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Citation: Appl. Phys. Lett. 98, 252903 (2011); doi: 10.1063/1.3601487
View online: http://dx.doi.org/10.1063/1.3601487
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High-\(k\) (\(k=30\)) amorphous hafnium oxide films from high rate room temperature deposition

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(Received 29 April 2011; accepted 28 May 2011; published online 23 June 2011)

Amorphous hafnium oxide (\(\text{HfO}_x\)) is deposited by sputtering while achieving a very high \(k \sim 30\). Structural characterization suggests that the high \(k\) is a consequence of a previously unreported cubiclike short range order in the amorphous \(\text{HfO}_x\) (cubic \(k \sim 30\)). The films also possess a high electrical resistivity of \(10^{14} \, \Omega \, \text{cm}\), a breakdown strength of \(3 \, \text{MV cm}^{-1}\), and an optical gap of \(6.0 \, \text{eV}\). Deposition at room temperature and a high deposition rate (\(~25 \, \text{nm min}^{-1}\)) makes these high-\(k\) amorphous \(\text{HfO}_x\) films highly advantageous for plastic electronics and high throughput manufacturing. © 2011 American Institute of Physics. [doi:10.1063/1.3601487]

Hafnium oxide (\(\text{HfO}_x\)) has received significant attention in recent years as a potential replacement for \(\text{SiO}_2\) as the gate dielectric material in complementary metal oxide semiconductor (CMOS) technology due to its high dielectric constant (high-\(k\)).\(^1\)–\(^6\) The use of a gate dielectric with an increased \(k\) allows a reduction in driving voltage of a transistor or an increase in dielectric film thickness while maintaining the same gate capacitance, thus suppressing the gate leakage current due to electron tunneling. There is also growing interest in using \(\text{HfO}_x\) as the gate dielectric for thin film transistors (TFTs) based on metal oxide channel materials such as \(\text{ZnO},\)\(^7\)–\(^10\) indium zinc oxide,\(^11\)–\(^12\) and indium gallium zinc oxide.\(^13\)–\(^15\) One of the key applications for such metal oxide TFTs is in the backplane for active matrix organic light emitting diodes (AMLCDs)\(^16\)–\(^20\) and also a high throughputs of plastic devices\(^21\).\(^22\)

In this work, this goal is achieved and \(\alpha\)-\(\text{HfO}_x\) has been deposited with a very high \(k\) of \(~30\). It is suggested that a previously unreported cubiclike short range order in the amorphous network enables such a high \(k\). The thin films of \(\alpha\)-\(\text{HfO}_x\) are deposited at room temperature from a metallic hafnium target using a high deposition rate, reactive sputter-deposition technique, called high target utilization sputtering (HiTUS).\(^23\) The HiTUS system (S500, Plasma Quest Ltd.) generates a remote, high-density, inductively coupled rf argon plasma in a sidearm, which is then amplified and directed onto a sputtering target. Sputter deposition is only achieved with the application of an additional target bias.\(^24\) This decouples the ion density (controlled by the rf antenna power supply) from the ion energy (controlled by the bias power supply) minimizing ion damage and providing finer control of the thin film microstructure compared to conventional magnetron sputtering. \(\text{HfO}_x\) films (50–300 nm thickness) were deposited onto n-type Si(100) wafers (\(\rho=0.015–0.025 \, \Omega \, \text{cm}\)) reactively without intentional substrate heating from a metallic hafnium target (99.95%, 4 in. diameter, 6 mm thickness, PI-KEM Ltd., 250 mm substrate-to-target distance) in an atmosphere (pressure 2 \times 10^{-3} \, \text{mbar}) of argon [55 SCCM (SCCM denotes cubic centimeter per minute at STP)] and oxygen gases (14–18 SCCM, both gases 99.999%, BOC Gases Ltd.). The argon is injected close to the target and the oxygen close to the substrate over a base pressure of 2 \times 10^{-5} \, \text{mbar}. The rf launch power is 1 kW and the dc bias power is 800–900 W.

Electrical parameters of the \(\alpha\)-\(\text{HfO}_x\) films were extracted from testing of metal–insulator–semiconductor (MIS) ca-
capacitor structures prepared by depositing HiTUS $a$-HfO$_x$ films on n-type silicon substrates and finished by the evaporation of chromium/aluminum metallic contacts. The capacitance-voltage ($C$-$V$) characteristics in Fig. 1(a) show very little hysteresis, and the fixed charge density and the flat band voltage is estimated to be $3.76 \times 10^{12}$ cm$^{-2}$ and 2.5 V, respectively. The average $k$ value of $a$-HfO$_x$ is 30 (as extracted from the accumulation region of the $C$-$V$ curve), which is notably higher than other $a$-HfO$_x$ reported previously, and is comparable to polycrystalline HfO$_x$ processed at higher temperatures. Figure 1(b) plots the leakage current density as a function of electric field for a typical $a$-HfO$_x$ film. A leakage current density in the range of 1–10 nA cm$^{-2}$ is observed for electric fields less than 1 MV cm$^{-1}$. The average electrical resistivity (at 1 MV cm$^{-1}$) is $10^{14}$ Ω cm, and the breakdown strength is in excess of 3 MV cm$^{-1}$. The $a$-HfO$_x$ is a wide band-gap material, with an optical gap of 6.04 eV extracted from its UV-visible transmission spectra.

The electrical resistivity, breakdown strength, and band gap of the $a$-HfO$_x$ is of the same order as for silicon nitride, and therefore passes these basic requirements for a TFT gate dielectric material. More importantly, the dielectric constant of the HiTUS $a$-HfO$_x$ ($k \sim 30$) is significantly higher than that for silicon nitride ($k \sim 7.5$) and standard rf magnetron sputter deposited HfO$_x$ ($k \sim 18$).

To understand the origin of the high $k$ in the HiTUS $a$-HfO$_x$, the microstructure of the films was studied by x-ray diffraction (XRD). The XRD scan of a typical as-deposited film in Fig. 2(a) shows only a broad/diffuse hump; this diffuse halo is commonly ascribed to an amorphous structure while that for silicon nitride ($k \sim 7.5$) and standard rf magnetron sputter deposited HfO$_x$ ($k \sim 18$).

To seek further insight into the structure, XRD scans were made of the $a$-HfO$_x$ films after vacuum annealing ($\sim 10^{-7}$ mbar) at up to $\sim 640$ °C for 35 min. A diffraction pattern corresponding to polycrystalline cubic HfO$_2$ emerges in the annealed films without appearance of any other phases [Fig. 2(b), crystallization from amorphous directly to cubic $\sim 550$ °C]. Amorphous to cubic transitions upon annealing are uncommon and usually accompanied by the evolution of other HfO$_x$ polymorphs as well. Hence, the observed crystallographic evolution in the HiTUS $a$-HfO$_x$ from an amorphous directly to an exclusively polycrystalline cubic phase suggests the presence of a cubic short range order in the as-deposited amorphous films. This cubiclike short range order (i.e., with Hf atoms eightfold and O atoms fourfold coordinated, as opposed to e.g., the monoclinic coordination of seven for Hf and either three or four for O) serves as nucleation sites for topotactic rearrangement of atoms to yield a polycrystalline cubic phase upon high temperature annealing. This is similar to topotactic crystallization previously found in ZrO$_2$—the material chemically and structurally most similar to HfO$_x$. The cubiclike coordination in the amorphous microstructure is also consistent with the measured high $k \sim 30$. A $k \sim 30$ is common for cubic HfO$_x$, but much higher than the suggested $k \sim 22$ for amorphous HfO$_x$ with monocliniclike atomic coordination.

A link between local atomic structure and dielectric properties was recently suggested in amorphous ZrO$_2$ films. Our results imply that the uniquely high $k \sim 30$ in our amorphous films is linked to a particular cubiclike local coordination. Radial distribution function determination will provide further insight into the suggested local structure but is beyond the scope of this present letter. Capacitance-voltage measurements performed on the films after annealing reveal that the polycrystalline cubic HfO$_2$ has an even higher dielectric constant than the amorphous precursor. Values of $k$ as high as 36 have been measured for these films, which is comparable with the highest $k$ values previously reported for any polycrystalline hafnium oxide films, including films that were impurity doped to maximize $k$.

The suggested cubiclike short range order in the HiTUS $a$-HfO$_x$ is analogous to the short range order in tetrahedral amorphous carbon ($ta$-C) or diamondlike carbon (DLC).
As in these materials, precise control of the ion energy and the plasma density is crucial for establishing this specific structure (or allotropy).\textsuperscript{32} Similar to \(ta-C\), formation of the high-\(k\) \(a\)-HfO\(_x\) is promoted by the deposition from medium energy ions (40–100 eV) in a highly ionized plasma \((10^{10}–10^{14} \text{ cm}^{-3})\) and at a high deposition rate \((>25 \text{ nm min}^{-1})\). These conditions can be satisfied by the HiTUS system.\textsuperscript{39} Since its remote plasma design allows independent control of sputtering plasma density and sputtering ion energy, the deposition conditions can be tuned to allow a sufficiently high ion flux to promote densification of the thin film (hence, local cubic coordination), but this is combined with sufficiently low ion energy to avoid crystallization and relaxation (leading to an amorphous structure). In analogy to the amorphous carbon materials, we henceforth refer to the HiTUS HfO\(_x\) as cubiclike amorphous HfO\(_x\) (ca-HfO\(_x\)).

It was previously reported that impurities in HfO\(_x\) can stabilize metastable polymorphs (e.g., Zr stabilizes monoclinic, \(Y\) cubic, and La \(a\)-HfO\(_x\)).\textsuperscript{39–41} Thus the composition of HiTUS deposited ca-HfO\(_x\) was closely examined to rule out such impurity effects. Depth resolved x-ray photoelectron spectroscopy (XPS), energy-dispersive x-ray spectroscopy (EDX), and Auger electron spectroscopy (AES) confirmed stoichiometric HfO\(_2\) \((1.2:1.4 \text{ for Hf:O from XPS})\) and did not show any elements other than Hf and O in the films. This sets the upper bound for contamination levels to the detection limit of these techniques \((<0.1–1 \text{ at. %})\), which is much lower than the impurity levels commonly required to stabilize nonequilibrium polymorphs.\textsuperscript{39–41} Thus the unique film properties are solely related to the HiTUS deposition.

In summary, this work demonstrates that amorphous hafnium oxide with a very high \(k\) of \(\sim 30\) exists, grown by the HiTUS system at room temperature and at high deposition rates \((>25 \text{ nm min}^{-1})\). The ca-HfO\(_x\) film displays good electronic-grade dielectric properties, as characterized by a high electrical resistivity of \(10^{14} \Omega \text{ cm}\), a high breakdown strength in excess of \(3 \text{ MV cm}^{-1}\), and a wide optical gap of 6.0 eV. XRD suggests that the very high \(k\) in the amorphous films is related to a local short range order dominated by cubiclike atomic coordination. Analogous to \(ta-C\) or DLC, this ca-HfO\(_x\) is formed under specific circumstances, which require a high plasma density to improve film density (thus inducing cubic coordination) but low-to-medium ion energy to avoid crystallization (thus ensuring an amorphous structure). The combination of a high dielectric constant and amorphous microstructure is itself of significance to both the large area electronics and CMOS industries. In addition, the low temperature deposition of ca-HfO\(_x\) is compatible with plastic substrates, and the high growth rate achieved by HiTUS makes this technique intrinsically more cost effective and scalable from a manufacturing perspective.

The authors acknowledge the support of this project provided by the Centre for Advanced Photonics and Electronics (CAPE) through the HiMo Project and the EPSRC through the Cambridge Integrated Knowledge Centre’s HiPZOT Project (Grant No. EP/E023614/1) and through the FIRE-BIRD project (TS/G001960/1). TEM measurements were performed by Dr. Simon Newcomb (Glebe Scientific Ltd., Newport, Eire).