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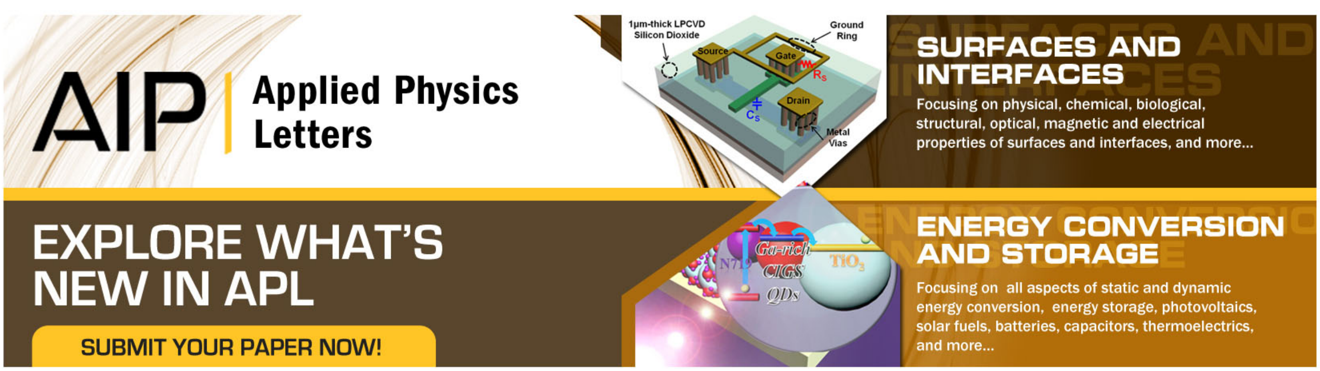

High-k (k=30) amorphous hafnium oxide films from high rate room temperature deposition

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Amorphous hafnium oxide (HfO_x) is deposited by sputtering while achieving a very high $k\sim30$. Structural characterization suggests that the high k is a consequence of a previously unreported cubiclike short range order in the amorphous HfO_x (cubic $k\sim30$). The films also possess a high electrical resistivity of 10^{14} Ω cm, a breakdown strength of 3 MV cm^{-1}, and an optical gap of 6.0 eV. Deposition at room temperature and a high deposition rate ($\sim$25 nm min^{-1}) makes these high-k amorphous HfO_x films highly advantageous for plastic electronics and high throughput manufacturing. © *2011 American Institute of Physics*. [doi:10.1063/1.3601487]

Hafnium oxide (HfO_x) has received significant attention in recent years as a potential replacement for 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 HfO_x as the gate dielectric for thin film transistors (TFTs) based on metal oxide channel materials such as 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 diode displays to which the high mobility and switching speed, but low cost of metal oxide TFTs, are well-suited.[16] This application will require a dielectric that is amorphous to allow the desired level of uniformity over a whole display area and also a high k to reduce the voltages required for operation.

Deposition of HfO_x which can potentially fulfill these requirements has been demonstrated with pulsed laser deposition, atomic layer deposition, and rf magnetron sputtering.[1] However, these approaches require deposition or annealing at elevated temperatures to attain good electrical characteristics while lower processing temperatures are desirable for compatibility with plastic substrates for flexible electronics.[17] The elevated temperatures also lead to polycrystalline films, which may consist of various crystalline phases, including monoclinic, cubic, tetragonal, and orthorhombic.[1–4] These different polymorphs of HfO_x however have very different k values: the monoclinic phase (which is the most stable under normal conditions) has the lowest k ($\sim$20), the cubic phase (which is metastable, but can exist indefinitely under normal conditions) has a higher k ($\sim$30) while the tetragonal phase has the highest k ($\sim$35 or higher).[18,19] Thus, polycrystalline HfO_x films can contain phases of different k values at local sites; such a multiphase nature can reduce the films' physical stability[1,20] and the presence of grains and grain boundaries can lead to instability and nonuniformity issues in devices. An amorphous gate dielectric material is therefore preferable for better device stability, reduced leakage currents, and improved device-to-device uniformity. However, it has been suggested that amorphous HfO_x is similar in local atomic coordination to the monoclinic polymorph and has a limited k of only $\sim$22.[21] A method of producing amorphous *and* high-k HfO_x, let alone at high deposition rates and at room temperature, has been elusive so far.[1]

In this work, this goal is achieved and a-HfO_x has been deposited with a very high k of $\sim$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 a-HfO_x are deposited at room temperature from a metallic hafnium target using a high deposition rate, reactive sputtering technique, called high target utilization sputtering (HiTUS).[22] 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.[22] 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. HfO_x films (50–300 nm thickness) were deposited onto n-type Si(100) wafers (ρ=0.015–0.025 Ω 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 2×10^{-3} 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 2×10^{-6} mbar. The rf launch power is 1 kW and the dc bias power is 800–900 W.

Electrical parameters of the a-HfO_x films were extracted from testing of metal–insulator–semiconductor (MIS) ca-

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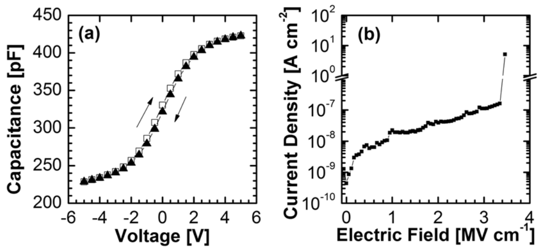

FIG. 1. (a) Capacitance-voltage characteristics and (b) leakage current density as a function of electric field for a HiTUS a-HfO_x thin film (thickness ~100 nm). Measurements were performed using an MIS (Cr–Al/a-HfO_x/n-Si) capacitor structure.

pacitor 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 3.76×10^{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,[23–27] and is comparable to polycrystalline HfO_x processed at higher temperatures.[28] 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,[29] and therefore passes these basic requirements for a TFT gate dielectric material. More importantly, the dielectric constant of the HiTUS a-HfO_x ($k\sim30$) is significantly higher than that for silicon nitride ($k\sim7.5$) and standard rf magnetron sputter deposited HfO_x ($k\sim18$).

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[30] which, by definition, refers to a solid with no long-range order, but with possible local short-range order over a distance of one to two bond lengths. The amorphous nature of the film is confirmed by the plan-view high resolution transmission electron microscope (TEM) image and diffuse electron diffraction pattern in Fig. 3.

To seek further insight into the structure, XRD scans were made of the a-HfO_x films after vacuum annealing ($\sim10^{-7}$ mbar) at up to ~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 ~550 °C]. Amorphous to cubic transitions upon annealing are uncommon and usually accompanied by the evolution of other HfO_x polymorphs as well.[31,32] 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

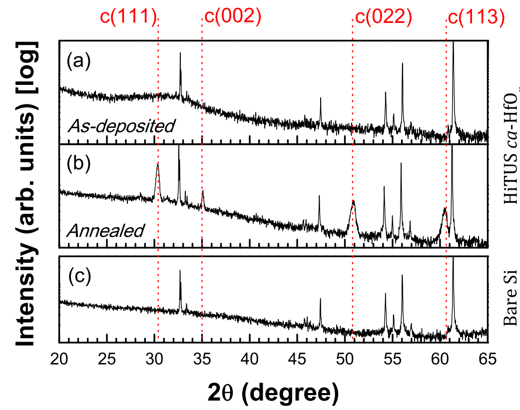

FIG. 2. (Color online) XRD scans of a typical (a) as-deposited and (b) vacuum annealed (640 °C) HiTUS a-HfO_x. The broad diffraction feature around $2\theta\sim32°$ in (a) is ascribed to amorphous HfO_x while (b) matches the diffraction pattern of polycrystalline cubic HfO_2 (ICDD-PDF file 53-0550). (c) shows an XRD scan of a bare Si wafer for reference highlighting substrate-related reflections.

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)[33] 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.[34,35] The cubiclike coordination in the amorphous microstructure is also consistent with the measured high $k\sim30$. A $k\sim30$ is common for cubic HfO_x,[18,19] but much higher than the suggested $k\sim22$ for amorphous HfO_x with monocliniclike atomic coordination.[21] A link between local atomic structure and dielectric properties was recently suggested in amorphous ZrO_2 films.[36] Our results imply that the uniquely high $k\sim30$ 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_x 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.[28]

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).

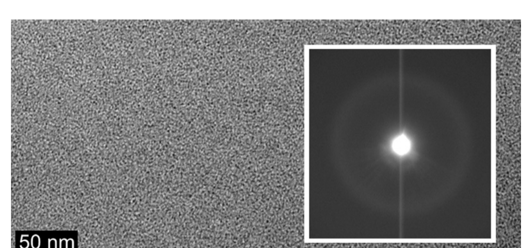

FIG. 3. A plan-view TEM image of a typical as-deposited HiTUS a-HfO_x demonstrating the amorphous nature of the a-HfO_x layer and the absence of nanocrystallites. An electron diffraction pattern is inset which shows diffuse halos, also consistent with the fully amorphous nature of the a-HfO_x layer.

As in these materials, precise control of the ion energy and the plasma density is crucial for establishing this specific structure (or allotropy).[37] 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 ($10^{10}-10^{14}$ cm^{-3}) and at a high deposition rate (>25 nm min^{-1}). These conditions can be satisfied by the HiTUS system.[38] 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).[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 (1:2.14 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 ($<0.1-1$ at. %), which is much lower than the impurity levels commonly required to stabilize nonequilibrium polymorphs.[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 ~ 30 exists, grown by the HiTUS system at room temperature and at high deposition rates (>25 nm min^{-1}). The *ca*-HfO_x film displays good electronic-grade dielectric properties, as characterized by a high electrical resistivity of 10^{14} Ω cm, a high breakdown strength in excess of 3 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.

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