• **\( M_0 \)** is the initial dipole moment
• **\( k = \frac{9\alpha \theta}{a_1^3} \)**, \( \alpha \) denotes the effective polarizability and \( a_1 \) is the distance between the dipoles at \( \Theta = 1 \)

The existing classical point dipole model is based on 2-D square lattice of parallel point dipoles with axis perpendicular to the line joining them. [A. R. Miller, Proc. Cambridge philos. Soc. 42, 292 (1946)]

• The Classical point dipole model deviates at high coverage for Cs/W. Why?
Density Functional Theory Approach

\[ \phi = \phi_{\text{Vacuum}} - E_{\text{Fermi}} \]

- DFT solves the Kohn-Sham approximation of TISE.
- DFT works in terms of electron density \( n(r) \).
- Ground state energy \( E(n(r)) \) is a functional of electron density.
- Can calculate work function from \( n(r) \) and matches experimental curve.

Model for Cs over layer on W[110]

- Wood’s notation:

  - Low coverage
    \[ \theta = 0.25 \]
  - Medium coverage
    \[ \theta = 0.5 \]
  - High coverage
    \[ \theta = 1 \]

\[ p(2 \times 2) \quad c(2 \times 2) \quad \text{2-D square array} \]
Role of angular orientation of dipoles: a phenomenological model

\[ \Delta \phi = 4\pi e \sigma_1 \theta \frac{M_0}{1 + k} \cos(\beta) \]

• Where, \( \cos(\beta) \) is the effective Angular Orientation Factor (AOF).

\[ \beta = c(\theta - \theta_0); \quad 0 \leq \theta \leq 1 \]

• At low coverage of adatoms, surface dipoles are non-interacting owing to which they tend to form an array of mutually parallel dipoles and perpendicular to the line joining them.

• However, at high coverage in addition to the point depolarization we propose that the self-interaction of dipoles may lead to change in the orientation of the dipoles with respect to surface normal.

• The nature of orientation follows a fitting equation which is function of coverage fraction \( \theta \) and needs deeper investigation to understand the relationship.
Dependence of work function on dipole orientation

\[ \cos \beta = 1.3 (\theta - 0.3) \]
Summary

• **Phenomenological model** is an extension of existing electric dipole based classical model, which able to explain full work function variation experimental curve as a function of Cs monolayer coverage.

• With increasing monolayer fraction coverage, **repulsive interaction between dipoles** increases, which lead to the orientation factor in the Phenomenological model.

• A fitting equation as a function of Cs monolayer coverage is identified.

• **Further investigation is needed to verify our conjecture and to connect with the physical picture of electronic structures of Cs and W within the electric dipole layer between interacting dipoles.**
Thank You!