

# **TIGHT-BINDING POTENTIALS FOR SPUTTERING SIMULATIONS WITH FCC AND BCC METALS**

**M. A. KAROLEWSKI\***

*Department of Chemistry, University of Alberta, Edmonton, AB,  
Canada T6G 2G2*

The parameters of many-body tight-binding (TB) potentials have been determined for 26 fcc and bcc metallic elements. The potentials are intended for application in classical dynamics simulations of sputtering phenomena. The potentials are fitted to the cohesive energy, lattice constant, elastic constants and vacancy formation energy of each element, using a cut off beyond the second (fcc) or third (bcc) neighbour distance. The surface binding energies, surface energies, and cluster (dimer and trimer) binding energies predicted by the TB potentials are reported. Practical issues relating to the incorporation of the potentials into sputtering simulation codes are discussed.

*Keywords:* Sputtering; Computer simulation; Potentials

## **INTRODUCTION**

The bombardment of solids by fast atomic or molecular projectiles results in the erosion of the target material through sputtering of its surface constituents as single atoms or bound clusters. Sputtering phenomena play an important role in a number of modern technologies and industries, and in techniques for materials modification and analysis. The current understanding of sputtering at the microscopic level has been achieved partly through the use of classical dynamics computer simulations [1 – 3]. Computer simulations offer the possibility

---

\*e-mail: mkarol@ualberta.ca

of characterising many aspects of the sputtering process, including the yield and origins of sputtered atoms, their angular and energy distributions, the distribution of sputtered clusters, adatom yields, and the emission statistics.

An important aspect of a sputtering simulation is the description of the target lattice potential energy. Sputter yields, adatom yields, and the clustering propensity of sputtered atoms all depend upon the properties of this potential. The potentials used for metal targets in contemporary molecular dynamics simulation models are typically empirical many-body potential schemes based on pair functionals [4]. Embedded-atom method potentials (EAM) [5], and tight-binding (TB) potentials based on the second-moment approximation [6, 7] are typical choices. (For elemental targets, the TB potential is formally equivalent to an EAM potential which has a square root embedding function). These potentials are usually fitted to bulk lattice properties, but often display good transferability to surface and cluster environments. In addition, their computational cost is low. TB potentials based on the second-moment approximation are an attractive choice for sputtering simulations because of their simple analytic form (see next section), which is easily programmed and which facilitates the development of reusable codes for production calculations. The capabilities and limitations of TB potentials for modelling the lattice properties of real materials have been analysed by Paidar *et al.* [8] (for EAM-like potentials in general, see Johnson [9]).

The aim of the present work is to determine the parameters of second-moment approximation TB potentials for a number of cubic metallic elements, and to characterise the properties of the potentials so obtained. TB potentials generally outperform pair potentials in terms of their ability to model solid state properties, and have properties similar to those of EAM potentials. The formalism of the potentials is not new, and the motivation for generating the parameter sets is largely to satisfy a perceived need for a wider range of potentials describing a variety of metals beyond those commonly studied. The potentials are envisaged for use in simulations of sputtering and other bombardment phenomena. A molecular dynamics computer program ('Kalypso') designed to use TB potentials has recently been developed, and may be obtained at no charge on application to the author.

A large number of excellent many-body potentials exists in the literature for solid-state simulations of fcc and bcc metals, but on

investigation, many of these are found to be difficult to apply to sputtering simulations. Typical reasons for this difficulty are: (a) the potential has too long a range, (b) the potential is ill-behaved in the core region, or (c) the functional form is too complex to implement efficiently. A present day molecular dynamics sputtering simulation might involve the computation of  $10^6$  time-steps for each of  $\sim 10^4$  atoms in a simulation target. Thus, attractive potentials of short range which can be efficiently implemented (*via* look-up tables rather than analytical evaluations) are mandatory in order to keep computation times to reasonable levels.

The potentials have been fitted in this work on the assumption of a second neighbour cut off for fcc metals, and a third neighbour cut off for bcc metals, using the exponential form (see next section) proposed by Rosato *et al.* [6] This range is typical for EAM potentials, but many TB potentials reported in the literature have been fitted for longer ranges, which has restricted their application in sputtering studies. Potentials have been obtained in this work for most of the metals which exhibit stable bcc or fcc crystal structures (excluding only Ce, Eu, Yb). Rosato *et al.* have previously fitted TB potentials based on exponential functions for 8 fcc metals assuming a first neighbour cut off [6], while Cleri and Rosato subsequently reported parameters of TB potentials for 17 fcc, bcc and hexagonal close-packed (hcp) metals, which were fitted up to the fifth neighbour distance [7]. TB potentials of similarly long range have been fitted for Cu, Ag and Au by Kallinteris *et al.* [10] for Ni, Pd, Au and Ag by Rey *et al.* [11] and for hcp and bcc Zr by Williams and Massobrio [12].

The paper is organised as follows. In the following section, the functional forms and method of parameterisation of tight-binding potentials are described. The properties of the fitted potentials are then reviewed, followed by a discussion on the integration of the potentials into simulation codes. The last section of the paper presents concluding remarks.

## METHODOLOGY

The assumptions underlying the tight-binding model of metallic cohesion in the second-moment approximation are reviewed by Clari and Rosato [7]. Within this approximation, the band energy of the

system is proportional to the square root of the second moment of the density of states. The system potential energy,  $U_s$ , is written in the following form, where  $E_i^R$  and  $E_i^B$  represent respectively a repulsive core interaction and the band energy associated with the  $i$ th atom:

$$U_s = \sum_i (E_i^R + E_i^B), \quad (1)$$

where  $E_i^R$  is a repulsive pair potential:

$$E_i^R = \sum_{j \neq i} U_{ij}(r_{ij}), \quad (2)$$

$$U_{ij}(r_{ij}) = A \exp(-p(r_{ij}/r_0 - 1)), \quad (3)$$

and  $E_i^B$  represents the cohesive band energy term:

$$E_i^B = - \left( \sum_{j \neq i} \phi(r_{ij}) \right)^{1/2}, \quad (4)$$

$$\phi(r_{ij}) = \xi^2 \exp(-2q(r_{ij}/r_0 - 1)). \quad (5)$$

In Eqs. (2)–(5),  $r_{ij}$  is the separation between atoms  $i$  and  $j$ , and  $A, \xi, p, q, r_0$  are adjustable parameters governing the interaction between those atoms. Eqs. (1) to (3) are similar to the Finnis–Sinclair (FS) scheme [13], but Eq. (1) uses a double summation convention for the repulsive functions, whereas the convention in the FS scheme is to sum this term for  $j > i$  rather than  $j \neq i$ . For  $s, p$ -bonded metals there is no strong theoretical motivation for representing the band energy part of the potential by a square-root term. However, this functional form can be rationalised as an empirical representation of the volume-dependent term required by the electron gas model of simple metals [7].

The length scale parameter,  $r_0$ , in Eq. (1) is set to the lattice nearest neighbour distance. The remaining parameters ( $A, \xi, p, q$ ) of the TB potentials were fitted for each element using the lattice constant, cohesive energy ( $E_c$ ), elastic constants ( $C_{11}, C_{12}, C_{44}$ ) and vacancy formation energy ( $E_v$ ). The uncertainties in experimental values of elastic constants and vacancy formation energies are typically on the order of 10–20%. The lattice constant and cohesive energy were fitted exactly, while the remaining properties were fitted using equal weights.

Fitting was carried out using a combination of genetic algorithm and downhill simplex methods. The cut off distance ( $r_{\text{cut}}$ ) used for the fitting procedure was chosen to lie between the second and third neighbour distances for the fcc elements, and between the third and fourth neighbour distances for the bcc elements. For those metals whose elastic constants approximate the Cauchy relation ( $C_{12} = C_{44}$ )—for example Rh, Ir, Th, Ca and Sr—the vacancy formation energy is the only property in the fitting set which strongly manifests many-body behaviour. The inclusion of vacancy formation energies in the fitting procedure should thus be particularly important for fixing the parameters of the potential for these metals. Unfortunately, reliable experimental measurements of  $E_v$  are not available for Ca, Rh or Th, so  $E_v$  has been estimated in these cases as  $E_c/3$ .

## LATTICE PROPERTIES

The potential parameters obtained from the fitting procedure are shown in Tables I and II [14–22], while the experimental and predicted values of the bulk properties used in the fits are compared in Tables III and IV (the meaning of the additional parameter  $G$  listed in Tables I and II will be explained later). The predicted elastic constants listed in Tables III and IV were calculated from the TB potentials using the standard tensor formulae, *e.g.*, Eqs. (8)–(10) in Ref. [23],

TABLE I Parameters of tight-binding potentials for fcc metals. The potentials are cut off beyond the second neighbour distance ( $r > \sqrt{2}r_0$ )

	$A(\text{eV})$	$\xi(\text{eV})$	$p$	$q$	$r_0(\text{\AA})$	$G/\xi$
Al	0.1602	1.5074	7.5681	2.7456	2.8634	3.552
Ca	0.0492	0.6842	11.2115	2.6841	3.9471	3.557
Ni	0.0565	1.4005	14.0867	1.7937	2.4918	3.655
Cu	0.0783	1.2355	11.1832	2.3197	2.5560	3.589
Sr	0.0257	0.5557	12.3406	1.8105	4.3027	3.652
Rh	0.1086	1.9776	14.1315	2.5555	2.6901	3.567
Pd	0.1223	1.5193	11.3225	3.0697	2.7511	3.532
Ag	0.0812	1.1081	11.5597	2.8316	2.8890	3.546
Ir	0.2141	2.7082	12.8986	3.4541	2.7145	3.513
Pt	0.2906	2.6715	10.1423	3.7878	2.7746	3.501
Au	0.1935	1.7581	10.4342	3.9472	2.8838	3.497
Pb	0.0851	0.8699	10.0667	3.3563	3.5003	3.517



TABLE II Parameters of tight-binding potentials for bcc metals. The potentials are cut off beyond the third neighbour distance ( $r > \sqrt{8/3}r_0$ )

	$A(eV)$	$\xi(eV)$	$p$	$q$	$r_0(\text{\AA})$	$G/\xi$
Li	0.0488	0.5729	6.3675	1.3969	3.0391	3.734
Na	0.0353	0.4083	7.8536	1.7477	3.7158	3.579
K	0.0230	0.3170	9.3093	1.6143	4.6073	3.633
V	0.2572	2.3126	6.8543	2.1886	2.6223	3.435
Cr	0.0407	1.1012	13.1852	0.8993	2.4981	4.048
Fe	0.1184	1.5418	10.7613	2.0379	2.4824	3.479
Rb	0.0292	0.3233	8.1532	1.9235	4.9363	3.516
Nb	0.4546	3.6302	5.2702	2.0552	2.6033	3.474
Mo	0.2043	2.5097	10.0154	2.0511	2.7253	3.475
Cs	0.0270	0.3036	8.4120	1.9433	5.3174	3.509
Ba	0.0400	0.6167	10.1835	1.5070	4.3466	3.680
Ta	0.3281	3.3008	8.2764	2.2371	2.8601	3.422
W	0.2490	3.2055	10.3715	1.9916	2.7410	3.493

TABLE III Experimental and fitted lattice properties for fcc metals. The first lines contain the experimental values, while the second lines contain the values predicted by the fitted TB potentials. Unless indicated otherwise, lattice constants ( $a_0$ ) are from Ref. [14], cohesive energies ( $E_c$ ) from Ref. [15], elastic constants ( $C_{11}$ ,  $C_{12}$ ,  $C_{14}$ ) from Refs. [16–18]; vacancy formation energies ( $E_v$ ) from Refs. [19, 20]

	$a_0(\text{\AA})$	$E_c(eV)$	$C_{11}(GPa)$	$C_{12}(GPa)$	$C_{44}(GPa)$	$E_v(eV)$
Al	4.0495	3.39	108	62.0	28.0	0.67
			87.8	72.3	27.3	0.71
Ca	5.582	1.84	27.8	18.2	16.3	0.61 <sup>a</sup>
			28.9	20.2	12.7	0.54
Ni	3.524	4.44	261	151	132	1.8
			251	159	130	1.9
Cu	3.6147	3.49	176	125	81.8	1.3
			177	122	83.6	1.3
Sr	6.0849	1.72	15.3	10.3	9.9	0.66 <sup>b</sup>
			16.4	10.7	8.43	0.71
Rh	3.8044	5.75	422	192	194	1.9 <sup>a</sup>
			357	231	169	2.2
Pd	3.8907	3.89	221	171	70.8	1.7
			205	146	83.1	1.2
Ag	4.0857	2.95	131	97.0	51.0	1.1
			128	89.6	55.4	1.0
Ir	3.8389	6.94	600	270	260	1.8
			494	342	196	2.2
Pt	3.9239	5.84	347	251	76.5	1.3
			308	246	85.5	1.2
Au	4.0783	3.81	202	170	45.4	0.93
			192	153	51.3	0.74
Pb	4.9502	2.03	48.8	41.4	14.8	0.58
			48.3	37.0	16.3	0.50
Th	5.0843	6.20	753	489	478	2.1 <sup>a</sup>
			855	503	359	2.4

<sup>a</sup> Estimated as  $E_c/3$ .

<sup>b</sup> Ref. [21].

TABLE IV Experimental and fitted lattice properties for bcc metals. The first lines contain the experimental values, while the second lines contain the values predicted by the fitted TB potentials. The meanings of symbols, and literature sources for experimental values, are given in the caption to Table III

	$a_0(\text{\AA})$	$E_v(\text{eV})$	$C_{11}(\text{GPa})$	$C_{12}(\text{GPa})$	$C_{44}(\text{GPa})$	$E_v(\text{eV})$
Li	3.5092	1.63	14.4 17.3	12.1 12.5	10.7 8.02	0.48 0.56
Na	4.2906	1.113	8.16 8.79	6.79 7.30	5.70 4.83	0.34 0.38
K	5.32	0.934	4.15 4.15	3.40 3.57	2.84 2.69	0.34 0.36
V	3.028	5.31	230 124	120 109	43.1 51.9	2.2 1.3
Cr	2.8846	4.10	347 93.7	66 83.1	100 75.5	2.0 1.9
Fe	2.8664	4.28	230 159	135 155	117 115	1.6 1.6
Rb	5.70	0.852	3.12 3.15	2.62 2.73	1.86 1.76	0.27 0.28
Nb	3.006	7.57	245 136	132 117	28.4 34.5	2.6 1.3
Mo	3.1469	6.82	459 183	168 173	111 124	3.2 2.5
Cs	6.14	0.804	2.47 2.45	2.06 2.16	1.48 1.42	0.26 0.27
Ba	5.019	1.90	12.5 <sup>a</sup> 10.2	7.1 <sup>a</sup> 8.94	10.5 <sup>a</sup> 7.10	0.65 0.76
Ta	3.3026	8.10	264 173	158 158	82.6 93.5	3.0 2.5
W	3.165	8.90	517 236	203 224	157 165	3.6 3.3

<sup>a</sup> Estimated from data compiled in Ref. [22].

while predicted (unrelaxed) vacancy formation energies were estimated using the method of Eq. (12) in Ref. [23]. The accuracy (in the least-squares sense) of the predicted lattice properties ranges from moderate to good for the fcc metals (except Ir), the alkali metals and Fe. However, for several bcc metals (V, Cr, Ta, Nb, W, Ba, Ta) the potentials substantially underestimate  $C_{11}$  (and in some cases  $E_v$ ), resulting in a much larger fitting error. The error seems to reflect a fundamental limitation of the TB form, which always produces a  $C_{11}/C_{12}$  ratio near 1.1 for metals with bcc structures. This is realistic for alkali metals, but not for bcc transition metals, for which a ratio near

or above 2 is more typical. Nevertheless, the fitted TB potentials do provide better predictions of the lattice properties of bcc transition metals than can be achieved by pair potentials (which always predict  $E_v = E_c$ , and  $C_{12} = C_{44}$ ), and this justifies their use in sputtering simulations in preference to pair potentials.

Potentials used in sputtering simulations should be transferable to low-coordination environments such as defects, surfaces and clusters. Some representative predictions of the TB potentials for surfaces and clusters will be presented in the following sections. The theoretical relationship between the performance of EAM-like potentials in bulk and low-coordination environments is quite complex. Johnson draws attention to the importance of correctly modelling the shear moduli,  $C_{44}$ , and,  $C' = (C_{11} - C_{12})/2$  [9]. Although the fitting procedure used for this work yields reasonable predictions of  $C_{44}$ , the predictions of  $C'$  are poor for most of the bcc transition metals. The failure of TB and EAM-like potentials to model the elastic properties of bcc metals has been attributed to their lack of angular dependence [5, 24], which can be remedied (with a considerable increase in complexity) by incorporating explicit angular functions, as in the modified embedded atom method (MEAM) [25] or angular-dependent TB potentials [26]. To the author's knowledge, such potentials have not yet been used for sputtering simulations. The use of an oscillating function in the cohesive term of the potential (*i.e.*,  $\phi_{ij}(r_{ij})$  in Eq. (5)) can also improve the accuracy of EAM-like potentials for modelling the bulk properties of bcc metals [27, 28], but renders the potentials unsuitable for sputtering models due to the introduction of repulsive regions in the effective pair potential.

The centrosymmetric character of the interaction terms in Eqs. (3) and (5) tends to favour the stability of fcc structures over bcc structures. The fcc-bcc energy difference is generally small ( $\sim 0.1$  eV), and depends on the cut off distance. However, it should be pointed out that small structural energy differences of this kind are rather less important in keV sputtering simulations than in other types of atomistic modelling (of defects, phase transformations *etc.*). Energetic barriers to phase transformation are sufficient to constrain the structure of a nominally metastable bcc target lattice for the duration of a sputtering simulation ( $\sim 1$  ps). It is possible to formally stabilise the bcc structure of a lattice at zero temperature by the artifice of

placing the TB potential cut off distance between the third neighbour shells of the most stable bcc and fcc structures respectively [7]. This produces stability by virtue of the greater number of interacting neighbours included in the bcc lattice sum (for example, bcc W and Ba are respectively found to be 0.17 eV and 0.08 eV more stable than the fcc phases by this method). However, for sputtering simulations at finite temperature it is necessary to cut off the potential halfway between the third and fourth bcc neighbour shells, in order to reduce overlap between displaced atoms and the cut off boundary, and this standard choice of cut-off distance results in preferential fcc stability.

## SURFACE BINDING ENERGY AND SURFACE ENERGY

Analytic sputtering theory deduces an inverse dependence of sputter yield on the surface binding energy [29]. This dependence has been demonstrated by classical dynamics sputtering simulations based on both pair and many-body potentials [30,31]. In the context of sputtering, an appropriate measure of surface binding energy ( $E_{SB}$ ) is the energy required to extract an atom from a surface lattice site (as opposed to the average cohesive energy of atoms in the surface layer). Tables V and VI summarise the values of  $E_{SB}$  predicted by the potentials fitted in this work for low-index surfaces of fcc and bcc metals.  $E_{SB}$  increases with the density of surface packing. For low-index surfaces, predicted values of  $E_{SB}$  are typically 10–20% higher than the bulk cohesive energy. For classical dynamics simulations, it is unnecessary to evaluate the surface binding energy explicitly, but an

TABLE V Energy (in eV) required to remove an atom from (100), (110) and (111) fcc metal surfaces ( $E_{SB}$ ), as predicted by tight-binding potentials

	<i>Al</i>	<i>Ca</i>	<i>Ni</i>	<i>Cu</i>	<i>Sr</i>	<i>Rh</i>	<i>Pd</i>
(100)	3.83	2.15	5.32	4.11	2.06	6.78	4.50
(110)	3.61	1.99	4.89	3.80	1.89	6.27	4.19
(111)	3.91	2.22	5.44	4.23	2.10	7.04	4.66
	<i>Ag</i>	<i>Ir</i>	<i>Pt</i>	<i>Au</i>	<i>Pb</i>	<i>Th</i>	
(100)	3.43	8.01	6.55	4.26	2.31	7.24	
(110)	3.19	7.47	6.19	4.03	2.17	6.71	
(111)	3.56	8.35	6.76	4.41	2.38	7.70	

TABLE VI Energy (in eV) required to remove an atom from (100) and (110) bcc metal surfaces ( $E_{SB}$ ), as predicted by tight-binding potentials

	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>V</i>	<i>Cr</i>	<i>Fe</i>	<i>Rb</i>
(100)	1.85	1.26	1.06	5.82	4.78	4.82	0.96
(110)	1.90	1.31	1.11	6.13	4.91	5.12	1.00
	<i>Nb</i>	<i>Mo</i>	<i>Cs</i>	<i>Ba</i>	<i>Ta</i>	<i>W</i>	
(100)	8.17	7.66	0.90	2.18	8.97	10.03	
(110)	8.51	8.12	0.95	2.27	9.50	10.62	

estimate of  $E_{SB}$  is needed (normally for an a randomly oriented surface) as an input parameter for binary collision approximation (BCA) sputtering models [32]. In many BCA studies  $E_{SB}$  has been equated to the bulk cohesive energy (this choice is justified in Ref. [33]). The predictions listed in Tables V and VI should provide better estimates of  $E_{SB}$  for undisturbed crystalline surfaces than values derived from pair potentials [34]. TB and EAM potentials fitted by other authors give estimates of  $E_{SB}$  for (100) fcc surfaces which differ by up to 0.3 eV from the predictions listed in Table V [33].

The surface energy ( $E_S$ ) is a fundamental property of a metal surface which can also be modelled using TB potentials. The surface energy is of interest because it offers a means of testing the transferability of the TB potentials to the surface environment. Tables VII and VIII compare TB potential estimates of  $E_S$  for unrelaxed low-index fcc and bcc metal surfaces with experimental estimates for polycrystalline metals [35]. Surface energies predicted by the TB potentials are systematically lower than the experimental values for both fcc and bcc metals. The surface energy predictions of the TB potentials are similar or higher than those predicted by EAM potentials for the metals Cu, Ag, Ni, Mo, Ta and W but are substantially lower (by as much as 30%) than the EAM predictions for Au, Pd, Pt, V and Nb [5, 36] Johnson found that the surface energy predicted by EAM-like potentials was nearly proportional to the predicted vacancy formation energy [9]. The unusually low surface energies predicted for V and Nb may be related to the poor modelling of the vacancy formation energies for these metals (Tab. IV).

TABLE VII Surface energies ( $\text{J m}^{-2}$ ) predicted for (100), (110) and (111) fcc metal surfaces by tight-binding potentials, and experimental surface energies (for polycrystalline metals) [35]

	<i>Al</i>	<i>Ca</i>	<i>Ni</i>	<i>Cu</i>	<i>Sr</i>	<i>Rh</i>	<i>Pd</i>
(100)	0.66	0.25	1.81	1.21	0.23	1.88	1.05
(110)	0.75	0.29	2.05	1.37	0.26	2.11	1.18
(111)	0.59	0.23	1.73	1.11	0.22	1.68	0.92
Expt.	1.16	0.49	2.45	1.83	0.41	2.70	2.05
	<i>Ag</i>	<i>Ir</i>	<i>Pt</i>	<i>Au</i>	<i>Pb</i>	<i>Th</i>	
(100)	0.76	1.94	1.18	0.70	0.29	1.13	
(110)	0.85	2.17	1.33	0.79	0.33	1.24	
(111)	0.67	1.66	0.98	0.58	0.25	0.93	
Expt.	1.25	3.00	2.48	1.50	0.56	1.55	

TABLE VIII Surface energies ( $\text{J m}^{-2}$ ) predicted for (100) and (110) bcc metal surfaces by tight-binding potentials, and experimental surface energies (for polycrystalline metals) [35]

	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>V</i>	<i>Cr</i>	<i>Fe</i>	<i>Rb</i>
(100)	0.43	0.19	0.11	1.50	1.96	1.72	0.081
(110)	0.40	0.18	0.10	1.31	1.90	1.54	0.073
Expt.	0.53	0.26	0.13	2.55	2.30	2.48	0.11
	<i>Nb</i>	<i>Mo</i>	<i>Cs</i>	<i>Ba</i>	<i>Ta</i>	<i>W</i>	
(100)	1.46	2.23	0.066	0.27	2.14	2.92	
(110)	1.25	1.99	0.060	0.25	1.88	2.63	
Expt.	2.70	3.00	0.095	0.37	3.15	3.68	

## CLUSTER PROPERTIES

One of the goals of sputtering simulations has been to elucidate the mechanisms of cluster (especially dimer and trimer) formation [37]. Simulations of this type require the use of a potential which is capable of describing the dynamics of cluster emission in both solid state and gas phase environments. Although clusters are sputtered with a distribution of electronic states, a given simulation model only follows clusters with a specific potential energy curve. Normally the simulation potential is evaluated on its ability to model the ground state properties of the cluster, since excited state species comprise a small fraction of the total cluster yield. Pair potentials predict a linear dependence of binding energy on primary coordination. This is adequate for some *s*, *p*-bonded metals (*e.g.*, Ca), but is normally a poor description of transition metal clusters. TB and EAM potentials

are known to be deficient in the opposite sense, in that they tend to overbind small clusters [11]. Table IX summarises the binding energies predicted by the TB potentials for dimer and trimer ( $D_{3h}$ ) species. Experimental (*or ab initio*) binding energies are also shown for the dimers [38–42]. In some cases large experimental uncertainties arise because of difficulties in establishing the ground state of the molecule. Table IX provides an indication of the transferability of the TB potentials to the gas phase environment. The potentials tend to overestimate the dimer binding energies. For half of the potentials (*i.e.*, Al, Ca, Sr, Pd, Ir, Pt, Au, Pb, V, Fe, Nb, Ba, Ta), the predicted dimer binding energies differ from the measured values by more than 50%. This error would presumably disqualify these potentials for quantitative simulations of (ground-state) cluster formation in

TABLE IX Binding energies (eV per atom) predicted by tight-binding potentials (TB) for dimers and trimers ( $D_{3h}$ ). Experimental (Expt.) binding energies are also shown for dimers

	<i>Dimer (TB)</i>	<i>Dimer (Expt.)</i>	<i>Trimer (TB)</i>
Al	1.93	$0.6 \pm 0.1^a$	2.24
Ca	0.76	$0.07^b$	0.96
Ni	1.45	$1.034 \pm 0.005^c$	1.94
Cu	1.34	$1.01 \pm 0.04^c$	1.73
Sr	0.58	$0.07^b$	0.77
Rh	2.11	$1.46 \pm 0.1^c$	2.76
Pd	1.74	$0.52 \pm 0.08^c$	2.16
Ag	1.24	$0.83 \pm 0.02^c$	1.56
Ir	3.10	$1.85 \pm 0.04^c$	3.86
Pt	3.49	$1.86 \pm 0.6^c$	4.02
Au	2.32	$1.15 \pm 0.01^c$	2.65
Pb	1.07	$0.51^d$	1.27
Th	2.38	$1.5^e$	3.10
Li	0.58	$0.52^e$	0.75
Na	0.42	$0.37^e$	0.53
K	0.31	$0.26^e$	0.41
V	2.58	$1.25 \pm 0.07^c$	3.10
Cr	1.07	$0.89 \pm 0.18^c$	1.48
Fe	1.54	$0.45 \pm 0.05^c$	2.01
Rb	0.33	$0.24^e$	0.42
Nb	4.58	$2.5 \pm 0.2^c$	5.19
Mo	2.53	$2.19 \pm 0.05^c$	3.27
Cs	0.31	$0.22^e$	0.40
Ba	0.61	$0.10^b$	0.81
Ta	3.49	$2.0 \pm 0.5^c$	4.34
W	3.21	$2.5 \pm 0.5^c$	4.18

<sup>a</sup> Ref. [38]; <sup>b</sup> Ref. [39]; <sup>c</sup> Ref. [40]; <sup>d</sup> Ref. [41]; <sup>e</sup> Ref. [42].

sputtering, although they could be used to estimate upper limits to cluster yields. For the remaining metals, the TB potentials predict dimer binding energies which are within 50% of the experimental values, and should prove more useful for quantitative simulations of cluster sputtering. Previous work indicates that the partial sputter yields of clusters increase linearly with binding energy [43], so it is possible to estimate the magnitude of the sputter yield error caused by moderate cluster overbinding in a simulation model. Experimental binding energies and structures for trimers are often controversial, and require a more detailed review and evaluation than is possible in this paper. However, errors in the binding energies predicted by the TB potentials for trimer (and larger) clusters will generally be lower than those for the corresponding dimers, since the error in predicted binding energy declines to zero in the bulk limit.

There are several reasons why TB potentials should model some clusters adequately and others badly, including the limitations inherent in the TB potential functional form [11], and the restricted data set of the fitting procedure, which only uses information from the metallic environment. Thus, the binding energy predicted by the TB potential for  $\text{Al}_2$  (1.93 eV) is comparable to the predictions of local density approximation (LDA) calculations for 1-dimensional linear (1.3 eV) and zig-zag (2.1 eV) metallic Al chains [44]. The prediction of dimer binding energies is a stringent test of any model of atomic structure, including first principles methods. In fact, the TB potential predictions for the binding energies of first row transition metal dimers ( $\text{V}_2$ ,  $\text{Fe}_2$ ,  $\text{Ni}_2$ ,  $\text{Cu}_2$ ) are quite similar to those obtained from the LDA [45].

## COMPUTER IMPLEMENTATION

Sputtering simulations typically employ composite potentials. These consist of a repulsive short-range screened Coulomb potential which is splined to an attractive potential at internuclear separations somewhat below the first neighbour distance [2]. For a many-body attractive potential of the pair functional type (TB, EAM *etc.*), this normally entails joining one of the nodes of the spline function to an effective pair potential,  $V_{ij}$ , which is derived from a series expansion of the many-body potential in the bulk environment [5, 46]. For TB

potentials of the form of Eqs. (1)–(5), the effective pair potential acting between atoms  $i$  and  $j$  is given by:

$$V_{ij}(r_{ij}) = 2U_{ij}(r_{ij}) - \frac{\phi(r_{ij})}{G} + \frac{[\phi(r_{ij})]^2}{4G^3}. \quad (6)$$

Equation (6) assumes the usual pair potential evaluation convention, *viz.* that interaction terms are only counted once for each distinct pair of atoms (in contrast to Eq. (1)). The functions  $U_{ij}(r_{ij})$  and  $\phi(r_{ij})$  are defined in Eqs. (3) and (5) respectively.  $G$  is a lattice sum which represents the value of the total band energy associated with any atom  $k$  in the reference environment (normally a site in the bulk of the ideal lattice):

$$G = \left( \sum_{k \neq l} \phi(r_{kl}) \right)^{1/2}. \quad (7)$$

Tables I and II give the values of the dimensionless ratio  $G/\xi$  for a lattice sum (Eq. (7)) corresponding to a bulk metallic environment. In all cases, this ratio takes values between 3.4 and 4.0. The larger values imply relatively greater long-range contributions to the potential. The attractive part of an effective pair potential derived for a surface environment may differ somewhat from that of a bulk environment, because of fewer contributions to the lattice sum in Eq. (7) [5]. However, this should have minimal impact on a composite potential designed for sputtering simulations, since the splining is carried out at a separation where the repulsive part of the potential dominates.

In practical applications of TB potentials, it is also desirable to employ a switching function in order to terminate the potential and forces smoothly at the cut off distance, thereby preventing energy book-keeping errors due to the non-conservative nature of the many-body potential at the cut off distance. For this purpose, a simple polynomial switching function,  $S(x)$ , can be applied to the potential in a region just below the cut off distance ( $r_{\text{cut}}$ ) [47]:

$$S(x) = 1 - 6x^5 + 15x^4 - 10x^3, \quad r_{sw} \leq r \leq r_{\text{cut}}, \quad (8)$$

where  $x = (r - r_{sw}) / (r_{\text{cut}} - r_{sw})$ , and  $r_{sw}$  is the distance at which the switching function is applied.

Finally, the TB potential formalism can be extended to describe bimetallic systems, using the fitting methods described in Refs. [7, 33, 48, 49]. In general, the fitting parameters for a bimetallic system cannot be deduced from those of the pure elements alone. However, an approximate combination rule which has been used for TB and Finnis–Sinclair potentials may be useful in the absence of specific parameterisations [33, 50]. This entails choosing the potential parameters in such a way that the heteronuclear interaction terms ( $\alpha-\beta$ , for elements  $\alpha$  and  $\beta$ ) correspond to the geometric means of the respective elemental terms ( $\alpha-\alpha$ ,  $\beta-\beta$ ):

$$\begin{aligned}\phi^{\alpha\beta}(r_{ij}) &= [\phi^{\alpha\alpha}(r_{ij})\phi^{\beta\beta}(r_{ij})]^{1/2}, \\ U^{\alpha\beta} &= [U^{\alpha\alpha}(r_{ij})U^{\beta\beta}(r_{ij})]^{1/2}.\end{aligned}\tag{9}$$

The accuracy of this approximation needs to be evaluated on a case-by-case basis using suitable thermodynamic measures, and corrections may be required. In-depth investigations of bimetallic systems have not yet been carried out using the potentials discussed in this work, but preliminary calculations indicate, for example, that alloy heats of solution and surface segregation for several pairs of fcc transition metals with similar atomic radii (Ni–Cu, Rh–Pd, Pd–Ag) may be estimated with a typical error of 0.1 eV by this method [52].

## CONCLUSION

Exponential tight-binding (TB) potentials have been fitted for 26 fcc and bcc metals with a view to application in sputtering simulations, which demand a computationally non-intensive calculation scheme and a relatively short range of interaction. These analytic many-body potentials can be readily implemented into sputtering simulation codes, and it is hoped that the availability of a large set of parameters will further encourage their use in production calculations of sputtering and other bombardment phenomena.

The ability of the fitted potentials to model bulk, surface and cluster properties varies from metal to metal, being generally less satisfactory for bcc metals (except alkali metals) than for fcc metals. The properties and limitations of TB potentials in this respect are comparable to

those of EAM potentials, namely that surface energies tend to be underestimated, while small cluster binding energies are overestimated [5]. Sputter yield predictions are sensitive to the details of coordination-dependent bonding at the target surface. This is an environment in which many-body potentials, despite their shortcomings, are known to perform better than pair potentials [51]. It would be of interest to compare the predictions of sputtering simulations based on TB potentials with those based on other functional forms; good agreement between TB and EAM potentials has recently been found for Cu and Ni targets [37, 52].

## References

- [1] Urbassek, H. (1997). *Nucl. Instr. Meth. B*, **122**, 427.
- [2] Smith, R., Jakas, M., Ashworth, D., Oven, B., Bowyer, M., Chakarov, I. and Webb, R., In: Smith, R. Ed., *Atomic and Ion Collisions in Solids and at Surfaces: Theory, Simulation and Applications*, (Cambridge University Press, Cambridge, 1997).
- [3] Chatterjee, R. and Garrison, B. J. (1997). *Radiat. Eff. Def. Solids*, **142**, 127.
- [4] Carlsson, A. (1990). *Solid State Phys.*, **43**, 1.
- [5] Daw, M. S., Foiles, S. M. and Baskes, M. I. (1993). *Mater. Sci. Rep.*, **9**, 251.
- [6] Rosato, V., Guillope, M. and Legrand, B. (1989). *Phil. Mag. A*, **59**, 321.
- [7] Cleri, F. and Rosato, V. (1989). *Phys. Rev. B*, **48**, 22.
- [8] Paidar, V., Larere, A. and Priester, L. (1997). *Modelling Simul. Mater. Sci. Eng.*, **5**, 381.
- [9] Johnson, R. A. (1988). *Phys. Rev. B*, **37**, 3924 and **37**, 1621.
- [10] Kallinteris, G. C., Papanicolaou, N., Evalgelakis, G. A. and Papaconstantopoulos, D. A. (1997). *Phys. Rev. B*, **2150**, 55.
- [11] Rey, C., Gallego, L. J., Garcia-Rodeja, J., Alonso, J. A. and Iñiguez, M. P. (1993). *Phys. Rev. B*, **48**, 8253.
- [12] Williams, F. and Massobrio, C. (1991). *Phys. Rev. B*, **43**, 11653.
- [13] Finnis, M. W. and Sinclair, J. E. (1984). *Phil. Mag. A*, **50**, 45.
- [14] West, A. R., *Solid State Chemistry and its Applications* (Wiley, New York, 1984).
- [15] Kittel, C., *Introduction to Solid State Physics*, (Wiley, New York, 1986) 6th Ed.
- [16] Simmons, R. O. and Wang, H., *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook* (MIT Press, Cambridge, MA, 1977).
- [17] *Landolt-Börnstein New Series*, Vols. III-11 and III-18 (Springer-Verlag, Berlin, 1991).
- [18] Mishra, S. K. and Singh, T. N. (1990). *Phys. Stat. Sol. (b)*, **158**, 153.
- [19] *Landolt-Börnstein New Series*, Vol. III-25 (Springer-Verlag, Berlin, 1991).
- [20] Puska, M. and Nieminen, R. M., In: *Density Functional Methods in Chemistry and Materials Science*, M. Springborg Ed., (Wiley, New York, 1997) pp. 310, 323.
- [21] Ziesche, P., Perdew, J. P. and Fiolhais, C. (1994). *Phys. Rev. B*, **49**, 7916.
- [22] Moriarty, J. A. (1986). *Phys. Rev. B*, **34**, 6738.
- [23] Daw, M. S. and Baskes, M. I. (1984). *Phys. Rev. B*, **29**, 6443.
- [24] Pasianio, R., Farkas, D. and Savino, E. J. (1991). *Phys. Rev. B*, **43**, 6952.
- [25] Baskes, M. I. (1992). *Phys. Rev. B*, **46**, 2727.
- [26] Wang, C. Z., Pan, B. C. and Ho, K. M. (1999). *J. Phys. C*, **11**, 2043.

- [27] Adams, J. B. and Foiles, S. M. (1990). *Phys. Rev. B*, **41**, 3316.
- [28] Ackland, G. J. and Thetford, R. (1987). *Phil. Mag. A*, **56**, 15.
- [29] Sigmund, P. (1969). *Phys. Rev.*, **184**, 383.
- [30] Gades, H. and Urbassek, H. M. (1995). *Nucl. Instr. Meth. B*, **102**, 261.
- [31] Garrison, B. (1982). *Surface. Sci.*, **114**, 23.
- [32] Eckstein, W., *Computer Simulation of Ion- Solid Interactions* (Springer, Berlin, 1991).
- [33] Gades, H. and Urbassek, H. M. (1994). *Nucl. Instr. Meth. B*, **88**, 218.
- [34] Jackson, D. P. (1973). *Radiat. Eff.*, **18**, 185.
- [35] de Boer, F. R., Boom, R., Mattens, W. C. M., Miedema, A. R. and Niessen, A. K., *Cohesion in Metals* (North-Holland, Amsterdam, 1988).
- [36] Guellilil, A. M. and Adams, J. B. (1992). *J. Mater. Res.*, **7**, 639.
- [37] Colla, Th. J., Urbassek, H. M., Wucher, A., Staudt, C., Heinrich, R., Garrison, B. J., Dandachi, C. and Betz, G. (1998). *Nucl. Instr. Meth. B*, **143**, 284.
- [38] Calaminici, P., Russo, N. and Toscano, M. (1995). *Z. Phys. D*, **33**, 281.
- [39] Allouche, A. R., Aubert-Frécon, M., Nicolas, G. and Spiegelmann, F. (1995). *Chem. Phys.*, **200**, 63.
- [40] Morse, M. D. (1986). *Chem. Rev.*, **86**, 1049.
- [41] Stranz, D. D. and Khanna, R. K. (1981). *J. Chem. Phys.*, **74**, 2116.
- [42] Radzig, A. A. and Smirnov, B. M. (1985). *Springer Ser. Chem. Phys.*, **31**, 378.
- [43] Gades, H. and Urbassek, H. M. (1995). *Nucl. Instr. Meth. B*, **103**, 131.
- [44] Heine, V., Robertson, I. J. and Payne, M. C. (1991). *Phil. Trans. Royal Soc. A*, **334**, 393.
- [45] Painter, G. S. and Averill, F. W. (1994). *Phys. Rev. B*, **50**, 5545.
- [46] Shapiro, M. H. and Tombrello, T. A. (1994). *Nucl. Instr. Meth. B*, **84**, 453.
- [47] Goldstein, A. S. and Jónsson, H. (1995). *Phil. Mag. B*, **71**, 1041.
- [48] Mazzone, G., Rosato, V. and Pintore, M. (1997). *Phys. Rev. B*, **55**, 837.
- [49] Levanov, N., Stepanyuk, V. S., Hergert, W., Trushin, O. S. and Kokko, K. (1998). *Surf. Sci.*, **400**, 54.
- [50] Rafi-Tabar, H. and Sutton, A. P. (1991). *Phil. Mag. Lett.*, **63**, 217.
- [51] Garrison, B. J., Winograd, N., Deaven, D. M., Reimann, C. T., Lo, D. Y., Tombrello, T. A., Harrison, D. E. and Shapiro, M. H. (1988). *Phys. Rev. B*, **37**, 7197.
- [52] Karolewski, M. A. (1999). *Surf. Sci.*, **440**, 87.