

Ab initio Study of LuN (001) Surface

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Structural and electronic properties of the lutetium nitride (001) surface have been studied with the density functional theory calculations and *ab initio* thermodynamics. A clean termination may be obtained in a wide range of the N chemical potential, whereas terminations with N vacancies and Lu adatoms may only be formed in Lu-rich conditions. The clean termination exhibits relatively small relaxations of interlayer distances near the surface, which leads to little changes in electronic properties compared to the bulk case. The presence of N vacancies and Lu adatoms may result in charge imbalance at the LuN surface. The findings presented in this work encourage further experimental search for novel rare earth nitride materials.

topics: lutetium nitride, surface, electronic structure, DFT

1. Introduction

Recent theoretical investigations of the electronic structure of LuN indicated an indirect (Γ -X) band gap of 1.08 eV in this semiconductor [1], which is close to those of ScN and YN (0.92 and 1.22 eV, respectively). The doping with Lu is expected to be a promising strategy for band gap engineering in rock salt and wurtzite solid solutions of rare earth (RE) [2] and group III nitrides [3–5]. Furthermore, the metastable hexagonal BN-like phase reported in experimental studies for ScN [6] has also been predicted for LuN in nonequilibrium conditions [3]. The novel hexagonal phase of LuN may exhibit a bigger band gap (1.56 eV [7]) than that of the rock salt compound. The electronic structure of the hexagonal LuN monolayer is interesting because of characteristic valence band splittings, which are driven by strong spin-orbit coupling and may be promising for applications in spintronics [7].

Among RE nitrides (REN), high-quality thin films were reported only for ScN [8, 9]. The (001) oriented ScN materials grown with the molecular beam epitaxy exhibit an atomically smooth surface of the rock-salt structure. Further theoretical investigations based on the density functional theory (DFT) suggested that the ideal (clean) terminations of ScN and YN systems are energetically favorable in a wide range of nitrogen chemical potentials [10–12]. The structural and electronic properties of the LuN surface have not been studied up to now.

In this work, the structure and band gap of the rock salt LuN (001) surface are investigated with the DFT calculations and *ab initio* thermodynamics. The structural relaxation is performed within the generalized gradient approximation (GGA) approach [13], whereas the band gaps and densities of states (DOS) are studied with the Tran-Blaha exchange-correlation functional [14], which is based on the modified Becke-Johnson potential. The discussion of the results is focused on the nitrogen chemical potential required for the formation of particular terminations of the LuN surface. The comparative analysis of electronic structures of bulk and most favorable surface types is presented.

2. Computational details

The calculations have been performed with the use of the Vienna *Ab initio* Simulation Package (VASP) [15, 16] and projector augmented wave method (PAW) atomic data [17]. The fully relativistic approach was used (spin-orbit coupling included). The generalized gradient approximation (GGA) [13] and Tran-Blaha modified Becke-Johnson generalized gradient approximation (MBJGGA) [14] parameterizations of exchange-correlation were employed for geometry optimization and calculations of electronic structure, respectively. The force condition for ionic relaxation was set to 10^{-3} Å/eV. All ionic positions were relaxed. The plane-wave basis of 500 eV was used.

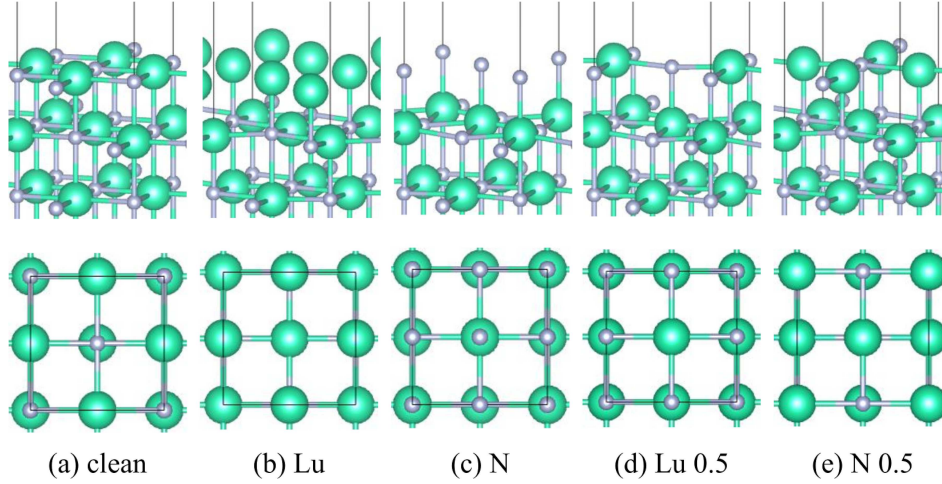


Fig. 1. Side and top views on terminations of LuN (001) surface: clean (a), Lu-terminated (b), N-terminated (c), Lu-deficient (d), and N-deficient (e). Lutetium and nitrogen ions are marked with green and gray colors, respectively.

The $16 \times 16 \times 16$ and $8 \times 8 \times 1$ $\mathbf{k}$ -point meshes were selected for bulk and slab calculations, respectively. The surface was modeled with 14 atomic layers of 2×1 symmetric (bottom and top) rock salt slabs with a vacuum region of $15 \text{ \AA}$. The surface energy was studied based on *ab initio* thermodynamics [18]. Namely, for the chemical potential of the surface assumed to be in equilibrium with that of the bulk, the surface energy can be expressed as a function of the nitrogen chemical potential according to the formula

$$\sigma = \frac{1}{2A} \left[E_{\text{slab}} - N_{\text{Lu}} \mu_{\text{LuN}}^{\text{bulk}} + (N_{\text{Lu}} - N_{\text{N}}) \mu_{\text{N}} \right], \quad (1)$$

where A is the surface area, $N_{\text{Lu/N}}$ are the numbers of Lu/N ions, $\mu_{\text{LuN}}^{\text{bulk}}$ and μ_{N} are the chemical potentials of bulk LuN and gas nitrogen, respectively. The range of possible μ_{N} was limited by the heat formation of bulk LuN (3.53 eV) and the half energy of N_2 molecule (8.32 eV), calculated from first principles, which allows investigations from Lu- to N-rich conditions. A similar approach was employed in previous theoretical investigations of TiN surface [19].

3. Results and discussion

The set of terminations considered in this work corresponds to possible structures grown in various conditions. The clean (ideal), Lu- and N-terminated LuN (001) surfaces, as well as more complex Lu- and N-deficient cases (marked Lu 0.5 and N 0.5), are depicted in Fig. 1. The additional layers of Lu/N ions are present in Lu-/N-terminated structures, whereas in deficient terminations half of Lu/N sites are empty (vacancies).

The cubic lattice parameter a of $4.762 \text{ \AA}$ obtained for rock-salt LuN from the GGA calculations is slightly bigger than the local density approximation

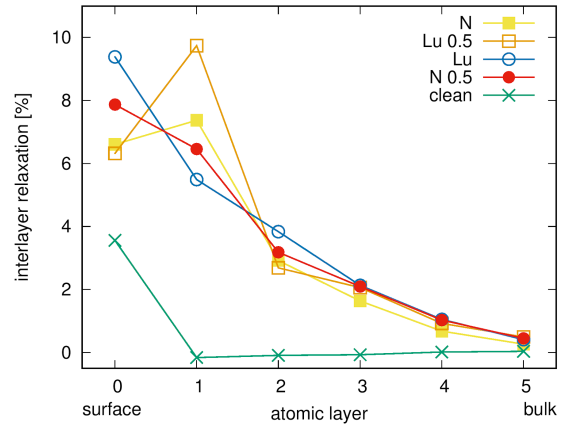


Fig. 2. Interlayer distance relaxations calculated (using GGA) for various terminations of LuN (001) surface.

(LDA) results [1, 2] and in very good accordance with experimental ($4.766 \text{ \AA}$) [20] and previous GGA data ($4.77 \text{ \AA}$) [21]. The bond relaxations of the clean termination are relatively small and limited to the topmost atomic layer, as presented in Fig. 2. It is a characteristic feature of ideal rock-salt REN surfaces in general [10–12]. The modified terminations exhibit significant relaxations of interlayer distances (up to 10%) when compared to the bulk one), which are proportional to the content of Lu ions in the particular material. The bulk-like structure is restored at several layers below the surface. It is worth mentioning that a faster convergence of interlayer distances was revealed in the rock-salt TiN (111) surface [19], which is probably connected with relatively small ionic radii of Ti ions. Comparable amplitudes of interlayer distance relaxations were reported for the 001 terminations of the PbS surface [22].

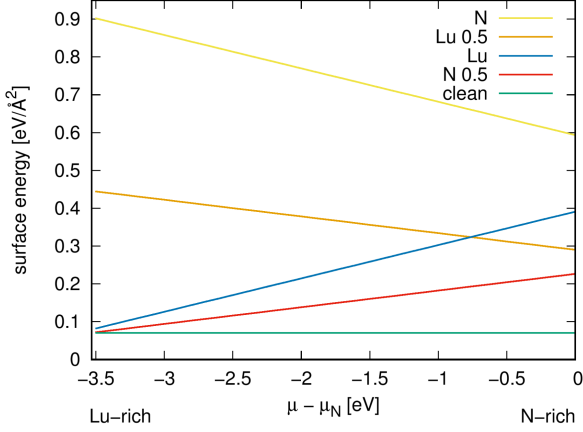


Fig. 3. Surface energy calculated (using GGA) for various terminations of LuN (001) surface as a function of the N chemical potential.

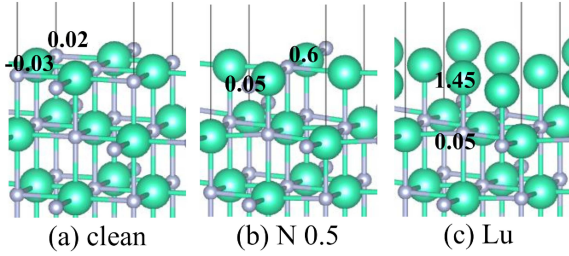


Fig. 4. The change in Bader charge with respect to the bulk system (GGA) for clean (a), N-deficient (b), and Lu-terminated (c) LuN (001) surface. Lutetium and nitrogen ions are marked with green and gray colors, respectively.

The surface energy plots for the terminations considered in this work are presented in Fig. 3. Similarly to previous results for ScN [10, 11] and YN [12], the clean termination of the LuN surface is energetically favorable in a wide range of the N chemical potential. The N-terminated systems are clearly unfavorable. Although N vacancies were found favorable at the ScN surface in Sc-rich conditions [11], the presence of N-deficient termination at the LuN surface is rather diminished. The N-deficient and Lu-terminated structures are only expected to form as a metastable phase in Lu-rich conditions. The results presented here indicate a relatively strong effect of nitrogen ions on the surface energy of LuN, which is difficult to be balanced.

According to the Bader charge analysis, the charge state of Lu and N ions is affected only in the topmost layers of the systems, as presented in Fig. 4. Compared to the bulk case, the charge modifications at the clean surface are negligible. N vacancies may lead to increased charges of surface Lu ions. This effect is significantly enhanced in the case of a Lu-terminated system, in which there are no N ions at the surface, and one may expect relatively high charges of the Lu ions (increased

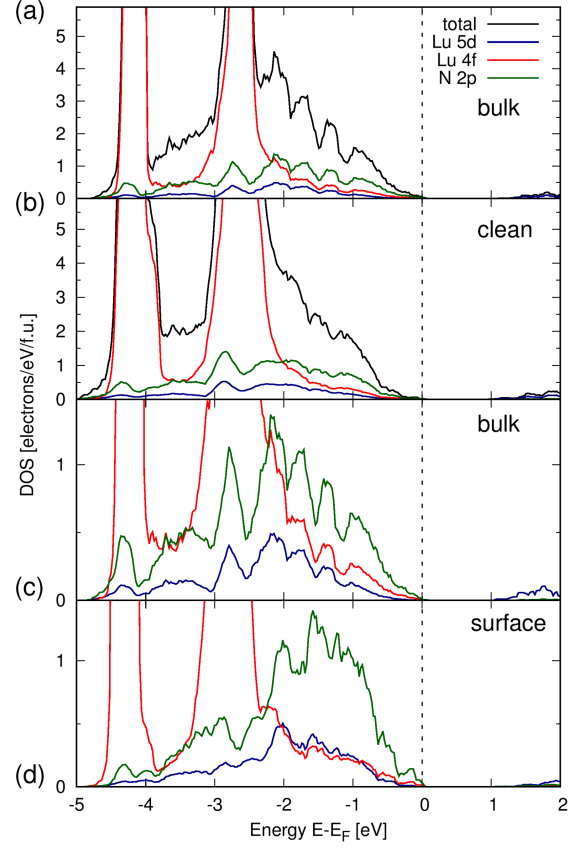


Fig. 5. Density of states (DOS) calculated (using MBJGGA) for bulk LuN (a) and clean LuN (001) surface (b). Partial DOS for bulk (c) and surface (d) ions. The Fermi energy is marked with the horizontal dashed line.

by 1.45 electrons with respect to the bulk ones). The topmost ions are strongly bound to the LuN surface due to a high symmetry of the rock-salt structure. It prevents lateral relaxation of ionic positions and a further charge flow. It is worth mentioning that some O-terminated oxide materials may exhibit very complex relaxation and reconstruction of the topmost atomic layers [23].

The DOS plots for bulk and clean surface systems are presented in Fig. 5a–b. The vicinity of the valence band maximum (VBM) in LuN is dominated by the N 2p states with minor contributions of the Lu 4f and 5d states. The characteristic nitride-like tails of conduction band minima in the systems are barely visible in a scale of Fig. 5. The band gap of bulk LuN, $E_g = 1.16$ eV, calculated with the MBJGGA approach is bigger than the modified Becke–Johnson local density approximation (MBJLDA) result (1.08 eV [1, 2]) obtained with the full potential calculations. The clean LuN surface is expected to exhibit a slightly reduced band gap of 1.06 eV because of the subtle structural and electronic relaxation in this case. As seen in Fig. 5c–d, the electronic structures of Lu and N ions at the clean surface are modified with respect to the bulk

cases, i.e., the bandwidths of the N 2*p* and Lu 5*d* contributions are slightly reduced, and the peaks are more asymmetric and closer to VBM. An additional local maximum of the N 2*p* states is formed below the E_F at the surface. The Lu 4*f* contributions, which are split by spin-orbit coupling and dominate valence DOS for binding energy higher than 2 eV, are noticeably flattened in the surface Lu ions. Furthermore, DOS in the conduction band region is clearly diminished at the surface. All DOS features discussed here suggest that the electronic structures of the clean (001) termination and bulk LuN are very similar to each other. The presence of N vacancies and Lu adatoms may lead to a strong charge imbalance at the surface (not shown in Fig. 5). However, such terminations are expected to form only in Lu-rich conditions and are generally unstable in a wide range of the N chemical potential.

4. Conclusions

Theoretical investigations based on the *ab initio* thermodynamics indicate that a clean LuN (001) surface is stable in a wide range of the N chemical potential and exhibits a band gap of 1.06 eV, which is close to the bulk one. The N vacancies and Lu adatoms may be present in Lu-rich conditions and induce a charge imbalance at the surface of the material. The findings presented in this work encourage further experimental efforts on the synthesis of high-quality thin films of LuN and following studies of electronic structures of such novel systems.

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