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XPS and ab initio study of the interaction of PbTe with molecular oxygen

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Abstract

Density functional (B3LYP) calculations have been performed to investigate the adsorption of $O_2(^3\Sigma_g^-)$ molecule on the surface of cluster $(PbTe)_4$. To study the influence of point defects (namely, impurity atoms and cation and anion vacancies) on the reactivity of PbTe surface, clusters $(PbTe)_3GeTe$, $(PbTe)_3GaTe$, $(PbTe)_3Te$, and $(PbTe)_3(Pb)$ were investigated. The adsorption of oxygen on the surface of $(PbS)_4$ cluster was calculated to evaluate the role of anions in the adsorption process. It was shown that the formation of the peroxide-like complex is the first step of adsorption. The calculated tendency to surface oxidation increases in sequence: PbTe with cation vacancies <PbS < pure PbTe < PbTe doped with Ga < PbTe doped with Ge < PbTe with anion vacancies. The results of quantum-chemical calculations correlate with X-ray photoelectron spectroscopy data.

Keywords: Density functional calculations; X-ray photoelectron spectroscopy; Oxidation; Lead telluride; Sulphides

1. Introduction

Over the last decade, the number of experimental and theoretical methods of the surface reactivity studies has markedly grown [1]. The application of quantum chemical approaches to the interpretation of experimental data became one of the most powerful tools of surface investigation. Quantum chemical calculations are especially important in the case of atomic-scale experimental methods (e.g. STM/STS, SR XPS, PED, SEXAFS, XSW, etc.). They may be of great help for both the comprehensive interpretation of experimental results and quantitative assessment of different groups of experimental data, i.e. the spectroscopic data, which show energetic features,

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and the microscopic or diffraction ones, which concern the atomic-scale geometry.

Lead chalcogenides belong to A^4B^6 semiconductors; they are widely applied for infra-red devices production [2]. It is commonly accepted that the reactions at semiconductor surfaces may lead to certain changes in electrophysics and exploitation characteristics; they should be also taken into account during heterostructures preparation and film growth [3]. The surface reactivity of lead chalcogenides was thoroughly investigated for PbS only; the reactions at the surfaces of other A^4B^6 compounds are less explored.

The interaction of PbS(1 0 0) surface with oxygen has been studied using a wide range of surface analysis methods. Lead sulphide, which occurs naturally in the form of galena mineral, was investigated particularly relative to its industrial and environmental importance. Galena was found to be rather resistive to air oxidation, e.g. in [4] the sample was exposed to air for 4 days before any oxidation products were revealed at the surface. The mechanism of galena oxidation was found to be rather complex. It includes the initial formation of sulphoxy species [5], which is followed by the formation of PbO, $Pb(OH)_2$, $PbCO_3$, SO_2 and $PbSO_4$ depending on the conditions and duration of the oxidation experiment [4–6]. The results of XPS and STM studies suggest that after the formation of sulphoxy species some sulphur atoms can leave the surface in the form of SO_2, this being followed by the formation of lead hydroxide and carbonate [5,6]. Lead sulphate was concluded to be the main oxidation product after prolonged exposure to air [4,7]. It was reported that the concentration of point [8] and dimensional defects [9] plays key role in the oxidation mechanism, in particular, the surface of a natural galena with ∼1000 ppm impurities oxidises much faster than that of a synthetic sample [8].

The oxidation of lead telluride surface is less explored [10–14]. The absorption study of PbTe(1 0 0) surface by Green and Lee [10] allowed to suggest that during the oxygen adsorption the peroxide-like surface complex is formed up to 70% coverage of the surface, this being proved by the calculation of the corresponding chemisorption heats. The adsorption of oxygen is a two-step process, as the initial weak bonding of oxygen is followed by the chemisorption. The two-step oxygen absorption was also observed for (1 1 1)-oriented films of PbTe in the XPS study [11]; it was shown that the rate of the second step is lower than that of the first step of oxygen uptake. The main oxidation products were proposed to be PbO and TeO_2 [12]. However, recently we have shown that the oxidised layer stoichiometry is close to lead tellurite ($PbTeO_3$) [13]. Hagström and Fahlman [14] performed a comparative study of the interaction of oxygen with PbTe and PbS(1 0 0) surfaces by means of UPS and XPS. They found that PbS surface is hardly oxidised even at 10^{12} L exposures, whereas for PbTe the oxidation starts at ca. 10^7 L exposures and includes two steps, as described above.

The introduction of Sn and Ge impurities into PbTe leads to changes in the surface oxidation mechanisms. For $Pb_{0.8}Sn_{0.2}Te(1 1 1)$ films the fast oxidation of Sn atoms to +4 state was observed in the XPS study [12]; during the oxidation process the surface is strongly depleted in tellurium and is enriched with lead and especially tin. The dominant role of Sn impurity atoms in the chemisorption of oxygen on $Pb_{0.8}Sn_{0.2}Te(1 1 1)$ surface was proved in [15] by means of XPS, AES and UPS. It was shown that the oxidation of Sn starts at exposures of 10^4 L, whereas the oxidation of Pb and Te starts at exposures $>10^6$ L. The oxidation of $Pb_{0.93}Ge_{0.07}Te(1 0 0)$ crystal surface is observed even after few minutes of air exposure; after 20 min of exposure the surface germanium atoms are fully oxidised to oxidation state +4, this being followed by slow oxidation of Te and Pb atoms [16]. However, in this case no surface enrichment in Ge was observed, in contrast to $Pb_{0.8}Sn_{0.2}Te$. It should be mentioned that some surface enrichment in lead was observed for pure, Ge- and Sn-doped PbTe [12,15,16].

Recently several ab initio quantum chemical studies of the reactivity of lead chalcogenides surfaces have been undertaken; most of them deal with the interaction of clean PbS(1 0 0) surfaces with water molecule, which can be of great importance for galena industry [17–19]. The interaction of oxygen with PbS surface was studied in [20] in attempt to predict the STM images, STS