Applied Surface Science 344 (2015) 65–78

Contents lists available at ScienceDirect

Applied Surface Science

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

Methane adsorption characteristics on β-Ga_2O_3 nanostructures: DFT investigation

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ARTICLE INFO

Article history:
Received 10 December 2014
Received in revised form 12 March 2015
Accepted 13 March 2015
Available online 21 March 2015

Keywords:
Ga_2O_3
Adsorption
Density of states
Mulliken population
Nanostructures

ABSTRACT

The electronic properties, structural stability and adsorption properties of methane on pristine, Sn, Cu and N substituted β-Ga_2O_3 nanostructures are successfully investigated through density functional theory with B3LYP/LanL2DZ basis set. The structural stability of β-Ga_2O_3 nanostructures is described in terms of formation energy. The electronic properties of pristine, Sn, Cu and N substituted β-Ga_2O_3 nanostructures are discussed with electron affinity, HOMO–LUMO gap and ionization potential. Dipole moment and point symmetry of pristine, Sn, Cu and N substituted β-Ga_2O_3 nanostructures are also discussed. The adsorption properties of CH_4 on β-Ga_2O_3 materials are studied and the suitable adsorption sites are reported. The important parameters such as energy gap, adsorbed energy, Mulliken population and average energy gap variation are used to identify the prominent site of CH_4 adsorption on β-Ga_2O_3 base material. β-Ga_2O_3 nanostructure can be tailored with proper substitution impurity to improve the adsorption characteristics of methane on β-Ga_2O_3 nanostructures in mixed gas atmosphere.

1. Introduction

Methane (CH_4) is a flammable, colorless and odorless gas, which finds its importance in industrial and domestic applications. Methane is piped into homes for cooking, domestic heating and also used as chemical feedstock to provide methanol, hydrogen and so on. Moreover, methane is non-toxic and highly flammable gas, which is evolved due to the reaction with other hazardous gases in the air. The explosive threshold limit for methane is reported to be approximately 5% [1]. Besides, low cost, high performance, real time and high sensitive sensor are required to detect methane.

Monoclinic gallium oxide (β-Ga_2O_3) is a wide band gap material with a band gap of 4.2–4.9 eV [2]. Pristine or doped Ga_2O_3 has a wide range of application in gas sensors [3–6], phosphors [7], transparent conducting electrodes [8] and dielectric gates [9]. Thin film based Ga_2O_3 is a promising material to sense oxygen at high temperature in the range of 600–1000 °C [10,11]. Ga_2O_3 can also be utilized for sensing reducing gases such as CO, H_2, CH_4 at high temperature [12,13]. Nanostructured semiconductor gas sensors attract scientific community owing to its superior spatial resolution, high sensitivity and rapid response due to high surface to volume ratio in thin films [14–18]. However, enhancing the detection limit and response toward target gas is a challenging task. In addition to surface functionalization [19,20], doping [21–23] and fabrication of heterostructures [24–26] are the general techniques for improving the stability, sensitivity and response of metal oxide sensors. Among these techniques, doping of Pt and Pd in pristine Ga_2O_3 is effective since, the sensor resistance varies exponentially when target gas is exposed to Ga_2O_3 base material at an ambient temperature. Kim et al. [27] reported that the enhancement of CO gas-sensing properties of Pt-functionalized Ga_2O_3 nanowires is possible. Fleischer and Meixner [28] reported selective CH_4 sensor using semiconducting Ga_2O_3 thin films based on temperature switching of multigas reactions. From the reports, it is inferred that the doping of foreign elements in β-Ga_2O_3 nanostructures will enhance the gas sensing properties. Zhang et al. [29] reported the first-principles study on the electronic structure and optical properties of Sn-doped β-Ga_2O_3. Pandeeswari and Jeyaprakash [30] reported the sensing response of β-Ga_2O_3 thin film toward ammonia vapors and its influencing factors at room temperature. Xiao et al. [31] studied the electronic structure and magnetic interactions in Ni-doped β-Ga_2O_3 from first-principles calculations. Guo et al. [32] reported the electronic structure and magnetic interactions in Zn-doped β-Ga_2O_3 from first-principles calculations. Yan et al. [33] reported the first-principles study on the electronic structure and optical properties of Cu-doped β-Ga_2O_3. Density functional

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http://dx.doi.org/10.1016/j.apsusc.2015.03.069
0169-4332/

theory (DFT) is a promising method to investigate the interaction between compounds and adsorption properties of compounds [34]. Based on these facts, literature survey was conducted and it was known that no major work is reported based on DFT methods to study the adsorption characteristics of CH_4 on β-Ga_2O_3 nanostructures. The inspiration behind this work is to enhance the CH_4 adsorption characteristics on β-Ga_2O_3 nanostructures with dopants. The novel aspect of the present work is to investigate the adsorption properties of CH_4 on various sites of β-Ga_2O_3 nanostructures with the incorporation of Sn, Cu and N as substitution impurities.

2. Computational details

The pristine, Sn, Cu and N substituted β-Ga_2O_3 nanostructures are successfully optimized using Gaussian 09 package [35]. This package is used to study the adsorption properties of CH_4 gas molecules on β-Ga_2O_3 base material. In this work, DFT is used in accordance with Becke's three-parameter hybrid functional in combination with Lee–Yang–Parr correlation functional (B3LYP) with LanL2DZ basis set. The selection of the proper basis set is an important key factor for optimizing β-Ga_2O_3 nanostructures. Since the atomic number of gallium and oxygen is thirty-one and eight respectively, LanL2DZ basis set is a good choice among other sets and it provides a consistent output with pseudo potential approximation [36,37]. The density of states (DOS) spectrum and HOMO–LUMO gap of β-Ga_2O_3 nanostructures is obtained using Gauss Sum 3.0 package [38]. The energy convergence is attained in the range of 10^{-5} eV, during the optimization of β-Ga_2O_3 nanostructure.

3. Results and discussion

The main focus of the present work is in the investigation of HOMO–LUMO gap, ionization potential (IP), Mulliken population, electron affinity (EA), dipole moment and adsorption characteristics of CH_4 gas molecules on β-Ga_2O_3 base material with the substitution impurities such as Sn, Cu and N in β-Ga_2O_3 nanostructures. The reason behind the selection of Sn, Cu and N as dopants is that Cu belongs to fourth period like Ga. Moreover, Cu has two electrons deficient when compared to Ga atom, which will change the electronic properties. In the case of Sn substitution, Sn is also a group IVA elements with the electronic configuration of *[Kr] $4d^{10}$ $5s^2$ $5p^2$*. The substitution of Sn with gallium results in the change of electron density, which consequences the conductivity of β-Ga_2O_3 base material. Besides, nitrogen is deficient in electrons compared to oxygen, which also exhibits the change in electronic properties. Based on these reasons, the impurities are chosen to substitute in Ga_2O_3 base material and these elements change the conducting property enormously in β-Ga_2O_3 base material. Thus, the adsorption properties of CH_4 on β-Ga_2O_3 nanostructures can be enhanced with the dopant. Fig. 1(a)–(d) refers to the structure of pristine, Sn, Cu and N substituted β-Ga_2O_3 nanostructures respectively. The structure of β-Ga_2O_3 is taken from International Centre for Diffraction Data (ICDD) card number: **74-1776**. The pristine β-Ga_2O_3 nanostructure has twenty Ga atoms and twenty-five oxygen atoms. Sn substituted β-Ga_2O_3 nanostructure contains eighteen Ga atoms, twenty-five O atoms and two Ga atoms are replaced with equivalent two Sn atoms for enhancing adsorption properties of CH_4 on β-Ga_2O_3 base material. Similarly, Cu substituted β-Ga_2O_3 nanostructure has twenty-five O atoms, eighteen Ga atoms and two Ga atoms are replaced with two Cu atoms. N substituted β-Ga_2O_3 nanostructure has twenty Ga atoms, twenty-two O atoms and three O atoms are replaced with three N atoms.

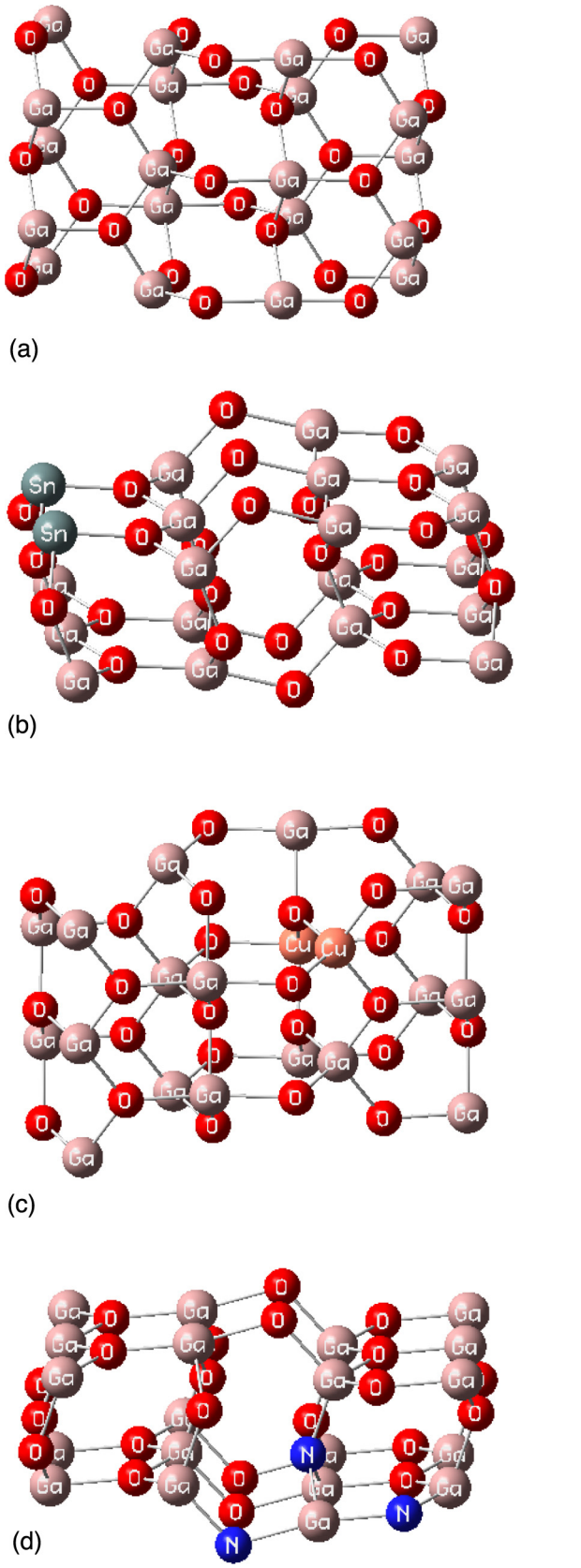

Fig. 1. (a) Pristine β-Ga_2O_3 nanostructure, (b) Sn substituted β-Ga_2O_3 nanostructure, (c) Cu substituted β-Ga_2O_3 nanostructure, (d) N substituted β-Ga_2O_3 nanostructure.