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# Surface properties of YN(001): A first-principles calculation

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We have studied the structural and electronic properties of the YN(001) surface by first-principles total energy calculations. In analogy with the ScN(001) surface, we have restricted our study to models having a $(1\times1)$ periodicity. Our calculations predict that the relaxed bulk terminated surface has the lowest formation energy for most of the range of allowed chemical potentials. Electronic properties of this surface are similar to those of the bulk, and the surface is a semiconductor. For strongly Y-rich conditions, a pure $(1\times1)$-Y terminated structure is more favorable than the ideal-relaxed surface. In this case, the surface is found to be metallic.

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Transition metal nitrides have a wide range of technological applications, due to their excellent physical properties that include high hardness, mechanical strength, and high melting point. In particular, titanium nitride, with a high hardness H$\sim$20 GPa, have been extensively used in optical and hard coatings.[1,2] These materials crystallize in the rocksalt structure and they can be either metals or semiconductors. There has been a recent interest in another transition metal nitride: ScN. Early experiments[3] and first-principles calculations based on the local density approximation[4] seemed to indicate that ScN was a semimetal with an almost zero indirect band gap. However, recent experiments have shown that ScN is a semiconductor.[5–8]. These results have been confirmed by calculations using techniques such as screened-exchange (SX) and quasiparticle corrections.[9,10] They have shown that ScN, YN, GdN, and LaN are indirect semiconductors with gaps of $\sim$1–2 eV. Therefore, transition metal nitrides represent a novel and probably technologically important group of semiconductor materials. ScN has a very small lattice mismatch with GaN ($<2\%$), and therefore it has been thought to be useful to combine ScN with GaN as GaN/ScN heterostructures or ScGaN alloys. A similar situation occurs with YN and InN (the difference in lattices constants is $\sim2\%$) and therefore combinations of InN and YN could also be useful in the growth of YN/InN heterostructures or YInN alloys.

Smith *et al.* have reported the growth of ScN smooth films using radio frequency molecular beam epitaxy (RF-MBE).[11–13] In particular, they have found that under N rich conditions, the growth in the (001) orientation is two dimensional, and it results in atomically smooth surfaces with $(1\times1)$ reflection high-energy electron diffraction (RHEED) patterns.[11] This result was confirmed by atomic resolution scanning tunneling microscope (STM) images showing clearly the square $(1\times1)$ unit cell. However, only one of the two sublattices (Sc or N) was observed. An ideally bulk terminated (001) plane contains the two kinds of atoms. Dual bias images obtained at $\pm1$ V showed a very small shift, less than the expected $a/2$, indicating that they were observing the same atoms at both polarities. These results could be due to missing N or Sc atoms, or it could be due to electronic effects of the bulk terminated relaxed surface. In a following paper, Smith *et al.* reported a study of the growth of ScN epitaxial layers for different Sc/N flux ratios. They have found that under Sc rich conditions the growth is also epitaxial, but the Sc excess leads to the formation of N vacancies, and the surfaces are metallic.[12,13]

First-principles calculations have shown that for N-rich surfaces, the most stable configuration corresponds to the ideal relaxed surface.[14,15] Moreover, simulated STM images indicate that the experiments are observing the Sc atoms.[15] Instead, for the Sc rich regime, the most stable configuration corresponds to N vacancies in the first layer, and the surface is metallic.

We are not aware of any experimental or theoretical article on the (001) surface of YN. To be able to use YN in combination with the technologically important GaN, AlN and InN, the nature of its surface becomes important: for example, the stability, the ability to form atomically smooth surfaces and interfaces, its electronic properties, etc. Some differences between the bulk behavior of ScN and YN at high pressures have been recently found. First-principles calculations indicate that ScN is stable up to 340 GPa.[16] Instead, they indicate that at $\sim$140 GPa, YN transforms to a CsCl structure.[17] Therefore, it is also possible that the surface properties of ScN and YN are different. In this paper, we present first-principles total energy calculations of the (001) surface of YN. We have optimized several structures having different number of surface atoms. Similar to ScN(001), our calculations show that for most of the allowed chemical potential range, the most stable configuration corresponds to a relaxed bulk terminated surface. Electronic properties are similar to those of the bulk, and the surface is a semiconductor. Only for a strongly Y-rich surface, the most favorable configuration corresponds to a surface with N vacancies in the first layer. In this case the surface is metallic.

The calculations were performed in the framework of density functional theory. We have employed the full potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN97 code.[18] The exchange and correlation effects were treated using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof.[19] We have used a repeated slab geometry consisting of five atomic (001) planes with one Y and one N atom in a $(1\times1)$ configuration. Resulting atomic relaxations are very small, with the atoms very close to bulk ideal positions. Therefore, the

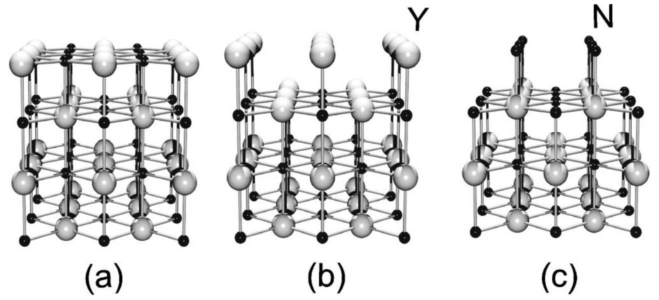


FIG. 1. Schematic view of the surface structure of the $(1\times1)$-YN(001) surface (a) ideal bulk terminated surface, (b) Sc terminated, (c) N terminated surface. Large and small spheres indicate Y and N atoms, respectively.

use of a larger cell containing more layers should not affect the results. A more serious restriction is the use of a $(1\times1)$ periodicity, since some surface structures with larger periodicities may have lower energies. However, this is not the case of ScN(001), and since there are no experimental results on YN(001) to guide us on possible reconstructions, we have restricted the calculations to structures compatible with a $(1\times1)$ cell. The calculated bulk lattice constant of 4.93 Å was used in this work. To decouple two consecutive slabs, we have separated them by an empty region of $\sim$10 Å, corresponding to four atomic layers. We have used muffin-tin radii of $R_N=1.8$ and $R_Y=2.2$ a.u. for the N and Y atoms, respectively, angular momenta up to $l=10$, and 28 $k$ points in the irreducible part of the surface Brillouin zone (SBZ). The atomic positions are relaxed until the forces are less than $10^{-4}$ Ry/a.u. To investigate several possible surface structures that may form under different conditions of growth, we have first determined the optimal geometry of the (001) surface of YN according to three different models, each one having a $(1\times1)$ periodicity. The first one corresponds to an ideally bulk terminated surface [Fig. 1(a)]. The second and third models correspond to a surface in which N [Fig. 1(b)] or Y [Fig. 1(c)] atoms are missing from the first layer.

To compare the relative stability of structures containing different number of atoms, we use the surface formation energy, defined in terms of the thermodynamic potential:

$$\Omega=E_{\mathrm{slab}}(n_Y,n_N)-TS-n_Y\mu_Y-n_N\mu_N,$$

where $E_{\mathrm{slab}}(n_Y,n_N)$ is the total energy of the YN system, $n_Y$ and $n_N$ are the number of Y and N atoms, and $\mu_Y$ and $\mu_N$ are the chemical potentials of Y and N, respectively. The entropy term $TS$ is assumed to contribute very little to the differences in $\Omega$ for the various structures, and it is therefore neglected. The surface formation energy $E_s$ is equal to $\Omega/2A$, where the 1/2 factor comes from the two surfaces that we have in our slab. $A$ is the surface area, which in the present case is the same for all the structures, and it corresponds to the $(1\times1)$ unit cell. The sum of the N and Y chemical potentials is constrained to be equal to the energy per unit cell in bulk YN: $\mu_Y+\mu_N=\mu_{YN(\mathrm{bulk})}$. In addition, $\mu_Y\leqslant\mu_{Y(\mathrm{bulk})}$, and $\mu_N\leqslant\mu_{N(\mathrm{bulk})}$, otherwise a bulk Y or a bulk N would precipitate. These three equations limit the allowed values of their difference $\Delta\mu=\mu_Y-\mu_N$ in the following way:

$$\mu_{Y(\mathrm{bulk})}-\mu_{N(\mathrm{bulk})}-\Delta H<\Delta\mu<\mu_{Y(\mathrm{bulk})}-\mu_{N(\mathrm{bulk})}+\Delta H,$$

where $\Delta H=\mu_{Y(\mathrm{bulk})}+\mu_{N(\mathrm{bulk})}-\mu_{YN(\mathrm{bulk})}$ is the heat of formation of bulk YN from bulk Y and bulk N.

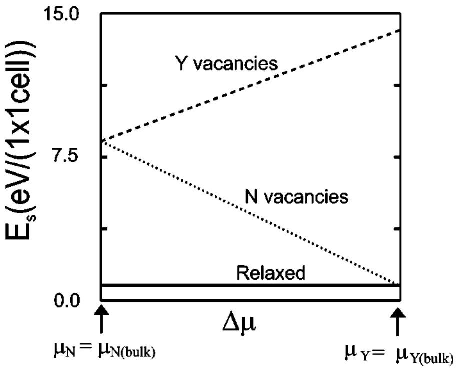


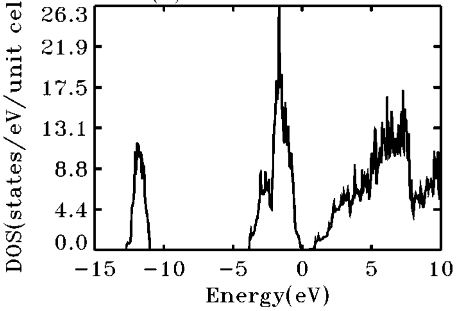
FIG. 2. Surface formation energies for several models of the YN(001) surface as a function of the difference in chemical potentials for Y and N, $\Delta\mu=\mu_Y-\mu_N$. The lower limit for $\Delta\mu$ corresponds to $\mu_N=\mu_{N(\mathrm{bulk})}$ and the upper limit to $\mu_Y=\mu_{Y(\mathrm{bulk})}$. Solid, horizontal line corresponds to the simply relaxed surface, with the lowest energy but near $\mu_Y\simeq\mu_{Y(\mathrm{bulk})}$.

One can then write down the surface formation energy $E_s$ in function of $\Delta\mu$ as

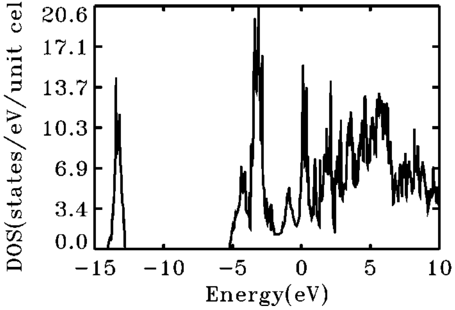
$$E_s=\frac{1}{2A}\left\{E_{\mathrm{slab}}(n_Y,n_N)-\frac{1}{2}(n_Y+n_N)\mu_{YN(\mathrm{bulk})}\right.$$
$$\left.-\frac{1}{2}(n_Y-n_N)\Delta\mu\right\}.$$

The surface formation energies of the structures considered as function of $\Delta\mu$ over the permitted range of $2\Delta H$ are shown in Fig. 2. It can be observed that the N-terminated (Y vacancies) structure is energetically very unfavorable. The relaxed bulk terminated structure (solid, horizontal line) is the most stable one for most of the range of allowed $\Delta\mu$. For the strongly Y-rich condition ( when the Y chemical potential is near is maximum, $\mu_Y\simeq\mu_{Y(\mathrm{bulk})}$, and the N chemical potential is low) the structure with N vacancies becomes slightly more stable (although it can hardly be noticed, the dashed line is lower than the full line at $\mu_Y=\mu_{Y(\mathrm{bulk})}$ in Fig. 2). Different from the case of ScN(001), the difference between the pure $(1\times1)$ Sc terminated and the ideal structure is now very small, and it is close to the limit of the precision of the calculations.

Figures 1(a)–1(c) shows schematically the fully relaxed atomic positions of the relaxed bulk terminated, the Sc, and the N terminated structures. In the relaxed bulk terminated structure, atoms hardly move from their original bulk sites. This result is not surprising, since the ionic character in the bonding of the rock-salt structure tends to suppress charge transfers, and it therefore prevents drastic changes in the surface. There is a small rumpling (0.03 Å) of the Y and N atoms, with both atoms moving slightly inwards, with the N atom being further down. The energy gain associated with



(a) Relaxed



(b) Sc−terminated

FIG. 3. Local density of states for (a) the relaxed ScN(001) surface. (b) Yttrium terminated surface.

the surface relaxation is rather small: $\Delta E \sim 0.04$ eV/ $\times[(1\times1)$ cell]. The other two structures show larger relaxations: the rumpling in the first full layer of the Y and N terminated surfaces are $\Delta z \sim 0.18$ and 0.26 Å, respectively. In general, the changes in atomic positions are larger than in the ScN(001) surface.

To understand the electronic nature of these surfaces, we have calculated the local density of states (LDOS). We have first considered the simple relaxed surface. Figure 3(a) shows the total (LDOS) of the slab. It is very similar to the LDOS of bulk YN, showing a very small gap, indicating that the surface is a semiconductor. Our calculations have been performed using density functional theory, and therefore we expect the gap to be larger. Three main regions can be observed in this figure: one below $-10$ eV and mainly due to nitrogen $2s$ electron, another between $-5$ eV and the Fermi level due to nitrogen $2p$ electrons with a small contribution from Y $4d$ electrons, and the last one in the empty states region with the biggest contribution from Y $4d$ electrons and a smaller contribution from the other electrons. The behavior of the LDOS of this surface is very similar to the one in bulk YN.[17] It basically shows the ionic character of the bonding.

A drastically different situation is obtained in the structure with N vacancies in the Y rich regime. The surface becomes metallic, as the general shape of the LDOS is maintained with respect to the relaxed bulk structure, but with the introduction of new peaks close to the Fermi level in the gap. With the absence of the first layer N atoms, the metallic behavior of first layer Sc atoms is in some way recovered.

Summarizing, in this paper we have performed first-principles total energy calculations of the YN(001) surface. Different structures with periodicity $(1\times1)$ were fully optimized. Calculations of the surface formation energies indicate that for most of the allowed range of chemical potentials, the stable structure corresponds to a simply relaxed bulk terminated surface. There is a very small buckling between the first layer Y and N atoms, with the N atoms being pushed 0.03 Å further down. Electronic properties are similar to those of the bulk, and the surface is a semiconductor. For a strongly Y-rich surface, the most favorable configuration corresponds to a surface with N vacancies in the first layer. In this case the surface is metallic.

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