

Ordered arrays of identical Nb₄ clusters on the GaN(0001) surface studied with first-principles calculations

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Based on the first-principles total-energy calculations within the density-functional theory, the (2×2) and (3×3) arrays of tetrahedron- and quadrangle-Nb₄ clusters on the GaN(0001) surface have been studied. We show that the periodically two-dimensional arrays of Nb₄ clusters on the GaN(0001) surface are very stable at two of the surface adsorption sites. Once the Nb₄ clusters locate at the stable sites, it is difficult for them to diffuse, since the potential barriers for the diffusions are relatively high. We also predict that on the GaN(0001) surface, the well-ordered (3×3) arrays of identical Nb₄ clusters are the ones with maximum density for the tetrahedron- and quadrangle-Nb₄ quantum dots.

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The fabrication and understanding of nanostructures have become an exciting area of research. For example, the recently discovered ordered array of metal clusters on semiconductor substrate is a form of artificial two-dimensional (2D) lattice,¹⁻⁷ which has not only advanced the control of nanofabrication to ultimate atomic precision but also provided a platform for studying next-generation microelectronics such as tuning the Schottky contact, 2D spintronics, surface superconductivity, and nanocatalysis. To date, few research has been done on the ordered arrays of metal clusters on the wurtzite GaN(0001) surface. The physics of such ordered cluster arrays is rich but has not yet been fully explored. For example, the limit of density about the separated ordered metal clusters on this substrate is not understood, even though such a maximum density could be vital to the eventual application of the cluster arrays, for example, in microelectronics, ultrahigh-density recording, and nanocatalysis.

The system of Nb₄ clusters on the GaN(0001) surface is unique because the Nb₄ cluster has two stable structures, the quadrangle-form (2D-Nb₄) and the tetrahedron-form (3D-Nb₄), which contains the least atoms among the three-dimensional clusters, and the 3D-Nb₄ is the smallest one among the most stable magic Nb_n clusters.⁸ The particularly strongly bound system of Nb₄ suggests the importance of the electronically and atomically closed-shell structure.⁹ These special properties help the Nb₄ clusters to form separated arrays with maximum density on the semiconductor substrate. It is noteworthy, however, that, despite many studies on the free Nb clusters^{8,9} and the ones adsorbed on the Cu surface,¹⁰ a phase with an ordered clusters array on the semiconductor GaN(0001) surface has not been investigated.

In this paper, we carry out a comprehensive study of the atomic and electronic properties of the (2×2) and (3×3) arrays of Nb₄ clusters adsorbed on the GaN(0001) surface, including the preferred adsorption sites, the distortion of Nb₄ upon adsorptions, the relaxation of substrate, the adsorption cohesive energies, and the charge density redistributions, using first-principles total-energy calculations within density-functional theory. The calculations are performed using the Vienna *ab initio* simulation package (VASP), which is based on the Perdew-Wang 1991 version of the generalized gradi-

ent approximation¹¹ and the projector augmented wave representation.^{12,13} A six-bilayer slab and a four-bilayer slab, both separated by a 16 Å vacuum region, are used to model the (2×2) Nb₄ adsorption and the (3×3) -Nb₄ on the wurtzite GaN(0001) surface, respectively, with the bulk GaN lattice constant are taken to be $a=3.21$ Å and $c=5.24$ Å. The Nb₄ clusters are adsorbed only on one side of the slab, and the other side are passivated by pseudohydrogen atoms. A default plane-wave cutoff energy of 520 eV is used for all the elements in the calculations. The surface Brillouin zone is sampled by using the $2 \times 2 \times 1$ **k**-point mesh in all calculations. In the energy minimization, we allow all atoms in the slab to fully relax except for the atoms in the bottom four bilayers for the (2×2) supercell and two bottom bilayers for the (3×3) supercell, which are fixed at their respective bulk positions. Energy convergence is reached when the forces on the relaxed atoms are less than 0.05 eV/Å.

We first discuss the adsorption sites and binding energies of the (2×2) arrays of Nb₄ clusters on the GaN(0001) surface. The most probable adsorption sites are shown in Figs. 1(a)–1(f); among them, the most stable adsorption site for a 3D-Nb₄ cluster in a (2×2) supercell is the T3_H3 site, with a binding energy of 6.72 eV/cluster. For a 2D-Nb₄ cluster, the most stable adsorption site is the T3_2D one with a binding energy of 8.71 eV/cluster. For the T3_H3 site, the three bottom atoms of the Nb₄ cluster prefer the on-top site of the N atoms (T3), while the other Nb atom locates at above the hollow site (H3) of the GaN(0001) surface (this site is then named as the T3_H3 site, other sites are named according to the same rule). The binding energy is defined as the energy required to separate a single Nb₄ cluster from the GaN(0001) surface. The binding energies for various adsorption sites are shown in Fig. 1(i). The Nb₄ clusters at the T3_H3 and T3_2D sites have the highest binding energies for 3D- and 2D-Nb₄ adsorptions on the surface, respectively. Other adsorption sites, i.e., the top site T3_Ga, the hollow sites H3_T3, H3_Ga, and H3_2D, are all metastable. All the binding energies of the 3D-Nb₄ adsorptions are lower than those of 2D-Nb₄ adsorptions. For example, the binding energy of the 3D-Nb₄ at the T3_H3 site is the highest one among the 3D-Nb₄ clusters on the GaN(0001), but it is lower than the 2D-Nb₄ adsorptions at T3_2D and H3_2D sites by 1.99 and 0.69 eV/cluster, re-

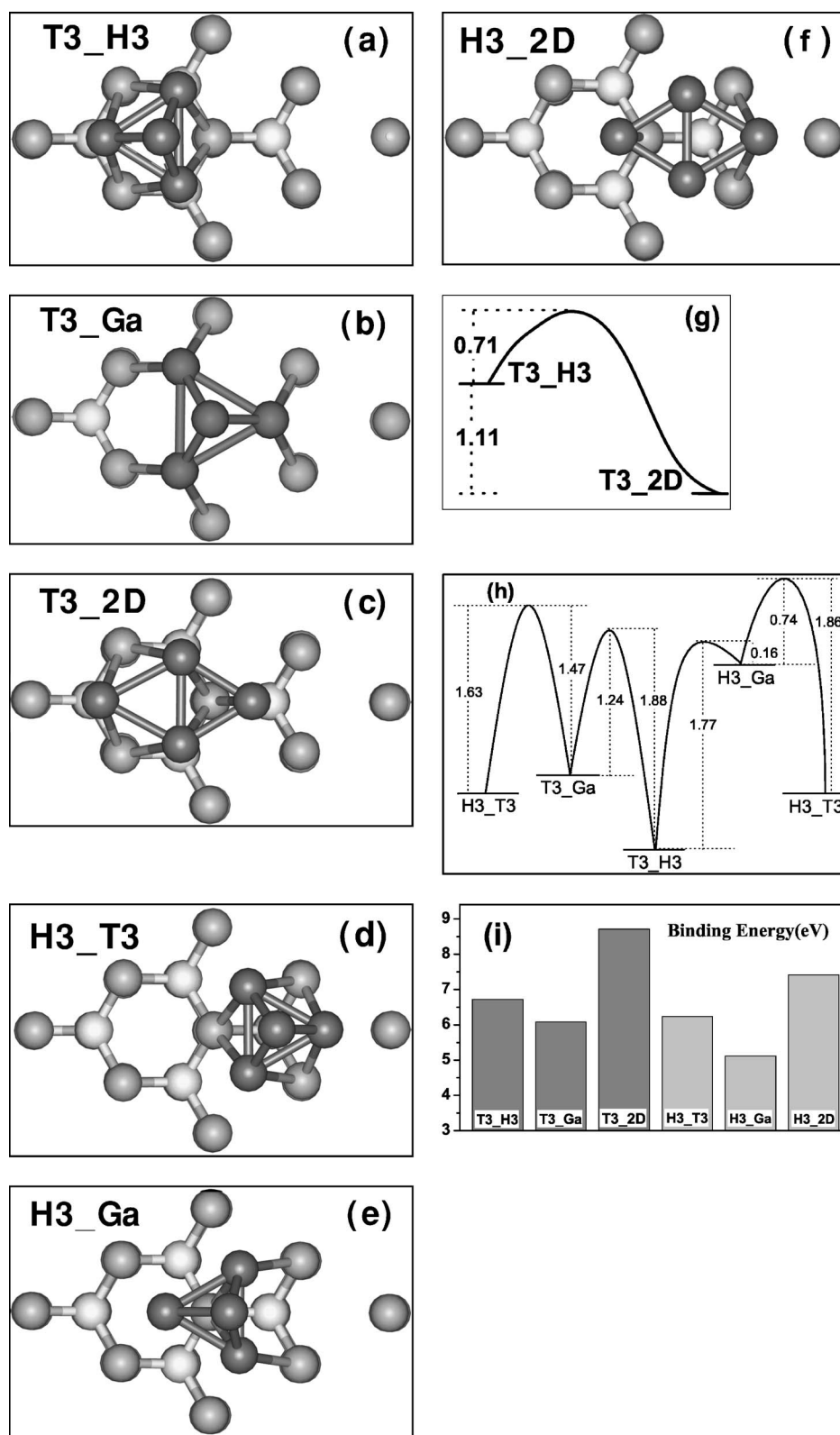


FIG. 1. [(a)–(f)] Top view of six different adsorption sites for the (2×2) arrays of 3D- and 2D-Nb₄ clusters on the GaN (0001) surface: (a) T3_H3 site, with three bottom Nb atoms locate at the top sites (T3) and the top Nb atom at the hollow site (H3). Other sites are named according to the same rule; (b) T3_Ga site, the same as T3_H3 but the top Nb atom locates at the top of surface Ga atom; (c) T3_2D site, the four Nb atoms are at the same plane; [(d)–(f)] the H3_T3, H3_Ga and H3_2D sites. (g) Diffusion barrier between the most stable sites: T3_H3 for the adsorption of (2×2) 3D-Nb₄ clusters and T3_2D for the 2D-Nb₄ clusters on the GaN(0001). (h) Diffusion barriers between various adsorption sites for the 3D-Nb₄ clusters. (i) Binding energies of a Nb₄ cluster at different sites. All the energies are in eV.

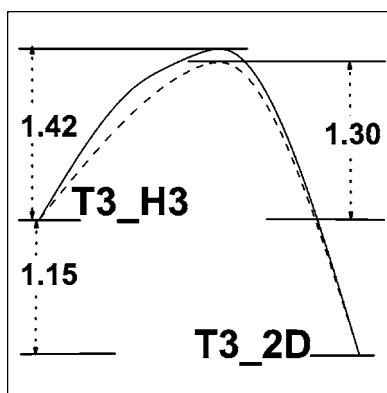


FIG. 2. The potential barrier for the transition from the T3_H3 to the T3_2D, for the (3×3) arrays of Nb₄ clusters on the GaN(0001) surface. Solid curve for the adiabatic movement method, and the dashed curve for the climbing image nudged elastic band method. All energies are in eV.

spectively. These data suggest that the adsorption of Nb₄ with quadrangle shape is more stable than the tetrahedron one on the GaN(0001) surface. This is similar to the case when Nb₄ clusters are adsorbed on the Cu(111) surface.¹⁰ The absolute binding energies for both the T3_H3 and T3_2D sites are higher than the counterparts on the Cu(111) surface by 1.00 and 0.71 eV/cluster, respectively,¹⁰ which indicates that there are stronger interactions between the clusters and the substrate for the Nb₄/GaN(0001), as compared with Nb₄/Cu(111). The ideal GaN(0001) surface is not stable due to the presence of unsaturated dangling bonds; however, for the (2×2) adsorption of Nb₄ clusters the dangling bonds can be effectively saturated, that is, for each (2×2) supercell there are four Ga atoms carrying dangling bonds, one adsorbed Nb₄ cluster can effectively saturates all the dangling bonds due to the short distances between the Nb and Ga atoms.

Diffusion barriers between various adsorption sites for the arrays of (2×2) Nb₄ clusters on the GaN(0001) surface are shown in Figs. 1(g) and 1(h). The diffusion barriers between various adsorption sites have been calculated by adiabatic movements of corresponding atoms. For example, to calculate the diffusion barrier as shown in Fig. 1(g), the top Nb atom of Nb₄ is moved from Figs. 1(a) and 1(c) by several steps along an arc which is estimated according to the hard-sphere model. Except for the last step, we keep the positions of all the other three Nb atoms and the substrate atoms unchanged. For the last step, the atoms move directly to the fully relaxed configurations, as shown in Fig. 1(c). Our calculations on the diffusion barriers are verified by a checking calculation based on the climbing image nudged elastic band method.¹⁴ Comparison between our method and the climbing image nudged elastic band method is shown in Fig. 2, and the barrier difference between two methods is around 8%. The calculation results for the arrays of (2×2) Nb₄ on the GaN(0001) surface show that the 3D-Nb₄ cluster at T3_H3 site can transfer to 2D-Nb₄ cluster at T3_2D site by overcoming an energy barrier about 0.71 eV/cluster, whereas the activation energy of the reverse process is about 1.82 eV/cluster. As the facts mentioned above, the Nb₄ clus-

ters at T3_H3 and T3_2D sites are the lowest adsorption sites for the 3D- and 2D-Nb₄ adsorptions, respectively. Since the energy barriers between various adsorption sites are relatively high (e.g., almost all barriers are larger than 1 eV), both the T3_H3 and T3_2D adsorption sites are quite stable, which suggests that the adsorption of Nb₄ clusters would prefer these two sites under moderate temperatures. On the other hand, it should be pointed out that the calculations on the differences of electron densities for the (2×2) arrays of Nb₄/GaN(0001) show that there are areas of slightly charge overlaps between the neighboring Nb₄ clusters for both the 3D- and 2D-Nb₄/GaN(0001) systems. This indicates that Nb₄ clusters with (2×2) arrays on the GaN(0001) surface are not completely separated. We, therefore, enlarge the supercell from (2×2) to (3×3) in order to increase the distances between the adsorbed Nb₄ clusters on the GaN(0001) surface and to find a system with a separated array of quantum dots.

Now we turn to the (3×3) arrays of 3D- and 2D-Nb₄ clusters on the GaN(0001) surface. We discuss here only the most stable adsorption sites, i.e., the T3_H3 and T3_2D sites for the adsorptions of 3D- and 2D-Nb₄ clusters, respectively, as shown in Figs. 3(a) and 3(b). The binding energy of T3_H3 is now 7.59 eV/cluster which is 0.87 eV/cluster larger than the (2×2) -Nb₄ arrays. For 2D-Nb₄ cluster, the binding energy at T3_2D is now 9.64 eV/cluster, which is also 0.93 eV/cluster larger than the (2×2) arrays. These binding energy data indicate that the interactions between the Nb₄ clusters and the GaN substrate for the (3×3) -Nb₄ adsorptions are stronger than the (2×2) adsorptions. Again, the 2D-Nb₄ adsorptions are more stable than the 3D-Nb₄ ones on the GaN(0001) surface. For the geometry of (3×3) -Nb₄ adsorptions, the positions of surface layer atoms have been found to relax a little, for example, the surface Ga atoms beneath the 2D-Nb₄ clusters are observed to shift their positions down by 0.30 Å. The potential barrier for the transition from T3_H3 to T3_2D, i.e., from Figs. 3(a) and 3(b), is estimated to be 1.42 eV/cluster, which is noticeably larger than the (2×2) surface which is only 0.71 eV/cluster. This remarkable potential barrier for the (3×3) adsorptions makes the transition from 3D-Nb₄ to 2D-Nb₄ on the GaN(0001) surface more difficult than the (2×2) adsorptions, and thus both the 3D-Nb₄ and 2D-Nb₄ adsorptions on the (3×3) surface are more stable than the (2×2) surface. Compared with the case of Nb₄/Cu(111), where the diffusion energy barriers are relatively low (by 0.21 eV/cluster),¹⁰ the transition from 3D-Nb₄ to 2D-Nb₄ on the Cu(111) surface becomes relatively easier. Due to the high diffusion barriers and strong interactions within the Nb₄ clusters, it is difficult for the Nb₄ clusters to transform into other forms on the GaN(0001) surface, in contrast to the phenomenon happened on Si(111)- 7×7 , where Pb clusters could easily transform into other forms when the growth temperature deviated slightly from the optimal value.¹⁵

The differences of electron charge densities for the (3×3) array of 3D- and 2D-Nb₄/GaN(0001) systems have been shown in Figs. 3(d)–3(g), in order to see the nature of interactions between the adsorbed Nb₄ clusters and the GaN(0001) surface and between the neighboring Nb₄ clus-

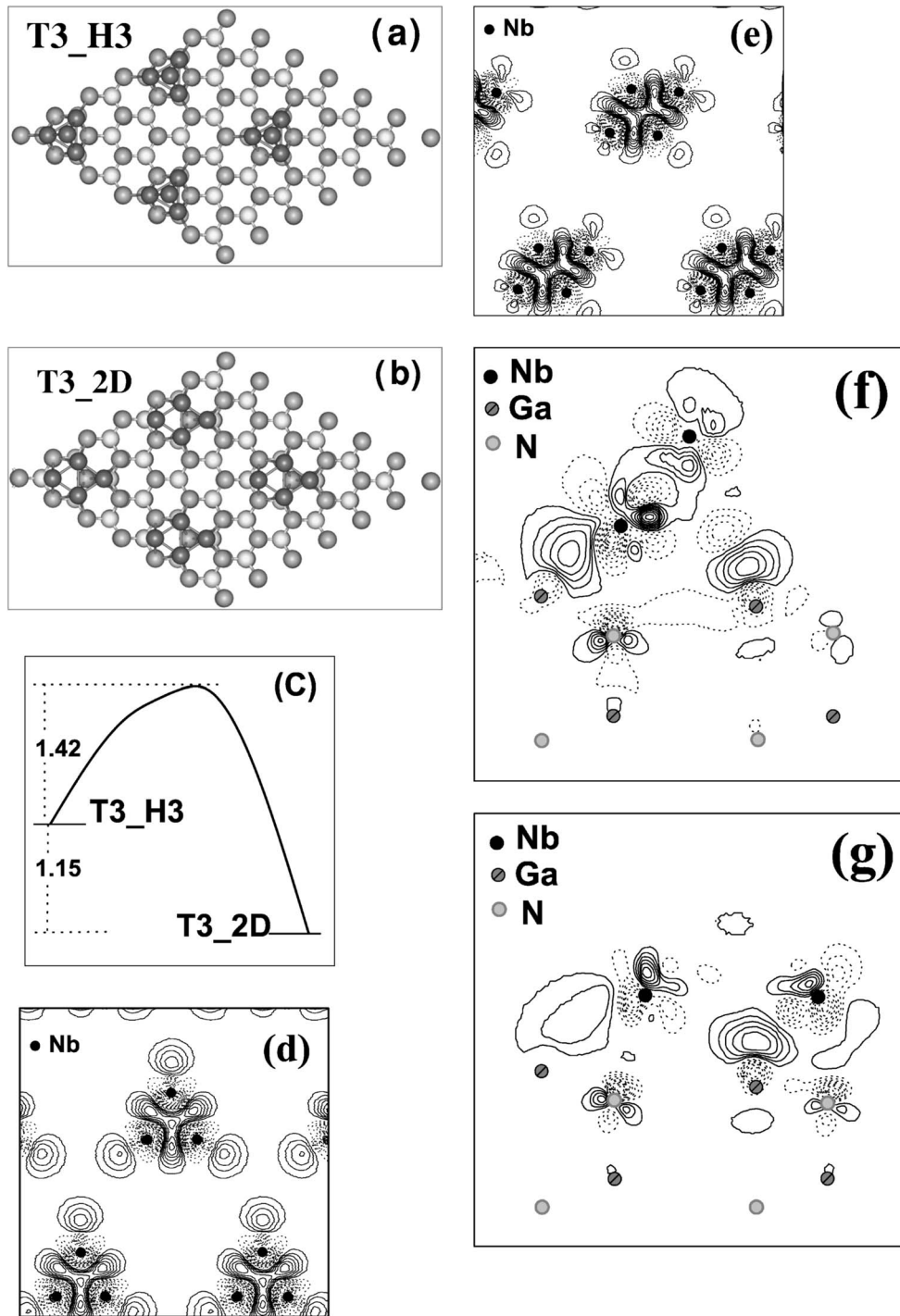


FIG. 3. [(a) and (b)] Top view of (3×3) arrays of Nb_4 clusters on the GaN(0001) surface, showing (a) the T3_H3 sites for the adsorption of 3D- Nb_4 clusters and (b) the T3_2D sites for the 2D- Nb_4 clusters. (c) The potential barrier for the transition from the T3_H3 to the T3_2D. All energies are in eV. [(d)–(g)] Contour plots of two kinds of charge density differences (see text for detailed definitions): (d) $\Delta\rho_1(\vec{r})$ for the 3D- $\text{Nb}_4/\text{GaN}(0001)$ at the T3_H3, the plotted plane is parallel to the GaN surface and crossing the three bottom Nb atoms; (e) same as (d), but for the 2D- $\text{Nb}_4/\text{GaN}(0001)$ at the T3_2D; (f) $\Delta\rho_2(\vec{r})$ for the 3D- $\text{Nb}_4/\text{GaN}(0001)$ at T3_H3, the plotted plane is vertical to the GaN surface and crossing the two Nb atoms; (g) the same as (f), but for the 2D- $\text{Nb}_4/\text{GaN}(0001)$ at T3_2D. Solid and dashed lines correspond to $\Delta\rho > 0$ and $\Delta\rho < 0$, respectively.

ters. One of the contour plots of the charge density differences, which helps to visualize the characteristics of bonding, is defined as the differences between the adsorbed Nb₄/GaN(0001) systems and the superposition of atomic charge densities, i.e., $\Delta\rho_1(\vec{r}) = \rho[\text{Nb}_4/\text{GaN}(0001)] - \sum_{\mu} \rho_{\text{atom}}(\vec{r} - \vec{R}_{\mu})$. Such contour plots for the most stable (3×3) arrays of 3D- and 2D-Nb₄ clusters on the GaN(0001) surface are, respectively, presented in Figs. 3(d) and 3(e). A feature of strong covalent bonding within each cluster can be clearly found for both the 3D- and 2D-Nb₄ clusters, which is similar to the free Nb₄ clusters.¹⁰ In particular, the overlap of charge densities between the neighboring Nb₄ clusters, which has been found in the (2×2)-Nb₄/GaN(0001) system, has completely disappeared in the present (3×3)-Nb₄/GaN(0001). Such a picture reveals that the neighboring Nb₄ clusters have now been fully separated physically, indicating that there are no direct interactions between the neighboring Nb₄ clusters and the arrays of (3×3) Nb₄ on the GaN(0001) surface form separated quantum dots. The results also mean that the (3×3) array of Nb₄ on the GaN(0001) surface is the array with maximum density of separated quantum dots on the GaN(0001) surface. In order to visualize the charge transfers between the adsorbates and the substrate, another contour plot for the charge density differences is defined as the difference between adsorbed Nb₄/GaN(0001) and the independent two-dimensional Nb₄ sheet and the clean GaN(0001) surface, i.e., $\Delta\rho_2(\vec{r}) = \rho[\text{Nb}_4/\text{GaN}(0001)] - \rho(2\text{D-Nb}_4) - \rho[\text{GaN}(0001)]$. Such contour plots for the most stable (3×3) arrays of 3D- and 2D-Nb₄ clusters on the GaN(0001) surface are presented in Figs. 3(f) and 3(g). Significant charge redistribution can be clearly visible between the Nb₄ adsorbate and the GaN surface layer. In particular, the plots show that the charge redistribution happened significantly only around the surface GaN bilayer, i.e., electron charge densities of GaN subsurface layers are rarely disturbed upon the Nb₄ adsorption. Both the charge redistribution and charge-transfer plots, as shown, indicate that the interactions between the adsorbates and substrate should be strong. Furthermore, with quite strong interactions between Nb atoms in the free Nb₄ clusters (the binding energy of a free Nb₄ cluster is 15.0 eV/cluster for 3D-cluster and 14.1 eV/cluster for 2D cluster¹⁰), the adsorbed Nb₄ clusters tend to maintain their compactness structures on the GaN(0001) surface. Each cluster should be able to be well identified on this surface. Importantly, the electronic density calculations also show that the neighboring Nb₄ clusters of the (3×3) adsorptions are now well separated from each other by zero regions of $\Delta\rho$, as shown in Figs. 3(d) and 3(e). In contrast, the electronic densities of the neighboring Nb₄ clusters are slightly overlapped with each other when Nb₄ are adsorbed with a (2×2) array. These results suggest that the (3×3) ordered arrays of Nb₄ clusters on the GaN(0001) surface is the array with maximum density for separated 3D-quantum dots, which should offer significant help for the experiments of quantum-dot growth on this surface. Noted that for both (3×3) arrays of 3D- and 2D-Nb₄/GaN(0001) systems, the densities of separated Nb₄ quantum dots are very high which may also have important applications, e.g., in the high-density memories, catalysis, and the developing nanostructure devices.

The differences of Nb₄ structural stabilities adsorbed on different supercells of the GaN(0001) surface are tied to the different behaviors of Nb₄ bonding with the substrate atoms. For example, for the (2×2) array 3D-Nb₄ at the T3_H3 sites, each of the three bottom atoms of Nb₄ makes bonds with three Ga surface atoms, in which there is one Ga atom who is shared by three neighboring Nb₄ clusters simultaneously. In contrast, for the (3×3) array of 3D-Nb₄ adsorptions at T3_H3, the Ga atom shared by neighboring Nb₄ clusters at (2×2) now makes bond with only one cluster, due to the larger distance between the (3×3)-Nb₄ clusters. As a result, the interactions between the adsorbates and the substrate become stronger for the (3×3) array of 3D-Nb₄ on the GaN(0001). Furthermore, compared to the (2×2) adsorptions, the larger distance between the (3×3)-Nb₄ clusters leads to weaker interactions between the neighboring Nb₄ clusters. The electrons which contribute to the interaction between the neighboring Nb₄ clusters at (2×2) now join in the interaction with the substrate at (3×3), which also contributes to the increase of the interaction between the adsorbates and the substrate. For both the (2×2) and (3×3) arrays of Nb₄ on the GaN(0001) surface, due to the planar structure, the 2D-Nb₄ cluster has more nearest-neighbor Ga atoms to interact with than the 3D-Nb₄ cluster, leading to larger binding energies (better stabilities) of 2D-Nb₄/GaN(0001) than 3D-Nb₄/GaN(0001). Experimentally, most of the stable metal clusters adsorbed on semiconductor surfaces also have two-dimensional structures (2D cluster).¹⁻⁷ For the (3×3)-Nb₄ adsorption on the GaN(0001), the surface dangling bonds are not all effectively saturated. For example, for each (3×3) supercell, there are nine Ga atoms carrying dangling bonds, one adsorbed Nb₄ can saturate only the dangling bonds from six surface Ga atoms, as seen from Figs. 3(a), 3(d), and 3(f), with dangling bonds from the other three Ga atoms unsaturated due to the large spacing between the Nb₄ cluster and the Ga atoms. Such a surface structure, however, should correspond to a local minimum on the potential-energy surface.

The theoretical results presented here should have important implications for the experimental studies of the high-density quantum-dot arrays on the semiconductor surface. The high stability of both the 3D- and 2D-Nb₄ on the GaN(0001) surface as predicted here offer alternative systems whose special characters remain to be explored experimentally. In addition, the comparative studies of the (2×2) and (3×3) arrays of Nb₄ clusters on the GaN(0001) surface have shown a density limit for the separated quantum dots, which should also be realized and checked experimentally. For artificial two-dimensional metal clusters on semiconductor substrate, our research also suggests that GaN(0001) surface should be a potential candidate, in addition to the Si(111) 7×7 surface.¹⁻⁷

In summary, the first-principles density-functional total-energy calculations have been used to map out the important adsorption sites and diffusion barriers for the (2×2) and (3×3) arrays of 3D- and 2D-Nb₄ clusters on the GaN(0001) surface. The periodically two-dimensional arrays of Nb₄ clusters are shown to be very stable on the GaN(0001) surface at two of the surface adsorption sites. For both the

(2×2) and (3×3) arrays of Nb_4 clusters, the 2D- Nb_4 adsorptions are more stable than the 3D- Nb_4 ones. The energy barriers between the stable adsorption sites are estimated to be high, suggesting that the Nb_4 clusters would prefer these stable sites under moderate temperatures. Furthermore, there are no electronic density overlaps between neighboring Nb_4 clusters for the (3×3) adsorption in contrast to the case of (2×2) array, showing that the (3×3) array of Nb_4 on the

GaN(0001) is the one with maximum density for the separated quantum dots on this surface. Several implications as predicted are awaiting confirmations in the future experimental studies.

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