Available online at www.sciencedirect.com
SCIENCE DIRECT®
Surface Science 598 (2005) 276–284
SURFACE SCIENCE
www.elsevier.com/locate/susc

Surface atomic structure and energetics of tantalum

A. Kiejna *

Institute of Experimental Physics, University of Wrocław, Plac M. Borna 9, PL-50-204 Wrocław, Poland

Received 25 July 2005; accepted for publication 2 September 2005
Available online 27 October 2005

Abstract

Electronic and structural properties of the unreconstructed low-index Ta surfaces are studied from first principles. Results for multilayer relaxations, surface energy, and work function of fully relaxed slabs are presented. All considered surfaces exhibit a large contraction of the first interplanar distance, which at the most open (1 1 1) surface amounts to 26%. The calculated surface energy anisotropy is discussed in connection with the stability of surfaces, the equilibrium shape of tantalum crystal, and the adsorbate induced faceting.

Keywords: Density functional calculations; Tantalum; Lattice relaxation; Surface energy; Work function

1. Introduction

Tantalum is a 5d transition metal which finds many useful applications, particularly within the chemical industry, electronics, in the medicine, and in the vacuum systems applications. Similarly to molybdenum and tungsten, its neighbor elements from the group VIB of the periodic table, tantalum crystallizes in a bcc structure. The lattice constants of the three metals differ within 5%. This similarity of the atomic dimensions of these metals makes them useful substrates for comparative studies of the electronic structure effects in different adsorption systems. For example, the adatom structures formed during the transition and noble metal adsorption on Ta differ qualitatively from those observed on the 5d W and 4d Mo surfaces [1]. This is rather surprising because Ta has only one electron less than W, while Mo is one period below W in the periodic table.

In order to be able to draw quantitative conclusions on the adsorption system a reliable information on the clean surface properties is necessary. Surface properties of tantalum are relatively rarely studied compared to molybdenum and tungsten. To our knowledge, no atomistic calculations of surface energy and work function of Ta surfaces, which take into account a complete relaxation of

* Tel.: +48 71 3759264; fax: +48 71 3287365.
E-mail address: kiejna@ifd.uni.wroc.pl

0039-6028/$ - see front matter
doi:10.1016/j.susc.2005.09.029

the atomic positions, have been reported so far. The existing first principles database calculations of the face-dependent surface energies [2,3], and work function [3], of numerous metals, as well as of the selected crystal planes of Ta [4] have assumed from the outset a truncated bulk geometry of the surface. However, to understand the complex reconstructions and the adsorbate-induced faceting phenomena, a detailed information on the relaxed geometry and energetics is required.

In this work the electronic and structural properties of the low-index tantalum surfaces are examined from first principles. Although their anisotropy is of fundamental interest by itself, our main motivation is to provide a solid base for the calculation of adsorption systems. It is demonstrated that surface relaxations of Ta crystal are large and affect the calculated energetic properties significantly.

2. Details of calculation

First-principles calculations are performed within density-functional theory (DFT) in the generalized gradient approximation (GGA) for the exchange-correlation energy functional [5], as implemented in the VASP (Vienna Ab initio Simulation Package) code [6,7]. A plane wave basis set with the energy cutoff of 250 eV is applied and the electron ionic–core interactions are represented by the projector augmented-wave (PAW) potentials [8]. The standard PAW potentials for Ta with 5p and 6s states treated as valence states are applied. As it was checked, using PAW potentials including 5d states into valence changed the bulk and surface properties negligibly. For the Brillouin zone integrations a set of Monkhorst–Pack [9] special k-points is applied ($18 \times 18 \times 18$ mesh for the bulk), together with a Methfessel–Paxton method [10] for the fractional occupancies, with a broadening of 0.2 eV. The calculated bulk crystal properties of bcc Ta: the lattice parameter of 3.311 Å (3.303 Å [11]) and the bulk modulus of 1.96 Mbar (2.00 Mbar [12,13]), are in a very good agreement with the experimental values (given in the brackets).

The low-index tantalum surfaces are modeled by periodic slabs consisting of 11 and 15 Ta layers, separated by several equivalent layers of vacuum, giving the total separation greater than 10 Å. In principle, an 11-layer slab is sufficiently thick to represent well all the low-index surfaces considered, to capture all relevant physics, and to avoid perturbation connected with the finite/periodic geometry. However, to account for the large and persistent relaxations at open surfaces, and to check the convergence of the results, calculations were also performed for the slabs of 15 atomic layers. The coordinates of all atoms are optimized until the forces on atoms converge to less than 0.02 eV/Å. The meshes of at least 100 special k-points [9] are used to sample the Brillouin zone of supercells representing the surfaces.

3. Results and discussion

3.1. Surface lattice relaxation

Table 1 presents calculated relaxations of atomic layers, expressed as the percentage change $\Delta_{i,i+1}$ of the interplanar distance $d_{i,i+1}$, with respect to the bulk interplanar spacing d. All considered tantalum surfaces exhibit inward relaxation of the topmost layer (Table 1), in accordance with a simple electrostatic argument [14,15]. The amount of this contraction varies however, from 5% for Ta(1 1 0) to 27% for the (1 1 1) plane. As is seen, the magnitude of the top-layer relaxation $\Delta_{12}(1\,1\,0) < \Delta_{12}(1\,0\,0) < \Delta_{12}(1\,1\,2) < \Delta_{12}(1\,1\,1)$ increases in the same order as the roughness [16] of the surface. These results for tantalum surfaces agree qualitatively with the first-principles calculations for the low-index Mo surfaces [18–20], and the measurements for the Mo(1 1 2) surface [21]. Compared to the Mo, the relaxation of Ta surfaces is substantially increased. To our knowledge the experimental data on Ta relaxation are available only for the Ta(1 0 0) [17]. They compare well with our results (Table 1). The top-layer relaxation changes only a small amount when the number of layers in a slab is increased. For deeper layers, the relaxations vary in an oscillatory way. The relaxation pattern as a function of an increasing