Study of Hybrid Semiconductor Nanoclusters and Hydrogen Storage Materials by using Density Functional Theory

Synopsis

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by

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Contents

1. Introduction

Germanium and silicon both are the most important elements in the semiconductor industries due to their scientific and technological applications **[1-3]**. The results of theoretical and experimental research, suggest that the properties of small sized clusters are quite different from the bulk materials due to the surface effect (atoms at surfaces have fewer neighbuors than atoms in the bulk) and quantum size effects (electronic wavefunction of conduction electron are delocalized over the entire particle). However pure germanium and silicon cluster cannot be directly used in application since they are chemically reactive due to their reactive nature. Proper doping with the transition metal atoms absorbs the unsaturated bonds on the cluster surface and improves is thermodynamic as well as chemical stability **[4-8]**. Metal doped cage like nanoclusters are found to be more interesting for their potential applications. There are many reports on metal doped silicon nanocluster. The system chosen in this present work is transition metal doped germanium nanoclusters because in the field of semiconductor materials, germanium is one of the most important alternatives to silicon due to its superior electron and hole mobilities. Therefore metal doped cage like clusters are expected to become important materials for a new generation of electronic devices and optoelectronic applications.

2. Motivation and problem statement

In the semiconductor cluster science, study of the electronic and thermodynamic stability, magnetic and optical properties are of main interest. In the last few decades, cluster science has become a rapidly growing interdisciplinary field of study with the advancement of experimental, theoretical and computational techniques. Therefore, research on the cluster science has increased rapidly. There are several reasons for that. Firstly, clusters provide a bridge between the limits of isolated atoms or molecules with the bulk matter. Therefore, it is interesting to study the evolution of the cluster properties with size in a particular composition. Such knowledge provides new viewpoint on and would improve the understanding of the behavior that occurs at the more familiar limits. This enthusiasm is still a primary influential force for cluster science and this thesis will touch upon some aspects of the size evolution of cluster properties. A second motivation in the cluster science is to study the reasons behind the nucleation at an atomistic level, which is able to form thermodynamically and chemically stable structures. Most of the current work in this area is now no longer directed at clusters as a model of a (critical) nucleus, but instead, at

clusters as an environment in which nucleation can occur on fast time scales and for which only a single nucleation event is required to transform the cluster.

3. Overview of thesis

We start by introducing elementary concepts from molecular quantum mechanics, and then we use central idea of Schrodinger equation. After that we explain principle of antisymmetry and use of Born-oppenhiemer approximation. To get idea about energy functional we gave a brief description of variational principle. Followed by Hohenberg- Kohn sham theory and Slater determinant, that uses the electron density as basic variable. The concept of basis set, local density approximation (LDA) and exchange correlation functional are also described. With this background of understanding the cluster, the present thesis focused on main two research sides in the cluster science and described in four chapters. Two chapters described the investigation and analysis of the inherent science of the stability of the clusters and super atoms. The latter chapters are more practical application oriented where the metal nanocluster have been used to investigate as effective hydrogen storage elements to solve the possible fuel problems.

4. Brief survey of earlier work

Experimental and theoretical investigation on the transition metal (TM) doped germanium and silicon clusters disclose a novel insight towards the understanding of cluster stability. The physical and chemical properties of germanium and silicon clusters, besides their scientific concernment, are also very important for nanotechnology in view of the continued miniaturization of the electronic devices. At the same time the physics of small magnetic clusters with extended magnetic moment has a great significance and has been the focus of both experimental and theoretical research. It is now become one of the main issues in condensed matter physics and material science. When the size reaches the nanometer scale, quantum confinement and low dimensional effects lead to a rich variety of structural and electronic behaviors usually electronic structures and stabilities of nanoclusters are very sensitive to the addition or subtraction of a single atom or slight changes of composition. Some of these properties can be of interest in molecular electronics, spintronics and catalysis. Concerning the magnetic properties, one of the main challenges is to fabricate performant magnetic storage devices. Intense research has been carried out in recent years

[9-11]. On the other hand one of the major elaborations of the past century was the identification of cluster science as a field that impact on so many others. Attributable to the reduced size and related phases of quantum confinement, an exciting achievement in cluster science is the realization that chosen stable clusters can mimic the chemical property of an atom or a group which is similar to an element in periodic table. This major finding known as a superatom concept came from the study of aluminium clusters **[12]**, where interesting size-dependent reactivity was noted. In the chasing to find other superatoms, it is necessary to develop the nature of superatom chemistry and identify the composition and size that can form superatoms. Therefore, one has to give a big effort to understand the electronic, physical and chemical properties to predict possible stable clusters.

In last few decades study of the interaction between hydrogen with the materials is the fundamental interest in research in the field of hydrogen storage. To solve the future energy problems it is important to understand the science behind this interaction from theory and experiment knowledge. Theory and computation can be used not only to understand experimental results, but also to design low cost materials with improve hydrogen storage efficiency. It is well known that magnesium and magnesium alloys have potential as high hydrogen storage elements **[13-15]**. Moreover, these alloys are lightweights, cost effective and hence the most promising candidates for hydrogen storage. However, due to the physical nature of hydrogen, it is difficult to store it in a large quantity in small materials volume **[16]**. Therefore modeling and its experimental verifications for the safe, reliable and cost effective hydrogen storage elements is one of the main challenges in this field.

Therefore theoretical prediction of the nano-structures of the size in nano order dimension is very much important. Experimental production and characterization of nanoclusters, based on the demand of devices are not always possible experimentally in a controlled manner because of high probability of reaction affinity. So, theoretical prediction and characterization of the nanoclusters and assembly of the nanoclusters are very hot topic of research at the present age.

5. Major contribution in the thesis –

The thesis consists mainly in two parts. The first part describes the electronic structure and stabilities of TM (Mo, Nb) doped hybrid semiconductor nanoclusters. The second part discuss the use of TM (Co, Rh) doped magnesium nanoclusters as a effective hydrogen storage candidates.

5.1 - *Study of electronic properties, stabilities and magnetic quenching of molybdenum doped germanium cluster: a density functional modeling*

In this chapter we presented the study of geometry and electronic properties of neutral and cationic Mo-doped Ge_n (n =1-20) clusters within the framework of density functional theory. Identification of the stable species, and variation of chemical properties with the size $MoGe_n$ clusters are the main focuses help to understand the science of Ge-Mo based clusters and superatoms that can be future building blocks for cluster-assembled designer materials and could open up a new field in electronic industry. The present work is the preliminary step in this direction. On the basis of the results, the following conclusions have been drawn.

1. The growth pattern of Ge_nMo clusters can be grouped mainly into two categories. In the smaller size range i.e. before encapsulation of Mo atom, Mo or Ge atoms are directly added to the Ge_n or $Ge_{n-1}Mo$ respectively to form Ge_nMo clusters. At the early part in this region the binding energy of the clusters increase in a much faster rate than the bigger clusters as discussed in chapter 3. After encapsulation of Mo atom by the Ge_n cluster for n>9, the size of the Ge_nMo clusters tend to increase by absorbing Ge atoms one by one on its surface keeping Mo atom inside the cage.

2. It is favorable to attach a Mo-atom to germanium clusters at all sizes, as the embedding energy (EE) turns out to be positive in every case. Clusters containing more than nine germanium atoms are able to absorb Mo atom endohedrally in a germanium cage both in pure and cationic states. In all Mo-doped clusters beyond n > 2, the spin magnetic moment on the Mo atom is quenched in expenses of cluster stability. As measured by the binding energy (BE), embedding energy (EE), HOMO-LUMO gap, fragmentation energy (FE), stability and other parameters both for neutral and cationic clusters, it is found that those are having 18 valence electrons show enhanced stability which is in agreement with shell model predictions **[17]**. This also shows up in the IP values of the Ge_nMo clusters, as there is a sharp drop in IP when cluster size changes from n=12 to 13. Validity of nearly free-electron shell model is

similar to that of transition metal doped silicon clusters. The signature of stability is not so sharp in the HOMO-LUMO gaps of these clusters. However there is still a local maximum at n=12 for the neutral cluster, indicating its enhanced stability, whereas, this signature is very much clear in cationic $Ge_{13}Mo$ cluster. Variation in HOMO-LUMO gap in different sized clusters could be useful for devise applications. The large HOMO-LUMO gap (2.25 eV) of $MoGe_{12}$ could make this cluster as a possible candidate as luminescent material in the blue region.

3. Major contribution of the charge from the d-orbital of Mo in hybridization and its dominating contributions in DOS indicate that the d-orbitals of Mo atom in different clusters are mainly responsible in the hybridization and stability of the clusters. Presence of the dominating contribution of Mo d-orbital close to the Fermi level in DOS is also significant for ligand formation and a strong indication of possibility to make stable cluster assembled materials.

4. Computations and detailed orbital analysis of the clusters confirm the rapid quenching of the magnetic moment of Mo in Ge_n host cluster while increasing the size from n=1 to 3. Beyond n=2, all hybrid clusters are in singlet state with zero magnetic moment. Following the overall shape of the delocalized molecular orbitals of $MoGe_{12}$ cage like clusters, the valance electrons of Ge_{12} cage can be considered as forming a spin compensating electron cloud surrounding the magnetic element Mo as like a screening electron cloud surrounding Mo which is similar to the magnetic element doped bulk materials. Therefore, the system may be interpreted as very similar to that of a finite-size Kondo system.

5. Variation of calculated NICS values with the distance from the center of the $MoGe_{12}$ cluster clearly indicates that the cluster is aromatic in nature and the aromaticity of the cluster is one of the main reasons for its stability.

(RSC. 2014; 4; 64825-64834)

4.2 - Role of NICS and shell closing model in the stability of neutral and cationic $NbGe_n$ (n= 7-18) clusters: a density functional investigation

As pointed out earlier in the thesis that the electronic shell model can be used efficiently to understand the stability and the electronic properties of the clusters. In this chapter we explain the enhanced stability of neutral $NbGe_{12}$ and cationic $NbGe_{16}$ clusters and also superatomic behavior of cationic $NbGe_{16}$ cluster. The results can be summarized as follows:

1. We have done theoretically study of the electronic properties, vibrational properties and superatomic behavior of Nb doped germanium clusters at different sizes in neutral and cationic states. Different physical and chemical parameters of the clusters show that neutral $NbGe_{12}$ and cationic $NbGe_{16}$ are the most stable species in the whole range of study. In addition, neutral $NbGe_{10}$ and $NbGe_{16}$; and cationic $NbGe_{13}$ also show enhanced stability.

2. To identify the most stable behavior, we have further studied NICS and closed shell model in both neutral and cationic state of these clusters. We found that the NICS behavior of the ground state $NbGe_{12}$ cluster supports the aromatic behavior, whereas, cationic $NbGe_{16}$ follow the closed shell superatomic model. The large HOMO-LUMO gap of 1.85eV makes this cluster suitable for optoelectronic devices and chemical stable. Further, the absence of any imaginary frequencies in these clusters shows that there is no presence of imaginary bonds in the clusters and clusters can be physically acceptable.

(To be communicated in RSC Advance)

4.3 - *Hydrogen storage in small size Mg_nCo clusters: A density functional study*

In this section of thesis, keeping the development in the theoretical studies of hydrogen storage elements **[13-15]**, we proposed a simple model to find out how transition metal Co plays an important role in the hydrogen dissociation process on Mg clusters and the reaction with H_2 using density functional theory based calculations. The present theoretical study gives a number of useful understandings of hydrogen storage in Mg_nCo nanoclusters. The conclusion of the study can be summarized as follows:

Present study reports the use of Mg_nCo as an effective hydrogen storage element in the form of nanoclusters. From the growth pattern of Mg_nCo (n=1-10) clusters it is found that Mg_4Co and Mg_6Co both are stable in the series where Co prefers to take peripheral position. From the chemisorptions and physisorptions energies and VIP and VEA parameters, we found Mg_5Co only can be used as effective hydrogen storage and dissociate element. After addition of H_2, H2-Mg_5Co is appears as efficient hydrogen catalyst. Together with these two, H2-Mg_5Co shows highest reaction energy in IRC path and we found the same activation barrier during the chemical process as we calculated in our simulation. The complete study shows that in the Mg_nCo (n=1-10) series, Mg_5Co can be selected as an efficient hydrogen storage element.

(International journal of Hydrogen energy. 2015; 40; 12727-12735)

4.4 - *Study of adsorption and dissociation pathway of H_2 molecule on Mg_nRh (n =1-10) clusters: a first principle investigation*

This section of the thesis presented hydrogen adsorption and dissociation process of Rh doped magnesium Mg_nRh nanocluster within the range of n=1-10. Our previous theoretical work over Co transition metal atom doped with Mg clusters found that Co plays an important role in the hydrogen dissociation process on magnesium clusters. Research on Mg is aiming to reduce the high temperature required for the dissociation of its hydride phase and to accelerate the H2 adsorption kinetics. So in the same direction, in this work we studied the importance of Rh transition metal to improve the hydrogen adsorption energy and enhance the hydrogen storage capacity. It is also qualify as good catalysts for accelerating the kinetics of hydrogen adsorption. The conclusion of the study can be summarized as follows:

We have studied the adsorption and dissociation behavior of hydrogen molecule on Mg_nRh (n=1-10) clusters by DFT calculation. Mg_6Rh cluster is found as physically as well as chemically most stable species in the whole series. In the different optimized adsorption modes, H_2 molecule can be easily adsorbed on the top of the Rh atom. Due to this the increasing H-H bond length exhibit relaxation of hydrogen bonds when adsorbed on the cluster. The vibrational frequency of hydrogen in Mg_nRh-H_2 cluster also varies. In Mg_nRh-H_2, H-H bond frequency is in the range from1000-1554 cm^{-1}, while in the gaseous phase it is 4650 cm^{-1}. So the H-H vibrational frequency shifted

towards low wave number after adsorption. The shift towards low vibrational frequency in adsorbed clusters is recognized to the increase of H-H bond length. Following the calculated IRC path of H2-Mg_9Rh cluster, it is found that H_2 molecule adsorbs at the Rh atom site in Mg_9Rh with low coordinate number and then moves to the Mg atom to form Mg-H bonds by overcoming the energy barrier of 15.73 kcal/mol. The maximum chemisorptions energy, low activation barrier and large value of reaction energy indicate that though Mg_6Rh is more stable compare to Mg_9Rh cluster, but, Mg_9Rh is the most qualified candidate for adsorption and dissociation of hydrogen; and hence can be used as an effective hydrogen storage element.

(Communicated in Int. J. of Hydrogen energy)

6. Future scope

The work done in this thesis will lead to the DFT investigation of other transition metal doped germanium and silicon semiconductor nanocluster. There are many scopes of transition metal doped cluster studies in magnetic superatom and cluster assemblies. These materials are now being considered as the building blocks of future modern technologies due to their size dependent electronic properties which can be tuned easily. It has numerous and important applications in the field of electronics, chemistry and biology, which become possible considereing these facts. This thesis gives an additional chance to prepare and to apply semiconducting nanocluster in the fields of electronic devices in the near future.

In near future, enormous number of hybrid nanoclusters are possible, so it is a research problem to model these types nanoclusters and to understand their physical and chemical properties. On the other side doping of TM in metal clusters like magnesium can be used as an effective hydrogen storage medium for future fule problem. So the present thesis makes an effort towards an interesting field of research in the cluster science. The future scope of the present research can be summarized as follows:

[1] Investigation of more hybrid TM metal doped Ge, Si, and Sn semiconductor cage cluster. Transition metal doped semiconductor nanoparticles have attracted scientific attention due to their prospective applications in optoelectronic devices or electronic devices. Many other composition can also form hybrid semiconductor clusters with characterstics physical and chemical properties that will be haelpful to understand the superatom building blocks.

[2] Investigation of metal clusters as catalysis and hydrogen storage materials. The interaction of hydrogen with metal clusters and their cations in the gas phase is also enabling the design and synthesis of a new class of hydrogen storage materials.

[3] It is quite important to study of the clusters assembled materials to make nanodevices and quantum dots. Cluster assembled materials are of interest because of their ability to tune component properties. It is one path way towards nanomaterials with controllable band gaps and hence cluster assembled materials. By controlling the cluster assembled building blocks into quantum dots and bulk is the next step towards achieving superatom materials with tunable physical properties. Clusters assembled materials can also be used to make nanotubes and 2D graphene nanosheet having different physical and chemical properties that can be useful for device applications and future building blocks.

[4] Supported clusters these are more nearer to practical application but they need huge computational facilities. Numerous attemps have been made to prepare supported metal clusters with nearly uniform structures. It is a new class of catalyst made possible by synthesis involving organometallic chemistry in surfaces, gas phase cluster chemistry. The relevance of ligand stabilized metal clusters on support to the supported metal clusters on interest for their role as precursors.

So the studies of clusters have been useful to gain a fundamental understanding of catalysis, magnetism, superatomic and hydrogen storage. It is possible to create a magnetic cluster from nonmagnetic materials by controlling its size and composition. The challenges still remain……

7. References

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7. List of Publications

- Electronic structure and stabilities of Ni- doped germanium nanoclusters: A density functional modeling study, J Mol Model. 2013; 19; 1473-1488
- Magnetic behavior in Cr_2Ge_n (n= 1-12) clusters- A density functional investigation, AIP. 2014; 1591; 1498
- Study of electronic properties, stabilities and magnetic quenching of molybdenum-doped germanium clusters: A density functional investigation, RSC Advance. 2014; 4; 64825-64834
- Hydrogen storage in small size Mg_nCo nanocluster- A density functional investigation, International journal of Hydrogen energy. 2015; 40; 12727-12735
- Role of NICS and shell closing model in the stability of neutral and cationic $NbGe_n$ (n= 7-18) clusters: A density functional investigation (*To be communicated in RSC Advance*)
- Study of adsorption and dissociation pathway of H_2 molecule on Mg_nRh (n =1-10) clusters: A first principle investigation (*Communicated in Int. J. of Hydrogen energy*)

8. List of attended conferences and workshop

- Poster presentation in "international E – Workshop/Conference on Computational Condensed Matter Physics and Material Science (IWCCMP – 2015), ABV – IIITM, Gwalior" 18-22 Oct, 2015
- Oral presentation on " Research Scholar day 2015, BITS- Pilani, Pilani campus" on 15 March, 2015
- Oral presentation on "Study of Magnetic Quenching and Aromatic nature of Mo doped germanium cluster – A density functional investigation at IUAC New Delhi during HPC workshop on 11-13 march 2015.
- Poster presentation in "International Conference on Current Trend in Condensed Matter Physcis" (CTCMP-2015), IOP, Bhubaneswar, Feb 19-22, 2015
- Present Oral presentation on Research Scholar day in BITS, Pilani, Pilani campus, March 23, 2014
- Attended "Workshop and Training on current Research trends in Condensed matter- Material Science", BITS, Pilani, Pilani campus, March 7-8, 2014
- Attended " WORKSHOP ON HIGH PERFORMANCE COMPUTING, Inter University Accelerator Centre, New Delhi" during 5-6 May, 2014

- Attended "International symposium on Science of Clusters, Nanoparticles and Nanoscale Materials (SOCNAM)", Central university of Rajasthan and Virginia commonwealth university, USA, March 4-7, 2013
- Attended "International Conference and Workshop on Nanostructured Ceramics and other Nanomaterials (ICWNCN)", University of Delhi, March 13-16, 2012