Metallic to insulating nature of TaN$_x$: Role of Ta and N vacancies

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(Received 24 June 2002; revised manuscript received 2 October 2002; published 28 February 2003)

It has been demonstrated recently that the stoichiometry of rocksalt TaN can be tuned by N$_2$ pressure and temperature, yielding material that ranges from highly conductive to insulating. Using density functional theory, we investigate the atomic and electronic structure and formation energy of defective TaN structures. The calculations predict that Ta and N vacancies form under N-rich and N-poor conditions, respectively, where the presence of Ta vacancies reduces the density of states (DOS) around the Fermi level ($E_F$). We also studied the Ta$_n$N$_4$ and Ta$_n$N$_5$ structures which occur in nature. The former phase, consisting of an ordered arrangement of Ta vacancies, also exhibits a notable decrease in the DOS at $E_F$, while the latter is a semiconductor with a band gap of 1.5 eV within the local density approximation. Our results suggest that the formation of Ta-deficient structures is directly related to the metal-to-insulator transition.

I. INTRODUCTION

Recent experiments have shown that the NbN/TaN$_x$/NbN system exhibits desired parameters for RSFQ circuitry when the barrier material TaN$_x$ has a resistivity close to the metal-insulator transition. The resistivity can be tuned by the growth conditions, namely, by the nitrogen pressure and temperature. For example, the stoichiometry (properties) can be varied from Ta$_{1.12}$N (metallic) to Ta$_{0.46}$N (barely metallic) to Ta$_{0.66}$N (insulating), by increasing the N$_2$ pressure. X-ray diffraction experiments indicate that the (metastable) rocksalt structure is essentially maintained. Thus, the local atomic geometries in these nonstoichiometric structures likely involve native defects. Tantalum nitride was also found to be a promising material for other applications, such as diffusion barriers in copper interconnects on Si chips and to make compact thin-film resistors. The Ta-N system is relatively unexplored and, unlike, e.g., the Ti-N system, it exhibits a remarkable richness in the array of equilibrium and metastable phases that can form; indeed more than 11 have been reported, where very little is known about their relative stability.

In this paper, we investigate the atomic and electronic structure and formation energies of defective TaN structures in order to gain insight into the mechanism giving rise to the variation in conductivity. We focus in particular on N-rich structures which are found to have dramatically increased resistivities compared to stoichiometric rocksalt TaN. For comparison, we also perform calculations for two other phases which form in nature and which also have N-rich stoichiometries, namely, Ta$_4$N$_5$ (Ref. 10) (a defective rocksalt structure) and Ta$_2$N$_6$ (Ref. 11) (an orthorhombic structure). Based on the calculated energetics and electronic structures, our results point to Ta vacancies as being largely responsible for the metallic-to-insulating transition. This prediction is consistent with indications from early work that higher nitrides of Ti, Zr, and Hf involve metal vacancies, on the basis of experiments (Ti, Zr, Hf) (Ref. 12) and theory (Zr) (Ref. 13). Investigations of the electronic properties of refractory compounds of transition-metal nitrides and carbides containing typical structural defects such as vacancies, interstitial, and substitutional impurities have been reported; to our knowledge, however, there have been no such studies for TaN. Some results that were briefly reported in Ref. 3 are presented in detail here.

II. CALCULATION METHOD

The density functional theory (DFT) calculations are performed using the first-principles full-potential linearized augmented-plane-wave (FLAPW) method and in its parallelized form with the local density approximation (LDA) for the exchange-correlation functional. We treat the core states fully relativistically and the valence states scalar relativistically, and use angular momenta up to $l=8$ in the muffin-tin spheres for both the wave functions and charge density in the self-consistent cycles. We consider high and low defect concentrations by using 8- and 32-atom cells to model the defect systems. For the former, the energy cutoff for the plane-wave expansion in the interstitial region be-
between the muffin-tin spheres is taken to be 25 Ry, and also for the 18-atom Ta$_3$N$_5$ structure. For the larger 32-atom systems, which include the Ta$_3$N$_5$ structure, a slightly lower (but still high) cutoff of 20.7 Ry was used. Thirty-five k points are taken in the irreducible part of the Brillouin zone (IBZ) for the “8-atom” cells and 27 for the Ta$_3$N$_5$ structure. For the larger 32-atom cells, we used (2 × 2 × 2) (defect cells) and (4 × 4 × 4) (Ta$_3$N$_5$ phase) Monkhorst-Pack grids. The muffin-tin radii $R_{MT}$ for all calculations are $R_{N} = 1.4$ bohr for the N atom and $R_{Ta} = 2.47$ bohrs for the Ta atom, with the exception of the N interstitial, for which we used $R_{Ta} = 2.10$ bohrs, due to the closer Ta-N distances caused by the interstitial N atom, and $R_{interstitial~N} = 5.2$ bohrs, due to the closer N-Ta distance. Clearly, in the calculation of the formation energy, we define the formation energy as

$$E_f = \left( E_{\text{defect}}^{\text{tot}} - n E_{\text{Ta-bulk}}^{\text{tot}} - m/2 E_{N_2}^{\text{tot}} \right)/(m+n),$$

where $E_{\text{defect}}^{\text{tot}}$, $E_{\text{Ta-bulk}}^{\text{tot}}$, and $E_{N_2}^{\text{tot}}$ are the total energies of the system without changing the temperature or pressure. We refer to this value of $\mu_N$ as the so-called “N-poor” condition.

Because the total energy of the nitrogen molecule obtained from DFT-LDA (and the generalized gradient approximation) is well known to be significantly overbound, we observe the heat of formation per atom of the structure under consideration, per N atom. We refer to this value as $\mu_N$ as the “nitrogen-rich” condition. The $p,T$ dependence of $\mu_N$ can be evaluated using tabulated data for $\mu_N(T,p_N^0)$. In general, the typical range of the chemical potential is determined and limited by the pressures and temperatures used in industry and laboratories, namely, from several to thousands of kelvin, and from ultrahigh vacuum ($<10^{-12}$ atm) to several hundreds of atmospheres.

The value of $\mu_N$ at which a given tantalum-nitrogen structure becomes unstable, i.e., where $E_f(\mu_N) = 0$, is obtained from rearrangement of Eq. (2) as

$$\mu_N = \frac{E_{\text{defect}}^{\text{tot}} - n E_{\text{Ta-bulk}}^{\text{tot}}}{m}.$$  

and with respect to the zero reference state of $\mu_N(T,p_{N_2})$, this becomes

$$\mu_N - 1/2 E_{N_2}^{\text{tot}} = \left[ E_{\text{defect}}^{\text{tot}} - n E_{\text{Ta-bulk}}^{\text{tot}} - m/2 E_{N_2}^{\text{tot}} \right]/m,$$

which is, by definition, the heat of formation of the Ta-N structure under consideration, per N atom. We refer to this value of $\mu_N$ as the “N-rich” condition.

The nitrogen chemical potential depends strongly on the nitrogen molecule. The quantity in Eq. (5) is actually the “grand potential,” where we have neglected vibrational contributions of the bulk systems since $p$ and $T$ effects are much stronger for the gas phase species; $<10^{-12}$ atm) to several hundreds of atmospheres.

III. RESULTS

A. Atomic structure

For the “high-concentration” defect structures, as modeled in the “8-atom” cells, we have Ta:N ratios of 2.0, 1.33, 0.75, 0.80, and 0.60 corresponding to two N vacancies, one N vacancy, one Ta vacancy, one N interstitial, and one N antisite (N on a Ta site), respectively. These structures are shown in Fig. 1. The structure containing two N vacancies is just as for Fig. 1(b), but with an additional nearest-neighbor N atom missing. Due to the relatively high defect concentrations, we optimized the equilibrium volume. The vacancy structures are found to have a reduced volume compared to the equivalent (calculated) stoichiometric TaN value: by $-1.91\%$, $-0.85\%$, and $-2.55\%$ for the two and one N vacancies and for the Ta vacancy, respectively. The greater contraction for the latter may be anticipated due to the larger size of the missing Ta atom. The N antisite also yields a
smaller volume, by $-1.52\%$. The N-interstitial defect induces a larger equilibrium volume than the ideal bulk stoichiometric TaN (by $3.15\%$) since the lattice expands to accommodate the additional N atom. Due to the high symmetry of these systems, internal relaxations are not possible with the exception of the N interstitial. For the N interstitial and the N antisite, we also consider lower-symmetry geometries which are described below.

The “low-concentration” (“32-atom”) defect systems are calculated using the theoretical bulk TaN lattice constant of 4.37 Å (the experimental value is 4.385 Å). The fully relaxed atomic geometry of the defects is described as follows: for the Ta vacancy, the six surrounding, nearest-neighbor N atoms move inwards by about $3\%$ relative to the unrelaxed positions, and for the N vacancy, the six surrounding nearest-neighbor Ta atoms move inwards by $7\%–10\%$ relative to the unrelaxed positions. Through this latter large relaxation, the Ta atoms approach the Ta-Ta distance that they have in bulk Ta, thus achieving a stronger Ta-Ta bonding; in the ideal rocksalt TaN structure, the Ta-Ta distance is $8\%$ larger than in bulk Ta (see, e.g., Ref. 23). For the N antisite, the six neighboring N atoms move inwards by a large $8\%–10\%$ relative to the unrelaxed positions. In each system there are also smaller relaxations of the atoms that are more distant from the defect. The energy gains due to all the atomic relaxations are $0.21$ eV and $0.69$ eV, respectively, for the Ta and N-vacancy structures. The large value of the latter is mainly due to the large relaxations of the Ta atoms and is similar to the energy loss when expanding bulk bcc Ta by $8\%$, where the calculated value is $0.56$ eV.

The ordered structures $\text{Ta}_4\text{N}_5$ and $\text{Ta}_3\text{N}_5$ which form in nature are depicted in Figs. 2 and 3. The former has a rocksalt structure and contains an ordered arrangement of Ta vacancies, while the latter (tritantalum pentanitride) has the orthorhombic structure, where each Ta atom is surrounded by six N atoms; more specifically, the structure is composed of irregular edge- and corner-sharing TaN$_6$ octahedra, where the N atoms are threefold and fourfold coordinated. The equilibrium volume of $\text{Ta}_4\text{N}_5$ is calculated to be $1.81\%$ smaller than the corresponding theoretical bulk TaN volume and is $1.2\%$ smaller than the experimental value. The fully relaxed internal coordinates, given using standard crystallographic notation, are listed in Table I where they are compared to the theoretical values.

<table>
<thead>
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<th>Atom type</th>
<th>$x$ coordinate</th>
<th>$y$ coordinate</th>
<th>$z$ coordinate</th>
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<tbody>
<tr>
<td>8 Ta in 8(h)</td>
<td>$-0.2$</td>
<td>$0.213$</td>
<td>$-0.4$</td>
</tr>
<tr>
<td>8 N in 8(h)</td>
<td>$-0.1$</td>
<td>$0.092$</td>
<td>$-0.7$</td>
</tr>
<tr>
<td>2 N in 2(b)</td>
<td>$0.0$</td>
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FIG. 1. Atomic geometries of the defect structures: (a) the Ta vacancy $V_{\text{Ta}}$, (b) the N vacancy $V_{\text{N}}$, (c) the N antisite $N_{\text{Ta}}$, and (d) the N interstitial $N_{\text{i}}$. The large shaded and small dark balls represent Ta and N atoms, respectively.

FIG. 2. Structure of $\text{Ta}_4\text{N}_5$: (a) top view and (b) perspective view. The large shaded and small dark balls represent Ta and N atoms, respectively.

FIG. 3. Structure of $\text{Ta}_3\text{N}_5$: (a) view of the $(001)$ plane, (b) view of the $(100)$ plane where the unit cell is indicated, and (c) perspective view. The large shaded and small dark balls represent Ta and N atoms, respectively. The arrows in (c) indicate the sixfold coordination of the Ta atoms, and the threefold and fourfold coordination of the N atoms.

TABLE I. Internal atomic coordinates of $\text{Ta}_4\text{N}_5$ relative to the unit cell dimensions as obtained by the present calculations (Theory) and experiment (Expt.), Ref. 10, given in standard crystallographic notation. The experimental lattice constants are $a = 6.831$ Å and $c = 4.269$ Å, and the space group is $I4/m$ ($C_{4h}^5$).
In particular, for the N interstitial we considered a “split-interstitial” geometry where two N atoms share a single N-atom site with a N-N distance similar to that in an N₂ molecule. For the N antisite, we considered the possibility that the N antisite moves away from its ideal Ta site towards a neighboring N atom. These geometries, however, had similarly high formation energies.

The structure containing the lower concentration of N vacancies, as calculated in the 32-atom supercell (not shown), is less stable than the one containing the higher concentration (8-atom supercell, Ta₁₃₃N) for all ranges of the chemical potential of nitrogen. This can be understood in that on removal of sufficient N atoms, the loss in bonding of neighboring Ta atoms is compensated for by the formation of Ta-Ta metallic bonds. The structure containing the higher concentration of Ta vacancies (8-atom supercell, Ta₀₇₅N) is more stable than the one containing the lower concentration (32-atom supercell) (not shown) for strongly N-rich conditions (higher values of μₕ), while for more N-poor conditions (lower values of μₕ), the lower concentration structure is preferred. The latter is, however, notably less favorable than the structures containing N vacancies.

We point out that there is a considerable vacancy-vacancy interaction in these systems so that even with the large 32-atom cells, the energetics obtained may differ from the situation of truly isolated defects. As noted above, the formation energy of Ta₈N₅ is lower than for the other Ta vacancy structures. This is consistent with the fact that Ta₈N₅ represents a phase that is formed in nature. Whether it can actually form under the given experimental conditions in Refs. 2 and 3 will, however, depend on the kinetics of the system.

To give some idea of the relationship between the pressure and temperature and μₕ for the present system, we consider the following: For a pressure of 5 × 10⁻³ Torr (0.66 × 10⁻⁵ atm), which is of the order of magnitude used in the experiments,²,³ it can be obtained, using Eq. (3), that at temperatures of 300, 600, and 900 K, μₕ takes the values −0.40, −0.87, and −1.37 eV, respectively. Inspecting Fig. 4, it can be seen that these values correspond to the region where Ta₁₂N₆ is most stable. However, if kinetic effects prevent the long-range ordering of this phase, the next most energetically favorable structures are the (“high-concentration”) N and Ta vacancies. In particular, the latter is preferred for smaller absolute values of μₕ (lower temperatures, higher N-pressure) and the former for larger absolute values of μₕ (higher temperatures). Thus, by “toggling” the temperature, the energetically preferred structure can change between these systems. A similar effect occurs for variations in pressure. We propose that this effect is related to the experimentally observed stoichiometry dependence of Ta-N structures on nitrogen pressure and temperature.

C. Electronic structure

Having investigated the atomic structure and energetics of the various systems, we now consider the electronic properties. The total and partial density of states (DOS) of the high-concentration defect systems are shown in Fig. 5. It can be noticed that for the Ta-vacancy [Fig. 5(a)], the N-antisite [Fig. 5(c)], and the N-interstitial [Fig. 5(d)] structures, addi-
tional states (compared to the single N 2s state of bulk TaN at \( \approx -16.5 \) eV) occur in the region \(-10\) to \(-20\) eV. They arise from the N atoms that have a reduced Ta coordination (e.g., the partial DOS of the atom labeled N for the Ta vacancy) or that are bonded to other N atoms (e.g., the partial DOS of the atom labeled N’ for the N antisite). The N vacancy [Fig. 5(b)] and the N antisite [Fig. 5(c)] have a high DOS at the Fermi energy, \( E_F \), while the Ta vacancy has a notably reduced DOS at \( E_F \) as compared to bulk TaN [see Fig. 5(a)]. In order to compare the relative DOS about the Fermi level for the different structures more quantitatively, we consider the ratio of the integrated total DOS from \(-0.15\) eV up to \(0.15\) eV to that of the whole valence energy region up to \( E_F \). We find that the “low-concentration” Ta-vacancy structure shown in Fig. 6(b) (labeled as \( \text{Ta}_{0.93}\text{N} \)) has an intermediate DOS at \( E_F \) (with ratio 0.025) with respect to the stoichiometric TaN (with higher ratio 0.031) and the high-concentration Ta vacancy in Fig. 5(a) (with lower ratio 0.020). The DOS of the high-concentration Ta-vacancy system is shown again in Fig. 6(c) (labeled as \( \text{Ta}_{0.75}\text{N} \)) to indicate the relative ratio of Ta to N atoms. Also shown in Fig. 6(d) is the DOS of a Ta-vacancy system containing an even higher vacancy concentration, namely, \( \text{Ta}_{0.6}\text{N} \). This is a defective rocksalt structure calculated in a cell containing 10 N atoms and 6 Ta atoms, i.e., the same cell as for the \( \text{Ta}_{0.75}\text{N} \) structure (Fig. 2), but with an additional Ta vacancy. The relative DOS about \( E_F \) for this system is higher than for the other structures (ratio 0.032), but it drops sharply above \( E_F \).

We expect that a lower relative DOS would be found if this structure was calculated in a larger supercell, where additional atomic relaxations could take place. Despite this exception, these results generally show that the presence of Ta vacancies decreases the DOS at and around the Fermi level.

For the Ta-vacancy structures [Figs. 6(b), 6(c), and 6(d)], states in the region \(-1\) to \(-4\) eV below \( E_F \) can also be seen, where for the “low-concentration” case only a sharp feature around \(-4\) eV occurs. Inspection of the band structure (see below) shows that defect-related bands contribute to the DOS in this region, which become narrow for the low-concentration case and give rise to the narrow peak. The Ta-vacancy-induced features are consistent with recent experimental results using x-ray emission spectroscopy where it is reported that nonbonding N 2p-like states form in the energy region between the hybridized Ta-5d–N-2p band and the higher-lying Ta-5d band, for the material containing highest Ta vacancies (i.e., \( \text{Ta}_{0.85}\text{N} \) in Ref. 4). There is also a

**FIG. 5.** Total (upper curve in each figure) and partial (lower curves in each figure) density of states for the high-concentration defect structures shown in Fig. 1: (a) the Ta vacancy \( \text{V}_{\text{Ta}} \), (b) the N vacancy \( \text{V}_N \), (c) the N antisite \( \text{N}_{\text{Ta}} \), and (d) the N interstitial \( \text{N}_i \). The labeling on the partial DOS means the following: For \( \text{V}_{\text{Ta}} \), \( \text{N}_8 \) corresponds to the atom having 6 Ta neighbors, and that labeled N \( \text{V}_N \) corresponding to the atom having 6 N neighbors, and that labeled Ta \( \text{V}_{\text{Ta}} \); the Ta atom having 4 N neighbors, and that labeled \( \text{V}_{\text{Ta}} \), the Ta atom having 4 N neighbors. For \( \text{N}_{\text{Ta}} \), the partial DOS labeled by N is for the N atom having 4 Ta and 2 N neighbors, \( \text{N}_8 \) is for the substitutional N atom having 6 N neighbors, and \( \text{N}_9 \) is for the N antisite N \( \text{Ta} \). For \( \text{N}_i \), the partial DOS labeled N corresponds to the atom having 6 Ta neighbors, and that labeled N’, the interstitial atom.

**FIG. 6.** Density of states (DOS) for (a) bulk TaN, (b) the low-concentration \( \text{V}_{\text{Ta}} \) (calculated in the “32-atom” cell), (c) the high-concentration \( \text{V}_{\text{Ta}} \) (calculated in the “8-atom” cell), (d) an even higher-concentration \( \text{V}_{\text{Ta}} \) (calculated in a cell containing 10 N atoms and 6 Ta atoms), and (e) the \( \text{Ta}_{0.75}\text{N} \) and (f) \( \text{Ta}_{0.6}\text{N} \) compounds. Total DOS (upper curves), total N and Ta partial DOS (lower curves), as indicated by the labels. N’ and N correspond to the partial DOS at the N atom away from and neighboring the Ta vacancy, respectively.
defect-induced band related to the N-2s states of the N atoms neighboring the vacancy [see Fig. 7(d)].

The total and partial density of states for the Ta₂N₅ and Ta₃N₅ phases are shown in Figs. 6(e) and 6(f). It can be seen that for the former, the DOS at $E_F$ exhibits a sharp minimum (with ratio 0.016), in contrast to bulk TaN, and there are also new features (compared to bulk TaN) below $E_F$, at around $-3$ to $-5$ eV, as for the high-concentration Ta-vacancy structure described above. There is also an upward shift in the N-2s level as seen for the Ta-vacancy systems. For the Ta₃N₅ structure, there is complete filling of the electronic shells and the system exhibits a band gap of 1.5 eV. We note that in reality the band gap will be larger due to the well-known underestimation as obtained when using the LDA. The positions of the N-2s states are even higher in energy, which can be correlated with a lower Ta coordination of the N atoms in this system compared to the Ta₂N₅ and Ta vacancies structures. The insulating nature can be understood from electron counting in that the number of valence electrons in Ta₂N₅ is 40 ($3 \times 5$ from Ta plus $5 \times 5$ from N) and that the $s$ and $p$ bands of the five nitrogen atoms can accommodate exactly ($5 \times 8$) 40 electrons.

The band structures for systems containing N- and Ta vacancies, as well as for ideal bulk TaN, are shown in the upper panels (b), (c), and (d) of Fig. 7. For the Ta vacancy, a defect-related state can be seen clearly around $-17$ eV, as well as new states in the energy range $-1$ to $-4$ eV, around the M-R-Γ region. In comparison, the band structure corresponding to the N vacancy exhibits an increased number of bands about $E_F$ as indicated by the higher DOS at $E_F$ mentioned earlier. In the lower panels (e), (f), (g), and (h), the band structure of the Ta₂N₅ phase is shown, as well as that of the ordered Ta-vacancy rocksalt Ta₄N₅ phase. In addition, for comparison the band structure for ideal stoichiometric TaN is given (calculated in a cell containing 20 atoms to facilitate comparison), as well as that for the highly defective Ta-vacancy structure Ta₀.₉N. On going from ideal TaN to Ta₂N₅ to Ta₀.ₙN, the upward movement and increase in the number of N-2s related states can be seen, as well as the appearance of new states in the region $-4$ to $-1$ eV [seen at $-4.0$ to $-3.5$ in Fig. 7(g) and moving up in energy to $-2$ to $-1$ in Fig. 7(h), about the R point].

We note that the present results are based on ground-state electronic structure calculations and do not take into account entropy effects of the extended systems. Furthermore, we have considered only a limited number of the many possible arrangements of the defects. Nevertheless, our results, predicting the formation of Ta-deficient structures (vacancies) for nitrogen-rich material and reduced DOS about $E_F$ and thus reduced conductivity, are all consistent with and help provide an understanding of recent experimental results.

IV. CONCLUSIONS

In summary, we have performed FLAPW calculations to investigate defective TaN structures. Structures containing Ta and N vacancies are found to have the lowest formation energies for N-rich and N-poor conditions, respectively. The presence of Ta vacancies reduces the density of states at $E_F$ by an amount that generally increases with decreasing Ta atom content. This will result in an increased resistivity and a reduction in conductivity compared to stoichiometric TaN. Similarly, the electronic structure of the Ta₄N₅ phase, which forms in nature, exhibits a notable decrease of electronic states at $E_F$ compared to bulk TaN, and for the Ta₂N₅ phase, it is a semiconductor with a (DFT-LDA) band gap of

FIG. 7. Upper panel, from left to right: (a) the Brillouin zone indicating the high-symmetry points and lines and the band structure of (b) the N vacancy, (c) ideal bulk TaN, and (d) the Ta vacancy as calculated in “8-atom” cells. Lower panel, from left to right: band structure of (e) the Ta₂N₅ phase, (f) ideal bulk TaN as calculated in a 20-atom cell (for comparison), (g) the Ta₂N₅ phase, and (h) a higher-concentration Ta-vacancy structure Ta₀.₉N, calculated in a cell containing 10 N atoms and 6 Ta atoms.
1.5 eV. Given that in the experiments the systems with dramatically reduced conductivity were prepared for strongly N-rich conditions and no new long-range-ordered structures were observed (i.e., in addition to the rocksalt structure), we propose that Ta vacancies and/or regions of Ta-deficient structures are primarily responsible for the metal-to-insulator transition observed experimentally.

ACKNOWLEDGMENTS

This work was supported by the Department of Energy (Grant No. DE-F602-88ER45372) and computing resources provided at NERSC and at the Arctic Region Supercomputing Center. We thank Nate Newman for stimulating discussions.