The transport properties of oxygen vacancy-related polaron-like bound state in HfO$_x$

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The oxygen vacancy-related polaron-like bound state migration in HfO$_x$ accounting for the observed transport properties in the high resistance state of resistive switching is investigated by the density functional theory with hybrid functional. The barrier of hopping among the threefold oxygen vacancies is strongly dependent on the direction of motion. Especially, the lowest barrier along the $<001>$ direction is 90 meV, in agreement with the experimental value measured from 135 K to room temperature. This hopping mainly invokes the z-directional motion of hafnium and threefold oxygen atoms in the vicinity of the oxygen vacancy resulted from the synergized combination of coupled phonon modes. In the presence of (111) surface, the lowest barrier of hopping between the surface oxygen vacancies is 360 meV along the $<101>$ direction, where the significant surface perpendicular motion of hafnium and twofold oxygen atoms surrounding the oxygen vacancy is identified to facilitate this type of polaron-like bound state migration. Thus, the migration on the surfaces could be more important at the high temperature.
high temperature. Polaron migration may be important to the observed transport at 

Surface phonon modes, localizing on vacancy-neighbouring hafnium atoms, are identified to facilitate this hop-

The experimentally observed barrier in the high temperature 

Results
The imperfect treatment of self-interaction in density functional theory tends to overly delocalize d electrons and yield an under-

In this case, about 50% of the electron spin density is localized pre-

vacancy-neighbouring threefold oxygen and hafnium atoms. In the presence of (111) surface, the kinetic barrier of the symmetrical hopping is significantly higher than that of the hopping in the bulk. Surface phonon modes, localizing on vacancy-neighbouring hafnium and twofold oxygen atoms, are identified to facilitate this hopping. The experimentally observed barrier in the high temperature range from 320 K to 400 K is clearly about two to three times larger than that in low temperature. Thus, this work suggests that surface polaron migration may be important to the observed transport at high temperature.

Table 1 | Calculated spin distribution over vacancy neighboring hafnium atoms

| Lower vacancy site (i) | Upper vacancy site (i') |
|-----------------------|------------------------|
| 0.11                  | 0.01                   |
| 0.16                  | 0.01                   |
| 0.22                  | 0                      |

Figure 1 | (a) The optimized 1 × 1 × 2 lattice with two threefold oxygen vacancies. Hafnium, oxygen atom, and vacancy are represented by blue, red and grey balls, respectively. An isosurface (Isovalue = 0.05 Å⁻¹) shows the spin distribution. The black dashed line and labels indicate interatomic distances in angstroms between the vacancy-neighbouring hafnium atoms. The spin mainly localizes on the lower oxygen vacancy site. (b) (100) and (001) slice view of the electron localization function calculated from valence electrons of the configuration in (a). The arrows point to the original positions of the oxygen vacancies. An attractor is located at the site of the lower vacancy while the value of electron localization function of the upper site is close to zero. (c) Atom projected density of states for the upper unit cell (non-polar site) and lower unit cell (polar site) in (a). Fermi level is set to be zero eV. The polaron-like bound state is mainly composed of Hf 5d atomic orbital.
which confirms the asymmetrical spin localization. Figure 1(b) shows the atomic projected density of states. The polaron-like bound state occupies the spin-up state at the Fermi level, and is mainly composed of hafnium 5d orbitals on which the electron is localized. The localization splits the original degenerate bandgap states induced by oxygen vacancies by pushing up the un-occupied spin-down state 2 eV above the Fermi level. Weak coupling between vacancies leads to the small band dispersion (~0.26 eV) of the polaron-like bound state, implying electron localization in the low density limit.

The polaron-like bound state migration is strongly dependent on the direction of motion in bulk HfO_x. Polaron-like bound states migrate along three different directions (i.e. <010>, <001>, and <100>) between two equivalent neighboring vacancies. The hopping direction dependent barriers unravel the anisotropic characteristics in transport process as presented in Table 2. Austin and Mott have proposed that the relationship between polaron hopping activation energy and distance is $W_H = \frac{e^2}{4} \left( \frac{1}{\kappa_e} - \frac{1}{\kappa} \right) \left( \frac{1}{r_P} - \frac{1}{R} \right)$, where $e$ is the electron charge, $\kappa_e/\kappa$ is the high-frequency/static dielectric constant, $r_P$ is the polaron radius, and $R$ is the distance between hopping centres. However, the application of this formula in anisotropic transport needs more caution. In Figure 2(a), the transition state displacement is mainly a superposition of two motion of hafnium atoms and threefold oxygen atoms. Higher order effect of the phonon eigenvectors are also estimated by varying the amplitude of the displacements, where the modes could be grouped based on the inter-mode anharmonic coupling. The transition state displacement is mainly a superposition of two groups of phonon modes, one concerning the modes localized on hafnium atoms with energy from 8 to 14 meV while the other consisting of motion of threefold oxygen atoms parallel to z-axis (i.e. O3 and O4) with energy from 24 to 45 meV, as illustrated in the inset of Figure 3(a) and Figure 3(b). The synergized combination of strongly coupled phonon modes play important roles in the migration may closely relate to the migration of polaron along the <001> direction.

| Direction | Hopping Barrier (meV) | Distance (Å) |
|-----------|----------------------|--------------|
| <010>     | 661.19               | 4.62         |
| <001>     | 281.47               | 4.76         |
| <001>     | 90.47                | 4.80         |

Table 2| Calculated lowest polaron-like bound state migration barriers between threefold oxygen vacancies in the equivalent sites in the bulk HfO_x along <100>, <010> and <001> directions.

Figure 2 | Calculated transition states of (a) <100> directional hopping in a 2 x 1 x 1 lattice with two threefold oxygen vacancies (b) <010> directional hopping in a 1 x 2 x 1 lattice with two threefold oxygen vacancies (c) <001> directional hopping in a 1 x 1 x 2 lattice with two threefold oxygen vacancies. The polaron-like bound states are originally localized on lower oxygen vacancies. The black dashed lines and labels indicate changes of interatomic distances in angstroms between the vacancy-neighbouring hafnium atoms. Green labels are major bond length changes given in angstroms.
McKenne and Shluger have found that grain boundaries act as sinks for oxygen vacancies so percolation paths are preferentially located along grain boundaries. Thus it is interesting to investigate the polaron-like bound state migration pathways in the vicinity of the boundaries. In this work, we focus on the migration dynamics near the \((111)\) surface which possesses the lowest surface energy (1.105 J/m²) among various low index surfaces. For simplicity, symmetrical hopping between equivalent sites on \((111)\) surfaces are investigated along either \(<110>\) or \(<101>\) direction with sixteen different paths. By using the slab model with two layers of \(\text{HfO}_x\) structure (\(a = 6.27\ \text{Å}, b = 13.76\ \text{Å}\)), the lowest activation barrier is found to be 360 meV along the \(<101>\) direction over 6.24 Å as given in Table 3. Experimentally, the trap depth in \(\text{HfO}_x\) which presumes a Poole-Frenkel emission model, was found to fall in the range from 210 meV to 350 meV in the elevated temperature region from 300 K to 400 K. As Poole-Frenkel behaviours are likely to have an origin of the polaron-like bound state migration near surface dominates over the bulk hopping in the high temperature region due to oxygen vacancy segregation near surfaces and the subsequent suppression of inter-grain coherent linkage.

Figure 4 (a) is the projected phonon density of states. Projecting the displacement vector onto the phonon eigenvectors at \(\Gamma\)-point, the modes with largest projections are below 48 meV, especially in the range from 7 to 20 meV. The dominant contribution to branches with large projections comes from the vibration of hafnium and twofold oxygen atoms neighbouring oxygen vacancies, as shown in Figure 4(a). Analysis of the phonon eigenvector with largest projection reveals the vibration is mainly polarized perpendicular to the surface. It is also noted that relatively large projection comes from branches with energy 45 meV to 48 meV, passing through the forbidden regions between the bulk continuums at non-zero \(q\)-points in Figure 4(b), which reveals the importance of surface modes to polaron hopping along the surface. These branches are also noticed to be almost dispersionless along the symmetry directions due to the very large mass difference between hafnium and oxygen atoms. We have also computed the phonon structure of the \((111)\) surface without oxygen vacancies and strong resemblance is found in dispersion.

An exception, however, is that the branches appearing in the forbidden region between the acoustic and optical bulk phonon modes are drastically changed due to oxygen vacancies induced surface relaxation. Like the bulk case, anharmonic coupling between modes is estimated by varying the amplitude used in the finite displacement method. The displacement of the transition states is mainly composed of the group of coupled modes in the energy range from 7 to 13 meV, as shown in Figure 4(c), localized on the hafnium and twofold oxygen atoms in the vicinity of the oxygen vacancies.

**Discussion**

The oxygen vacancy-related polaron-like bound state is clearly localized in the high resistance state of \(m\)-\(\text{HfO}_x\) investigated by the density functional theory with the hybrid functional including proper portion of non-local exact exchange. Anisotropic migration barriers are found for polaron-like bound state hopping between the equivalent threefold oxygen vacancies. The lowest barrier of threefold oxygen vacancy-related polaron-like bound state along the \(<001>\) direction is 90 meV, in agreement with the experimental value. The \(z\)-directional motion of the neighbouring hafnium and threefold oxygen atoms are identified to play important roles in the hopping of polaron-like bound state. In the presence of \((111)\) surface, lowest migration hopping path is

| Direction | Hopping Barrier (meV) | Distance (Å) |
|-----------|-----------------------|--------------|
| \(<110>\)| 519.70                | 6.88         |
| \(<101>\)| 360.93                | 6.24         |

**Table 3 | Calculated lowest polaron-like bound state migration barriers between threefold oxygen vacancies in the equivalent sites on the \((111)\) surface of \(\text{HfO}_x\), along \(<110>\) and \(<101>\) directions**
found to be along $<101>$ direction with displacements mainly invoking the surface perpendicular motion of phonon modes localized on the vacancy-neighbouring hafnium and twofold oxygen atoms. The present work based on the oxygen vacancy-related polaron-like bound state sheds light on the microscopic nature of the transport process in the high resistance state of $m$-HfO$_x$ resistive memory devices.

**Method**

Here we use the plane wave pseudo-potential code CASTEP with norm-conserving pseudopotentials method aided by B3LYP functional and an energy cutoff at 450 eV. The calculation is performed by using the spin polarized density functional theory. For cell optimization, the supercell parameters are optimized in their charge states using PRE version of GGA with norm-conserving pseudopotentials. The geometry is further optimized by B3LYP method. The transition state search is implemented by the combination of linear synchronous transit and quadratic synchronous transit schemes with 0.1 eV/Å convergence threshold for the root mean square forces on the atoms$^{31,46,47}$. K-point convergence test has been done and 5 irreducible k-points are used in sampling. For transition state search related calculations, only $\Gamma$ point is used to reduce computational cost. Phonon dispersion and density of states calculation are computed by the finite displacement method implemented in CASTEP$^{48}$.

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**Figure 4** | (a) Calculated atom projected phonon density of states and (b) phonon dispersion of (111) HfO$_x$ 2-layer vacuum slab model with lowest symmetrical migration energy along $<101>$ direction. The projected bulk phonon dispersion of HfO$_x$ is shown by the hatched region. The branches within energy range from 45 to 48 meV pass through the forbidden regions between the bulk continua at non-zero q-points, representing surface modes. (c) Illustration of the dominant phonon packet. Arrows are the superposition of coupled modes where the vibration is mainly with the vacancy-neighbouring hafnium and twofold oxygen atoms.
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