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M. V. Strikha[1,2], D. V. Antoniuk[1]

A theoretical model for estimation of work function reduction for MXenes with hydroxyl termination

[1]*Taras Shevchenko National University of Kyiv, Faculty of radiophysics, electronics and computer systems, Akademika Hlushkova Ave 4g, Kyiv, Ukraine*
[2]*V.E. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Nauky Ave, 41Kyiv, Ukraine, maksym_strikha@hotmail.com*

This article presents a simple model that explains significant reduction of work function in MXenes $Ti_{n+1}C_n$ with hydroxyl termination and demonstrates matching results to ones in the existing literature, obtained via complex computing based on the first principles. This model can be applied for results evaluation of the hydroxy functionalization of various MXene types, due to prospects of the creation of novice emission electronics devices

Keywords: MXenes, work function, surface termination, hydroxy group.

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Introduction

MXenes are a type of two-dimensional materials that has been firstly described in 2011 in work [1] co-authored by Yuri Gogotsi, Ukrainian by origin, who still retains his professor position at Sumy State University. Generalized formula for MXene $M_{n+1}X_nT_x$ includes n+1 atomic layers of transition metal M (denoted as M_{n+1}), with n monoatomic layers of carbon or nitrogen in-between them (X_n); such sandwich-like structure can include different terminations (F, O, Cl, OH), denoted as T_x (see Fig. 1). Currently, a term "multi-layer MXene" describes a structure with five or more layers of transition metal.

The distinctive features of MXenes gained public attention: within a decade after the discovery of MXenes, articles about MXenes were published in more than 400 journals by more than 8300 researchers from 1450 institutions in 62 countries (according to estimations in [2]). Due to the varying stoichiometry and surface organization, MXenes have a range of physical and chemical features that can be controlled. MXenes have a variable band gap, which depends on the method of surface termination, high electric conductivity, high Young's modulus, ultra-low optical attenuation etc. Currently MXenes are used in modern energy storage and conversion devices, electronics, sensors, medicine etc (see review article [3] with references therein).

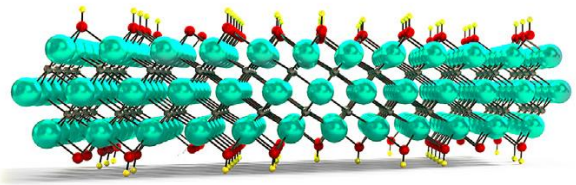

Fig. 1. The first MXenes structure $M_3X_2T_x$, described in [1], that contains three layers of transition metal Ti (big lighter balls), two carbon layers between them (small darker balls), and surface termination of hydroxy groups OH (oxygen atoms are located closer to atoms of metal, while atoms of hydrogen are farther from atoms of metal) above and below.

MXenes can potentially be used for the creation of cathodes with low work function for emission electronics. As per today, caesium is standard material with low work function 2.1 eV [4], its usage, however, is limited due to its high toxicity. Thus, alternative approaches for creation of modern cathodes are considered that are based on the adsorption of alkaline and rare earth metals (Ce, Gd, Eu),

and co-adsorption on surfaces of Si, Ge, and Mo, also in nanostructured state, where double-charged layers can be created, which significantly reduce work function [5, 6].

Work function of MXenes with surface O, F, OH functionalization was estimated in [7] based on the first principles. It shows that oxygen or fluorine functionalization leads to insignificant increase or reduction of work function, while hydroxyl-terminated MXenes can show low work function in 1,6-2,8 eV range. Here, the intrinsic dipole moment of the OH hydroxyl group is the main factor in work function reduction.

The computations in [7] were carried out with the use of bulky computing packages, and therefore lack the necessary clarity. Thus, a simple theoretical model is needed that allows estimate a possible range of changes in work function affected by MXenes' surface functionalization by hydroxy groups.

Theoretical model

Generally, the change in work function under the influence of adsorbates applied to the surface is caused by three factors: a) redistribution of electronic charge between the surface and adsorbates; b) relaxation of the surface caused by adsorbates; c) polarity of adsorbates [8]. In this paper, we consider MXenes that can be associated with lower work function, i.e., MXenes based on titan and carbon layers (the type, first studied in [1]; see Fig. 1).

Generally, unterminated MXenes are metals or semimetals (semiconductors with a zero-band gap); the high value of density of electronic states close to the Fermi level is caused by the outer layers of transition metals (see [3]). However, already in [1] it was experimentally shown that surface termination of Ti_3C_2 by a hydroxy group led to the creation of a band gap of ca 50 meV, turning such MXene into a semiconductor.

Thus, surface concentration of hydroxy groups exceeds concentration of conductivity carriers in this material. As Fig. 1 demonstrates, these hydroxy groups create on the surface a monolayer with the same number of dipoles as the number of atoms in the transition metal layer under it. Since the band gap width exceeds 26 meV (which is an energy at the room temperature), then under ambient conditions, each of these metal atoms corresponds to less than one conduction electron, while each of the dipoles corresponds to a negative electronic charge localized near the oxygen atom and a positive one localized near the hydrogen atom. Terminalization shown in Fig. 1, is also not accompanied by a noticeable surface reconstruction of Ti atoms. This means that in the first approximation for the functionalized MXenes based on titanium and carbon, we can neglect the redistribution of the electronic charge between the surface and the adsorbates, and the relaxation of the surface caused by the adsorbates, so that the work function reduction will be caused mainly by the dipole moments of the hydroxyl groups.

The energy level structure, which arises at the boundary between hydroxyl terminated MXene and vacuum, is shown in Fig. 2 (We presented a similar model in [9] to explain the reduction of the electron affinity caused by the presence of two layers of adsorbates, negatively and positively charged, on the semiconductor surface, which corresponds to the experimental situation studied in [5, 6]). At the same time, we assume that the Fermi level coincides with the edge of the conduction band in MXenes).

Since the distance between the hydrogen and oxygen atoms in the hydroxyl group is d = 0.97 A, this gap is tunnel-transparent for thermal electrons near the bottom of the conduction band in the MXene (whose wavelength is an order of magnitude longer), and they freely tunnel from the MXene into vacuum. Therefore, the effective work function from hydroxylfunctionalized MXene (see Fig. 2) is equal to:

$$e\Phi_k = e\Phi_0 - e\Delta\Phi. \qquad (1)$$

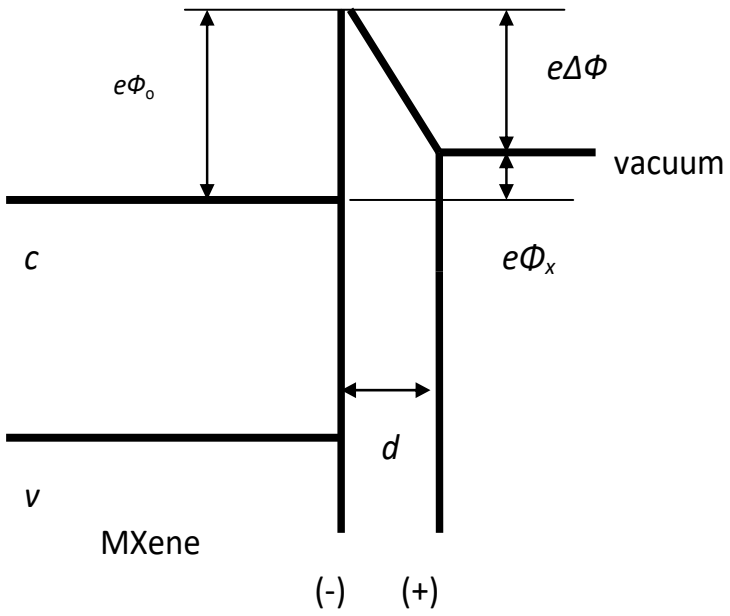

Fig. 2. MXene's work function reduction affected by dipole moment of the hydroxyl group on the surface.

ΔΦ in the right-hand side of (1) can be estimated from the flat capacitor formula:

$$\Delta\Phi = \frac{eN_S d}{\varepsilon_0 \varepsilon}, \qquad (2)$$

where N_s is surface density of dipoles, ε_o – a dialectic constant of vacuum, ε – a dielectric permittivity of the gap between charged planes.

Discussion

Assuming that $N_s \sim 5 \cdot 10^{18} м^{-2}$, $\varepsilon \sim 10$ (typical value of the dielectric permittivity for semiconductors) and $d \sim 1 \times 10^{-10}$ m, we obtain $\Delta\Phi \sim 3$V. The value of the work function of MXene non-functionalized by hydroxy groups is equal ~ 4,5 eV and does not depend on surface number of Ti and C (in a 1-9 range that could be estimated by computation packages in [7]); after the functionalization, the value lowers to ca 1,6 eV and similarly does not depends on the amount of MXene' surfaces [7].

Thus, the proposed model not only provide qualitative explanation of the significant work function reduction in $Ti_{n+1}C_n$ with hydroxy termination (clearly illustrated in fig. 2), but also matches the results of a complex and cumbersome numerical calculation of [7] based on first principles. This model can be used for evaluation of the hydroxy functionalization results of various MXene types, based on their application prospects in modern emission electronics.

Strikha M. V. – Doctor of Sciences in Physics and Mathematics, Professor, Professor of the Physical electronics department of the Faculty of radiophysics, electronics and computer systems at Taras Shevchenko National university of Kyiv, chief researcher at V.E. Lashkaryov Institute of Semiconductor Physics, National Academy of Science of Ukraine;
Antoniuk D.V. – student of the Faculty of radiophysics, electronics and computer systems at Taras Shevchenko National university of Kyiv.

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М.В. Стріха[1,2], Д.В. Антонюк[1]

Теоретична модель для оцінки зниження роботи виходу максенів з гідроксильною термінацією.

[1]Київський національний університет ім. Тараса Шевченка, факультет радіофізики, електроніки і комп'ютерних систем, пр. Глушкова, 4г, Київ, Україна;
[2]Інститут фізики напівпровідників ім. В.Є.Лашкарьова НАН України, пр. Науки, 41, Київ, Україна,
maksym_strikha@hotmail.com

Запропонована проста теоретична модель для пояснення значного зниження роботи виходу в максенах $Ti_{n+1}C_n$ з гідроксильною термінацією. Модель демонструє добрий чисельний збіг із наявними в літературі результатами складного комп'ютерного розрахунку виходячи з першопринципів. Вона може бути використана для оцінки наслідків функціоналізації гідроксильними групами різних типів максенів, з огляду на перспективу створення новітніх приладів емісійної електроніки.

Ключові слова: максени, робота виходу, термінація поверхні, гідроксильна група.