Available online at www.sciencedirect.com
SCIENCE DIRECT®
Nuclear Instruments and Methods in Physics Research B 243 (2006) 43–50
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Repulsive interatomic potentials for noble gas bombardment of Cu and Ni targets

M.A. Karolewski *

Department of Chemistry, University of Brunei Darussalam, Jalan Tungku Link, Gadong BE 1410, Brunei Darussalam, Borneo

Received 18 May 2005; received in revised form 3 July 2005
Available online 31 August 2005

Abstract

Interatomic potentials that are relevant for noble gas bombardment of Cu and Ni targets have been calculated in the energy region below 10 keV. Potentials are calculated for the diatomic species: NeCu, ArCu, KrCu, Cu_2, ArNi, Ni_2 and NiCu. The calculations primarily employ density functional theory (with the B3LYP exchange–correlation functional). Potential curves derived from Hartree–Fock theory calculations are also discussed. Scalar relativistic effects have been included via the second-order Douglas–Kroll–Hess (DKH2) method. On the basis of a variational argument, it can be shown that the predicted potential curves represent an upper limit to the true potential curves. The potentials provide a basis for assessing corrections required to the ZBL and Molière screened Coulombic potentials, which are typically found to be too repulsive below 1–2 keV. These corrections significantly improve the accuracy of the sputter yield predicted by molecular dynamics for Ni(100), whereas the sputter yield predicted for Cu(100) is negligibly affected. The validity of the pair potential approximation in the repulsive region of the potential is tested by direct calculation of the potentials arising from the interaction of either an Ar or Cu atom with a Cu_3 cluster. The pairwise approximation represents the Ar–Cu_3 potential energy function with an error <3 eV at all Ar–Cu_3 separations. For Cu–Cu_3, the pairwise approximation underestimates the potential by ca. 10 eV when the interstitial atom is located near the centre of the cluster.

PACS: 31.15.Ew; 31.50.Bc; 79.20.Ap; 79.20.Rf

Keywords: Interatomic potentials; Molecular dynamics; Sputtering

1. Introduction

Molecular dynamics (MD) simulations provide a description of atomic collisions in solids within the framework of classical dynamics. In MD, atomic interactions are typically described by means of composite interatomic potentials. These consist of a repulsive screened Coulombic potential at short internuclear distances (R), which is interpolated to an attractive potential at internuclear distances that are shorter than chemical bond lengths.

For a pair of interacting atoms with atomic numbers Z_1, Z_2 respectively, the repulsive potential may be expressed as the product of the Coulombic potential and a screening function, $\phi(R)$, whose effect is to attenuate the internuclear repulsion

$$V(R) = (Z_1 Z_2 e^2/4\pi\varepsilon_0 R)\phi(R). \quad (1)$$

For the most commonly used screened Coulombic potentials, the screening function is expressed as

$$\phi(R) = \sum_{k=1}^{N} c_k \exp(-b_k R/a). \quad (2)$$

For the Bohr potential, $N = 1$; for the Molière potential, $N = 3$; and for the Ziegler–Biersack–Littmark (ZBL) potential, $N = 4$ [1]. Standard values for the parameters c_k, b_k are defined for each potential. The definition of the screening length a involves Z_1 and Z_2, e.g. for the ZBL potential

* Tel.: +673 246 3001; fax: +673 246 1502.
E-mail address: mkarol@fos.ubd.edu.bn

0168-583X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2005.07.192

$$a = 0.4685(Z_1^{0.23} + Z_2^{0.23})^{-1}\ (\text{Å}). \quad (3)$$

Experimental determinations of repulsive interatomic potentials in condensed matter rely on fits to data obtained from scattering experiments. Low-energy ion scattering spectrometry (ISS) can be used to fit effective screening lengths up to several keV, but ISS data are mainly confined to light projectiles such as He^+ [2]. Schüller et al. made use of rainbow structures in the angular distributions of surface-channelled projectiles to test different functional forms of the repulsive projectile-target potential (up to ~40 eV) [3]. MD simulations of the Doppler broadening of gamma radiation produced during nuclear recoil de-excitation [4,5] or nuclear beta decay [6] can be used to evaluate potential functional forms in the approximate energy range 50–500 eV. For example, gamma ray induced Doppler shift data obtained for recoiling nuclei in Ni, Fe and Cr crystals have been used to fit the screening length for the ZBL potential [5]. ZBL screening length correction factors inferred in [5] were ca. 0.91 for the Fe–Fe and Ni–Ni potentials and ca. 0.78 for the Cr–Cr potential. Similarly, measured range parameters for heavy ions in amorphous solids can be compared with ranges simulated on the basis of an assumed potential function [7].

Repulsive interatomic potentials can be calculated via ab initio (first principles) quantum mechanical methods. For an isolated diatomic species (molecule or collision complex), the potential energy can be expressed in terms of the total electronic energy, $E_e(R)$ and the Coulombic internuclear repulsion, $U_n(R)$, as follows:

$$V(R) = U_n(R) + E_e(R) - E_e(\infty). \quad (4)$$

The final term in Eq. (4) arises because the potential energy is referenced to the energy of the separated atoms, i.e. $V(\infty) = 0$ by convention. Broomfield et al. calculated the $ArCu^+$, ArSi and Si_2 potentials [8,9], while Kuwata et al. calculated potentials for ArCu and ArAl [10]. Other groups have calculated repulsive potentials for a range of homonuclear diatomics (predominately of light atoms) [11–14]. Errors on the order of 10% in the ZBL potential have been inferred from most of these studies.

In this paper, repulsive interatomic potentials have been calculated using ab initio methods for a number of heavy-atom diatomic species that are relevant for noble gas bombardment of Cu and Ni targets: NeCu, ArCu. KrCu. Cu_2, ArNi, Ni_2, NiCu. Sputter yield predictions for Cu(1 0 0) and Ni(1 0 0) targets from MD simulations based on the ZBL and the ab initio potentials respectively, are then compared.

Several sources of errors in calculated potentials can be identified, including basis set limitations and neglect of correlation and relativistic effects. Errors due to basis set limitations are expected to increase at small internuclear separations [12]. There is no reliable database of potentials against which the accuracy of theoretical repulsive potentials can be tested. However, it will be shown in Section 4.1 that variational arguments can be used to identify regions in which an assumed analytic potential function is too repulsive. This method of evaluation provides a lower limit to the correction required for a particular form of analytic potential (e.g. the ZBL potential).

2. Computational methods

2.1. Interatomic potentials

Interatomic potentials were calculated using the Gaussian 03 suite of programs (revision B.05) [15]. A variety of theoretical methods and basis sets was employed. The calculations are primarily distinguished according to whether they employed the Hartree–Fock (HF) theory or the density functional theory (DFT). The hybrid B3LYP exchange–correlation functional was used for all of the DFT calculations reported here [16,17]. Both relativistic and non-relativistic HF and DFT calculations were carried out. Scalar (spin-independent) relativistic effects were taken into account using the second-order Douglas–Kroll–Hess (DKH2) method [18]. The relativistic calculations will be indicated in this paper using the notation HF–DKH2 and DFT–DKH2, while the unqualified designations of HF and DFT will be used for non-relativistic calculations.

The majority of calculations discussed in this paper employed the large all-electron basis set designated as 6-311 + G(3df), as implemented in Gaussian 03. This is a triple-zeta basis set (available for elements up to Kr) that is supplemented by polarization and diffuse functions. In Section 3.1 a number of calculations are reported that used the smaller all-electron 3-21 G and 6-31 G basis sets that lack polarization and diffuse functions. The Cu_2 DFT calculations from Gaussian were also compared with (non-relativistic) DFT calculations performed using the DMol3 quantum chemical package [19,20]. The DMol3 calculations used the hybrid BYLP exchange–correlation functional and the all-electron, double-numeric precision (DNP) basis set, which is comparable to the Gaussian 6-31G(d) basis set.

Potential energy curves $V(R)$ for the diatomic species NeCu, ArCu, KrCu, Cu_2 and NiCu were calculated at 0.05 Å intervals of R for electronic states of the lowest spin multiplicity. For ArNi and Ni_2, both singlet and triplet state potential energy curves were obtained. Calculations were performed for a range of R down to 0.3 Å, such that typically $V(R)$<5–8 keV. The potential energy scale is referenced either to the sum of free atom energies (the normal case, when the diatomic ground state dissociates into ground state atoms), or (for Cu_2, Ni_2 and NiCu) to the diatomic energies at $R = 100$ Å.

2.2. Molecular dynamics

MD sputtering simulations were carried out using the Kalypso package (version 2.0) [21]. The projectile species was 3 keV Ar, incident from the normal direction. The Cu(1 0 0) and Ni(1 0 0) targets consisted of 13 atomic layers