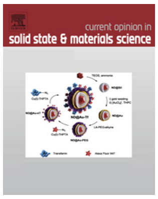
Current Opinion in Solid State and Materials Science xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Current Opinion in Solid State and Materials Science

journal homepage: www.elsevier.com/locate/cossms



Electronic band structure and electron transfer properties of two-dimensional metal oxide nanosheets and nanosheet films

J.E. ten Elshof

MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, Netherlands

ARTICLE INFO

Article history:
Received 21 July 2017
Revised 21 August 2017
Accepted 29 August 2017
Available online xxxx

Keywords:
Two-dimensional materials
Oxides
Semiconductors
Band gap
Conductivity
Defects
Langmuir-Blodgett films
Heterostructures

ABSTRACT

The electronic properties of 2-dimensional metal oxide nanosheets are reviewed. Although the band structures of 2D nanosheets bear some resemblance with the band structures of the 3D parent compounds from they are derived, their 2D nature may have a profound influence on the location of the valence and conduction bands. The presence of structural defects, aliovalent dopants, and adsorbed molecules affects the mobility and concentration of charge carriers, and may even influence the band structure. The ability to transfer electrons to and from nanosheets is controlled by the charge density of the nanosheet, and/or the presence of electron donating or accepting species in the immediate vicinity. Charge transport and electron transfer in multilayer films and heterostructures are also discussed.

1. Introduction

Two-dimensional materials have been receiving considerable attention since the discovery of graphene in 2004 [1]. There is currently still a large interest in graphene and other Van der Waals materials like h-BN, transition metal dichalcogenides such as MoS_2, and several others [2]. Somewhat less well known are the two-dimensional metal oxide equivalents of Van der Waals materials, commonly named 'oxide nanosheets'. They are two-dimensional ionic crystallites with a thickness of about 0.5–3 nm and lateral dimensions between ~50 nm and ~50 µm [3,4]. Single layer oxide nanosheets are derived from layered ionic parent compounds, such as layered titanates, niobates, tungstates, managanites, Dion-Jacobson phases, etc. using a chemical exfoliation process in a solvent, typically water [4–8]. The parent crystal structures can be thought of as consisting of anionic oxidic layers that are stacked and kept together via interlayers of exchangeable, monovalent cations. By removing the interlayer cations, the crystal delaminates into the anionic layers. For example, the Dion-Jacobson layered oxide $KCa_2Nb_3O_{10}$ can be exfoliated into unilamellar $Ca_2Nb_3O_{10}^-$ nanosheets of 1.44 nm thickness [9] by the following two-step process:

$$KCa_2Nb_3O_{10}(s) + H^+(aq) \rightarrow HCa_2Nb_3O_{10}(s) + K^+(aq) \qquad \text{step 1}$$

$$HCa_2Nb_3O_{10}(s) + TBAOH(aq) \rightarrow Ca_2Nb_3O_{10}^-(aq) + TBA^+(aq) + H_2O \qquad \text{step 2}$$

The first step is an ion-exchange process in which the interlayer cation K^+ is replaced by H^+. In the second step, the fast acid-base reaction between OH^- from tetrabutyl ammonium hydroxide (TBAOH) and the interlayer protons from $HCa_2Nb_3O_{10}$ ensures destabilization of the ionic interactions that keep the layered $HCa_2Nb_3O_{10}$ parent crystal intact, and results in the formation of a colloid of unilamellar nanosheets [10]. The negatively charged nanosheets in solution are charge-compensated and stabilized by quarternary ammonium ions, NR_4^+ (R = Bu, Pr, Et, Me) in their immediate vicinity, usually $N(C_4H_9)_4^+$ (TBA^+). Since the parent 3D crystals are grown by a solid state reaction at high temperatures, the nanosheets are thermodynamically equilibrated, i.e. they have a high crystallinity and low point defect density. Other oxide nanosheets can be made via the same or related soft exfoliation routes. The net negative ionic charge on nanosheets makes the presence of counter ions necessary in order to maintain local charge neutrality, and in this respect oxide nanosheets differ fundamentally from Van der Waals materials. But the counter ion is not an irreversible part of the ionic nanosheet lattice and can be replaced by exchange. Due to its close proximity and Coulombic charge, the counter ion may exert an influence on the physical properties of nanosheets.

E-mail address: j.e.tenelshof@utwente.nl

http://dx.doi.org/10.1016/j.cossms.2017.08.004
1359-0286/

Please cite this article in press as: J.E. ten Elshof, Electronic band structure and electron transfer properties of two-dimensional metal oxide nanosheets and nanosheet films, Curr. Opin. Solid State Mater. Sci. (2017), http://dx.doi.org/10.1016/j.cossms.2017.08.004

The as-prepared nanosheet colloids have been employed to fabricate monolayer and multilayer films, layered nanocomposites, superlattices, and porous microstructures using methodologies like layer-by-layer (LbL) assembly, controlled precipitation and Langmuir–Blodgett deposition [11–15]. The synthesis of nanosheets, their assembly into functional structures and several of their applications have been discussed comprehensively in several recent reviews [6,9,16–19]. For a general introduction into the topic of 2D oxide nanosheets, the reader is referred to these papers. Regarding their electronic behavior, metal oxide nanosheets present an extremely interesting class of 2D materials. Since most metal oxides are semiconductors, they have semiconducting, optical and charge transfer (redox) properties that make them potential candidates for application in a diverse range of technologies where such properties are of crucial importance, in particular in the areas of nanoelectronics [9,20], energy materials [17,21] and (bio)sensing [22–25]. The development of innovative materials and devices based on 2D materials such as Li batteries, photocatalysts, supercapacitors, field effect-based sensors, half-metals and high-*k* dielectric layers all require materials with tailored electronic properties.

In view of the importance of the electronic structure of 2D oxide materials for the above-mentioned range of applications, a concise review of experimental and theoretical studies on various aspects of the electronic band structure and transport properties of oxide nanosheets is presented here. At first glance, the electronic properties of nanosheets bear some resemblance with the electronic properties of their layered 3D parent compounds. However, the 2D nature has several specific consequences. Firstly, spatial confinement of the crystal in one dimension influences the band structure and splitting of the energy levels. Secondly, since all atoms in 2D materials are at or very close to the surface, all electronic properties are strongly influenced by the environment in which the nanosheets reside. Adsorbed species may act as dopants and influence the concentration and mobility of charge carriers within the sheet. Coulombic charges and fields generated within the oxide are screened by counter ions and the polarizability of the surrounding medium. Space charge layers which are common in 3D semiconducting oxides are therefore absent. Thirdly, the geometry of nanosheets imposes a highly anisotropic conductivity, allowing easy carrier transport in the plane of the crystal lattice, while electron transfer (redox) reactions are dominant in the out-of-plane direction.

In the next section, existing knowledge on the electronic band structure of various oxide nanosheets is summarized, with emphasis on the effect of quantum confinement and composition on the band gap. Then, the influence of point defects and aliovalent dopants in nanosheets on their electronic properties is discussed. The topic of ection 4 is charge transport through nanosheets, charge transfer to/from nanosheets, and electron-hole generation and annihilation within the nanosheet. Charge transfer in nanosheet assemblies, i.e., restacked powders, Langmuir-Blodgett multilayer films and heterostructures is discussed in ection 5, followed by some concluding remarks in the final section.

2. Electronic band structure of metal oxide nanosheets

Most oxide nanosheet compositions that are discussed in this paper are *n*-type semiconductors with a relatively wide band gap. The most thoroughly explored class are titanate nanosheets $Ti_{1-x}O_2$ ($x = 0.09–0.13$). The main contribution to the valence band of titanium oxide nanosheets are Ti 3*d*-O 2*p* bonding interactions. The conduction band mainly consists of Ti 3*d* states antibonding with O 2*p*. The octahedral oxygen ligand shell surrounding Ti centers splits the conduction band further into Ti 3*d* e_g states at 5–8 eV, and t_{2g} states at 2–5 eV [26]. In some cases the band structure of oxide nanosheets can be considered as a 2-dimensional analogue of the band structure of structurally similar 3-dimensional oxides. For example, the calculated band energy diagrams of stacked and single-layered $Ti_{1-x}O_2$ nanosheets are very similar to the band structure of anatase [26], see Fig. 1. The structural similarity between (restacked) $Ti_{1-x}O_2$ nanosheets and anatase is well known. Restacked nanosheets can even be transformed topotactically into anatase [27].

The band gap of 2D titanate crystals (0.75 nm thick) is considerably larger than that of bulk anatase, however. Band gap values for $Ti_{1-x}O_2$ nanosheets as determined by electrochemical (Mott-Schottky method), photochemical, optical (Tauc plot), conductive atomic force microscopy and scanning tunneling microscopy are consistently reported to be in the range of 3.8–4 eV, compared to ~3.2 eV for anatase [28–31]. Absorption at sub-band gap wavelengths has also been observed and is ascribed to intraband transitions by electrons occupying conduction band states. A difference of ~0.6 eV is also found between the band gaps of the layered protonated titanates $H_yTi_{1-x}O_2$, and their exfoliated 2D counterparts, i.e. unilamellar titanate nanosheets in water [32], as well as in other layered titanates [33]. The larger band gap in nanosheets has been attributed to the influence of quantum confinement in a quasi-2D arrangement, although the additional influence of structural changes upon exfoliation cannot be excluded [28]. In quantum mechanics, the particle in a box model predicts that the energy level E_n of a quantum mechanical particle-wave that is confined to a box of dimensions L, scales with L^{-2}. Hence, for an oxide nanosheet with lateral dimensions L_x and L_y and thickness L_z, the

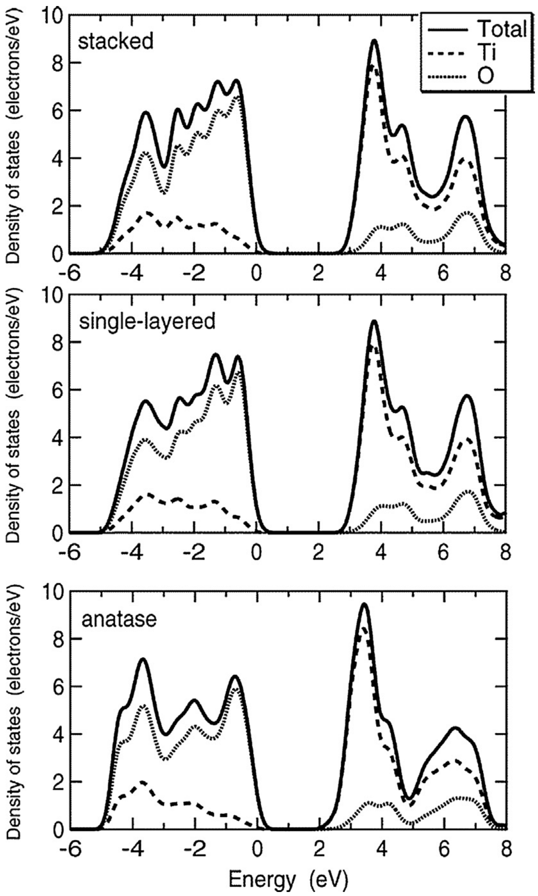


Fig. 1. Total and partial density of states for (a) restacked TiO_2 nanosheets; (b) a single-layered TiO_2 nanosheet, and (c) anatase. Adapted with permission from Ref. [26]. Copyright 2003 American Chemical Society.

Please cite this article in press as: J.E. ten Elshof, Electronic band structure and electron transfer properties of two-dimensional metal oxide nanosheets and nanosheet films, Curr. Opin. Solid State Mater. Sci. (2017), http://dx.doi.org/10.1016/j.cossms.2017.08.004