Adsorption Parameters of Cu and Ni on the \{110\} Plane of W and Mo

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Abstract. This paper reports on the embedded-atom method (EAM, developed by Johnson) calculations of adsorption parameters for Cu and Ni on unrelaxed \{110\} substrates of Mo and W. The following are calculated: (i) the equilibrium height \(h_e\) of an adatom; (ii) the optimum coefficients \(W_0A_{hk}\) of a truncated Fourier representation of the adatom-substrate interaction potential; (iii) the desorption energies \(E_{des}\); and (iv) the activation energies \(Q\) of surface migration. It is shown that (a) the calculated values of \(E_{des}\) agree satisfactorily with available empirical data; (b) the scale factor \(W_0\) is approximately proportional to the bonding as measured by \(E_{des}\), whereas the normalized coefficients \(A_{hk}\) are determined by the \{110\} substrate symmetry; (c) \(E_{des}\) and \(Q\) are respectively dominated by the embedding energy and pair potential of the EAM; and (d) \(W_0\) and \(E_{des}\) for an atom in a monolayer are only about half as much as the corresponding quantities for an isolated atom.

1. Introduction

Competing interactions play a determinative role in commensurate-incommensurate phase transitions in adsorbed layers. This has been appreciated ever since the Frenkel-Kontorova [1] model had been used by Frank and van der Merwe [2] to derive stability criteria for epitaxial monolayers in their transition from configurations of perfect registry (pseudomorphism) to incommensurate configurations with misfit dislocations at their interfaces. The two competing interactions are: (a) the intralayer atomic interaction that favors the crystalline structure of the overlayer and has been modeled by the harmonic approximation with structural and elastic properties of a bulk truncation; and (b) the interlayer (monolayer atom-substrate) interaction that has been modeled by a periodic potential with the periodicity of the substrate and approximated by a Fourier truncation. Frank and van der Merwe [2] already realized that realistic quantitative predictions require data on monolayer equilibrium structure, elastic properties, and substrate Fourier coefficients. They used 6–12 Lennard-Jones pair potentials in their calculations and derived surprisingly useful results. It has since been established that pair potentials are rather inadequate in describing metallic interaction and that embedded-atom methods (EAMs) [3, 4] are greatly superior for this purpose. Whereas more fundamental approaches produce more accurate results they are computationally very demanding. The application of EAMs are only slightly more complicated than pair potentials and have been proven to yield fairly accurate adsorption results [5, 6]. EAMs have indeed also been used to calculate structural and elastic properties of unsupported thin films [7, 8].

It has been observed that epitaxial systems with large negative misfit such as Ni on Mo \{110\} [9] and W \{110\} [10] show a tendency to initially
form pseudomorphic (ps) monolayer (ML) islands which undergo a ps-to-cp (closed-packed) transition when excess atoms are deposited on top of them. A first-order phase transition in a Cu double layer on a Mo \{110\} surface [11] in which the orientation of the interfacial misfit dislocations changes by 90° has also been reported. These observations, as well as the wealth of information generated by these studies, focused attention on these systems. The success already achieved by applying EAM models in the calculation of surface properties and the availability of fitting parameters for the relevant materials motivated a study of the adsorption parameters of these systems. These parameters are essential for the understanding of the above-mentioned and analogous phenomena at adsorbate substrate interfaces.

The main objective of the present investigation is to calculate optimized coefficients for a Fourier truncation of the adatom-substrate interaction for both isolated adatoms and atoms forming part of monolayers of Cu and Ni on Mo\{110\} and W\{110\}. Other important adsorption parameters that obtain as by-products of the calculation are desorption energies \(E_{des}\), activation energies of surface migration \(Q\), and atomic vibration frequencies \(\nu\). The calculation of \(E_{des}\) and \(Q\) is important as they have been measured and accordingly allow an assessment of the reliability of the EAM calculations. All these quantities are of paramount importance in understanding interface phenomena: \(E_{des}\), \(Q\), and \(\nu\) contribute to the understanding of adsorption at crystal-vacuum and crystal-vapor interfaces, whereas \(E_{des}\) and the coefficients of the truncated Fourier representation of the adatom-substrate interaction, govern the behavior of crystal-crystal interfaces. The decisive role of \(E_{des}\), \(Q\) and \(\nu\) in crystal growth at liquid- or gas-solid interfaces is well known. \(E_{des}\) and the relevant Fourier coefficients dominate the initial stages of epitaxial growth. Apart from its fundamental significance for crystal-crystal interaction, epitaxy is a most important process in the fabrication of electronic and optoelectronic devices. Whereas the individual epitaxial orientations are determined by the matching of interfacial atomic arrangements, as expressed in the row matching rule [12], the realization of a given orientation at the epilayer-substrate interface, when there is competition between two possible orientations, is determined by the magnitudes of the relevant Fourier coefficients. In the criteria for the accommodation of misfit [12] between the interfacial atomic arrangements by homogenous (misfit) strain and misfit dislocations the values of the Fourier coefficients are some of the key parameters. For a monolayer (ML) there is a critical misfit, depending on these coefficients, below which the ML is stable when the misfit is accommodated by misfit strain; the ML atoms are in registry with the substrate potential minima. The surface free energy of a growing ML, which may be expressed in terms of the ML "desorption" (adhesion) energy, together with the free energies of the substrate surface and the interface, determine the equilibrium growth mode [13]. Misfit accommodation and growth modes are key issues in the fabrication of electronic devices.

2. Model

2.1. Atomic interaction

The EAM models for bcc [14] and fcc [15] metals developed by Johnson et al. were used to describe the interaction between atoms. The basic equations of the embedded-atom method are

\[
E_t = \sum_{\text{bonds}} \phi(r_{ij}) + \sum_{\text{atoms}} F(\rho_a); \tag{1}
\]

\[
\rho_i = \sum_j f(r_{ij}), \tag{2}
\]

where \(E_t\) is the total internal energy of a system of \(N\) atoms. Here \(\rho_i\) can be interpreted as the electron density at atom \(i\) due to all other atoms independent of their type, and \(f(r_{ij})\) as the electron density at atom \(i\) due to the presence of atom \(j\). \(F(\rho_a)\), the energy to embed atom \(a\) in the electron density \(\rho_a\), is attractive, whereas \(\phi(\rho_b)\) is a two-body potential between atoms separated by a bond length \(r_b\), and it may or may not be purely repulsive.

For monatomic lattice model calculations the functions \(f\), \(F\), and \(\phi\) must be specified for each atomic species. For an alloy model [16], a two-body potential must additionally be specified for each combination of atomic species. For calculations involving atoms of two different kinds, e.g., \(a\)-and \(s\)-type, \(\phi^{as}\) and \(\phi^{aa}\) are given by the