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Citation for published version:

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Early version, also known as pre-print

Published In:
Physica Status Solidi (RRL)
Hydrogenation induced carrier mobility polarity reversal in single layer AlN

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Two-dimensional (2D) materials promote the development of nanoelectronic devices, which requires candidate systems with both a high carrier mobility and a sufficiently large electronic bandgap. We present a first principles calculation of the intrinsic carrier mobilities of pristine (1L-AlN) and hydrogenated (1L-AlN-H\textsubscript{2}) AlN nanosheets. Numerical results show that 1L-AlN shows a hole-dominated ultra-large carrier mobility (up to 3000 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}). Upon fully-hydrogenation (1L-AlN-H\textsubscript{2}), the polarity of carrier mobility is reversed from hole-dominated to electron-dominated. This tunable polarity of intrinsic carrier mobility indicates single layer AlN nanosheet a promising candidate for future nano-electronics.

High carrier mobility and moderate band gap are two most important factors of fabricating high-performance nanoelectronic devices. The former ensures efficient manipulation of charge carriers, and the later indicates the capability of controlling the charge carriers by the external electric field\textsuperscript{1}. Graphene and MoS\textsubscript{2} are two of the most important two-dimensional (2D) materials, which are extensively considered as good candidates of low dimensional nanoelectronic devices. However, the band gap of graphene is almost equal to zero although its mobility is ultra-high\textsuperscript{2}. 2D MoS\textsubscript{2} has finite band gap, but its carrier mobility is relatively low (60 ~ 200 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}) which is roughly one order smaller than that of conventional silicon-based semiconductors (~500 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1})\textsuperscript{3}. It is necessary and significant to explore a potential 2D material for assembling robust nanoelectronics devices, which has not only high carrier mobility but also controlling finite band gap.

Among the potential two-dimensional (2D) materials, single layer AlN (1L-AlN) is currently an object of much interest due to its semiconducting nature and its large band gap\textsuperscript{4, 5}. Recently, ultrathin (sub-monolayer to 12 monolayers) graphene-like hexagonal AlN has been realized experimentally by Tsipas \textit{et al.}\textsuperscript{6}. They reported that these ultrathin AlN nanosheets display good quality epitaxial growth characteristics and minimal residual oxygen incorporation on the surface. Motivated by this report, Bacaksiz \textit{et al.} investigated the frontier orbitals of 1L-AlN\textsuperscript{4}. They predicted that the valence band maximum (VBM) of 1L-AlN is mainly composed of out-plane N-p\textsubscript{z} orbitals\textsuperscript{5}, which may ultimately result in a high hole carrier mobility. In addition, fully-functionalization can saturate the N-p\textsubscript{z} orbitals and induce pucker of single layer AlN\textsuperscript{7, 8}, which may play an important role in modulating the carrier mobility of monolayer AlN.

Previous investigations indicated that the coherent wavelength of thermally activated carriers at room temperature is much larger than the bond length and is very close to the acoustic phonon wavelength in inorganic semiconductors\textsuperscript{9-11}. Thus, the scattering at low energy regime...
is mostly dominated by the electron-acoustic phonon coupling \(^{12,13}\). According to the arguments proposed by Bardeen and Shockley\(^ {14-16}\), the scattering due to the electron-acoustic phonon coupling can be described effectively by the deformation potential (DP) theory. Within the effective mass approximation, the DP theory can be effectively applied to the two-dimensional (2D) materials and the carrier mobility \(\mu_{2D}\) can be calculated by

\[
\mu_{2D} = \frac{2e\hbar^3C^{2D}}{3k_B T m^* T E_1^2},
\]

where \(m^* = \hbar^2[E(k)/\partial^2 k]^{-1}\) is the effective mass and \(T\) is the temperature. \(E_1\) represents the deformation potential constant of the valence-band minimum (VBM) for hole or conduction-band maximum (CBM) for electron along the transport direction, which is defined as \(E_1 = dE_{\text{edge}}/d\delta\) with \(E_{\text{edge}}\) the energy of CBM/VBM under proper cell compression and \(d\) the infinitesimal of structure deformation. \(C^{2D}\) is the in-plane elastic modulus and is defined as \(C^{2D} = [\partial^2 E/\partial\delta^2]/S_0\), where \(E\) is the total energy of the supercell, \(\delta\) is the applied uniaxial strain and \(S_0\) is the area of the supercell.

In the present work, we carried out first principles calculation using Vienna Ab-initio Simulation Package (VASP) to investigate the carrier mobilities of 1L-AlN and fully-hydrogenated 1L-AlN using Eq. (1). Numerical calculation is performed by using the projector augmented wave method with the Perdew-Burke-Ernzerhof functional (PAW-PBE), which has been extensively employed to study the geometric and electronic properties of AlN nanostructures\(^ {4,5,7,8,17,18}\). The energy cutoff for the plane-wave basis was set to 500 eV for all calculations. Numerical results show that the carrier mobility of 1L-AlN at room temperature is relatively high, which is up to \(-3000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) and is hole-dominated. While for the fully-hydrogenated 1L-AlN (1L-AlN-H\(_2\)), the carrier mobility is largely decreased and changes from holes-dominated to electrons-dominated. This behavior indicates that the 1L-AlN can be assembled to conductivity-adjustable nanoelectronics device by hydrogen saturation. The detailed analysis is shown as follows.

Firstly, we investigated the electronic structure and acoustic phonon-limited mobility of 1L-AlN. In order to intuitively demonstrate the carrier conduction along the zigzag and armchair directions, an orthogonal supercell is used. The corresponding atomic structure is shown in Fig. 1a, where the orthogonal supercell vectors \(a_{hx} = a(1, 0, 0)\) and \(a_{hy} = a(0, \sqrt{3}, 0)\) (the lattice constant \(a = 3.13 \text{ Å}\)) are signified with red arrows, together with the hexagonal primitive cell vectors \(a_{hx} = a(1, 0, 0)\) and \(a_{hy} = a(0.5, \sqrt{3}/2, 0)\) with black arrows for comparison. The right panel of Fig. 1a shows the first Brillouin zone (FBZ) and Fig. 1b shows the band structure of 1L-AlN. The K point (fractional reciprocal coordinates: 1/3, 2/3, unit is 2\(\pi/a\)) defined in reciprocal lattice of the primitive cell is folded into (1/3, 0) point sitting at the Γ-X branch in the FBZ of the orthogonal supercell (see Fig. 1a).

![Atomic structure model and band structure of single layer AlN (1L-AlN).](image)

**FIG. 1.** Atomic structure model and band structure of single layer AlN (1L-AlN). (a) Left panel: structural schematic diagram of 1L-AlN. The black and red arrow lines represent the hexagonal unit vectors \(a_{hx}\) and \(a_{hy}\) and the orthogonal supercell vectors \(a_{hx}\) and \(a_{hy}\), respectively. Right panel: the first Brillouin zone (FBZ) associated with two sets of k vectors. \(B_{hx}\) and \(B_{hy}\) are the k vector of hexagonal primitive cell. \(B_{hx}\) and \(B_{hy}\) are the k vector of orthogonal super cell. The green dashed line shows the folding of the K point from the FBZ of the hexagonal lattice to the FBZ of the orthogonal lattice. (b) Band structure of 1L-AlN (the orthogonal supercell). The large balls indicate the Al atoms and the small balls indicate the N atoms.

As described in Eq. (1), the carrier mobility of 2D materials is determined by \(m^*, C^{2D}\) and \(E_1\), so all these quantities are calculated firstly from first principles and the corresponding values are listed in Table 1. The effective mass \(m^*_{ab}\) tensor is calculated by \(\hbar^2[E(k)/\partial^2 k]^{-1}\) along \(a_{hx}\) and \(a_{hy}\) directions, respectively, which indeed reveals a different value for holes.
(1.33m_{e} along a_{ox} direction and 1.52m_{e} along a_{oy} direction) and an equal value for electrons (0.51m_{e} along both a_{ox} and a_{oy} directions). While, for C^{2D} and E_{1}, the values are very close along a_{ox} and a_{oy} directions for both electrons and holes.

As a result, the acoustic phonon-limited mobilities $\mu$ at room temperature (300 K) were calculated according to Eq. (1). As shown in Table 1, the electron mobility is 300.92 along zigzag direction (a_{ox} direction) and 298.33 cm$^2$V$^{-1}$s$^{-1}$ along armchair direction (a_{oy} direction), respectively. It is significantly larger than the electron mobility of single layer MoS$_2$ (60–72 cm$^2$V$^{-1}$s$^{-1}$). Simultaneously, we found that the hole mobilities (2795–3701 cm$^2$V$^{-1}$s$^{-1}$) is much higher than the electron mobility (almost 9–12 times), which is even higher than that of typical silicon-based devices (~500 cm$^2$V$^{-1}$s$^{-1}$). This strong electron/hole mobility polarization originates from a sharp difference (almost 9 times) of $|E_{1}|$ between hole and electron, which will be discussed later.

**TABLE I. Predicated Carrier Mobility in AlN nanosheets**

<table>
<thead>
<tr>
<th>Type</th>
<th>$m^{*}$</th>
<th>$E_{1}$</th>
<th>C^{2D}</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1L-AlN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e (a_{ox})</td>
<td>0.51</td>
<td>-5.08</td>
<td>143.89</td>
<td>300.92</td>
</tr>
<tr>
<td>e (a_{oy})</td>
<td>0.51</td>
<td>-5.08</td>
<td>143.75</td>
<td>298.33</td>
</tr>
<tr>
<td>h (a_{ox})</td>
<td>1.33</td>
<td>-0.55</td>
<td>143.89</td>
<td>3700.96</td>
</tr>
<tr>
<td>h (a_{oy})</td>
<td>1.52</td>
<td>-0.56</td>
<td>143.75</td>
<td>2795.66</td>
</tr>
<tr>
<td>1L-AlN-H$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e (a_{ox})</td>
<td>0.80</td>
<td>-2.38</td>
<td>84.40</td>
<td>326.24</td>
</tr>
<tr>
<td>e (a_{oy})</td>
<td>0.80</td>
<td>-2.38</td>
<td>84.30</td>
<td>327.18</td>
</tr>
<tr>
<td>h (a_{ox})</td>
<td>1.84</td>
<td>-2.94</td>
<td>84.40</td>
<td>40.20</td>
</tr>
<tr>
<td>h (a_{oy})</td>
<td>1.91</td>
<td>-2.94</td>
<td>84.30</td>
<td>37.51</td>
</tr>
</tbody>
</table>

$^{a}$“1L-AlN” and “1L-AlN-H$_2$” represent pristine and fully-hydrogenated AlN nanosheet, respectively. Types “e” and “h” denote the “electron” and “hole”, respectively. $m^{*}$ (in unit of m$_{e}$) represents the effective mass. $E_{1}$ (in units of electronvolts) is the deformation potential. C^{2D} is the 2D elastic modulus, which is in units of N/m. Carrier mobility $\mu$ (in units of cm$^2$V$^{-1}$s$^{-1}$) is calculated using Equation (1) with temperature $T = 300$ K.

In the following, we investigate the carrier mobility of 1L-AlN-H$_2$ and analyze the influence of fully-functionalization to the carrier mobility. The orthogonal super cell of 1L-AlN-H$_2$ resembles that of 1L-AlN except a litter larger lattice constant $a$ ($a = 3.14$ Å). The corresponding geometric structure and band structure of 1L-AlN-H$_2$ are shown in Fig. 2. Different from the pristine ones, the hydrogenated AlN nanosheet possesses a quasi-bulk-like wurzitite structure with a bandgap of 3.01 eV. Based on the band structure, the quantities $m^{*}$, C^{2D}, $E_{1}$ and finally $\mu$ were all calculated and listed in Table 1. Numerical results show that the effective masses $m^{*}$ of 1L-AlN-H$_2$ is larger than 1L-AlN for both electrons and holes along zigzag and armchair directions. In contrast, C^{2D} decreases after fully hydrogenation as a result of the change from $sp^{2}$ orbitals (1L-AlN) to tetrahedrally coordinated $sp^{3}$ orbitals (1L-AlN-H$_2$). Different from the monotone change of C^{2D} and $m^{*}$, $E_{1}$ show a diverse trend upon full-hydrogenation, where the hole $|E_{1}|$ increase upon fully-hydrogenation and electron $|E_{1}|$ decrease upon full-hydrogenation. Finally, the carrier mobility $\mu$ of electrons and holes of 1L-AlN-H$_2$ show different behaviors to the hydrogenation. The electron mobility remains the same level as that of 1L-AlN along both zigzag and armchair direction, which indicate week relevance between hydrogenation and electron mobility. While, the hole mobility plunges from roughly 3000 cm$^2$V$^{-1}$s$^{-1}$ to ~40 cm$^2$V$^{-1}$s$^{-1}$ for both directions due to the suddenly increase of hole $|E_{1}|$ after the hydrogenation. As a result, the hole dominated carrier mobility of 1L-AlN is changed to the electron dominated carrier mobility of 1L-AlN-H$_2$, which means a reversal of intrinsic carrier mobility polarity can be achieved via fully-hydrogenation.

Combining Eq.(1) and the data in Table 1, we concluded that $|E_{1}|$ plays an important role to the polarity-reversion of $\mu$ after the fully hydrogenation of 1L-AlN. The deformation of potential constant $E_{1}$ can be understood by analyzing the wavefunction distribution of CBM and VBM before and after the hydrogenation.$^{9,11,20,21}$

Fig.3 shows the real space distributions of CBM and VBM of 1L-AlN and 1L-AlN-H$_2$, respectively. We firstly analyze the CBM and VBM of 1L-AlN. The CBM of 1L-AlN is composed of the in-plane part and out-plane part as shown in Fig.3(a). The out-plane wavefunction is robust to in-plane strain and contributes a small $E_{1}$.$^{9,11,20}$ By contrast, the in-
plane wavefunction mainly consists of $s$ orbitals of N atoms ($N-s$) as shown in Fig. 3a, which are sensitive to in-plane strain and induce a large electron $|E_i|$ equal to 5.08 eV. While, the VBM of 1L-AlN mainly stems from $p_z$ orbitals of N atoms which are perpendicular to the 2D plane of 1L-AlN as shown in Fig. 3b. The $N-p_z$ orbitals make little change as the in-plane strain, resulting a very small hole $|E_i|$ roughly equal to 0.55 eV. The combination of in-plane $N-s$ orbitals associated with CBM and out-plane $N-p_z$ orbitals associated with VBM lead to the electron dominated polarity for 1L-AlN.

![FIG. 3. The band decomposed charge densities of conduction band bottom (CBM) and valence band maximum (VBM). (a, b) for 1L-AlN. (c, d) for 1L-AlN-H$_2$. The isosurface level is set at 0.02 eÅ$^3$. The big, middle and small balls represent Al, N and H atoms, respectively.](image)

Then we analyze the CBM and VBM of 1L-AlN-H$_2$. Similar to 1L-AlN, the CBM of 1L-AlN-H$_2$ also comprises crucial in-plane part and negligible out-plane part as shown in Fig. 3c. However, the in-plane part of 1L-AlN-H$_2$ only consists of partial $N-s$ orbitals different from that of 1L-AlN which consists of integral $N-s$ orbitals (see the difference between Fig. 3a and Fig. 3c). As a result, few $N-s$ orbitals of 1L-AlN-H$_2$ contribute a smaller electron $|E_i|$ compared to 1L-AlN as indicated in Table 1. While, for the VBM of 1L-AlN-H$_2$, although it mainly derive from $s$ orbitals of H atoms ($H-s$) as shown in Fig. 3b, the out-plane $H-s$ orbitals are not vulnerable to in-plane strain$^{9,11,20}$. Further analysis shows that the largely increased hole $|E_i|$ (2.94 eV) of 1L-AlN-H$_2$ compared to that of 1L-AlN comes from the in-plane $N-p_x,p_y$ orbitals as shown in Fig. 3b. The in-plane $N-p_x,p_y$ orbitals are more susceptible to in-plane strain than the partial $N-s$ orbitals$^{9,11,20}$, which ultimately induces a larger hole $|E_i|$ (2.94 eV) than electron $|E_i|$ (2.38 eV) in 1L-AlN-H$_2$ and polarity-reversed carrier mobility compared to 1L-AlN$^9$.

In conclusion, we have investigated the carrier mobilities of 1L-AlN and 1L-AlN-H$_2$ using first principles calculation. Numerical results show that monolayer AlN has larger and tunable carrier mobility. The carrier mobility of 1L-AlN is hole-dominated, while the carrier mobility of 1L-AlN-H$_2$ is electron-dominated, which indicates the polarity of carrier mobility can be adjusted and reversed by hydrogenation.

Project supported by the National Natural Science Foundation of China (51674205, 51474176, 51475378, 51575452), the Natural Science Basic Research Plan in Shaanxi Province of China (2016JQ5014). We would like to thank the National Supercomputer in GuanZhou for computational facilities.

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