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Atomistic modeling of Ag deposition on the low-index faces of Al and Al deposition on Ag

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Abstract

The deposition of Ag on low-index surfaces of Al, and the symmetric case of Al on Ag surfaces, are studied by means of a simple modeling approach based on a quantum approximate technique, the BFS method for alloys. For submonolayer deposits of Ag on Al, a preference is seen for growth of close-packed chains along nearest-neighbor directions on (100) and (110) surfaces, while cluster formation is preferred for growth on Al(111). For Al deposition on all three low-index Ag surfaces, diffusion of Al into the Ag surface layers is favored. The behavior seen on the various surfaces is attributed to a competition between the preference for Ag atoms to favor an Al environment, while Al atoms tend to avoid the increased energy associated with having Ag neighbors. The energies of the various atomic configurations are then determined by how the two competing effects manifest themselves for the corresponding geometric arrangements considered.

Keywords: Adatoms; Computer simulations; Silver; Aluminum; Semi-empirical methods and model calculations; Surface alloys; Surface structure

1. Introduction

Understanding the fundamental processes controlling heteroepitaxial growth is the focus of a large segment of the materials science community, yet we are still lacking a comprehensive model that can be used to predict the interface structure, composition, and stability for metal–metal interfaces.

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In particular, interfaces between aluminum and various transition metals play an important role in applications as catalysts, metallization layers in semiconductor devices, and thin films for magnetic data storage. The lack of inversion symmetry at the heteroepitaxial interface implies that reversing the role of substrate and film materials may result in different growth behavior as seen, for example, in Pd/Cu(110) vs. Cu/Pd(110) [1]. In cases with lattice mismatch, the stress in the film switches from compressive to tensile. This asymmetry is also seen in the chemical preference for element A to diffuse into element B, while atom B prefers to remain on the surface of substrate material A. In a series of papers [2,3], Bauer and co-workers address this asymmetric growth situation, assuming local thermodynamic equilibrium, and using the surface energies of elements A and B, and the energy of the associated interface. However, under typical conditions for heteroepitaxial growth, equilibrium may not be realized because of kinetic limitations and vapor pressures of the deposited material.

The interface between Al and a variety of transition metals has been studied in recent years. Films of Pd, Fe, Ni and Co were all shown to mix with and displace the substrate Al atoms from their equilibrium lattice positions at room temperature [4]. On the other hand, Ti films grow as an epitaxial, pseudomorphic fcc overlayer. Neither the aluminide formation energy, nor the lattice mismatch alone, serve as useful parameters to predict epitaxial growth. Instead, a correlation exists between the relative atomic sizes (i.e., the metallic radius) of the adatoms and the observed growth behavior for these metals on Al surfaces. Metal atoms with radii larger than that of Al form overlayers (Ti), and adatoms with radii smaller than that for Al form alloys at the interface (Pd, Fe, Ni, Co). All of the systems mentioned have bulk phase diagrams indicating formation of a variety of aluminide compounds, and in some cases the lattice matching is quite good (1% for Fe–Al).

Thus, we are motivated to go deeper in our understanding of the interface, and to establish an atomistic modeling scheme capable of predicting the evolution of metal–metal interfaces. From a modeling standpoint, it is essential to prove that the application of any given quantum approximate method can be effective when dealing with the fine energy balances which, if treated correctly, would help understand the driving forces that govern film growth and surface alloy formation as a function of coverage. In this sense, the Ag–Al interface was selected for study because it represents a good test case for the quantum approximate method used in this work, i.e., the Bozzolo–Ferrante–Smith (BFS) method for alloys [5]. Bulk Ag has a lattice mismatch with Al of only 0.9% [6], and a formation energy that is relatively small (<0.04 eV/atom) [7]. Since the mismatch-induced stress is small, we expect that chemical effects will have an important role.

The BFS method by construction characterizes the metal–metal interaction in terms of BFS strain and chemical contributions, and so is ideally suited to characterize these metal–metal interfaces. The primary purpose of the present paper is to establish appropriate parameters for the BFS model description of the Al–Ag system, using results from the literature for very low adatom coverage. Future work will apply these results to ongoing studies of Ag film growth on Al surfaces for a larger range of coverage.

While the present work deals primarily with submonolayer coverage of Ag on Al and the symmetric system, Al on Ag, it is interesting and useful to review the experimental work done on these systems so as to appreciate the complex behavior of these interfaces as a function of coverage and temperature, and the challenge for any model calculations. Egelhoff [8] studied thin Ag films grown on Al(100) using X-ray photoemission (XPS). In this case, Ag was observed to produce a (5 × 1) LEED pattern at submonolayer coverage, a disordered phase between 2 ML and 10 ML, and an ordered (1 × 1) epitaxial structure around 10–20 ML. X-ray photoelectron spectra of Ag/Al(100) films showed that the electronic structure of the Ag film does not converge to bulk Ag until about 20 ML, much more than the expected 3 or 4 ML that would correspond to layer-by-layer growth, suggesting a granular structure. Egelhoff concluded that prior to the onset of epitaxy, Ag was in the form of small, closely packed clusters (quasi-equilibrium structures) with a diameter that depends