Electronic structure and dispersion of optical function of tantalum nitride as a visible light photo-catalyst

CrossMark

A.H. Reshak *

New Technologies – Research Center, University of West Bohemia, Univerzitni 8, 306 14 Pilsen, Czech Republic
Center of Excellence Geopolymer and Green Technology, School of Material Engineering, University Malaysia Perlis, 01007 Kangar, Perlis, Malaysia

ARTICLE INFO

ABSTRACT

Tantalum nitride Ta_3N_5, as a visible light photocatalyst is studied using the state-of-the-art full potential linear augmented plane wave (FPLAPW) method in a scalar relativistic version. The calculated energy band gap values are vary between 1.1 eV (LDA), 1.2 eV (GGA), 1.5 eV (EVGGA) and 2.1 eV (mBJ). The band gap obtained using mBJ show excellent agreement with the experimental value 2.1 eV than the previous calculation. Thus mBJ potential is applied to investigate the ground state properties of tantalum nitride. The conduction band minimum is located at Y point of BZ, while the valence band maximum is located at the center of BZ indicates that the tantalum nitride is an indirect band gap semiconductor. The calculated electron charge density contours show that covalent bond exist between Ta and N atoms. The optical properties are discussed in details to seek deeper insight for the electronic structure. The calculated uni-axial anisotropy of Ta_3N_5, indicate a strong anisotropy of the optical dielectric functions. The absorption spectrum show that the absorption occurs in the visible region which makes Ta_3N_5 as an active photocatalyst under visible light irradiation. Ta_3N_5 crystal almost behaves as transparent in the higher wavelength light.

1. Introduction

The depletion of fossil fuels and environmental problems has greatly diverted the attention of researchers towards the clean, renewable and suitable alternative to fossil fuels. Hydrogen is considered to be the next generation energy carrier. Photocatalysis, the overall splitting of water is the potential method for production of hydrogen. Tantalum nitrides have attracted great deal of interest recently due to its potential technological application. It exhibits a remarkable richness with regard to the array of equilibrium and metastable phases that can form [1,2]. Among many applications of tantalum nitrides includes diffusion barrier in integrated circuit, wear-resistance layer, used as coating in cutting tools, thin film resisters [3]. TaN also gain its importance due to its growing interest regarding its potential as electronic materials especially as barrier layer in josephson junctions, consist of superconductor/normal-conductor/superconductor (SNS) interfaces which are of great interest in connection with high speed digital electronics [4]. Takata et al. found that TaON and Ta_3N_5 evolve O_2 or H_2 through band gap excitation in the presence of sacrificial electron

donor or accepter respectively. These materials remain stable against photo-corrosion under the reaction conditions for H_2 and O_2 evolution [5]. Tantalum nitride (Ta_3N_5) is considered as the pigment material [6]. It has an orthorhombic crystal structure as determined by Brese and O'Keeffe using time of flight neutron diffraction [7]. The structure of Ta_3N_5 is composed of irregular octahedron of N atoms centered by Ta atoms [7,8]. The difficulty in the developing the successful photocatalysts is due to the lack of fundamental requirements such as band edge potentials suitable for the overall splitting of water, energy band gap (E_g) smaller than 3.0 eV and stability of the materials in the photocatalytic reaction [9–22]. The water splitting reaction on a semiconductor photocatalyst is performed in three steps (a) the photocatalyst absorbs photon energy greater than the band gap energy of the materials and generated photoexcited electron–hole pairs in the bulk. (b) The photoexcited carrier separate and move to the surface without recombination. (c) Absorbed species are reduced and oxidized by the photo-generated electrons and holes to produce H_2 and O_2 respectively. The electronic and structural properties of the photocatalyst play important role in the first two steps. High crystallinity of the structure has a great effect on the activity since the density of defects decreases with the increasing crystallinity. The last step occurs due to the presence of solid catalyst [23]. Terao [2] reported many phases of tantalum nitride which were prepared by nitriding

* Address: New Technologies – Research Center, University of West Bohemia, Univerzitni 8, 306 14 Pilsen, Czech Republic. Tel.: +420 777 729 583.
E-mail address: maalidph@yahoo.co.uk

evaporated Ta films in an atmosphere of ammonia and nitrogen. $TaN_{-0.5}$, Ta_2N, Ta_5N_6, Ta_4N_5 and Ta_3N_5 phases were obtained at the temperature range of 600–1100 °C [2]. From above we notice that there is dearth of information about the electronic structure and optical properties of tantalum nitride as a visible light photocatalyst. Therefore we thought it would be worthwhile to perform comprehensive theoretical calculations based on the self-consistent first principle calculations to obtain comprehensive information about the crystal structure, electronic band structure and optical properties of tantalum nitride, Ta_3N_5.

The main goal of the present work is to investigate the electronic band structure and the dispersion of optical properties of tantalum nitride, Ta_3N_5 as a visible light photocatalyst to solve the environmental problems and use it as clean and renewable alternative resources to fossil fuels.

2. Structural properties and computational details

The state-of-the-art full potential linear augmented plane wave (FPLAPW) method in a scalar relativistic version within the frame work of density functional theory (DFT) as implemented in the WIEN2k package [24] was employed. We have calculated the electronic band structure, total and partial density of states, the electronic charge density distribution and the dispersion of optical properties for tantalum nitride, Ta_3N_5. The exchange correlation potential were treated by four kind of approximations namely local density approximation (LDA) the Ceperley–Alder (CA) approach, generalized gradient approximation (GGA-PBE) the Perdew Becke Ernzerhof approach, Engel Vosko generalized gradient approximation (EVGGA) and the modified Becke–Johnson potential (mBJ). We treat the core states fully relativistically and the valence state scalar relativistically. The value of the angular momentum is taken to be $\ell = 10$ inside the muffin-tin spheres for both the wave-function and charge density in the self-consistent cycles. Basis set convergence was controlled by the cutoff parameter $R_{mt}K_{max} = 7$. Where R_{mt} represent smallest atomic sphere radius in the unit cell and

K_{max} is the magnitude of the largest K vector. Calculations were performed using 168 K point mesh in the irreducible Brillouin zone (IBZ). The self-consistent convergence accuracy was set at 10^{-4} Ry. Since the value of the energy gap is very crucial for the photocatalysts, therefore we need to calculate the exact and accurate value of the energy band gap. Thus the mBJ considered to be one among the best approximations in obtaining very accurate results. The mBJ, a modified Becke–Johnson potential, allows the calculation of band gaps with accuracy similar to the very expensive GW calculations [25]. It is a local approximation to an atomic "exact-exchange" potential and a screening term. In 1991, Brese and O'Keeffe [7] reported that the tritantalum pentanitride (Ta_3N_5) has been prepared from the reaction of $TaCl_5$ with ammonia and refined structure was obtained by time of flight neutron diffraction data. They found that the crystal structure of Ta_3N_5 is orthorhombic with space group *Cmcm* (see Fig. 1). The atomic positions and lattice constants are given in Table 1.

3. Results and discussion

3.1. Band structure and density of states

Electronic band structure play vital role in studying the materials and show the value of energy gap E_g between the conduction

Table 1
Lattice parameter and atomic positions of Ta_3N_5 [7].

Lattice parameter (Å)		a	b	c
		3.8862	10.2118	10.2624
Atom	Wyckoff sites	x	y	z
Ta1	4c	0	0.1971	0.25
Ta2	8f	0	0.13455	0.55906
N1	4c	0	0.76322	0.25
N2	8f	0	0.04701	0.11949
N3	8f	0	0.30862	0.073378
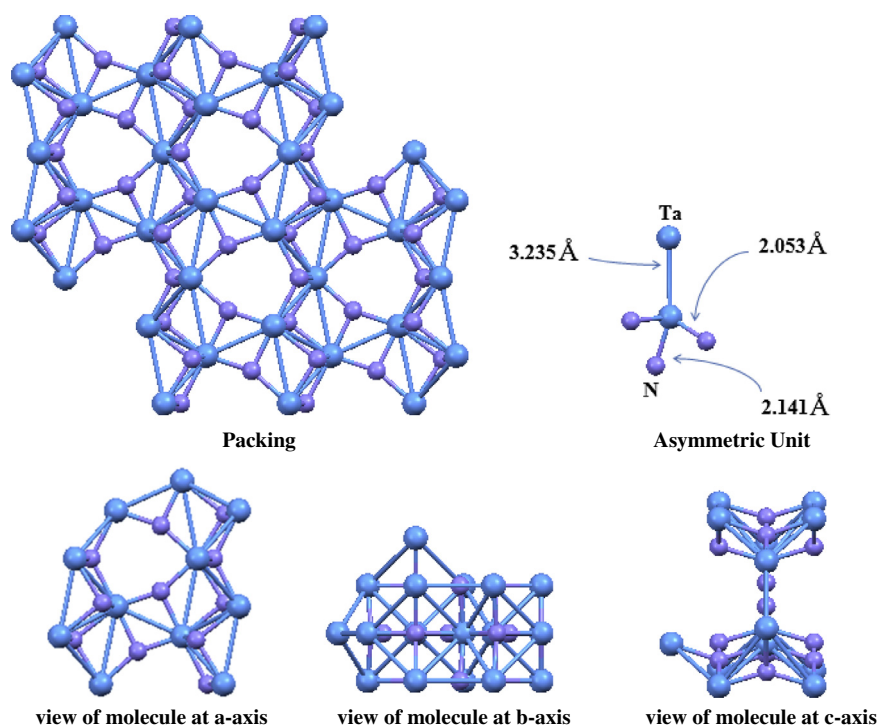
Fig. 1. Unit cell structure of Ta_3N_5.