Journal of Electron Spectroscopy and Related Phenomena 227 (2018) 15–22

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

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

First-principles insights on the electronic and field emission properties of Ga and Al doped germanium nanocones

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ARTICLE INFO

Keywords:
Germanium
Nanocone
Field emission
Charge transfer
Work function

ABSTRACT

Density functional theory (DFT) simulations have been performed to study the field emission characteristics of pristine, Ga, and Al substituted germanium nanocone (Ge-NC). The influence due to the substitution of group-III elements on Ge-NC is studied using the density of states (DOS) spectrum and electron density. As a matter of fact, from the molecular electrostatic potential surface, it is noticed that the impurity substitution at the apex of Ge-NC leads to increase in the field emission properties due to delocalization of electron by the charge transfer at the apex of nanocone. In addition, the Mulliken charge transfer, work function and current density of the emitted electron were calculated for the pristine and Ga and Al-doped Ge-NC. The results suggest that the substitution of group-III impurity along the apex of Ge-NC leads to the improved field emission, which can be used for the assembly of vacuum electronics and nanoelectronics.

1. Introduction

The impurity-doped semiconductor with different nanostructures is found to have more applications than the intrinsic one, which is the prime focus among the research community. Owing to the increase in conductivity (decrease in the band gap between the conduction band and the valence band), the doped semiconductors are employed in devices such as detectors, rectifiers, sensistors, thermistors, solar cells and in the components like integrated circuits (heavily doped one). Habib Ullah group [1–5] have broadly demonstrated the application of various organic compounds in the field of chemical sensors, various toxic gas/vapor sensors & photocatalyst and also studied the material properties with the doping using density functional technique. Germanium, which falls under the oxidation states II and IV can be utilized in the various fields like nanoelectronics, photonics, spintronics and optical fibers [6,7]. Moreover, due to their nontoxicity and biocompatible property, germanium fascinated many researchers. Further, it is also used in the fabrication of photodetectors, temperature sensors and biosensors [8–10]. The methods of synthesis of germanium include its extraction as a by-product of zinc and copper, extraction from coal sediments [11], segregation from the acid solutions, hydrometallurgy and many more. The properties like small effective mass, large absorption coefficient, high dielectric constant, narrow band gap, large Bohr exciton radius and strong effects of quantum confinement made Ge to stand unique among other semiconductor materials.

In the initial stages, the emission of electrons from metals/semiconductors, which is used in various devices are by the phenomenon of thermionic emission, i.e., by heating the material to high temperatures. The thermal breakdown of the material, high energy consumption, slow response and low efficiency in the above-said process is eliminated by adopting field emission phenomena. The field emission property of a nanostructure evaluates the emission of the electron under an applied electric field to categorize the material as a field emitter. Even though planar electrodes initially acquired the field emission theory, electrodes with sharp tips and small radius of curvature advance the flow of electrons from the cathode to anode when a local electric field ($\sim 10^6$–10^7 V/cm) is employed. Although carbon nanotubes (CNT) offer splendid field emission properties like low turn-on and threshold fields and high emission current density, they tend to have trivial emission stability. Thus, in order to eliminate this drawback, various nanomaterials are considered for field emission. Owing to the spiral inflexibility, conical shape and nanometric dimensions, nanocones are regarded as a prominent 1D nanostructure to be employed in scanning probes and field emitters. As a result of the augmented local electric field at the tip of the nanocone, the barrier width and the electric field strength to turn-on are decreased. The above reasons validate the electron emission characteristics of the nanocones. In addition, the materials suitable for field emitters are expected to have specific functionalities like low work function, high aspect ratio, high field enhancement factor and stable chemical and mechanical properties. These attributes make the particular material to yield high current density at a low applied potential. Besides, nanocone structure satisfies

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https://doi.org/10.1016/j.elspec.2018.06.002
Received 1 May 2018; Received in revised form 12 June 2018; Accepted 18 June 2018
Available online 19 June 2018
0368-2048/

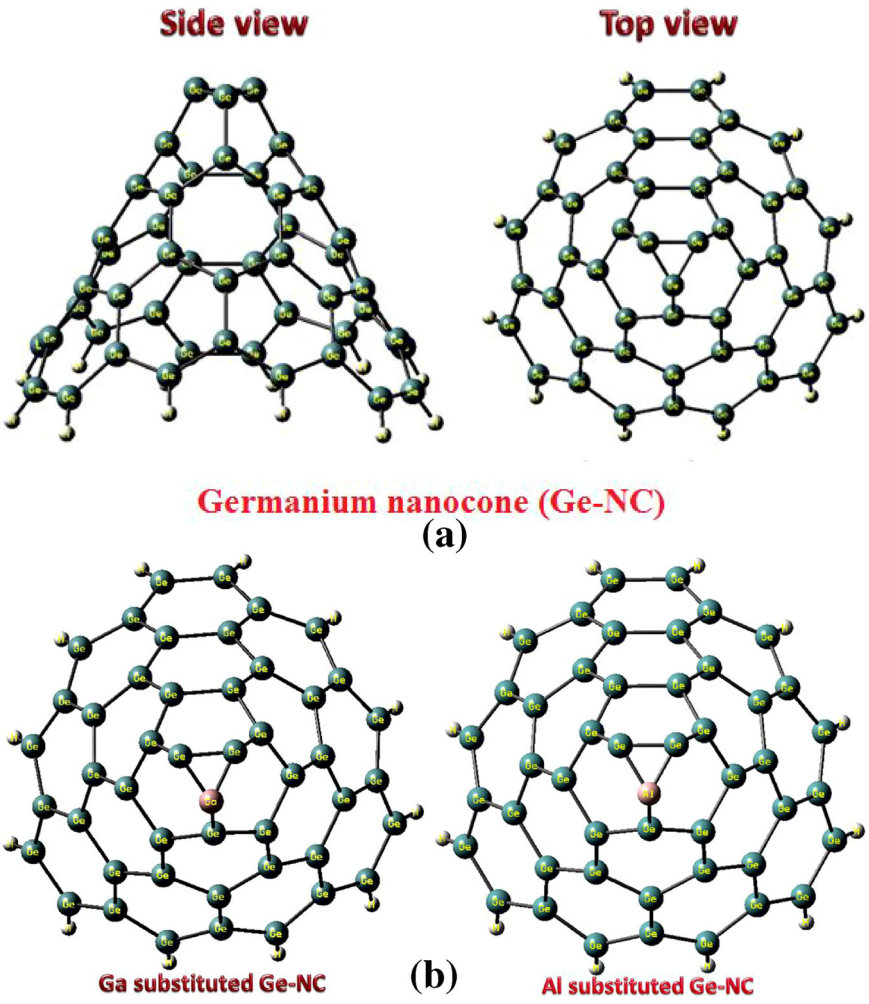

Fig. 1. (a) Pristine germanium nanocone (Ge-NC). (b) Ga substituted Ge-NC and (c) Al substituted Ge-NC.

these criteria. Moreover, the nanocone field emitters can be employed in X-ray sources (scanning electron microscopy, electron beam lithography), travelling wave tubes, flat-panel displays, cathode-ray tube monitors, high energy accelerators, microwave power amplifiers and other vacuum microelectronic devices. Moreover, the previously reported nanomaterials utilized for field emission are aluminum nitride (AlN), boron nitride (BN), graphene oxide (GO), ZnO, In_2O_3, SnO_2, TiO_2, MoO_3, SiC, WO_3, GaN, and LaB_6 [12–16].

The declination angle $\theta = n\pi/3$ commonly characterizes a nanocone. The angle of sector obtained from a flat nanosheet, which tends to form a cone is called the declination angle. Moreover, we would like to address the reason behind the selection of Ge nanocone as field emitters. The tunneling mechanism of an electron to vacuum is hastened in Ge nanocone by applying a large electric field, which arose due to high aspect ratio [17] and small radius of curvature of the nanocone. Furthermore, Ge nanocones possess electronic properties such as high conductivity and negative temperature coefficient of resistance. Ge nanocones are synthesized by various methods, namely electron-beam evaporation method, which manifests the field emission properties of Ge nanocone on vacuum nanoelectronics [18]. The novel aspect of the research work is to explore the prospects of germanium nanocone to tune its field emission properties upon doping the group-III elements such as gallium and aluminum in the Ge nanocone (Ge-NC).

2. Computational details

In the current work, we calculated the electronic properties of pristine and group-III doped Ge-NC with density functional theory (DFT) implemented by Gaussian 09 package [19] employing B3LYP hybrid functional along with 6–31 G (d) basis set in order to assess the frontier molecular orbitals, structural optimization, and electron density is accomplished [20]. The precise representation of the experimental data while exploring nanomaterials is considered as an important factor in choosing the B3LYP functional [21,22]. Moreover, the above literature validate the choice of B3LYP/6–31 G (d) exchange-correlation functional for Ge-NC [23,24]. Besides, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) along with the DOS spectrum is computed using GaussSum 3.0 package [25]. The variation in the band gap is (ΔE_g) is calculated as follows:

$$\Delta E_g = [(E_{g2} - E_{g1})/E_{g1}] \times 100\%$$

where E_{g1} represents the band gap energy for pristine Ge-NC and E_{g2} depicts the energy gap values of doped Ge-NC (with Ga/Al). To study the relative stability of Ga and Al elements substituted Ge-NC, the binding energy (E_b) of these complex must be determined using the following equation [26–30].

$$E_b\ (\text{GeNC-M}) = [E_{tot}\ (\text{GeNC-M}) - xE_{Ge} - yE_H - zE_M]^*(1/n)$$

where E_{tot}(GeNC-M) represents the total energy of impurity substituted germanium nanocone and 'n' is the total number of elements in Ge-NC material. E_{Ge}, $E_{H,}$ and E_M refer to the corresponding isolated energy of Ge, H and dopant elements. x, y and z illustrate the number of Ge, H and dopant atoms, respectively.