Supporting Information

For

Chemical bonding and Cu diffusion at the Cu/Ta$_2$N interface: a DFT study

by

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SI-1 Chemical potential and $S_{\text{bottom}}$ term.

In the main text, surface energy is calculated by the following equation: \(^1\)\(^2\)

$$E_s = \left( E_{\text{slab}} - \sum_i n_i \Delta \mu_i \right) / A - S_{\text{bottom}} \quad (S1)$$

where $\Delta \mu_i$ ($i = \text{N, Cu, Ta}$) is the chemical potential of constituent $i$. For Ta$_2$N, the chemical potentials $\Delta \mu_N$ and $\Delta \mu_{Ta}$ should satisfy following equation under thermal equilibrium growth condition:

$$2 \Delta \mu_{Ta} + \Delta \mu_N = E_{Ta_2N}^f = -2.43 \text{eV} \quad (S2)$$

where $E_{Ta_2N}^f$ is the formation energy of pure Ta$_2$N. Then, $\Delta \mu_N$ and $\Delta \mu_{Ta}$ under different growth conditions can be determined: under N-poor (Ta-rich) growth condition, $\Delta \mu_N = -2.43$ eV and $\Delta \mu_{Ta} = 0$ eV; under N-rich (Ta-poor) growth condition, $\Delta \mu_N = 0$ eV and $\Delta \mu_{Ta} = -1.22$ eV. Considering that the combination of N and Ta may form other materials such as TaN, Ta$_3$N$_5$ and Ta$_5$N$_6$, more restrictive conditions should be added to prevent formation of these materials. However, we merely want to compare surface stability among different surfaces, using more restrictive conditions only results in different surface energy values, while the order of surface stability will not be affected at all. Therefore, we only use the above chemical potential values to calculate surface energies because they are sufficient to get reliable conclusions. For Cu, the chemical potential $\Delta \mu_N$ is simply equal to the energy per atom (-4.10 eV) in bulk Cu.

In surface calculations, the surface slab models can be constructed to be symmetrical or non-symmetrical structures. Using Ta$_2$N (001) surface as an example, below Fig. S1a shows atomic structure of the symmetrical Ta$_2$N (001)$_{T1}$ termination. The top and bottom layers of Fig. S1a are both N layers and vacuum spaces are added on both sides. During geometry relaxation, the top and bottom layers are both allowed to be relaxed. Then, the surface energy of symmetrical Ta$_2$N (001)$_{T1}$ termination can be calculated by: \(^3\)

$$E_s = \left( E_{\text{slab}} - \sum_i n_i \Delta \mu_i \right) / 2A \quad (S3)$$

Without the factor ‘2’ in Eqn. (S3), the surface energy calculated by Eqn. (S3) is the sum of two sides. To obtain surface energy of one side of the slab model, the factor ‘2’ should be divided in Eqn. (S3). To calculate surface energy of Ta$_2$N (001)$_{T2}$ termination by symmetrical
structure, we must build another slab model which is shown in Fig. S1b. It is seen that, the top and bottom layers of Fig. S2 are both Ta layers. Then, surface energy of the symmetrical Ta$_2$N (001)$_{T2}$ termination can also be calculated by Eqn. (S3).

![Symmetrical slab model](image)

**Fig. S1** symmetrical slab model of (a) Ta$_2$N (001)$_{T1}$ and (b) Ta$_2$N (001)$_{T2}$ terminations. Non-symmetrical slab model of (c) Ta$_2$N (001)$_{T1}$ and (d) Ta$_2$N (001)$_{T2}$ terminations.

The symmetrical slab model needs more atoms and bigger cell size to simulate the surface. Thus, more computational resources are needed. In this study, we use the non-symmetrical structure to simulate Ta$_2$N surfaces. **Fig. S1c** shows the non-symmetrical structure of Ta$_2$N (001)$_{T1}$ termination. During geometry relaxation, the bottom three layers are fixed while other layers are allowed for relaxation. The surface energy of Fig. S1c can be calculated by the above Eqn. (S1). The $S_{bottom}$ term in Eqn (S1) is calculated by using slab model in Fig. S1a. However, the slab model in Fig. S1a are **NOT** allowed for any relaxation. In other words, we merely get the total energy of slab model in Fig. S1a. Then, the $S_{bottom}$ term is calculated by Eqn. (S3).

When we calculate surface energy of Ta$_2$N (001)$_{T2}$ termination, we can build the non-symmetrical structure which is shown in **Fig. S1d**. It is seen that, the bottom layer of Ta$_2$N (001)$_{T2}$ termination is still N layer while the top layer is Ta layer. Then, the value of $S_{bottom}$
term that obtained in calculation of Ta$_2$N (001)$_{T_1}$ termination can also be adopted to calculate surface energy of Ta$_2$N (001)$_{T_2}$ termination.

What is worthy of mentioning is that, the symmetrical and non-symmetrical models are both able to give reliable results. In our previous study of Ta$_3$N$_5$ surfaces,$^2$ symmetrical and non-symmetrical models were both adopted for the testing calculations. Our results revealed that surface energies of non-symmetrical models are nearly the same as that of symmetrical models. The above discussion of surface energy calculation method may be not very clear. We will use the SrTiO$_3$ (100) surface, which only has two terminations, to make a detailed discussion of surface energy calculation method. Some of the below discussion has been reported in supporting information of our previous work.$^4$

The surface energy can be calculated by the following equation: 

$$E_{surface} = \frac{1}{2A} (E_{slab} - nE_{bulk})$$  \hspace{1cm} (S4)

where $E_{slab}$ is the total energy of the slab model, $E_{bulk}$ is the total energy per unit cell of the bulk, $n$ is the number of unit cells that the slab model contains, and $A$ is the surface area of the slab model. The Eqn. (S4) is a classic surface energy calculation equation and is applicable to many situations, especially to the pure metal surfaces. However, the Eqn. (S4) has its limitations. We use the typical semiconductor SrTiO$_3$ as an example to discuss the limitation of Eqn. (S4).

As can be seen in below Fig. S2, the SrTiO$_3$ (100) surface is the stack of TiO$_2$ and SrO atomic layers. Therefore, the SrTiO$_3$ (100) surface can be exposed by TiO$_2$-termination or SrO-termination. Generally, when we calculate surface energy of the SrTiO$_3$ (100) surface with TiO$_2$-termination, the top and bottom ends of constructed slab model will be both exposed by the TiO$_2$ atomic layer. Then, the number of TiO$_2$ atomic layer will be more than that of SrO atomic layer. When the number of TiO$_2$ atomic layer is more than that of SrO atomic layer, the Eqn. (S4) is not suitable to calculate surface energy. Using Fig. S2 as an example, the TiO$_2$-terminated SrTiO$_3$ (100) surface contains 3 TiO$_2$ atomic layers and 2 SrO atomic layers. Since one TiO$_2$ atomic layer plus one SrO atomic layer equals to one unit cell of bulk SrTiO$_3$, the slab model in Fig. S2 contains 2 unit cells of bulk SrTiO$_3$ and one TiO$_2$ atomic layer. Then, we cannot give the factor ‘$n$’ in Eqn. (S4) and thus the Eqn. (S4) cannot
be used to calculate surface energy.

**Fig. S2** Schematic diagram of the symmetrical TiO$_2$-terminaed SrTiO$_3$ (100) surface.

To calculate surface energy of the slab model in **Fig. S2**, we can use the above Eqn. (S3). Compared with the Eqn. (S4) which requires the number of unit cells in the slab model, the Eqn. (S3) only needs the number of each constituent in the slab model. Therefore, the Eqn. (S3) has larger application range than the Eqn. (S4). Then, the surface energy of the TiO$_2$-terminated SrTiO$_3$ (100) surface in **Fig. S2** can be written as:

\[
E_{\text{surf}} = \frac{1}{2A} \left( E_{\text{slab}} - n_O \mu_O - n_{\text{Ti}} \mu_{\text{Ti}} - n_{\text{Sr}} \mu_{\text{Sr}} \right)
\]  
(S5)

where \(n_O, n_{\text{Ti}}\) and \(n_{\text{Sr}}\) are 8, 3 and 2, respectively.

It is necessary to discuss the relationship between Eqn. (S3) and (S4). We still use the semiconductor SrTiO$_3$ to carry out the discussion. Under the thermal equilibrium growth conditions, the chemical potential of SrTiO$_3$ is equal to the total energy of bulk SrTiO$_3$:

\[
\mu_{\text{SrTiO}_3} = E_{\text{SrTiO}_3}
\]  
(S6)

Since \(\mu_{\text{SrTiO}_3}\) can be expressed as:

\[
\mu_{\text{SrTiO}_3} = 3\mu_O + \mu_{\text{Ti}} + \mu_{\text{Sr}}
\]  
(S7)

then, based on Eqn.(S6) and (S7), we can get:

\[
3\mu_O + \mu_{\text{Ti}} + \mu_{\text{Sr}} = E_{\text{SrTiO}_3}
\]  
(S8)

If we replace Eqn. (S5) with Eqn. (S8) and eliminate the \(\mu_{\text{Ti}}\) term, we can get the surface energy as:

\[
E_{\text{surf}} = \frac{1}{2A} \left[ E_{\text{slab}} - n_{\text{Ti}} E_{\text{SrTiO}_3} + (3n_{\text{Ti}} - n_O) \mu_O + (n_{\text{Ti}} - n_{\text{Sr}}) \mu_{\text{Sr}} \right]
\]  
(S9)

S5
It is seen from the Eqn. (S9) that, when the number of unit cells in the slab is the integer multiple of the bulk, \( i.e. \), the ratio of \( n_{\text{Ti}} : n_{\text{Sr}} : n_{\text{O}} = 1 : 1 : 3 \), for example the situation in the above Fig. S3, the Eqn. (S9) becomes

\[
E_{\text{surf}} = \frac{1}{2A} \left[ E_{\text{slab}} - n_{\text{Ti}} E_{\text{SrTiO}_3} \right]
\]  

(S10)

which is exactly equal to the Eqn. (S4). Therefore, the Eqn. (S3) is essentially the general form of the Eqn. (S4).

What should be noted is that, surface energy of the slab in Fig. S3 calculated by Eqn. (S10) does not belong to the TiO_2-termiantion, but the average of the sum of TiO_2-termiantion and SrO-termiantion. If we want to obtain the surface energies of SrO-termination or TiO_2-termination, we must build a symmetrical slab model, \( i.e. \), the top ends should be the same as the bottom ends, like the situation in Fig. S2.

However, the non-symmetrical slab model can also be used to calculate surface energy. If we use the non-symmetrical slab model to calculate surface energy, we can use Eqn. (S1). There are two differences between Eqn. (S1) and Eqn. (S3). First, the factor ‘2’ is removed from Eqn. (S1). Second, there is an extra \( S_{\text{bottom}} \) term in Eqn. (S1). We still use the SrTiO_3 to discuss why the Eqn. (S1) can be used to calculate surface energy.

As can be seen in below Fig. S4(a), the top and bottom layers of the slab model are TiO_2 and SrO, respectively. If we want to obtain the surface energy of TiO_2-termination, the bottom SrO layer is fixed while other layers are allowed for relaxations when we perform geometry relaxation of the slab model in Fig. S4(a). Then, based on the Eqn. (S3), the surface energy of Fig. S4(a) is the sum of relaxed-TiO_2 and fixed-SrO:

\[
E_{\text{surf}} \text{ (Fig. S4(a))} = \frac{1}{2A} E_{\text{surf}} \text{ [(relaxed - TiO}_2) + (\text{fixed - SrO})]
\]  

(S11)

To obtain the surface energy of relaxed-TiO_2, we must subtract the energy of fixed-SrO from
Eqn. (S11). To obtain the energy of fixed-SrO layer, we calculate surface energy of the slab model in Fig. S4(b). The top and bottom layers of slab model in Fig. S4(b) are both SrO layers. Note that, to obtain the surface energy of fixed-SrO layer, the whole slab model in Fig. S4(b) is not allowed to perform geometry relaxation. Then, based on the above Eqn. (S3), the surface energy of Fig. S4(b) is:

$$E_{surf}(\text{Fig. S4(b)}) = \frac{1}{2A} E_{surf}(\text{fixed - SrO})$$  \hfill (S12)

The Eqn. (S12) is exactly the $S_{bottom}$ term in Eqn. (S1). The Eqn. (S11) is equal to the $\frac{1}{A}(E_{slab} - \sum_i n_i \Delta \mu_i)$ term in Eqn. (S1) without the factor ‘2’. Using the results of Eqn. (S11) and Eqn. (S12), we can get the surface energy of relaxed-TiO$_2$.

![Fig. S4](image)

**Fig. S4** Schematic diagram of three SrTiO$_3$ (100) surfaces. (a), (b) and (c) are used to calculate surface energies of relaxed TiO$_2$ layer, fixed SrO layer, and relaxed SrO layer, respectively.

One advantage of using Eqn. (S1) to calculate surface energy is that, one $S_{bottom}$ term can be used to calculate surface energies of different surface termination. For example, to calculate the surface energy of relaxed-SrO layer, we can use the slab model in Fig. S4(c). During the geometry relaxation, the bottom SrO layer is fixed and other layers are allowed for relaxation. Then, the value of $S_{bottom}$ calculated in Fig. S4(b) can also be used to calculate the surface energy of relaxed-SrO in Fig. S4(c). Since the SrTiO$_3$ (100) surface only has two possible terminations, this advantage of Eqn. (S1) is not obvious. When the surface of one material has many possible terminations (for example ten possible terminations), to calculate surface energy of each termination, this advantage of Eqn. (S1) will be very obvious.

The other advantage of using Eqn. (S1) to calculate surface energy is that, the computational cost of Eqn. (S1) can be substantially reduced compared with that of Eqn. (S3).
The below Fig. S5 and S6 are symmetrical slab models of SrO-termination and TiO$_2$-termination, respectively, of SrTiO$_3$ (100) surface. To test the dependence of surface energy on the number of atomic layers, slab models with increased number of atomic layers from (a) to (c) are built in Fig. S5 and S6. In Fig. S5 and S6, the central three atomic layers are fixed during relaxations. The below Fig. S7 and S8 are non-symmetrical slab models of SrO-termination and TiO$_2$-termination, respectively, of SrTiO$_3$ (100) surface. Similarly, to test the dependence of surface energy on the number of atomic layers, slab models with increased number of atomic layers from (a) to (c) are also built in Fig. S7 and S8. During relaxations, the bottom three layers are fixed. Table S1 lists the calculated surface energies of all slab models in Fig. S5 to S8. It is seen that, the surface energies calculated by non-symmetrical slab models based on Eqn. (S1) are nearly the same as that by symmetrical slab models based on Eqn. (S3). More importantly, to achieve the same surface energies, the number of atoms in non-symmetrical slab models is much lower than that in symmetrical slab models. Therefore, we use the Eqn. (S1) to calculate surface energy of non-symmetrical slab models in our study.

![Symmetrical slab model of SrO-termination of SrTiO$_3$ (100) surface](image)

**Fig. S5** symmetrical slab model of SrO-termination of SrTiO$_3$ (100) surface with increased atomic layers from (a) to (c).

![Symmetrical slab model of TiO$_2$-termination of SrTiO$_3$ (100) surface](image)

**Fig. S6** symmetrical slab model of TiO$_2$-termination of SrTiO$_3$ (100) surface with increased atomic layers from (a) to (c).
**Fig. S7** non-symmetrical slab model of SrO-termination of SrTiO$_3$ (100) surface with increased atomic layers from (a) to (c).

**Fig. S8** non-symmetrical slab model of TiO$_2$-termination of SrTiO$_3$ (100) surface with increased atomic layers from (a) to (c).

**Table S1** Surface energies ($E_{surf}$ J/m$^2$) of different terminations of SrTiO$_3$ (100) surface calculated by symmetrical and non-symmetrical models (under Ti-poor, O-rich and Sr-rich condition). The slab models for each surface termination can be found in Fig. S5 to Fig. S8.

<table>
<thead>
<tr>
<th>Termination</th>
<th>Slab models</th>
<th>Number of O</th>
<th>Number of Ti</th>
<th>Number of Sr</th>
<th>Total number of atoms</th>
<th>$E_{surf}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>symmetrical SrO</td>
<td>Fig. S5(a)</td>
<td>7</td>
<td>2</td>
<td>3</td>
<td>12</td>
<td>-2.32</td>
</tr>
<tr>
<td>termination</td>
<td>Fig. S5(b)</td>
<td>13</td>
<td>4</td>
<td>5</td>
<td>22</td>
<td>-2.36</td>
</tr>
<tr>
<td>symmetrical TiO$_2$</td>
<td>Fig. S5(c)</td>
<td>19</td>
<td>6</td>
<td>7</td>
<td>32</td>
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</tr>
<tr>
<td>termination</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>non-symmetrical SrO</td>
<td>Fig. S6(a)</td>
<td>8</td>
<td>3</td>
<td>2</td>
<td>13</td>
<td>4.42</td>
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<tr>
<td>termination</td>
<td>Fig. S6(b)</td>
<td>14</td>
<td>5</td>
<td>4</td>
<td>23</td>
<td>4.34</td>
</tr>
<tr>
<td>non-symmetrical</td>
<td>Fig. S6(c)</td>
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<td>7</td>
<td>6</td>
<td>33</td>
<td>4.33</td>
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<td></td>
</tr>
<tr>
<td>non-symmetrical</td>
<td>Fig. S7(a)</td>
<td>7</td>
<td>2</td>
<td>3</td>
<td>12</td>
<td>-2.33</td>
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<td>Fig. S7(b)</td>
<td>10</td>
<td>3</td>
<td>4</td>
<td>17</td>
<td>-2.35</td>
</tr>
<tr>
<td>non-symmetrical</td>
<td>Fig. S7(c)</td>
<td>13</td>
<td>4</td>
<td>5</td>
<td>22</td>
<td>-2.36</td>
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<td>SrO termination</td>
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<td></td>
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<tr>
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<td>Fig. S8(a)</td>
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<td>Fig. S8(b)</td>
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<td>3</td>
<td>15</td>
<td>4.34</td>
</tr>
<tr>
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<td>Fig. S8(c)</td>
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<td>4</td>
<td>4</td>
<td>20</td>
<td>4.33</td>
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</table>
SI-2 Convergence test and slab models

We select the (001), (100) and (110) low-index surfaces to perform surface investigations of Ta$_2$N. To ensure the reliability of our calculated results, the thickness of atomic layers for each slab model must be tested. For Ta$_2$N (001) surface, we further consider three possible terminations which are named as (001)$_{T1}$, (001)$_{T2}$ and (001)$_{T3}$. The atomic structures of (001)$_{T1}$, (001)$_{T2}$ and (001)$_{T3}$ with increased atomic layers are shown in Fig. S9, Fig. S10 and Fig. S11, respectively. For Ta$_2$N(100) surface, we also consider three possible terminations which are named as (100)$_{T1}$, (100)$_{T2}$ and (100)$_{T3}$. The atomic structures of (001)$_{T1}$, (001)$_{T2}$ and (001)$_{T3}$ with increased atomic layers are shown in Fig. S12, Fig. S13 and Fig. S14, respectively. For Ta$_2$N (110) surface, only one termination is considered. The atomic structures of (001) surface with increased atomic layers are shown in Fig. S15.

**Fig. S9** atomic structures of (001)$_{T1}$ termination with increased atomic layers from (c) to (a).

**Fig. S10** atomic structures of (001)$_{T2}$ termination with increased atomic layers from (c) to (a).
**Fig. S11** atomic structures of $(001)_{T3}$ termination with increased atomic layers from (c) to (a).

**Fig. S12** atomic structures of $(100)_{T1}$ termination with increased atomic layers from (c) to (a).

**Fig. S13** atomic structures of $(100)_{T2}$ termination with increased atomic layers from (c) to (a).

**Fig. S14** atomic structures of $(100)_{T3}$ termination with increased atomic layers from (c) to (a).
Fig. S15 atomic structures of Ta₂N (110) surface with increased atomic layers from (c) to (a).

Note that, to reasonably test surface energy convergence, the slab models of one given termination with increased atomic layers must have the same cell sizes. Using the Ta₂N (001)$_{T1}$ termination as an example, the slab cell size of Fig. S9a is the same as that of Fig. S9b and Fig. S9c. For each termination, the vacuum space must be thick enough to avoid interactions between neighboring images. We still use the Ta₂N (001)$_{T1}$ termination as an example, a vacuum space of 15 Å is added at one side of slab model in Fig. S9a. The 15 Å is thick enough to avoid interactions between neighboring images. Since the vacuum space in Fig. S9a is the smallest, the vacuum spaces in Fig. S9b and Fig. S9c are both larger than 15 Å and also thick enough to avoid interactions between neighboring images.

Table S2 lists the convergence test of atomic layer thicknesses for the Ta₂N (001), (100) and (110) surfaces by calculating surface energies. The surface energies in Table S2 are calculated by using Ta-rich growth condition. For each termination, the red italic texts in Table S2 are finally selected for the slab model constructions. The convergence test of Cu (111) surface is very simple. We use 3, 5 and 7 Cu atomic layers to test its convergence. The surface energies of 3, 5 and 7 atomic layers are 1.25, 1.29 and 1.28 J/m$^2$, respectively. Therefore, only 3 atomic layers are sufficient to simulate the Cu (111) surface.
Table S2  Surface energies (E_{surf}  J/m²) for Ta₂N (001), (100) and (110) surfaces with different number of atomic layers. The number of atomic layers for each surface termination can be found in Fig. S9 to Fig. S15.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Termination</th>
<th>Number of Atomic layers</th>
<th>Number of N</th>
<th>Number of Ta</th>
<th>k-points</th>
<th>E_{surf}</th>
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<td>(001)</td>
<td>(001)ₜ₁</td>
<td>Fig. S9a 5</td>
<td>8</td>
<td>12x12x1</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fig. S9b 4</td>
<td>6</td>
<td>12x12x1</td>
<td>0.28</td>
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<td></td>
<td>Fig. S9c 3</td>
<td>4</td>
<td>12x12x1</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>(001)</td>
<td>(001)ₜ₂</td>
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<td>0.34</td>
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<tr>
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<td></td>
<td>Fig. S10b 3</td>
<td>6</td>
<td>12x12x1</td>
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<tr>
<td></td>
<td></td>
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<td>4</td>
<td>12x12x1</td>
<td>0.34</td>
<td></td>
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<tr>
<td>(001)</td>
<td>(001)ₜ₃</td>
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<td>7</td>
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<td>Fig. S11b 3</td>
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<td>(100)</td>
<td>(100)ₜ₁</td>
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<td>Fig. S12b 7</td>
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<tr>
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<td></td>
<td>Fig. S12c 6</td>
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<td>2.53</td>
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<td>(100)</td>
<td>(100)ₜ₂</td>
<td>Fig. S13a 7</td>
<td>14</td>
<td>8x6x1</td>
<td>2.63</td>
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</tr>
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<td></td>
<td></td>
<td>Fig. S13b 6</td>
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<td>8x6x1</td>
<td>2.62</td>
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<td></td>
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<td>8x6x1</td>
<td>2.61</td>
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<td>(100)</td>
<td>(100)ₜ₃</td>
<td>Fig. S14a 7</td>
<td>13</td>
<td>8x6x1</td>
<td>2.97</td>
<td></td>
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<td>Fig. S14b 6</td>
<td>11</td>
<td>8x6x1</td>
<td>2.97</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>Fig. S14c 5</td>
<td>9</td>
<td>8x6x1</td>
<td>2.96</td>
<td></td>
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<tr>
<td>(110)</td>
<td>(110)</td>
<td>Fig. S15a 9</td>
<td>18</td>
<td>8x8x1</td>
<td>2.69</td>
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<td>Fig. S15b 8</td>
<td>16</td>
<td>8x8x1</td>
<td>2.70</td>
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<td>Fig. S15c 7</td>
<td>14</td>
<td>8x8x1</td>
<td>2.69</td>
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</table>

SI-3 Interface cohesive energies calculated by 2x2x1 K-point meshes

To test whether the single Gamma point is sufficient to compare different interface models, we use a 2x2x1 meshes (include two K-points) to re-calculate the interface cohesive energies. The calculated results are listed in below Table S3. It is seen that, the interface cohesive energies calculated by 2x2x1 meshes are close to that by single Gamma point. More importantly, the order of interface cohesive energies calculated by 2x2x1 meshes is the same as that by single Gamma point. Therefore, using single Gamma point is sufficient in our calculations.
Table S3 Interface cohesive energies ($E_c$ in J/m$^2$) of Cu/Ta$_2$N(001)$_{T1}$, Cu/Ta$_2$N(001)$_{T2}$ and Cu/Ta$_2$N(001)$_{T3}$ interface models calculated by 2×2×1 meshes and single Gamma point.

<table>
<thead>
<tr>
<th>Interface model</th>
<th>$E_c$ (J/m$^2$)</th>
<th>Interface model</th>
<th>$E_c$ (J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Ta$<em>2$N(001)$</em>{T1}$</td>
<td>3.64</td>
<td>Cu/Ta$<em>2$N(001)$</em>{T1}$</td>
<td>3.70</td>
</tr>
<tr>
<td>Cu/Ta$<em>2$N(001)$</em>{T2}$</td>
<td>0.58</td>
<td>Cu/Ta$<em>2$N(001)$</em>{T2}$</td>
<td>0.72</td>
</tr>
<tr>
<td>Cu/Ta$<em>2$N(001)$</em>{T3}$</td>
<td>3.56</td>
<td>Cu/Ta$<em>2$N(001)$</em>{T3}$</td>
<td>3.52</td>
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</table>

**SI-4 The NEB calculation of interstitial N atom diffusion from Ta$_2$N to Cu**

To investigate the interstitial N diffusion from Ta$_2$N to Cu, we simply choose the Cu/Ta$_2$N(001)$_{T2}$ interface model because only the T2 termination of Ta$_2$N (001) surface is exposed with N layer.

**Fig. S16(a) and (b)** show the relaxed initial state and relaxed final state of interstitial N diffusion at Cu/Ta$_2$N(001)$_{T2}$ interface. The N atom that participates in the diffusion *via* interstitial form is denoted as N$_{int}$. Note that, we choose the N$_{int}$ atom shown in Fig. S16(a) and (b) to perform calculations because there is a large gap between Cu atoms on the top of this N$_{int}$ atom. This will ensure larger possibility of N$_{int}$ diffusion into Cu phase *via* the interstitial diffusion mechanism. It is seen that, after geometry relaxations, the relaxed initial state is different from the relaxed final state. Therefore, we can perform NEB calculation to find out possible diffusion barriers.

**Fig. S17** shows the diffusion barrier of an interstitial N atom diffusion at Cu/Ta$_2$N(001)$_{T2}$ interface. We build four intermediate states between the relaxed initial state and relaxed final state. The NEB calculations reveal that the energy barrier of an interstitial N atom diffusion at Cu/Ta$_2$N(001)$_{T2}$ interface is 4.26 eV. To our knowledge, the energy barrier of Cu diffusion in TaN in the temperature range of 600-800 °C and 800-900 °C are 1.3 eV and 2.7 eV, respectively. The energy barrier of Cu diffusion in W$_2$N in the temperature of 600-800 °C is 1.0 eV. The energy barrier means that, when the external energies are larger than the energy barrier, the diffusion will happen. The energy barrier of N diffusion from Ta$_2$N to Cu is as large as 4.26 eV, suggesting that the interstitial N diffusion from Ta$_2$N to Cu is highly difficult.
Fig. S16 (a) relaxed initial state and (b) relaxed final state of N diffusion at Cu/Ta$_2$N(001)$_{12}$ interface. The N atom that participates in the diffusion via interstitial form is denoted as N$_{\text{int}}$.

Fig. S17 The diffusion barrier of an interstitial N atom diffusion at Cu/Ta$_2$N(001)$_{12}$ interface. The diffusion barrier is 4.26 eV.

References