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Si-Cluster Terminated by H, F, and O Atoms: A Correlation with Visible Luminescence of Porous-Si

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The effect of H, F, and O termination atoms together with size dependence of Si-cluster on the electronic structure are considered, using semi-empirical molecular orbital calculation. The results show that the electronic structure of Si-cluster is strongly affected by the presence of O terminators, which enhance the carrier localization. The transition probability between the electronic states support the high efficiency of visible luminescence. Our calculations suggest that O surface termination of Si-cluster is one of the requisite condition for the luminescence in the red-orange region.

1. Introduction

The efficient visible luminescence from porous-Si at room temperature is drawing a great deal of excitement in material research[1]. The low dimensional semi-conductor nanostructures usually exhibits new quantum phenomenon and have potential for becoming novel & future opto-electronic devices. However, the microscopic origin and mechanism of strong visible luminescence in this peculiar material are still controversial i.e., whether this is due to an intrinsic property of porous-Si [quantum size effect [2]] or an extrinsic effect [chemical modification[3]) i.e., polysilane, siloxene, etc.]. In this work, we have explored these two physical mechanisms by means of semi-empirical molecular orbital (MO) calculations. The focus of interest is role of Si-cluster surface conditions i.e., the effect of different kind of terminators viz., hydrogen (H), fluorine (F), and oxygen (O) atom on the electronic properties and whether geometrical confinement can lead to allowed optical transitions in the visible region.

2. Theoretical Model

A semi-empirical method[4], the modified neglect of diatomic overlap-parametric method 3 (MNDO-PM3) in the restricted Hartree-Fock approximation is used in the present work. In MNDO-PM3, linear combination of atomic orbital approximation is considered and only valence electrons are taken into account for the calculation of Si-cluster electronic states, treating the inner shell electrons as a core together with nucleus. The configurational interactions (CI) are also taken into consideration for the calculation of excited states. The Si atoms beyond the first neighbors to the terminators are fixed to simulate the Si-cluster. The calculated value of the total energy difference between the lowest excited and the ground electronic state is termed as the energy gap for an idealization. This work was performed by a CRAY Y-MP8/232 system using MOPAC program[5].

The Si-clusters considered for the present work range from 10 to 320 Si atoms. It is assumed that in these clusters, Si atoms occupy diamond crystal sites and are spherical. Different kind of termi-

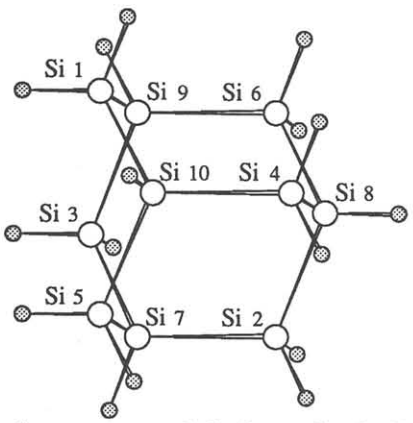

Fig. 1 Structure model of tetrahedrally symmetric Si-cluster used as initial cluster in MO calculations.

nation atoms viz., H, F, and O atom considered in this work, consistent with the SIMS and XPS analysis. The initial structure of Si-cluster is fixed to 10 Si atoms and the surface dangling bonds are terminated by H atoms. This structure has a T_d symmetry and corresponds to the carbon adamantane structure ($C_{10}H_{16}$) which is favored for Si_{10} cluster by stability consideration. Fig. 1 shows the atomic arrangement of initial Si-cluster, isolated in free space.

3. Results and Discussion

Our Si-cluster structure reflects confinement (Si network) as well as chemical effect (surface termination atoms). We considered H terminated Si-clusters ranging from 10 Si to 320 Si atoms. Fig. 2 shows a plot of calculated energy gap of unrelaxed and relaxed cluster structures versus number of Si atoms (N_{Si}). According to results, when a H terminated Si_{10} cluster is optically excited, the total energy gap of unrelaxed structure is about 3.43 eV. Here, the excitation is adiabatic so that the cluster structure is unchanged at the moment of electronic excitation. However, since the cluster structure with excited electronic states is unstable, it relaxes afterward which results in a reduction of energy gap down to 2.85 eV i.e., a Stokes shift of 0.58 eV. Alternatively, this implies that visible luminescence can be observed at 2.85 eV from optically excited $Si_{10}H_{16}$ cluster. The energy gap of H terminated Si-clusters show a continuous decrease with increasing size. The variation in energy gap is rather strong for small size clusters ($N_{Si} < 50$) compare to large one. A comparison of the features of electronic wave functions of unrelaxed and relaxed structure revealed that large clusters are stable under the photo excitation process. This implies that H termination makes the structure of Si-cluster stable. The energy gap of the largest Si-cluster ($Si_{320}H_{156}$: 2nm) is about 2.38 eV, which lies in yellow-green region. Results also indicate that Si-cluster of about 3nm size, which is a characteristic size of porous-Si will have the emission band in the same region. This emission region is well above the widely reported red-orange (1.6-2.2eV) region.

The effect of F and O termination atoms on the energy gap of Si-cluster is considered by assuming the initial structure of $Si_{10}H_{16}$. Usually, electro-negative atoms decrease the electron population in the bonding orbitals. This phenomenon leads to the weakening of bond and a decrease of bonding and antibonding splitting, which finally results in the decrease of energy gap. Different atomic arrange-ments are considered for same number of F or O termination atoms. The position of the termination atom in cluster is selected as marked on Si atoms in Fig. 1. The F terminated Si_{10} cluster shows the energy gap of about 2.30 eV. Although F termination change the energy gap, however, the number of F atoms produce no significant effect on the calculated energy gap of the cluster. It is almost independent of number of F terminators. On the other hand, O termination atoms show the dominant effect on the electronic structure of cluster as shown in Fig. 3(a). The O terminated Si_{10} cluster shows the energy gap of about 1.69 eV. The increasing number of O termination atoms produce a continuous decrease in the energy gap. The size dependence of the O terminated Si-clusters is shown in Fig. 3(b). It is found that energy gap of the O terminated Si-cluster also decreases with the increasing size, however, it strongly depends on the number of O atoms. The relaxed structure show large structural relaxation compare to H terminated cluster. The presence of O

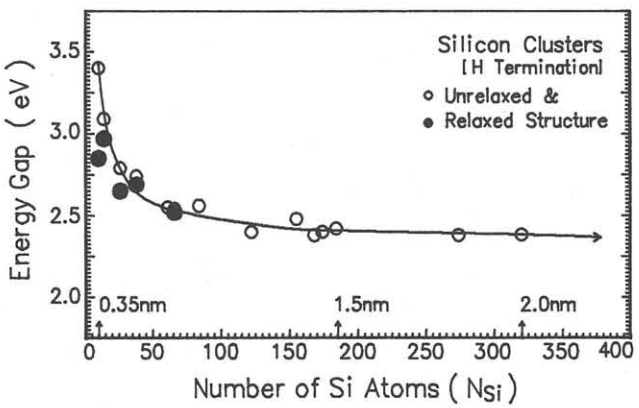

Fig. 2 Plot of energy gap as a function of number of Si atoms (N_{Si}) for H terminated Si-clusters.

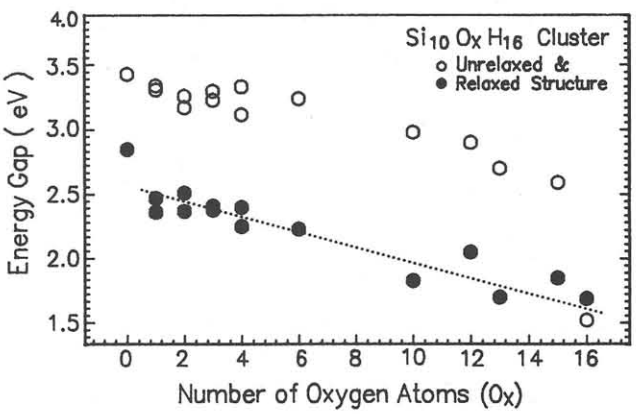

Fig. 3(a) Plot of energy gap versus number of O termination atoms (O_x) in the $Si_{10}O_xH_{16}$ cluster.

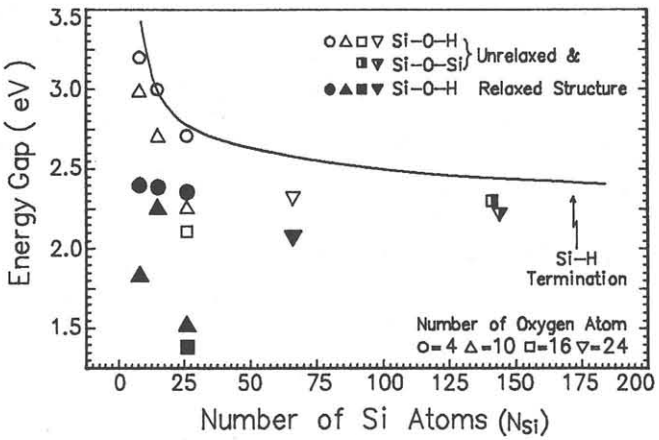

Fig. 3 (b) Plot of energy gap as a function of number of Si atoms (N_{Si}) for O terminated Si-cluster.

atoms also shift the energy gap towards the widely reported red-orange region. These results reveal that the energy gap of Si-cluster not only depends on the size but also on the kind of termination atom, especially O atom.

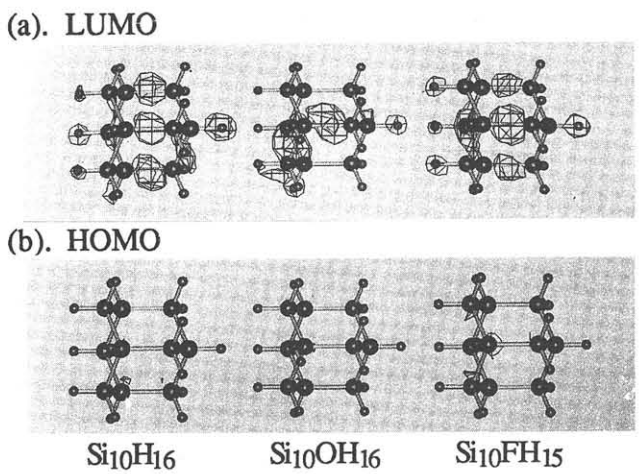

Fig. 4 MO contours for H, O, and F terminated initial Si-clusters. The terminator position is fixed to Si10 atom (Fig. 1). (a) HOMO and (b) LUMO.

In order to look deeper into the O termination effect, the MO distributions are considered. In Fig. 4, 3-dimensional MO contours are shown for the H, O, and F terminated Si-clusters. The MO distribution for the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) are shown in the figure. It can be seen that O termination atom in Si-cluster induces the localization of wave functions toward its position compare to other atoms. This behavior leads to the confinement of electrons in this region, which appears to be a peculiar characteristic of the O atom and is likely to enhance the carrier localization. The modification of electronic structure may be associated with this characteristic of O atom. Table 1 shows the s- and p-type atomic orbital contribution of the Si and termination atoms to the HOMO and LUMO of the ground electronic states for $Si_{10}H_{16}$, $Si_{10}OH_{16}$, and $Si_{10}FH_{15}$ clusters. It should be noted from table that the HOMO is mainly composed of p-type atomic orbitals and the LUMO is composed of s-type atomic orbitals. Since the transition between s-type and p-type atomic orbitals is optically allowed, the transition probability is expected to be very high i.e., high emission efficiency.

Table 1
The s- and p- type atomic orbital contribution (%) of the Si and termination atoms to the HOMO and LUMO of the ground electronic states.

Si-cluster	$Si_{10}H_{16}$		$Si_{10}OH_{16}$		$Si_{10}FH_{16}$	
MO	(H)	(L)	(H)	(L)	(H)	(L)
s- orbital	26	59	21	56	25	58
p- orbital	74	41	79	44	75	42

(H) : HOMO; (L) : LUMO

4. Conclusions

In conclusion, our simulations have shown that the electronic structure of Si-cluster not only depends on the size but also on the kind of termination atoms. The important feature of these calculations is the effect of O termination atom, which plays an important role in modifying the electronic structure. The number of O termination atoms virtually monitor the luminescence process. The H termination lead to a stable Si-cluster structure and the F atoms do not play significant role. We propose that the effect of O termination atoms should be considered for the visible luminescence process.

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