Atomic and electronic structure of amorphous and crystalline hafnium oxide: X-ray photoelectron spectroscopy and density functional calculations

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The atomic structure of amorphous and crystalline hafnium oxide (HfO2) films was examined using x-ray photoelectron spectroscopy and band data calculated by the density functional method, we found that the valence band of HfO2 consists of three subbands separated by ionic gaps. The upper subband is formed by O 2p, Hf 4f, and Hf 5d states; the intermediate subband is formed by O 2s and Hf 4f states, whereas the lower narrow subband is mainly formed by Hf 5p states. The energy gap of amorphous HfO2 is 5.7 eV as determined by electron energy loss spectroscopy. The band calculation results indicate the existence of light (0.3m0) and heavy (8.3m0) holes in the HfO2 film and the effective mass of electron lies in the interval of 0.7m0–2.0m0. © 2007 American Institute of Physics. [DOI: 10.1063/1.2464184]

I. INTRODUCTION

It is well known that the key dielectrics for manufacturing the silicon devices are amorphous silicon dioxide (a-SiO2) and amorphous silicon nitride (a-Si3N4). After 40 years of intensive study, the atomic and electronic properties of these dielectrics are now well understood.1–3 As the thicknesses of the silicon oxide and silicon nitride are being scaled down to their physical limits, a pressing problem in modern microelectronics is to replace the conventional dielectrics by high dielectric permittivity and monoclinic phase in three polymorphic modifications: a low-temperature monoclinic modification. A cubic modification was observed at temperatures above 2000 K, and the cubic phase (Fm3m) that forms at temperatures above 2870 K.12,13 In the cubic and tetragonal phases, the hydrogen is fourfold coordinated, and the Hf atom is eightfold coordinated. In the monoclinic phase, the coordination numbers for O atoms can be either three- or fourfold, and the Hf atoms can be seven- or eightfold coordinated.

At room temperatures, crystalline HfO2 exists in the monoclinic modification. A cubic modification was observed at 200 °C in thin HfO2 and ZrO2 films with thicknesses ranging from 100 to 500 Å.14–17 In the temperature range of 300–600 °C, films with thicknesses between 100 and 500 Å are a tetragonal modification of HfO2, with parameters substantially differing from the high-temperature bulk modification.14,17 Stable monoclinic phase is normally observed in films thicker than 500 Å.

The electronic structure of HfO2 in its cubic, tetragonal, and monoclinic modifications was theoretically examined by Demkov.18 This author found that the valence band of HfO2 is made up of two subbands. However, the band gap energy predicted by numerical calculations turned out to be substantially smaller than its experimental value. A theoretical study of the density of electronic states in the monoclinic modification of HfO2 was also reported by Foster et al.19 This study is important for investigating the charge transport through such thin films. Suppression of leakage currents across the gate dielectrics of MOS structures is currently the crucial issue. The large electric field across the thin dielectric film makes the direct and Fowler-Nordheim tunneling through the Si/dielectric energy barrier possible. The injection current exponentially depends on the effective mass m* of the tunneling charge carriers in the dielectric.20,21 Band calculation and experimental data show that in SiO2 and Si3N4 there...
exist “light” electrons with effective mass in the range of \(0.3m_0–1.4m_0\) and heavy holes with effective mass in the range of \(2.5m_0–10m_0\). The heavy holes in these materials are due to the narrow band formed by the antibonding O \(2p_\pi\) and N \(2p_\pi\) orbitals in SiO\(_2\) and Si\(_3\)N\(_4\), respectively. Neither theoretical nor experimental study on the effective electron or hole mass in HfO\(_2\) has been reported so far. The purposes of the present study is to examine, both experimentally and theoretically, the atomic and electronic structure of HfO\(_2\), and to use these results in estimating the effective electron and hole masses in this material.

II. EXPERIMENT

The starting materials were \(\langle 100 \rangle\)-oriented \(n\)-Si substrates with resistivity of 20 \(\Omega\) cm. Prior to the deposition, the Si substrates were cleaned with the standard RCA procedure. HfO\(_2\) films with thicknesses in the range of 200–600 \(\AA\) were then deposited onto the wafers using an ARC-12M sputter, with a purity of 99% hafnium target. Note that the objective of this work is to study the bulk properties of HfO\(_2\), and the density function calculations to be presented later are also focused on the bulk structure. To minimize the interface effects, the films prepared in this work are much thicker than those used in the current MOS devices for electrical properties characteristics. The vacuum chamber was pumped down to a pressure of \(10^{-6}\) Torr and then subsequently filled with an oxygen/argon mixture. The argon-to-oxygen flow ratio was \(2:23\). During the deposition of the HfO\(_2\) films, the pressure in the chamber was maintained at a level of \(10^{-3}\) Torr and the substrate temperature was 150 °C. The as-deposited films using this method are amorphous. The chemical composition and the stoichiometry were studied with x-ray photoelectron spectroscopy (XPS) measurements. The as-deposited film is slightly oxygen deficient. Part of the samples was further annealed at 800 °C in atmosphere for 30 min in order to improve the film stoichiometry and to have significant crystallization effects for the ease of experimental investigation. Lower annealing temperature and shorter duration may be adopted to minimize the crystallization effects, but the microcrystallites should still have notable effect as the crystallization phase can be found at processing temperature of 325 °C for sample being prepared using atomic layer deposition (ALD) method.

Various characterizations were conducted for the samples. X-ray phase analysis (XPA) was conducted by studying the diffraction of synchrotron radiation with wavelength \(\lambda = 1.5406 \text{ Å}\). X-ray diffraction patterns were registered on a high-resolution diffractometer in the Institute of Nuclear Physics at Novosibirsk. A glancing incidence scheme with \(\theta = 4°\) was used. The sample was rotated around the normal to the film surface. The x-ray diffraction patterns were recorded at a scanning pitch of \(\Delta(2\theta) = 0.05°\) with the interval \((2\theta)\) in the range of 20°–70°.

Edge x-ray absorption fine spectra (EXAFS) measurements of the HfO\(_2\) films were conducted to study the fine structure of the Hf \(K\) near-edge absorption. These characteristics were measured using the synchrotron radiation produced by the VEPP-3 storage ring (also in Institute of Nuclear Physics, Novosibirsk) with energy of 2 GeV and current ranging from 50 to 100 mA. The radiation detector was a gamma ionization chamber filled with Ar/He mixture and a double-crystal monochromator (a (111)-oriented split Si single crystal) was used in the detector. The EXAFS spectra were registered using the surface-sensitive fluorescent technique. By measuring the intensity of the secondary (fluorescent) radiation emitted by a decaying “hole” state of an atom where a deep vacancy was generated by gamma-quantum absorption, the x-ray absorption coefficient can be determined. To eliminate the reflections of the synchrotron radiation from the substrate, the sample was mounted on a turning table rotated with frequencies in the range of 10–15 Hz. Phase and amplitude characteristics of the EXAFS data were calculated through the X\(\alpha\)-DW (Debye-Waller factor) approximation using the EXCURV92 package. To analyze the local atomic environment, a fitting procedure with \(k\) weighting was applied to the Fourier-filtered data to yield the dependences \(k\chi(k)\), where \(\chi(k)\) is the normalized oscillating absorption coefficient and \(k\) is the wave number. The fitting was performed in the interval of photoelectron wave vectors from 3 to 12 Å\(^{-1}\).

X-ray and ultraviolet photoelectron spectra were measured using a VG ESCALAB 220i-XL spectrometer with an Al \(K\alpha\) monochromatic radiation source with energy of 1486.6 eV or helium plasma with energy of 21.2 eV (He I) or 40.8 eV (He II).

III. RESULTS AND DISCUSSIONS

A. Atomic structure of HfO\(_2\) films

Figure 1 shows a survey of the x-ray photoelectron spectrum on an amorphous HfO\(_2\) film. Estimations from the ratio of Hf \(4d\) and O \(1s\) peak intensities confirm that the chemical composition of this film is essentially stoichiometric. Figure 2 shows the x-ray diffraction patterns for as-deposited and annealed (800 °C for 30 min in ambient air) HfO\(_2\) films. Compared with the x-ray diffraction (XRD) pattern of monoclinic HfO\(_2\) powder (plotted in squares in the bottom picture), it suggests that the annealed HfO\(_2\) films are crystalline (with a monoclinic structure and a lattice parameter \(a\).
\[ = 5.08 \text{ Å} \). The formation of the monoclinic structure during the 800 °C annealing can be explained by the existence of a thermodynamically nonequilibrium amorphous modification of HfO\(_2\) in the initial state.

Figure 3 shows the modulus of the Fourier transform of the function \[ \kappa^2 \chi(k) \] extracted from the Hf \( K \) EXAFS spectrum (radial structural functions without phase corrections) for a HfO\(_2\) film, before and after thermal annealing. It indicates that the as-deposited films are completely amorphous as there is no detectable Hf–Hf separation. The annealed sample results in a rise in the Hf–O amplitude in the first coordination sphere of the metal atoms (ordering) and gives rise to a Hf–Hf peak and to peaks corresponding to the ordered arrangement of oxygen atoms in the farther coordination spheres of Hf (see Fig. 3, curve 2).

**B. Electronic structure of amorphous HfO\(_2\) films**

Figure 4 shows an ultraviolet photoelectron spectrum due to the valence band of amorphous HfO\(_2\) measured at an excitation energy of 21.2 eV. Also shown in the same figure is the Au spectrum to be used as a reference for determining the valence band level.

The low-energy part of the spectrum controls the energy position of the top of the valence band in amorphous HfO\(_2\). As the Au work function (Fermi-level position with respect to the vacuum level) is 5 eV and the top of the valence band of amorphous HfO\(_2\) is about 1.5 eV above the Au Fermi level, the top of the HfO\(_2\) valence band \( (E_V) \) is 6.5 eV lower than the vacuum level. Since the energy position of the Au Fermi level coincides with the top of Si valence band, \( E_V(Si) \), the height of the energy barrier for hole injection from Si into amorphous HfO\(_2\) thus amounts to 1.5 eV also.

The width of the energy gap in amorphous HfO\(_2\) was estimated from electron energy loss spectroscopy (EELS) data obtained with a 200 eV monochromatic electron beam (see Fig. 5). The zero energy in the figure refers to the position of the peak due to elastically reflected electrons. Negative energies refer to inelastically reflected electrons. The width of the forbidden gap \( (E_g) \) in amorphous HfO\(_2\) as extracted from Fig. 5 is in the range of 5.7 ± 0.3 eV. This value agrees with other reports.\(^{27,28}\)

The solid curve in Fig. 6 is an experimental XPS spectrum due to the valence band of amorphous HfO\(_2\). The dotted curve in this figure represents a Gaussian fit of the full density of valence band states predicted with allowance for the ionization cross sections of the 5\( p \), 4\( f \), 5\( d \), and 6\( s \) orbitals of Hf.
Hf and 2p and 2s orbitals of O. The values of the ionization cross sections are listed in Table I. The dispersion in each peak is assumed to be equal to the width at half-height of the corresponding peak in the experimental curve. The valence band of HfO$_2$ is split into three subbands with roughly identical widths at half-height of 3 eV. The prevailing contribution to the spectrum is due to the 4f, 5d, and 5p states of Hf and due to the 2p and 2s states of oxygen. An ultraviolet photoelectron spectrum of amorphous HfO$_2$ taken at an excitation energy of 40.8 eV is shown in Fig. 7. The prevailing contribution to the experimental spectrum is made by O 2s states.

C. Electronic structure of the three crystalline modifications

To construct the band diagrams of the cubic, tetragonal, and monoclinic modifications of HfO$_2$ and to determine the effective masses of holes and electrons in these crystals, quantum-mechanical calculation using the Amsterdam density functional (ADF) BAND program was conducted. The ADF program was used to calculate the electronic structure of atoms and molecules, and BAND is a subprogram in the ADF package for calculating periodic atomic systems (atomic chains and layers, and bulk crystals).

The program is based on the theory of the Kon-Shem density functional in the local-density approximation for the exchange and correlation energies. The program calculates the electron density and total energy of multielectron systems. It allows the user to reconstruct the band structure, to predict the total density of states (TDOS) and the partial densities of states (PDOS) for all spherical harmonics with a certain value l of the orbital momentum, and to analyze the charges at the atoms in the system.

The crystal structures and the respective Brillouin zones with singular points are shown in Fig. 8. In the cubic modification of HfO$_2$, the Bravais lattice is a face-centered-cubic lattice, and the unit cell is the primitive rhombohedric. The translation vectors are $\langle a/2, a/2, 0 \rangle$, $\langle a/2, 0, a/2 \rangle$, and $\langle 0, a/2, a/2 \rangle$, and the lattice constant is $a=5.08$ Å. The basis is formed by three atoms: one Hf atom is located at $(0, 0, 0)$ and two O atoms are located at $(a/4, a/4, -a/4)$ and $(a/4, a/4, a/4)$.

In the tetragonal modification of HfO$_2$ the unit cell is a regular prism with squared basis. The translation vectors are $(a, 0, 0)$, $(0, a, 0)$, and $(0, 0, c)$, where $a=3.56$ Å and $c=5.11$ Å. The structure of the tetragonal HfO$_2$ readily forms from the cubic phase of HfO$_2$: in the $\langle 001 \rangle$ direction, the lattice constant increases to $c=5.11$ Å, and the oxygen columns shift by $\delta=0.19$ Å, while the neighboring columns experiencing antiphase shifts. The basis consists of six atoms: two Hf atoms are located at $(0, 0, 0)$ and $(a/2, a/2, c/2)$ and four O atoms are located at $(a/2, 0, c/4-\delta)$, $(a/2, 0, -c/4-\delta)$, $(0, a/2, c/4+\delta)$, and $(0, a/2, -c/4+\delta)$.

The space lattice of the monoclinic modification of HfO$_2$ has primitive unit cell with the translation vectors $(a, 0, 0)$, $(0, b, 0)$, and $(c \cos \gamma, 0, c \sin \gamma)$, where $a=5.08$ Å, $b=5.19$ Å, $c=5.22$ Å, and $\gamma=99.77$. The basis consists of 12 atoms whose coordinates are listed in Table II. The unit cell of the monoclinic modification of HfO$_2$ involves two types of oxygen atoms, one (O1) is three-coordinated and the other (O2) is four coordinated.

![FIG. 6. An x-ray photoelectron spectrum of amorphous HfO$_2$ taken at an excitation energy of 1486.6 eV (solid curve) and the predicted photoionization cross section (dashed curve).](image1)

![FIG. 7. The photoelectron spectrum of amorphous HfO$_2$ measured with excitation energy of 40.8 eV and the predicted density of states in the valence band were normalized with the photoionization cross section.](image2)

| TABLE I. Photoionization cross-section coefficients for the 5p, 4f, 5d, and 6s orbitals of Hf and for 2p and 2s orbitals of O. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | Hf              |                |                | O               |                |                |
| $\hbar\omega$ (eV) | 5p       | 4f        | 5d       | 6s       | 2s       | 2p       |
| 40.8            | 7.9990 | 0.9905 | 2.5980 | 0.0755 | 0.8342 | 6.8160 |
| 1486.6          | 0.1014 | 0.1108 | 0.0245 | 0.0005 | 0.0190 | 0.0003 |
In computing the electronic structure of the cubic, tetragonal, and monoclinic crystalline modifications of HfO$_2$ with ADF and BAND programs, the Bloch electron functions in the crystal are sought in the form of an expansion in basis functions. For the basis functions, two types of functions are used: numerical orbitals (NO) and Slater orbitals (STO). The numerical orbitals are the wave functions predicted by the Herman-Skilman program, and the Slater orbitals are

$$X_{n,lm} = A n^{n-1} \exp(-\xi r)Y_{lm},$$  \hspace{1cm} (1)

where $n$ is the effective principal quantum number. Combination of NO and STO in the basis set imparts the set with a high variational flexibility that guarantees a good accuracy of the calculations with a comparatively limited number of basis functions. The molecular orbital is calculated by only involving the atomic orbital due to the valence electrons and the inner atomic shells are frozen.

The number of basis functions per unit cell in the cubic modification of HfO$_2$ is 75, and the values of cell numbers for the tetragonal and monoclinic configurations are 150 and 300, respectively. Integration over the Brillouin zone was performed with 65, 75, and 119 $k$ points in the irreducible part of the Brillouin zone for the cubic, tetragonal, and monoclinic modifications, respectively. Similar calculations for the band structure of the cubic, tetragonal, and monoclinic modifications of HfO$_2$, but with a basis set made up by plane waves were reported previously by Holgado et al.$^{14}$

Figures 9–11 show the theoretically predicted band diagrams of the cubic, tetragonal, and monoclinic crystalline modifications of HfO$_2$ drawn through the Brillouin zone singular points (see Fig. 8). Here and below, the zero energy is taken to coincide with the top of the valence band. With enlarged atomic basis, the band structure becomes more complicated, although having a similar appearance for all the three modifications. It can be concluded from the present results that the properties of HfO$_2$ are defined by the short range and not by the long-range atomic ordering.

In the cubic modification of HfO$_2$, the valence band top $E_V$ lies at the point $X$ of the Brillouin zone, and the conduction-band bottom $E_C$ at the point $\Gamma$. The band gap energy in the cubic modification of HfO$_2$ can be estimated as

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{X (Å)} & \textbf{Y (Å)} & \textbf{Z (Å)} \\
\hline
0 & 0 & 0 \\
Hf atoms & 2.4761 & 0.4516 & 2.1444 \\
& 2.9189 & 2.5951 & 0.4278 \\
& 0.4429 & 2.1434 & 2.5722 \\
& 1.1366 & 1.5898 & 0.6349 \\
& 1.3395 & 2.0414 & 2.7793 \\
& 1.7824 & 4.1848 & 0.2071 \\
O atoms & 1.5795 & 0.5536 & 3.2071 \\
& 0.5968 & 3.7156 & 1.4201 \\
& 3.0729 & 4.1673 & 3.5644 \\
& 3.5158 & 6.3106 & 0.9923 \\
& 0.1539 & 1.5723 & 3.9922 \\
\hline
\end{tabular}
\caption{Positions of the basis atoms in the primitive cell of monoclinic HfO$_2$ (Cartesian coordinate system).}
\end{table}
the difference between the valence band top and the conduction band bottom and is \( E_g = E_C - E_V = 3.2 \text{ eV} \). In the tetragonal modification, \( E_V \) and \( E_C \) lie at the \( H9003 \) and \( M \) points of the Brillouin zone, respectively, giving \( E_g = 3.8 \text{ eV} \). For the monoclinic modification, \( E_V \) lies at the \( /H9003/G \) point of the Brillouin zone and \( E_C \) at the \( B \) point, giving \( E_g = 3.5 \text{ eV} \). Thus, all the three modifications of HfO\(_2\) are indirect band gap dielectrics, and the band gap energies \( E_g \) are approximately in the range of 3.2–3.8 eV. These values are significantly less than the experimental values in the range of 5.3–5.8 eV, according to various authors.\(^2\)\(^7\),\(^2\)\(^8\) This discrepancy can be attributed to the fact that density functional theory (DFT) calculations normally yield an underestimated value for the band gap energy.

The effective masses of electrons and holes (see Table III) were calculated using a square approximation of the \( E(k) \) dispersion curves near the edges of the valence and conduction bands, i.e.,

\[
m^* = \frac{\Delta k^2}{2\Delta E},
\]

where \( \Delta E \) is the energy difference between the minimum and maximum energies at the points lying apart at the distance \( \Delta k \) in the inverse space in the corresponding direction.

Calculations show that in each crystalline modification of HfO\(_2\), there exist heavy as well as light holes, the effective hole masses exhibiting a large spread from 0.3\(m_0\) in cubic HfO\(_2\) to 8.3\(m_0\) in tetragonal HfO\(_2\). The conduction band electrons have effective masses of roughly identical order, the heaviest of 1.97\(m_0\) and the lightest one of 0.68\(m_0\), being observed in the case of cubic HfO\(_2\).

In the cubic modification of HfO\(_2\) for the conduction band bottom at the \( G \) point, there is a doubly degenerated state that splits along the \( G-X \) direction, being preserved in the \( G-L \) direction. In tetragonal HfO\(_2\) the top of the valence band is degenerated, the degeneration being preserved in the directions \( A-M \) and \( Z-A \). The conduction electrons are light in both directions. In monoclinic HfO\(_2\) the electronic states are nondegenerated for both the valence band top and the conduction band bottom.

Figures 12–14 show the PDOS predicted for the \( 4f, 5p, \) and \( 5d \) orbitals of Hf and for the \( 2s \) and \( 2p \) orbitals of O in cubic HfO\(_2\).

### TABLE III. Effective electron and hole masses in the atomic units for cubic, tetragonal, and monoclinic HfO\(_2\).

<table>
<thead>
<tr>
<th>Crystallographic direction</th>
<th>( m_{11}/m_0 )</th>
<th>( m_{22}/m_0 )</th>
<th>Crystallographic direction</th>
<th>( m_{11}/m_0 )</th>
<th>( m_{22}/m_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma-X )</td>
<td>0.32</td>
<td>...</td>
<td>( L-\Gamma )</td>
<td>0.86</td>
<td>0.86</td>
</tr>
<tr>
<td>( X-W )</td>
<td>3.04</td>
<td>...</td>
<td>( \Gamma-X )</td>
<td>1.97</td>
<td>0.68</td>
</tr>
<tr>
<td>( Z-A )</td>
<td>0.78</td>
<td>0.78</td>
<td>( M-\Gamma )</td>
<td>0.72</td>
<td>...</td>
</tr>
<tr>
<td>( A-M )</td>
<td>8.26</td>
<td>8.26</td>
<td>( \Gamma-Z )</td>
<td>0.94</td>
<td>...</td>
</tr>
<tr>
<td>( \Gamma-Y )</td>
<td>1.28</td>
<td>...</td>
<td>( A-B )</td>
<td>1.03</td>
<td>...</td>
</tr>
<tr>
<td>( Z-\Gamma )</td>
<td>0.85</td>
<td>...</td>
<td>( B-D )</td>
<td>1.21</td>
<td>...</td>
</tr>
</tbody>
</table>

FIG. 11. \( E-k \) diagram across the singular points of Brillouin zone for monoclinic HfO\(_2\).

FIG. 12. Partial densities of the states due to \( 4f \), \( 5p \), and \( 5d \) orbitals of Hf and of those due to \( 2s \) and \( 2p \) orbitals of O in cubic HfO\(_2\).
shown in the figure. It can be seen that the relative contributions of the various orbitals to the density of states for the three modifications are roughly identical.

It is further realized that, like most of the transition-metal oxides, the density of states in the conduction band of HfO₂ is made up by the d states of the transition metal, i.e., by the Hf 5d orbitals. The 5 eV wide upper subband of the valence band is formed mainly by the 2p electron states of oxygen with partially Hf 5d states. The intermediate subband, of 2 eV width, is formed by Hf 4f states with some O 2s states. Note that the peak due to the Hf 4f orbital in the figure is truncated as the actual intensity of the peak is five times larger. The lower narrow subband, 0.1 eV wide, is almost completely formed by the Hf 5p states.

The calculated total density of states agrees well with the valence band photoelectron spectrum (see Figs. 6 and 12–14). There are three subbands separated by ionic gaps. It is noted that the difference between the width of the predicted TDOS peaks (the two lower peaks have half-widths of 1.5 and 2.5 eV) and the width of the corresponding experimental peaks (half-width of 5 eV) is quite large. This discrepancy can be attributed to the finite lifetime of holes at the core levels which results in the broadening of the peaks in experimental spectra. However, taking into account the processes resulting in peak broadening (Auger processes, for instance) would require a more precise theoretical model and is out of the scope of the present study.

IV. CONCLUSIONS

In summary, the band structures of the cubic, tetragonal, and monoclinic polymorphous modifications of HfO₂ have been calculated with DFT. The results agree with the experimental photoelectron spectroscopy data. The valence band of HfO₂ consists of three subbands separated from each other by ionic gaps. The upper subband is formed by O 2p, Hf 4f, and Hf 5d states; the intermediate subband is formed by O 2s and Hf 4f states, whereas the lower narrow subband is mainly formed by Hf 5p states. We calculate the effective electron and hole masses in HfO₂. The effective electron masses for different directions in the Brillouin zone fall into the interval of 0.2m₀ – 2.0m₀. The calculations show that there exist heavy and light holes for various directions in the Brillouin zone for all the three modifications. The pronounced anisotropy of the electron and hole masses suggests that charge injection into Si may be effectively suppressed by growing a certain orientation crystalline HfO₂ film. Those effects would have significant impact on the current conduction over the dielectric films. The present calculations are based on bulk material structure. The results should be partially applicable to ultrathin (~2 nm) film where the effect of interfacial layer and the interface bonding must be taken into account. The crystallization effects, the fluctuation of effective masses, the anisotropy of electron, and the hole masses should still exist in the ultrathin films.

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