Influence of oxygen and titanium substitution on Vanadium nitride nanostructures - ADFT study

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Abstract: The structural stability and electronic properties of Vanadium Nitride, Oxygen substituted Vanadium Nitride and Titanium substituted Vanadium Nitride structures in the form of 2D and 3D structures were studied using Gaussian 09 program package with B3LYP/LANL2DZ basis set. The geometrical optimization of structures implies that the oxygen or titanium atom substituted. The dipole moment of the structures depends on the geometry of the structures and it found to be minimum in 2D Oxygen substituted Vanadium Nitridestructure represent more neutralized structures. The HOMO-LUMO, Ionization potential, binding energies and electron affinity, chemical hardness of different structures are calculated and reported.
Keywords: Vanadium Nitride nano structures, HOMO-LUMO, Binding energy, Ionization potential.

Introduction

The transition metal nitrides have attractive physical and chemical properties [1] which has been studies as additive in steels to enhanced their hardness, tenacity and abrasive resistance [2,3]. The applications of these materials are in magnetic and electrical components [4]. Vanadium nitride (VN) is one of the typical transition metal nitrides whose transition temperature is ranging from 2 to 9 K, depending on the nitrogen content and residual stress strongly [2].   VN high melting point, extreme hardness, wears resistance, high thermal conductivity, low electrical resistivity and corrosion resistance [5].VN films have been deposited by pulsed laser ablation [6], reactive electron beam evaporation [7], and reactive magnetron sputtering [8] etc. The VN film, a refractory nitride which has high melting point and low electrical resistivity, seem fit for the basic diffusion barrier requirement [9]. Theoretical studies of relative pure vanadium nitrides have not received their due attention[10]. In the present study the ground state properties and phase stability of pure vanadium nitrides and substitute either Ti or O in vanadium nitrides via density functional electronic structure calculations. This study also becomes important view of the potential application of pure and substituted vanadium nitrides.

Computational details

The different structure of Vanadium Nitride and Ti and O substituted Vanadium Nitride are geometrically optimized through Gaussian 09 package [11] employing Becke's three-parameter hybrid functional combined with Lee-Yang-Parr correlation functional (B3LYP) method optimized with LANL2DZ basic set[12,13]. HOMO-LUMO gap calculations for different optimized VN clusters are carried out using Gauss sum 3.0 packages [14]. To replace the complex effects of bound electrons in the atoms and the effective potential of the nucleus will have a modified potential term, the pseudopotential approximation [15], is in quantum chemical calculations.

Results and discussion

Structural stability of pure and impurity substituted Vanadium Nitride

The different Vanadium Nitride with substitution impurities of Ti and O, in the form of nanosheet (2D) and nanocone (3D) structures are optimized. The optimized structures of pure Vanadium Nitride (VN), O substituted vanadium nitride (VN-O) and Ti substituted vanadium nitride (VN-Ti) are shown in Fig..1. Further in both 2D and 3D structures, first one Ti atom substituted to V atom in pure Vanadium Nitride (VN-Ti1) and two Vanadium atoms replaced by two Ti atoms (VN-Ti2). Similarly one O atom substituted to N atom in pure Vanadium Nitride atom (VN-O1) and two N atoms replaced by two O atoms (VN-O2). For all the nanostructures the band length is kept as $1.7A^0$.All the nanostructures gas CS point group, molecules in this group have one symmetry operation which is a mirror plane except VN-Ti1 cone and VN-Ti2 cone structures. These two structures having C1 point group which is also called identity symmetry element.
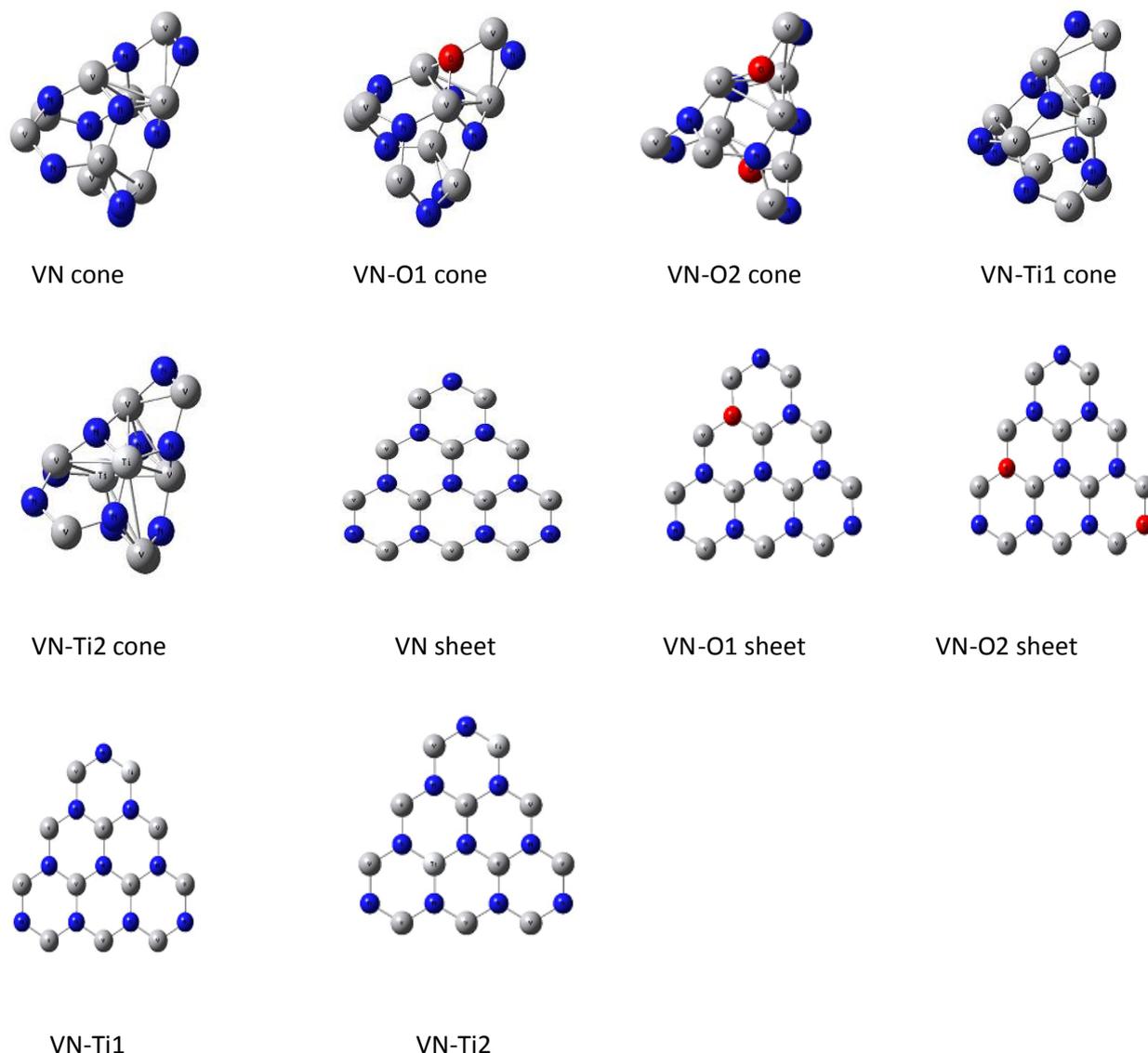
VN cone	VN-O1 cone	VN-O2 cone	VN-Ti1 cone
VN-Ti2 cone	VN sheet	VN-O1 sheet	VN-O2 sheet
VN-Ti1	VN-Ti2		

Fig. 1 The optimized 3D and 2D structures of VN,VN-O and VN-Ti

The calculated energy of optimized structures is shown in Fig.2. The energy observed for pure VN sheet and VN cone are -1398.70 and -1130.76 Hartrees respectively. The energy value decreases with O to N substitution and for Ti substitution it increases. Due to the increasing trend in Ti substituted atom resulting increase in stability in both 2D and 3D structures.

The calculated dipole moments are tabulated in Table.1. The dipole moments observed higher in 3D structure and lower in 2D structure which implies that the charge distribution. In case of, 3D structures, the dipole

moment almost equal because of balanced charges but in contract, the dipole moment of the 2D structure vary arbitrarily, which has not produced any sequence of changes due to unbalanced charges.
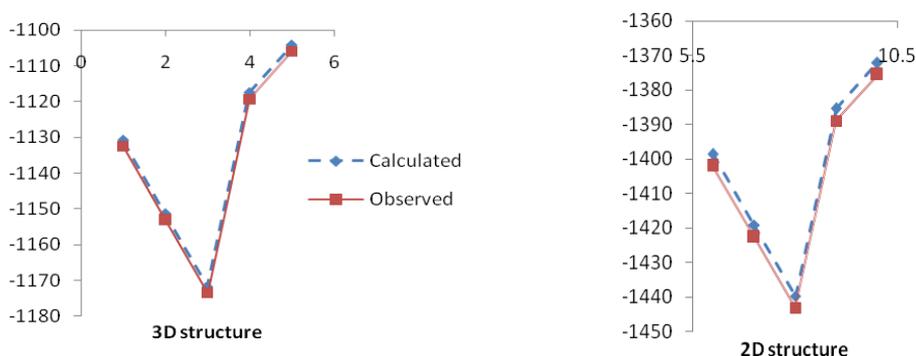

Fig.2. Calculated and Observed Energy for optimized 3D and 2D structures of VN,VN-O and VN-Ti

Electronic properties of VN and substituted VN

The electronic properties of VN,VN-O and VN-Ti structures for 2D and 3D are discussed in terms of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO). Fig..3. shows the range of Density of States (DOS) values provides insight to density of charge along the Fermi level.
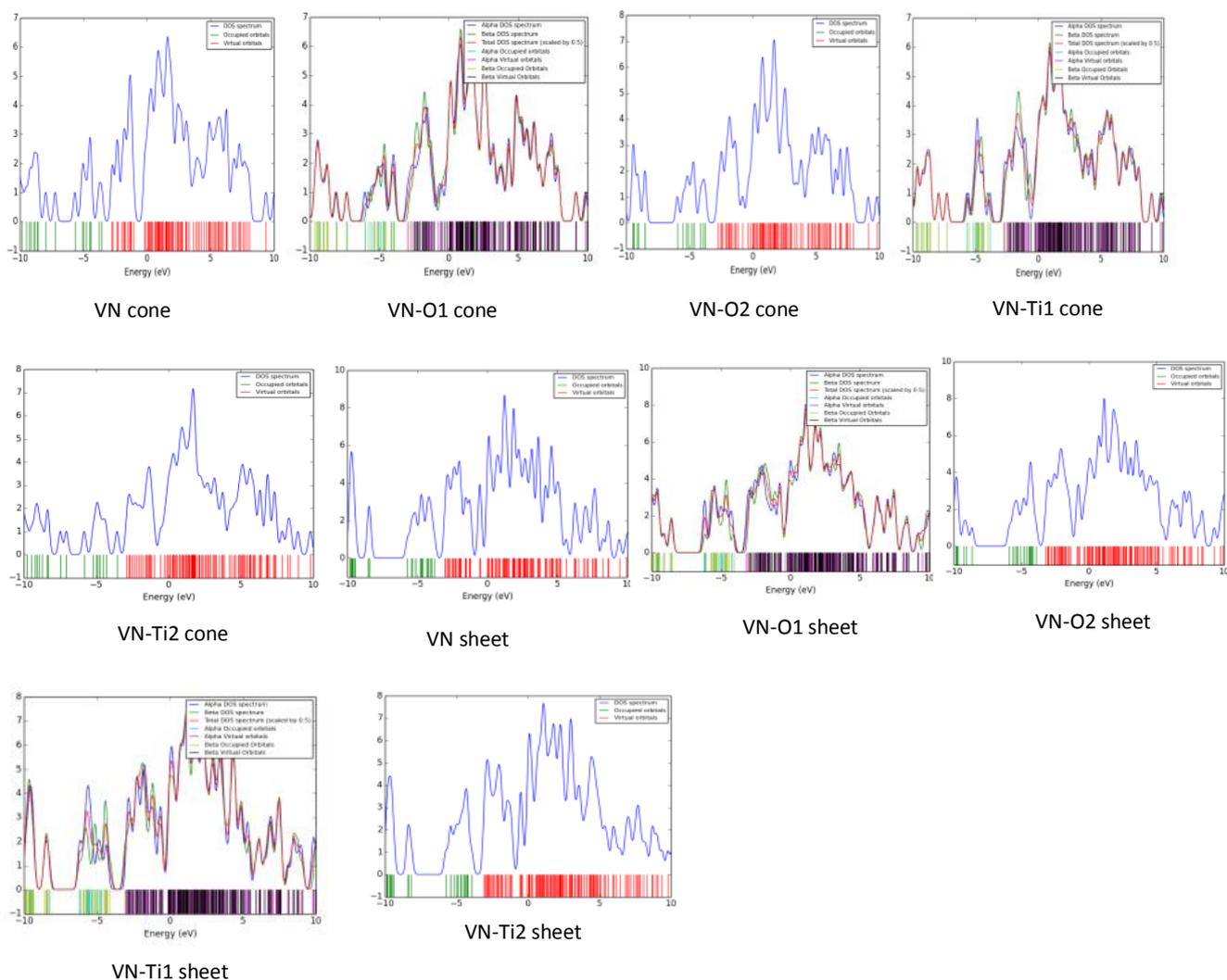

Fig. 3. The DOS image of optimized 3D and 2D structures of VN, VN-O and VN-Ti

The HOMO-LUMO gap varies arbitrarily because of overlapping of 3d orbitals of Vanadium and nitrogen 2p orbitals. From Fig..3 it is observed that VN-O1 and VN-Ti1 structures are exhibit alpha and beta energy bands due to its unbalanced spin up and spin down electrons. From table.1 the VN sheet and VN cone band gap are found 0.79eV and 0.8eV respectively. For 2D structure one oxygen or titanium substituted the band gap increases with respect to VN sheet structure due to the alpha and beta energy bands. And gradually increases the substituted atoms which give decrease in band gap due to single energy band. In contrast, in 3D structure the HOMO-LUMO gap which gradually increases with substituted either O or Ti due to its closed structure. The higher band gap restricts the movement of electron from HOMO to LUMO that will not actively take part in electrical conductivity and which are responsible for transparency for the material. In VN-Ti1 sheet and VN-Ti1 cone structure, the large HOMO-LUMO gap implies that the structure are chemically inert because it is unfavorable to add electrons to a high lying LUMO level or to remove electrons from a low-lying HOMO level [16,17].

Table 1. Dipole moment and Energy gap of geometrically optimized 3D and 2D structures of VN, VN-O and VN-Ti

S. No.	Structure	Dipole moment (Debye)	Eg (eV)
1	VN cone	4.826	0.8
2	VN-O1 cone	5.533	0.98
3	VN-O2 cone	5.549	1
4	VN-Ti1 cone	5.925	1.12
5	VN-Ti2 cone	5.294	0.67
6	VN sheet	1.385	0.79
7	VN-O1sheet	1.002	1.06
8	VN-O2 sheet	0.289	0.59
9	VN-Ti1 sheet	1.781	1.39
10	VN-Ti2 sheet	1.483	0.88

The HOMO-LUMO energy gap ($E_{homo} - E_{lumo} = \eta$) is used to calculate the chemical hardness of the structure. Usually a hard molecule has a wide HOMO-LUMO gap. The chemical hardness of various structures is tabulated in Table 1. The maximum hardness is found for VN-Ti1 sheet, VN-Ti1 cone and VN-O1 sheet structures. These structures are harder the other structures [18].

Ionization Potential and Electron Affinity

In density functional analysis, according to Koopman's theorem the obtained HOMO value can be considered as Ionization Potential (IP) and the LUMO value can be taken as Electron Affinity (EA) [19]. From Fig..4, we observe the variation of IP and EA for different structure of VN, VN-O and VN-Ti. The maximum IP is found 4.3eV in VN-Ti1 sheet structure and the minimum is in VN-Ti2 cone which is 3.55eV. However, both 2D and 3D structures IP is higher in VN-Ti1, VN-O1 and lower in VN-Ti2, VN-O2 to electron spin in molecular structure. In the case of substituted atom increases results gradual decrease in the IP value.
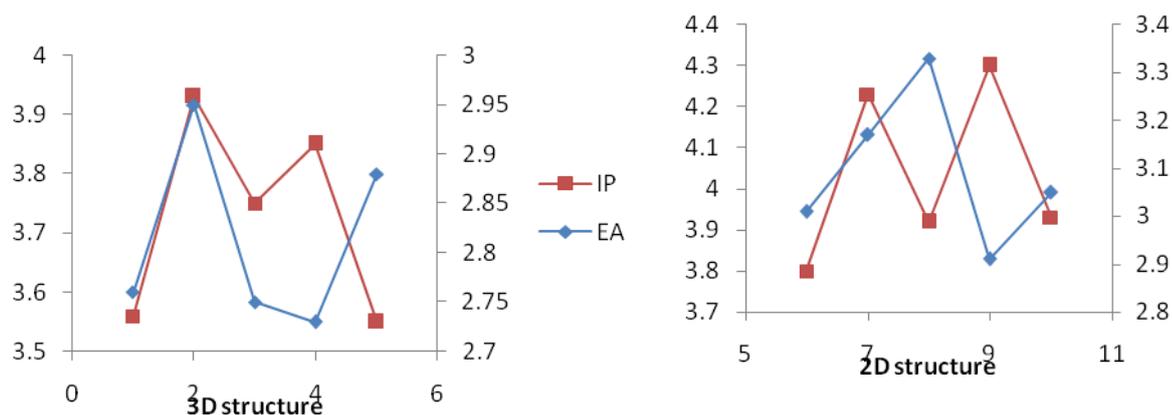

Fig.4. Variation of Ionization Potential and Electron Affinity withoptimized 3D and 2D structures of VN, VN-O and VN-Ti

The Electron Affinity (EA) represents how the structures can easily accept the electrons to it, the high value of EA indicates that the cluster has an active involvement in chemical reactions.   Among all the structures, the VN-O2 sheet and VN-O1 sheet structures have 3.33eV and 3.17eV respectively which are highly reactive. [20, 21].   In the impurity substituted to VN structure, the electron affinity increases gradually because the atomic number increases with same number of shells, so the nuclei of these elements will possess more positive charges.   Then the nuclei will be able to attract electron more tightly according to the rule of electrostatic forces.

Binding energy of VN

The binding energy per atom (BE) of nanoclusters can be found using the following relation (1)

$$E_{BE}=(n_1* E[V] + n_2* E[N]+ n_3*E[x] − E[VNx])/ (n_1+n_2+n_3) ---------- (1)$$

where E[V] is the energy of the Vanadium atom , E[N] is the energy of Nitrogen atom, E[x] is the energy of x=Ti, O atom and n_1, n_2, n_3 are the number of vanadium atom, nitrogen atom and Ti or O atom respectively [22].Fig..5 shows the variation of binding energy with 2D and 3D structure. From the plot, it is found that VNTi1sheet having higher value of BE than all VN structures and can be considered for higher stability. The maximum value of BE is calculated for 0.162eV and the minimum value is about 0.092eV for VN-Ti2cone and VN-Ti1 sheet respectively. More the electron affinity produce harder it is to form ions, in this study compare to 3D structure the 2D structures are harder to form ions. In 2D structures VN-Ti1, VN-O1and VN-Ti2 has greater electron affinity because their atomic structure allows them to gain electrons.
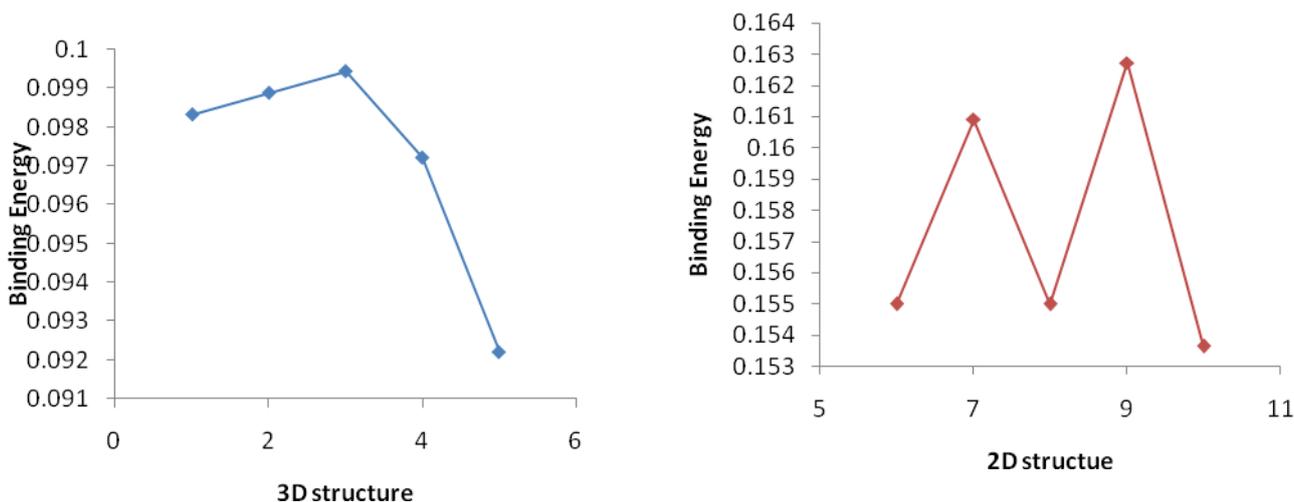

Fig. 5Variation of binding energy withoptimized 3D and 2D structures of VN, VN-O and VN-Ti

Conclusion

The realistic structures of VN and VN-O and VN-Ti are completely optimized using DFT technique. An important observation that needs to be highlighted is that the energy of the optimized VN-Ti structures is found to be stable than the other VN and VN-O structures. Using HOMO-LUMO energy gap the maximum chemical hardness is found for VN-Ti1 sheet, VN-Ti1 cone and VN-O1 sheet structures. The dipole moment of 2D structure like VN- O2 sheet is low since the atoms are not form a closed loop structure like cone structure but in 3D structures the dipole moment of VN and substituted VN having ~5Debye. Compare with the both 2D and 3D VN structures, the energy gap of the substituted VN structure is high and gradually decreases with increasing the substituted atom.The binding energy in 3D structure, which increases with Oxygen atom increases and decreases with Titanium atom increases. In contrast, in 2D structure, either single Oxygen or single Titanium substituted to base VN structure the Binding energy increases and then decreases with increasing the substituted atom.   The information given in this article provides a superfluity for the experimental lists to orient new materials for further development of the applications

References

1. Disalvo F.J, Clarke S.J, Ternary nitrides: a rapidly growing class of new materials Solid State Mater. Sci. 1996,1, 241-249
2. Xiangbo Liu , Huibin Lu, Meng He, Kuijuan Jin, Guozhen Yang ,Hao Ni, Kun Zhao, Epitaxial growth of vanadium nitride thin films by laser molecule beam epitaxy. Materials Letters, 2014,123,38–40
3. Shen YZ, Kim SH, Han CH, Cho HD, Ryu WS, Lee CB. Precipitate phases of a ferritic/martensitic 9% Cr steel for nuclear power reactorsJ Nucl Mater., 2008,374,403–12.
4. Yamada T, Shimada M, Koizumi M, Fabrication and characterization of titanium nitride by high pressure hot pressing. Am Ceram Soc Bull 1980,59, 611
5. Luyang Chen, Yunle Gu, Liang Shi, Zeheng Yang, Jianhua Ma, Yitai Qian, A room-temperature synthesis of nanocrystalline vanadium nitride Solid State Communications 2004,132, 343–346
6. D'Anna E, Cristoforo A.D, Fernández M, Leggieri G, Luches A, Majni G, Mengucci P,. Nanai L, Excimer laser reactive deposition of vanadium nitride thin films. Applied Surface Science 2002,186, 496–501
7. Wiklund U, Casas B, Stavlid N. Evaporated vanadium nitride as a friction material in dry sliding against stainless steel. Wear 2006,261,2–8
8. Glaser A, Surnev S, Netzer F, Fateh N, Fontalvo G, Mitterer C. Oxidation of vanadium nitride and titanium nitride coatings. Surface Science 2007,601(4), 1153–1159.
9. Xin-Ping Qu , Mi Zhou, Tao Chen, Qi Xie, Guo-Ping Ru, Bing-Zong Li, Study of ultrathin vanadium nitride as diffusion barrier for copper interconnect, Microelectronic Engineering 2006,83, 236–240
10. Chinnappan Ravi, First-principles study of ground-state properties and phase stability of vanadium nitrides, CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 2009,33, 469-477.
11. Frisch M. J et al., Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT., 2009.
12. Chandiramouli R., A DFT study on the structural and electronic properties of Barium Sulfide nanoclusters, Res. J. Chem. Environ., 2013, 17, 64-73.
13. Nagarajan V and Chandiramouli R., Effect on the structural stability and electronic properties of impurity substituted sodium selenide nanostructures – A quantum chemical study, Int.J. ChemTech Res., 2014,6(4), 2240-2246.
14. O'BOYLE N. M, TENDERHOLT A. L and LANGNER K.M., A Library for Package-Independent Computational Chemistry Algorithms, J Comput Chem., 2008, 29, 839–845.
15. Srinivasaraghavan R, Chandiramouli R, Jeyaprakash B.G. and Seshadri S., Quantum chemical studies on CdO nanoclusters stability, Spectrochim. Acta, Part A., 2013, 102, 242-249.
16. Nagarajan V and Chandiramouli R., Quantum Chemical Studies on ZrN Nanostructures, Int.J. ChemTech Res., 2014,6(1), 21-30.
17. Sriram S, Chandiramouli R, Balamurugan D and A. Thayumanvan., A DFT study on the structural and electronic properties of ZnTe nanoclusters, Eur. Phys. J. Appl. Phys., 2013, 62, 30101.
18. Pearson R.G.,Chemical hardness and density functional theory J. Chem. Sci., 2005, 117, 369-377.
19. Saravanakannan V , and Radhakrishnan T, Structural and Electronic studies on Al Substituted SnO2 nano structures a DFT Study, Research Journal of Pharmaceutical, Biological and ChemicalSciences, 2013,4(4),589-599.
20. Chang-Guo Zhan, Jeffrey A. Nichols and David A. Dixon, onization Potential, Electron Affinity, Electronegativity, Hardness, and Electron Excitation Energy: Molecular Properties from Density Functional Theory Orbital Energies, J. Phys. Chem. A, 2003,107, 4184- 4195.
21. Akola J., Hakkinen H. and Manninen M., Ionization potential of aluminum clusters, Phys. Rev. B: Condens. Matter, 1998, 58, 3601-3604.
22. Quantum chemical studies on (ZnO)n/(NiO)n heterostructured nanoclusters R. Chandiramouli, S.Sriram and D.Balamurugan, Molecular Physics, 2013,151-164.

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