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The electronic structure change with Gd doping of HfO₂ on silicon

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Gd-doped HfO₂ films deposited on silicon substrates undergo a crystallographic change from monoclinic to fluorite (cubic) phase with increasing Gd concentrations. The crystallographic phase change is accompanied by a small increase in the valence bandwidth and in the apparent band offset in the surface region. Electrical measurements show pronounced rectification properties for lightly doped Gd:HfO₂ films on p-Si and for heavily-doped Gd:HfO₂ films on n-Si, suggesting a crossover from n-type to p-type behavior with increasing doping level. © 2007 American Institute of Physics. [DOI: 10.1063/1.2787967]

While HfO₂ has attracted considerable attention as a high-κ dielectric oxide, the cubic phase of yttrium doped HfO₂ appears to have improved dielectric properties. It has been demonstrated that Y₂O₃ doping stabilizes HfO₂ in the cubic phase. Doping of HfO₂ by Er, Gd, and many other rare earth elements also induces a monoclinic to cubic phase transition. The gadolinium doping of a number of wide band gap semiconductors suggested that Gd doping of HfO₂ may lead to a dilute magnetic semiconductor. Moreover, semiconducting Gd-doped HfO₂ may provide a promising new class of materials for neutron detection technologies.

At 3% Gd substitution for Hf in HfO₂, Gd contributes to the density of states at 9.5–10.5 eV binding energy, as demonstrated by resonant photoemission. The lattice remains in the monoclinic phase, which is strained by about 3%. Here, we show that further doping leads to a structural phase change with subtle changes in the electronic structure.

The Gd-doped HfO₂ films were deposited on both p-type and n-type single crystal Si(100) substrates using pulsed laser deposition at a growth rate of about 0.15 Å/s. The Gd-HfO₂ target was prepared by standard ceramic techniques using HfO₂ and Gd₂O₃ powders, as described elsewhere. The films were deposited at a substrate temperature of 500 °C. The deposition was carried out in a mixture of H₂ and Ar (8% H₂) to introduce oxygen vacancies, and the vacuum was maintained at 10⁻⁵ Torr during the deposition. The doping level was determined from the target composition and confirmed by companion near edge x-ray absorption spectroscopy (NEXAFS) and by x-ray emission spectroscopy. The NEXAFS and EXAFS data indicate that the Gd atoms occupy the Hf sites in the Gd-doped HfO₂ films.

X-ray diffraction (XRD) patterns show that the resulting HfO₂ films with 3% Gd, which are approximately 250 nm thick, are in the single monoclinic phase with strong texture growth and about 3% strain compared to the undoped HfO₂ (Fig. 1), consistent with prior results. With increased doping levels, a new phase is evident, as seen from the x-ray diffraction patterns in Fig. 1. For 10% Gd doping levels, this new phase retains a minority monoclinic phase component, but for 15% Gd doping, the films are free of the monoclinic phase, i.e. stable. This new phase, apparent with the more highly Gd-doped HfO₂ films, is consistent with the fcc fluorite phase in XRD, as is expected. The presence of a small amount of the Gd:Hf₂O₇ pyrochlore phase cannot, a priori, be excluded, because it differs from fluorite only in the presence of ordering within the cation sublattice.

To determine the placement of the Fermi level, temperature-dependent angle-resolved photoemission experiments were performed using the 3 m toroidal grating monochromator beam line in an UHV chamber previously described. The Fermi level (EF) was established from a

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FIG. 1. (Color) Part of the XRD pattern for 3%, 10%, and 15% Gd doped doped HfO₂. The 3% Gd doped films are consistent with that of the HfO₂ in a simple monoclinic structure. The 10% doped samples are mixed monoclinic and majority cubic phases, as indicated, while 15% Gd-doped samples are in a fluorite phase. In the fluorite fcc phase, the lattice constant increases with increased Gd doping.
gold film in electrical contact with the sample, and a very
careful effort was undertaken to eliminate and exclude charg-
ing effects from the photoemission measurements of Gd-
doped HfO$_2$ films. Photoemission was undertaken over a
range of temperatures 100–700 K, but the data presented
here were taken at 320 °C, where surface charging was
found to be negligible. This is well below the temperature
dependent structural phase transition 700 °C.

From Fig. 2, it is clear that the valence band edge is
placed well away from the Fermi level for both Gd-doped
and undoped HfO$_2$ films. The Hf 4f binding energies of
18–21 eV are substantially larger than those reported by
Renault et al.\textsuperscript{19,20} Hf 4f binding energies and valence band
edge are similar\textsuperscript{9} or slightly larger than those reported
elsewhere.\textsuperscript{21–23} As seen in Fig. 2, the Hf 4f binding energies
increase when Gd doping is increased from 3% to 10%.

The increase with Gd doping in the intensity of the
photoemission features in the oxygen 2p region of the va-
lence band, at 5–10 eV binding energy, relative to the Hf 4f
features at 18–21 eV binding energies, suggests that Gd 4f
states contribute to the shoulder on the broad photoemission
peak at the binding energy of 9–10 eV. This contribution
was confirmed by resonant photoemission studies of lightly
doped Gd: HfO$_2$, by first-principles electronic structure calculations using
the full-potential linear augmented plane-wave method in the
site, as seen in the lower inset of Fig. 2. In this region, the
density of states suggested by photoemission decreases with
increasing yttrium doping levels\textsuperscript{5}, but is seen here to increase
with Gd doping. Indeed, the increase in binding energy of all
the major photoemission features seen with Gd doping is not
observed for (HfO$_2$)$_{1-x}$(Y$_2$O$_3$)$_x$ samples.\textsuperscript{5} The possibility
of surface defects or surface states pinning the Fermi level dif-
fently for the two different dopants (Y and Gd) cannot be
excluded and may in fact be likely. Yttrium segregates
away from the surface of zirconia,\textsuperscript{24} and may be seen in the upper inset
in Fig. 2, theoretical calculations (see below) suggest that the
phase transition from monoclinic to fluorite phase is also
accompanied by a transfer of the oxygen spectral weight to-
ward this shoulder, which makes it difficult to assign these
intensity changes precisely.

With Gd doping, there is also an increase in the small
density of states between 4 eV binding energy and the Fermi
level, as seen in the lower inset of Fig. 2. In this region, the
density of states suggested by photoemission decreases with
increasing yttrium doping levels,\textsuperscript{5} but is seen here to increase
with Gd doping. Indeed, the increase in binding energy of all
the major photoemission features seen with Gd doping is not
observed for (HfO$_2$)$_{1-x}$(Y$_2$O$_3$)$_x$ samples.\textsuperscript{18} The possibility
of surface defects or surface states pinning the Fermi level dif-
fently for the two different dopants (Y and Gd) cannot be
excluded and may in fact be likely. Yttrium segregates
away from the surface of zirconia,\textsuperscript{24} and may be seen in the upper inset
in Fig. 2, theoretical calculations (see below) suggest that the
phase transition from monoclinic to fluorite phase is also
accompanied by a transfer of the oxygen spectral weight to-
ward this shoulder, which makes it difficult to assign these
intensity changes precisely.

The assignment of the photoemission features was veri-
fied by first-principles electronic structure calculations using
the full-potential linear augmented plane-wave method in the
local density approximation. Excitations involving the 4f
shell of Gd or Hf were treated using the core-hole method, as
described previously.\textsuperscript{15} As reported previously,\textsuperscript{17} the calcu-
lated Gd photoemission binding energy in the fluorite phase
is 5.5 eV below the valence band maximum. Placing the va-
lence band maximum at about 4 eV below the Fermi level,
this results in a 9.5 eV binding energy for the Gd 4f states
with respect to the Fermi level, in agreement with resonant
photoemission data.\textsuperscript{17,18} To place this in context, the Gd 4f
binding energies for the gadolinium oxide are from
8.5 to 11 eV binding energies with respect to the Fermi
level, with smaller binding energies with respect to the
valence band maximum than observed here.\textsuperscript{26}

Similarity of the photoemission intensities (Fig. 2) for
monoclinic and fluorite phases of HfO$_2$ reflects the similarity
of the electronic structure. In particular, the upper inset in
Fig. 2 shows the calculated valence band density of states
(DOS) convoluted with a Gaussian of 0.8 eV width for the
two phases of pure HfO$_2$. Although the bandwidth is almost
1 eV larger for the fluorite phase (6.5 eV compared to
5.6 eV in the monoclinic phase), the DOS at the band bottom
is small. Therefore, if the finite linewidth is taken into ac-
count, the apparent bandwidth increases by less than 0.5 eV.
This generally agrees with the observed photoemission va-
lence bandwidths, if the peak is resolved into a sum of Gd 4f
peak and pure oxygen p band, and the tailing density of
states toward the Fermi level is neglected, as seems to often
be the practice.\textsuperscript{6}

Further, we calculated the Hf 4f excitation energies us-
ging the core-hole method for both the fluorite and the mono-
clinic phases. In both cases, we used a unit cell with four Hf
and eight O atoms and changed the 4f occupation from 14 to
13 on one of the Hf atoms (the excited core is spin polarized
and the calculations are done including the valence band spin
polarization self-consistently). The core is treated fully rela-
tivistically, and the hole is placed on the 4f$_{7/2}$ level which
has lower binding energy within the 4f doublet. The excited
electron fills a donor level which lies at about 0.6 eV below
the conduction band minimum (the level is broadened due to
the finite size of the supercell). Estimating the distance from
this level to the valence band maximum and subtracting it
from the energy difference between the photoexcited 4f$_{13}$
and the ground 4f$^{14}$ states, we find the Hf 4f$_{7/2}$ photoexcita-
tion energy of 14.4 eV for the fluorite phase and 14.1 eV for
the monoclinic phase. The 0.3 eV difference lies within the

FIG. 2. (Color) Different band intensities for (a) pristine: 0%, (b) 3%, and
(c) 15% Gd-doped films of HfO$_2$. The photon energy is 70 eV and the light
incidence angle is 45°. The increasing contributions to the density of states
near to the Fermi level are illustrated in the inset for 0% (black dots), 3%
(open triangles), and 15% (stars) Gd doping levels in the inset at the bottom
left, while the calculated density of states for the fluorite (black) and the
monoclinic (red) phases of pure HfO$_2$, in the region of the valence band
maximum (the O 2p bands) are shown in the upper left inset.
error associated with the finite supercell size. According to these results, the 4f photoemission peak should not shift appreciably relative to the valence band maximum at the transition from monoclinic to fluorite phase. We also found that the position of the HF 4f photoemission peak relative to the valence band maximum is insensitive to the presence of uncompensated Gd (this was done using the same supercell with 25% Gd substitution; the excited electron then fills the valence band). All these results are consistent with Fig. 2.

*p-n* heterojunction diodes can be formed with strongly textured monoclinic and fluorite Gd-doped HfO$_2$ on Si(100). We fabricated several diodes to illustrate that the overcompensation of the expected Gd acceptor states, by oxygen vacancies, as is seen with smaller (3 at. %) Gd doping levels is not sustained at the higher Gd doping levels. An *n*-type band offset of the lightly Gd-doped HfO$_2$ relative to *p*-type silicon is indicated by the excellent diode rectification seen for a heterojunction of 3% Gd-doped HfO$_2$ and *p*-type silicon, as shown in Fig. 3. For the 10% Gd: HfO$_2$/p-Si heterojunction, no rectification or diodelike characteristics are seen, but for the 10% Gd-doped HfO$_2$ to *n*-type silicon heterojunction, we do observe rectification or diodelike characteristics, shown in Fig. 3. While these data do not conclusively show the dominant carrier, they suggest that oxygen vacancies can overcompensate the Gd acceptor states without completely destroying the semiconductor properties for 3% Gd doping levels but not for 10% Gd doping levels or higher.

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