Band-Gap Engineering by III-V Infill in Sodalite

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We study the structure of III-V clusters in sodalite by *ab initio* molecular dynamics (Car-Parrinello) and find strong bonding of the group III atoms to the oxygens of the cage with loss of tetrahedral order. The clusters introduce optically active states in the zeolite energy gap and turn it into a semiconductor with energy gap determined by its chemical nature rather than by quantum confinement. Within the local density approximation we find values of ≈ 0.4 and ≈ 1.9 eV for InAs and GaN clusters of the same size. We suggest that the growth of selected compounds in zeolite may lead to wide gap semiconductors for blue light emitting devices.   [S0031-9007(96)01996-5]

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Semiconductor filling of mesoporous matrices such as zeolites, MCM-41, and asbestos is recently actively explored as an alternative route to the search for tunable light emitting devices exploiting quantum confinement effects in semiconductors [1,2]. The expected advantage of this approach with respect to conventional lithography is the possibility of including clusters of very small dimensions and uniform size distribution as well as reducing the production costs. It constitutes a self-organizing strategy to the growth of low-dimensional structures similar in spirit to the growth of porous silicon [3] or to growth on high index planes [4].

In this paper we report a first principles calculation of the sodalite ($Si_6Al_6O_{24}$) crystal with infilled III-V semiconductor clusters. We use the *ab initio* molecular dynamics, Car-Parrinello method [5], to identify the stable, energy minimized structures and the resulting electronic and optical properties. Our main findings can be summarized as follows: (i) Bulklike tetrahedral coordination is lost due to strong interactions with the zeolite cage: Only group III atoms bond to the oxygen in the cage, leading to segregation of saturated group V atoms in the interior of the cage. Therefore, the growth inside large pore materials is likely to stop after a bilayer of III-V is formed and a pronounced dependence of the luminescence on the pore size is not to be expected. (ii) The resulting energy gap of the cluster is determined by its chemical nature rather than by size quantization. We find a linear relation between the cluster energy gap and that of the corresponding bulk material for the three cases studied here (InAs, GaP, GaN). Conversely, only marginal variations of the energy

gap are found for clusters of the same material and different sizes. Therefore, tunability of the gap can be obtained by varying the infill material. In particular, blue light emitting devices could be obtained by GaN growth in zeolite matrices, bypassing the well-known problem of finding a suitable substrate for epitaxial growth of this material. In fact, within the usual local density approximation (LDA) underestimation of the energy gap, we find a gap value of ~1.9 eV for GaN clusters in sodalite.

Calculations of the structural stability and of the electronic properties are performed by means of the *ab initio* molecular dynamics, Car-Parrinello method [5]. We have recently studied, within the same theoretical approach, the sodalite crystal [6] and isolated hydrogen saturated III-V microclusters [7], wherein some details on the methodology may be found. We use the unitary cell of sodalite ($Si_6Al_6O_{24}$) with periodic boundary conditions to represent the full crystal. The volume of the unit cell is twice the volume of the sodalite cage, so that we can choose to fill either each cage with one cluster (filling factor 1) or every two cages with one cluster (filling factor $\frac{1}{2}$). We use first-principle soft pseudopotentials [8] for the first-row elements (O and N) and norm-conserving pseudopotentials [9] for the other elements. The chosen energy cutoff of 20 Ry for the plane-wave basis set ensures a good convergence of the results. In particular, we have checked that an increase of the cutoff from 20 to 25 Ry results in negligible changes of the structural properties of the sodalite cage [6]. The electronic properties are calculated only at the Brillouin zone center Γ, which in view of the large unit cell of the sodalite should yield a good

description of the electronic charge density. The favorable comparison of the structural parameters and of the electronic density of states calculated within this approximation with the experimental data for natural sodalite [6] supports this assumption. The extension of our calculation to a larger set of k points by use of parallel computers is planned for the future. The exchange-correlation functional is treated within the LDA. In a very recent calculation of methanol in sodalite [10] using a similar approach, generalized gradient corrections (GGA) to LDA were included in order to improve the description of the hydrogen bonds, which are poorly described in LDA. In the present calculation we believe that LDA is appropriate since it usually accurately describes strong covalent bonded systems. Moreover, the GGA do not significantly improve the LDA underestimation of the energy gap in semiconductors which is of interest here [11]. The search for the most stable geometry of the III-V cluster is performed using a simulated annealing approach [5], which allows one to pass over local minima in the potential energy surface. A typical total simulation time for each cluster is about 1 ps.

We focus first on the structural properties of the cluster in interaction with the sodalite cage. We have first considered a structure with one Ga_4P (In_4As, Ga_4N) tetrahedral cluster replacing the Na_4Cl present in natural sodalite in each cage. The equilibrium structure is found to have only three Ga (In) atoms bonded to the P (As, N) atom, with different bond lengths (see Table I). The fourth Ga (In) atom moves away and gets weakly bonded to the cage in the center of the opposite hexagonal face, rather than remaining attached to the cluster and starting to build a new shell of neighbors. We would expect this atom to move out of the structure were it not forced to remain in the simulation box. In Table I we summarize our findings concerning the interatomic distances and bond angles for each cluster studied.

We have next analyzed a structure with a Ga_3P cluster in each cage. The energy minimized structure appears to

be the same as in the previous case, suggesting the Ga_3P to be the stable structure for growth with 3:1 and 4:1 Ga:P ratios. The most remarkable feature is that only Ga atoms take part in the bonding to the active O sites of the cage, while the P atom remains in the interior of the cage. This tendency becomes even more evident for larger clusters such as the Ga_4P_4, which we describe next. In this case we chose a filling factor of $\frac{1}{2}$. We begin the simulation with the included cluster having the shape of a simple cube with alternating arrangements of Ga and P atoms at the corners. The motivation for considering this structure is twofold. (i) Our previous study of hydrogenated III-V clusters [7] had shown an unexpected structural stability of cubic clusters. (ii) This situation puts anions and cations in completely symmetric positions with respect to the cage, making the choice of the resulting bonding unbiased. At the beginning of the simulated annealing, the cluster remains for a while undistorted, as in the case of local energy minima, and then a sudden dramatic structural rearrangement takes place with an energy gain of ~5 eV. The resulting minimized structure is shown in Fig. 1. The tendency of Ga atoms to bond to the cage, together with that of P atoms to stay away from it, gives rise to complete
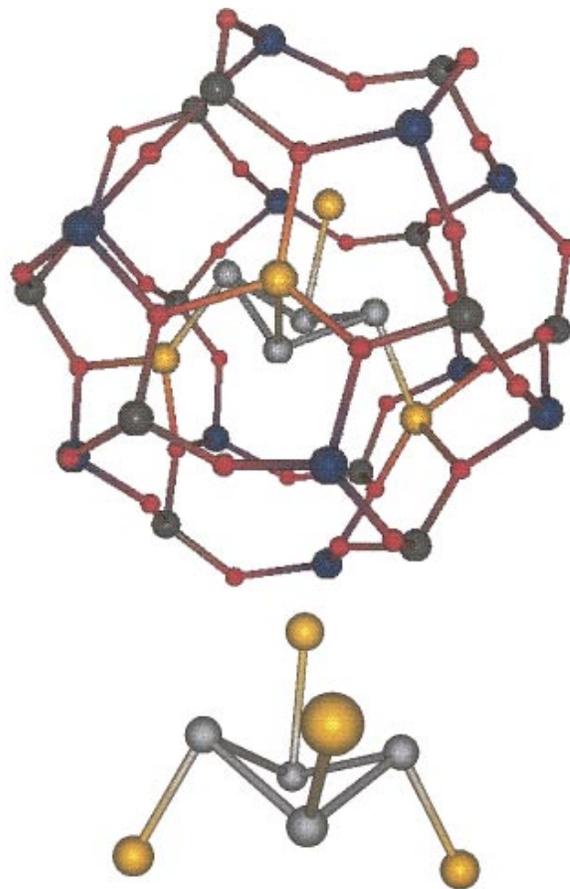
TABLE I. Geometrical parameters for all the studied III_4V clusters in sodalite. The notation $2(III_4V)$ indicates that we have two III_4V clusters per unit cell. In fact, the simulation box has a volume twice as large as the sodalite cage. Notice that the III-V bonding distances are similar to the bulk values: 2.36 Å (GaP), 2.61 Å (InAs), and 1.96 Å (GaN:zinc-blende).

	Distances III-V (Å)				Angles III-V-III (°)		
			$2(Ga_4P)$				
P_1-Ga	2.17	2.39	2.62	4.27	85.1	103.5	112.2
P_2-Ga	2.15	2.48	2.65	2.94	91.1	115.5	122.0
			$2(In_4As)$				
As_1-In	2.48	2.71	2.86	4.91	97.7	106.7	108.5
As_2-In	2.47	2.96	2.97	5.20	88.4	103.8	104.7
			$2(Ga_4N)$				
N_1-Ga	1.82	1.90	2.00	3.42	103.0	108.7	147.9
N_2-Ga	1.82	1.90	1.95	3.38	111.4	114.4	116.2

FIG. 1(color). Optimized geometry of Ga_4P_4 included in the sodalite unit. Silicon: blue balls; aluminum: dark grey balls; oxygen: red balls; gallium: yellow balls; phosphorus: light grey balls. In the inset we show for clarity the cluster alone.

segregation of P atoms in the center of the cluster. Each P atom is threefold coordinated with two P atoms (at distances of ~2.24 Å) and one Ga atom. Of the four Ga atoms, two have retained fourfold, almost tetrahedral, coordination to one P atom and three O atoms, the third Ga is bonded to one P and two O atoms, while the fourth has only one strong bond with the P atom. This fact suggests that the bonding to O occurs only up to the filling of the O $2p$ band with about six electrons. In the natural sodalite, the six electrons are provided by the two Na_4Cl clusters in the sodalite unit cell [6].

In view of the stability of the Ga_3P cluster we have also examined the Ga_6P_2 cluster in order to ascertain whether two such clusters are likely to form in the same cage. Furthermore, this study can also confirm whether the saturation of the Ga-O bonds stops after transfer of about six electrons. Also in this case, the minimal energy structure has undergone a deep transformation from the initial bipyramidal geometry: The cluster is reduced to a Ga_3P_2 fragment where, again, the P atoms are strongly bonded to each other and to two Ga atoms. The remaining three Ga atoms have very weak bonds to the cage and to the P atoms. Bonding to the cage occurs only via the Ga atoms, with a total of six strong O-Ga bonds per unit cell.

On the basis of our findings we predict that III-V infills in sodalite lead to a new artificial material where the strong interactions with the electronegative oxygen atoms of the cage strongly modify the III-V bulk bonding. Despite the relatively small size of the zeolite cage considered here, the tendency to form oxygen-cation and anion-anion bonds is so strong that we expect that the growth in zeolites with larger pore sizes is likely to stop after the formation of one shell of cations and one of anions. This result could explain the considerable disorder observed in the case of a larger GaP cluster in the supercage of the zeolite Y [1,12]. This finding is corroborated by Ref. [12] as well as by recent EXAFS results of InP infill in ALPO-5 [13] at the In K edge [14], displaying a double structure for the In first neighbors at ~2.0 and ~2.5 Å, which we interpret as due to bonding of In to O and P atoms, respectively. Unfortunately, to our knowledge no data exist for P coordination where we do not expect the 2.0 Å feature related to O-P bonding.

We close the discussion of the structural properties by noting that large rearrangements occur only for the included clusters, while the structural parameters of the cage are only slightly affected in all the cases presented: Only the Si-O-Al angles display fluctuations of about 10% around the undistorted values.

Despite the drastic changes in bonding and coordination, we show next that the electronic properties are determined by the local chemical bonding and remain directly related to those of the bulk semiconductor materials. In Fig. 2 we show the calculated electronic density of states for all the sodalite-III_4V samples studied, in comparison with that of natural sodalite. The common denominator is that the infill introduces a number of electronic states in the
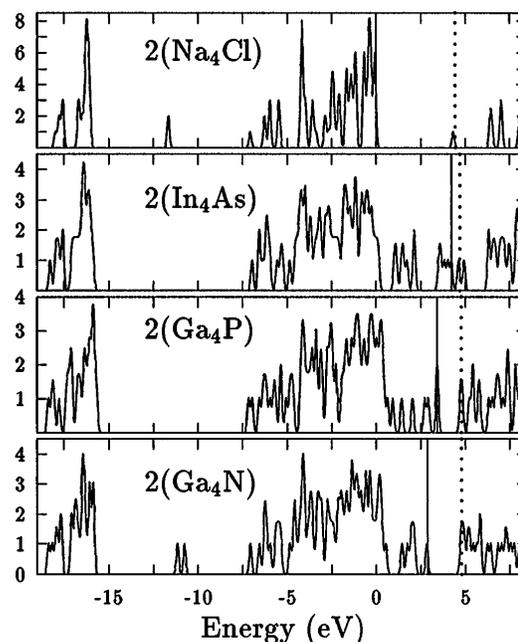

FIG. 2. Electronic density of states for Ga_4P, In_4As, and Ga_4N clusters infill in sodalite compared with that of natural sodalite (Na_4Cl: top panel). These curves are aligned using the center of the lowest energy band, around -17 eV. The full and dotted vertical lines indicate the position of the top of the valence band and the bottom of the conduction band, respectively.

large energy gap of the zeolite (between 0 and 4.4 eV in the figure) resulting in a semiconductor material. The energy gap shows a strong dependence on the particular chemical composition of the cluster in spite of the similar bonding and structure. Moreover, a clear correlation of the resulting gap to that of the corresponding bulk material is observed, as shown in Fig. 3. In view of the results of Table I, this result can be interpreted in terms of a tight binding picture [15]. In view of the structural stability of
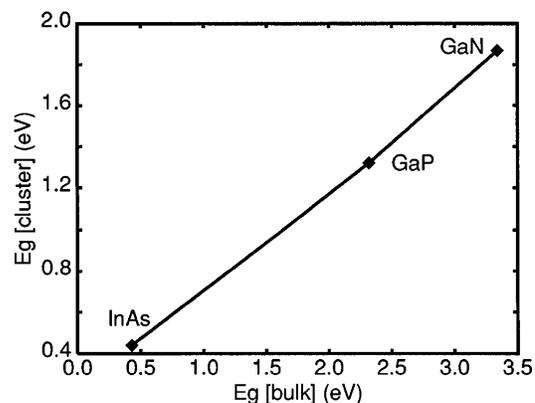

FIG. 3. The calculated LDA energy gap for three different III_4-V clusters in the sodalite unit as a function of the experimental energy gap of the corresponding bulk III-V material (from Cohen and Chelikowsky, *Electronic Structure and Optical Properties of Semiconductors,* Ref. [17]).

all these compounds, we believe that this finding could lead to successful growth of wide gap semiconductors by GaN infill in zeolites.

For all the GaP clusters studied with different Ga:P ratios, the resulting gap depends only marginally on the specific microcluster and remains at ~1.5 eV. Even considering that LDA usually underestimates the energy gap, this value is much smaller than expected on the basis of quantum confinement in nanometer size dots: In particular, in our previous study [7] of similar III-V clusters, where hydrogen termination did not lead to drastic structural rearrangements, the gaps were much larger (3–4 eV) and in the same range for all materials considered. We can interpret these results as due to the chemical bonding of the new segregated III-V material as resulting from the interaction with the cage. Therefore the standard picture of quantum confinement of III-V materials in zeolite cages [12,16] has to be thoroughly reexamined and is certainly inappropriate for the present system. One remarkable feature of the charge density of the highest valence and lowest conduction states is that the highest valence state is very well localized on the infill, whereas the lowest conduction state displays also small s-like contributions on the O atoms of the cage. It appears that the growth of the gap is limited on the high energy side by the presence of the O $3s$ orbitals. This is also consistent with the results of Fig. 2 which show that the lowest conduction state falls, for all infill materials, at an energy close to that of the O $3s$ orbitals, constituting the lowest conduction state of the natural sodalite [6].

Lastly, we focus on the optical activity of these systems. We have computed the matrix elements for optical transitions [7] which give a measure of the probability of light absorption. It is interesting to note that the fundamental interband transition has finite strength, particularly for the Ga_3P case, resulting in a promising candidate for light emission. We believe our results to be of importance for the interpretation of the recent experimental observations of Ref. 16; the luminescence spectra for InP infill in a number of zeolites with pore sizes varying from 7 to 40 Å remain, in all cases, very close to the InP bulk value, ranging from 1.4 to 1.6 eV. In particular, for InP infill in ALPO-5, which has a structure very similar to the sodalite, a large contribution around 1.5 eV is added to the weak luminescence of the cage. We suggest that the photoluminescence in these systems is related to the local chemical bonding rather than to confinement effects, and that a large shift to the blue with decreasing pore size is not to be expected. Rather, variations of the recombination efficiency may result from the particular microscopic structure realized. It may be possible to obtain sharp, intense luminescence by carefully adjusting the growth conditions so as to obtain only one type of included cluster.

In summary, we have shown on the basis of *ab initio* MD calculations that the inclusion of III-V clusters into sodalite cages is expected to lead to a new artificial semiconductor material with tunable electronic properties.

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