1
2 **Science and Technology of Diamond Films Grown on HfO₂ Interface Layer for**
3 **Transformational Technologies**

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14 **Abstract**

15 This paper describes the science underlying the synthesis and characterization of
16 microcrystalline diamond (MCD) to ultrananocrystalline diamond (UNCD) films on hafnium
17 oxide (HfO₂) thin films, grown on flat Si substrates and micro-pillars on Si substrates, for the
18 first time. Using as a novel inter-phase layer for the integration of microcrystalline (1-3 μm
19 grain size), nanocrystalline (10-200 nm grain size), and ultrananocrystalline diamond (3-5 nm
20 grain size) as coatings on substrates used in transformational technologies such as silicon,
21 oxides, and metals that need protective corrosion/mechanical abrasion resistant coatings is
22 developed in this work. Atomic layer deposition was used to grow HfO₂ films with 5, 10, 30 and
23 100 nm in thickness, while hot filament chemical vapor deposition was used to grow diamond
24 films, respectively. High resolution transmission electron microscopy, X-ray photoelectron and
25 Raman spectroscopies revealed the formation of an atomic scale hafnium carbide (HfC)
26 interphase layer on the surface of the HfO₂ film, which provides efficient nucleation for
27 diamond film growth to produce tailored diamond surfaces on flat Si substrates and Si micro-
28 pillars on flat Si substrates, for new transformational micro/nano-electronics and other high-tech
29 technologies.

30 **Keywords:** Diamond, films, HfO₂ interface layers, electrical properties

1. Introduction

Microcrystalline diamond (MCD, $\sim \mu\text{m}$ range grain size) exhibits high thermal conductivity (see Fig. 7a in ref. 1) to provide efficient cooling for the new generation of micro- and nano-electronic devices.^[1] On the other hand, nanocrystalline diamond (NCD, 10 to hundreds of nanometer grain size) and ultrananocrystalline diamond (UNCD, 3-5 nm grain size) films exhibit a unique set of multifunctionalities and properties, namely: a) Young's Modulus and hardness equivalent to those of single crystal diamond; b) lowest coefficient of friction for NCD films with O-plasma treatment^[2] and for as grown UNCD films^[1] among known thin films of any materials; c) high electrical conductivity^[1] and extremely low threshold electric fields for electron field emission^[1, 3-6] with nitrogen incorporated in grain boundaries of the so named N-UNCD films^[1-6] or boron atoms substituting C atoms in the diamond lattice and providing electrons to the conduction band for both NCD and UNCD films identified as B-NCD and B-UNCD;^[5] d) outstanding mechanical properties^[1,2] and biocompatibility for both NCD and UNCD films.^[1, 7, 8] All the diamond films properties mentioned above enable applications to a new generation of mechanical devices (microelectromechanical and nanoelectromechanical systems (MEMS/NEMS)),^[1, 9-11] electronic devices,^[1, 6] chemical and electrochemical systems^[1, 12] and bio-medical devices,^[1, 7, 13] respectively.

The applications of MCD, NCD, and UNCD films described above require the growth of these films on different substrates, like semiconductors, metals, and oxides among others, such that the atoms and/or molecules involved in the growth of diamond films do not diffuse into the substrates producing deleterious effects (e.g., corrosion and/or degradation of semiconductor properties, induced brittleness in metals, and undesirable stoichiometric changes in oxides to mention some).

1 The growth of MCD diamond layers on semiconductor substrates, to enable heat
2 dissipation to cool down the next generation of micro- and nano-electronic devices, will benefit
3 greatly if the MCD layer can be grown on the main oxide (HfO_2) used as a gate layer in silicon
4 (Si)-based complementary metal-oxide-semiconductor (CMOS) devices. Alternatively, the
5 growth of UNCD films on HfO_2 may provide the capability for encapsulation of Si-based
6 microchips for implantation inside the human body, as for example UNCD-encapsulated Si-
7 microchip implanted inside the eye to restore partial vision to people blind by retinitis
8 pigmentosa.^[7] On the other hand, a template oxide layer could be used as a strong diffusion
9 barrier, during growth of corrosion/abrasion-resistant UNCD protective coatings on metals, in
10 order to prevent diffusion of atoms (e.g., H) and molecules (e.g., H_2) used in the growth
11 process, which would induce degradation of the chemical and mechanical properties of the
12 metal substrate (work in progress in our laboratory has already shown that a 30-50 nm scale
13 HfO_2 layer grown on the surface of stainless steel inhibit diffusion of hydrogen atoms into the
14 SS substrate, enabling growing UNCD coatings on SS without the latter becoming brittle
15 (Patent pending).

16 An oxide layer that fits very appropriately the properties described above, as an interface layer
17 to grow diamond films on silicon-based CMOS devices and metals such as stainless steel or
18 aluminum is Hafnium Oxide (HfO_2), which currently is the main dielectric layer used in Si-
19 CMOS devices replacing the SiO_2 layer that was going to be < 2 nm thick for the current
20 generation of nanoscale gate CMOS devices, inducing gate leakage current of about 1 A/cm^2 at
21 1 V, rendering CMOS devices non-operational.^[14] HfO_2 , with the higher dielectric constant K
22 (25) than SiO_2 (3.9) provided the solution to keep the FET gate capacitance, $C = \epsilon_0 K A / t$, at a
23 device operational value with a physically thicker gate oxide layer with lower leakage than the

equivalent oxide thickness of the extremely thin unusable SiO₂ layer.^[14]

In addition, the integration of UNCD films with CMOS devices is possible because of the low temperature (~ 400 °C – within the CMOS thermal budget) UNCD film growth process already demonstrated.^[1, 15]

2. Experimental Method

With respect to the scientific and technological information presented above, this paper describes the underlying science related to the demonstration of the growth of carbon based MCD to UNCD films on oxide-based HfO₂ interface layers, using the hot filament chemical vapor deposition (HFCVD) technique. The HfO₂ thin films were grown via atomic layer deposition (ALD), using Tetrakis (dimethylamido) hafnium (Hf(NMe₂)₄) as Hafnium precursor and H₂O as oxidation precursor. HfO₂ films of 5, 10, 30 and 100 nm, thicknesses were grown on silicon and silicon oxide (SiO₂)/Si substrates heated up to 100 °C, and using nitrogen purge of 20 seconds between each precursor pulsing. All substrates with the HfO₂ layers on the surface were subjected to a diamond seeding process via immersion of the substrate in a commercial (supplied by Nanodiamond Laboratory, NC, USA) solution of methanol with functionalized diamond particles (to avoid seed particles agglomeration to induce high density pinhole free diamond films), in an ultrasound generator, which immerse UNCD (3-5 nm) particles from the seeding solution on the substrate surface via sound waves induced vibration. Details of the seeding process can be found in the literature.^[1] Following the seeding process, the substrates were placed inside the HFCVD chamber on a rotating substrate holder to promote film uniformity.

The experimental conditions for growing MCD to UNCD involved several critical parts as described below. Knowing the temperature of the substrate surface during the diamond film

1 growth is critical. However, the substrate surface temperature cannot be measured during growth
2 due to growth process interference. Thus, the substrate surface temperature reading was
3 calibrated using a K-type thermocouple in direct contact with the substrate surface previous to
4 film growth, compared against the reading of a thermocouple inserted in the substrate holder,
5 which is the temperature read in the HFCVD system during film growth. A calibration curve
6 correlating the substrate and sample holder temperatures was plotted to enable the accurate
7 measurement of the substrate surface temperature during film growth.

8 An array of 9 parallel W filaments ($\phi = 0.25$ mm, length ~ 14.2 cm) held on a Molybdenum
9 (Mo) frame was positioned above the substrate holder at a distance of 3 cm. The substrates were
10 positioned on a Mo disk that was rotated during film growth to induce film thickness uniformity
11 on up to 100 mm diameter substrates. The filaments were heated to 2200°C by passing a DC
12 current during the film growth. The filament temperature was measured by a two color
13 pyrometer. The substrate temperatures were ~ 800 °C for MCD and NCD film growth and ~ 650
14 °C for UNCD film growth. The gases flows used to grow the diamond films were: i) for MCD
15 and NCD films- CH_4 (3 sccm)/ H_2 (200 sccm) during 8 hrs. and 4 hrs. respectively, and for
16 UNCD films- CH_4 (2 sccm)/ H_2 (10 sccm)/ Ar (90 sccm) during 1 hr., keeping the
17 total chamber pressure at 10 Torr. The details of the HFCVD process to grown MCD to UNCD
18 films can be found in a recent paper. ^[16]

19 The microstructure (grain morphology and size) and films thickness were characterized
20 using scanning electron microscopy (SEM, ZEISS SUPRA-40) and high-resolution transmission
21 electron microscopy (HRTEM, JEOL 2100F). The samples for the HRTEM analysis were
22 prepared via focused ion beam (FIB, FEI Nova 200) process. The crystallinity and grain sizes of
23 the MCD and UNCD films were investigated via X-ray diffraction (XRD, Rigaku Ultima III, Cu

$K\alpha$ radiation, 1.542 Å). The film's growth rate was determined from the thickness measurement via cross section SEM. Chemical bonding in the films were analyzed by visible and UV Raman spectroscopy, using a Thermo Nicolet Micro and Macro Almega XR Raman spectrometer with 532 nm wavelength laser beam and near resonance Raman scattering measurements using a Horiba-Jobin T64000 micro-Raman spectrometer with 244 nm wavelength laser beam, respectively. The crystal structures of the films were analyzed using selected area electron diffraction (SAED) in HRTEM, and the surface chemistry was characterized using X-ray photoelectron spectroscopy (XPS, ULVAC PHI 5000 Versa Probe II) analysis.

3. Results and Discussion

Figure 1 shows the nanostructure of a 140 nm thick UNCD film grown uniformly on a 10 nm thick HfO₂ thin film on a Si substrate (**Fig. 1(a)**). **Figure 1(b)** shows a HRTEM image of the UNCD film with grain sizes of about 3~5 nm, with the diamond crystal structure confirmed in the diffraction pattern of the inset. **Figure 1(c)** shows a HRTEM image of the HfO₂ layer including the HfO₂/SiO₂ and UNCD/HfO₂ interfaces. The HfO₂ layer, amorphous as grown by ALD, is crystallized during the film's growth as indicated in the upper left inset diffraction pattern, showing clear spots characteristic of the HfO₂ crystalline structure. The UNCD/HfO₂ interface exhibits a wrinkled structure, highlighted with the orange rectangle in **Fig. 1(c)**. The upper right inset in **Fig. 1(c)** shows the diffraction patterns of the UNCD/HfO₂ interface. A comparison of the diffraction patterns of pure UNCD (inset in **Figure 1(b)**) and the UNCD/HfO₂ interface (inset in **Fig. 1(c)**), reveals the appearance of extra peaks in the case of the interface, which indicates that there is a new phase at the interface. This new phase most probably originates during the **first stages in the growth** of the UNCD films, as explained in detail later in this paper. HRTEM-EELS elemental analysis profile, shown in **Fig. 1(d)** (scanning direction is

1 indicated as a white arrow in **Fig. 1(a)**), confirms the elemental profile through the whole
 2 SiO₂/HfO₂/UNCD heterostructure).

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4

5 **Figure 1.** (a) Low Magnification TEM image of the UNCD/HfO₂/SiO₂/Si heterostructure; (b)
 6 High Resolution TEM (HRTEM) image of UNCD (yellow square in (a)) - the image shows the
 7 characteristic 3~5 nm grain size of the UNCD film; (c) HRTEM image of the HfO₂ layer
 8 including the SiO₂/ HfO₂ and HfO₂/UNCD interfaces, with the latter exhibiting a wrinkled
 9 structure as highlighted with the orange rectangle (the top insets show the diffraction patterns
 10 of HfO₂ (left) and the UNCD/HfO₂ interface (right), including the wrinkled structure that

corresponds to HfC (see XPS analysis in Fig.2B(a)); (d) TEM-EELS elemental profile of the UNCD/HfO₂/SiO₂ heterostructure. The scanning direction is indicated as a white arrow in (a).

Figure 2 A(a) shows visible Raman spectra from UNCD films grown on HfO₂ layers (with various thicknesses from 5 nm to 100 nm) grown by ALD on SiO₂ substrates. The Raman spectra were obtained with a visible 532 nm laser beam wavelength. The spectra show characteristic D band (1341.7 cm⁻¹) and G band (1588.5 cm⁻¹) peaks from the sp² C-atoms bond hybridization. Although the thickness of the HfO₂ layer changed from 5 nm to 100 nm, the Raman spectra showed identical peaks for all UNCD films, as shown in **Figure 2A(a)**. Deconvolution of the Raman peaks of the UNCD film grown on the 100 nm thick HfO₂ layer is shown in **Figure 2A(a)** as a representative characterization of all UNCD films. **Fig. 2A(a)** shows that there is a contribution of three extra peaks, green (at 1489.2 cm⁻¹), violet (at 1258.3 cm⁻¹) and yellow (at 1164.3 cm⁻¹), to the D and G peaks, reported as representative of C=C stretching of Trans-PolyAcetillene (T-PA), broadened vibrational density of states (VDOS) of small diamond clusters, and tetrahedral amorphous carbon, and T-PA C-H bending combined with C-C stretching, respectively. [17-20] The literature [1, 11, 17-20] shows that the diamond peak (1332 cm⁻¹) in UNCD films is always masked by the D mode peak of disordered carbon because visible Raman scattering from carbon is mainly sensible to the dominating sp² bonds in the large network of UNCD grain boundaries, and much less to the sp³ carbon bonds of diamond. In **Figure 2A(b)**, however, UV excitation produced by a 244 nm (5.1 eV) wavelength laser beam provides sufficient energy to excite the σ states of both sp² and sp³ C bonds, allowing a direct observation of the sp³ C bonds of diamond, [21, 22] and confirming the diamond phase revealed by a well defined 1332 cm⁻¹ peak from a single crystal diamond (black curve), a NCD film (blue curve) with 10-100s nm grain size, and although small, and even a UNCD film (red curve) (**Fig. 2A(b)**). From a comparison of Figs. 2A(a) and 2A(b), the UV Raman (244 nm) spectra for

1 UNCD films are quite different from visible Raman (532 nm) spectra. When a small H₂
2 concentration is used to grow UNCD films by HFCVD the resulting 3-5 nm grain size induce a
3 large band gap, possible due to quantum confinement. However, the disappearance of the 1150
4 and 1458 cm⁻¹ peaks, shown in the visible (532 nm) Raman spectra, for the UV (244 nm) spectra,
5 as in **Fig. 2A(b)**, indicate that those peaks are not the consequence of phonon confinement. This
6 is due to the fact that if these peaks were zone boundary phonons, then they should be present in
7 UV excitation as well.^[22] On the other hand, the visible Raman spectrum shows that the intensity
8 of a broad peak from the graphite D band (1340-1350 cm⁻¹) is inversely proportional to the
9 crystal size as indicated in Fig. 2A (a), although the appearance of this feature was attributed to
10 the breakdown of the q=0 selection rule. Ferrari and Robertson^[23] developed a Raman
11 interpretation model for these systems, which indicates that for nanocrystalline diamond, the
12 characteristic Raman diamond peak at 1332 cm⁻¹ is strongly reduced in intensity, and the D- and
13 G-band features dominate the visible Raman spectra.

14 In order to understand the growth of UNCD films on HfO₂, the activation energy for the
15 growth of UNCD films on HfO₂ layer was obtained from the Arrhenius plot (growth rate (*k*) vs.
16 1/T) as shown in **Fig. 2A(c)**. Fitting of the experimental points in the Arrhenius curve of **Fig.**
17 **2A(c)**. yields an activation energy of about ~ 18.4 kcal/mole (i.e. 77 kJ/mole) for the growth of
18 UNCD films on HfO₂. Reports of measurements of diamond film growth vs. substrate
19 temperature showed that low activation energies from 5.7 kcal/mol to 28 kcal/mole^[24, 25] are
20 most appropriate to grow high quality diamond films, and those results support the observation of
21 the high quality UNCD films grown on HfO₂ as reported in this paper, which shows an activation
22 energy for UNCD growth in the optimum range.

Figure 2. A: a) Raman spectra of UNCD films grown on HfO₂ layers, obtained with a 532 nm wavelength visible laser beam, showing characteristic D band (1341.7 cm⁻¹) and G band (1588.5 cm⁻¹) peaks; this figure includes a deconvolution of the Raman spectrum of the UNCD film grown on the 100 nm thick HfO₂ layer, showing the contribution of three peaks [green (1489.2 cm⁻¹), violet (1258.3 cm⁻¹) and yellow (1164.3 cm⁻¹) corresponding to the G band (1588.5 cm⁻¹) and D band (1341.7 cm⁻¹) peaks; (b) Raman spectra of a UNCD film grown on a HfO₂ layer, obtained with a 244 nm wavelength UV laser beam), showing a very small but visible 1332 cm⁻¹ peak characteristic of diamond, which is exactly at the position where the strong 1332 cm⁻¹ diamond peak of crystalline diamond appears; c) Arrhenius plot (growth rate (*k*) vs 1/*T*) for UNCD films grown on HfO₂ layers at different temperatures - fitting of the

1 experimental data points provides the activation energy for growth of UNCD films at ~ 18.4
2 kcal/mole, which is within the range of activation energies that yield high quality diamond
3 films. **B:** XPS spectra from UNCD films grown on HfO₂ layers for 5 min (a), 10 min. (b), and
4 15 min. (c). The spectra for the C1s and Hf4f peaks reveal the presence of peaks at ~ 284.5 eV
5 and ~ 14.7 eV, respectively, which confirm the formation of a HfC interface layer that induce
6 nucleation of diamond films.

7
8 XPS analysis was performed on the surface of the HfO₂ layer at the initial UNCD film
9 growth stage. The appearance of the C1s, Hf4f and O1s XPS peaks provided key information,
10 which, together with the HRTEM data, indicate that the UNCD films nucleate on HfO₂ due to the
11 formation of a nm thick HfC interface layer at the very initial growth stage. The first row of data
12 in **Fig. 2B (a)**, shows the XPS spectrums of C1s, Hf4f and O1s from the UNCD film grown for 5
13 min. **Figures 2B(b) and 2B(c)** show similar XPS data for UNCD films grown for 10 min. and 15
14 min., respectively. For UNCD films grown for 5 and 10 min., the Hf4f and O1s peaks dominate
15 the XPS spectra. However, a small but noticeable carbon (C1s) appears at the binding energy of $\sim$
16 281.8 eV, which correlates, within experimental error with the 284.5 eV C1s peak of HfC. [^{26, 27}]
17 The C1s peak of HfC does not appear in the spectrum of the UNCD film grown for 15 min,
18 which is due to the thickness of the UNCD film that covers completely the HfO₂ layer.
19 Confirmation of the formation of the HfC layer is provided by the appearance of, a shoulder peak
20 at ~ 14.7 eV binding energy in the Hf4f spectra shown in Figs. 2B(a) and 2B(b), which correlates
21 with the formation of HfC. [^{26, 27}] Prior research demonstrated that diamond films grow very well
22 on carbide forming substrates such as silicon (Si), [¹] tungsten (W), [^{1, 28}] and titanium (Ti) [¹] to
23 name a few. In general, the carbide layer contributes to the nucleation and subsequent growth of
24 diamond films grown by various CVD techniques. [^{1, 28-30}] In this respect, Auciello's group
25 demonstrated that a W layer grown on several substrates induces the growth of the densest

1 UNCD films, ^[1, 28] helped by the high thermal stability and thermal expansion coefficient of the
2 WC layer which is closely matched to diamond films grown by the MPCVD process. The
3 demonstration that UNCD films can be grown on HfO₂ adds to the prior work that demonstrated
4 that UNCD films are also grown on other oxides substrates. ^[1] The other oxides on which MCD,
5 NCD, and UNCD films were grown for the research described in this paper were tungsten oxide
6 (WO_x), silicon oxide (SiO₂) and titanium-aluminum oxide (TAO) nanolaminates. The results
7 shown in this paper reveal that UNCD films grown on HfO₂ layers exhibit higher density than the
8 UNCD films grown on the other oxides mentioned above, **Figure 3** shows SEM top view images
9 of UNCD film grown on a silicon wafer with a SiO₂ layer on the surface (Fig. 3a). As seen in that
10 figure, the UNCD films is porous, due to the fact that the SiO₂ attenuates the silicon carbide
11 formation, which promotes the UNCD growth (H₂ thermal annealing is needed to reduce the
12 porosity of UNCD films grown on SiO₂). ^[31] **Fig. 3b** shows a UNCD film grown on a
13 silicon wafer covered with a tungsten oxide (WO_x) layer on the surface. As it can be seen in that
14 figure, the UNCD layer is uniform, but during adhesion test the film was removed easily. In the
15 case of UNCD film grown on a TAO layer (**Fig. 3c**), the parts of the oxide layer were
16 delaminated during the diamond deposition process. Figs **3d, 3e and 3f** show UNCD films grown
17 on silicon wafers with HfO₂ layers on the surface. As it can be seen in all figures, UNCD, NCD
18 and MCD films are uniform and pinhole free, all of them exhibit excellent adhesion as
19 demonstrated by adhesion tests. **Figure 4** shows cross section SEM images of all diamond films
20 which top views are shown in Fig. 3. It is relevant to notice that the UNCD, NCD and MCD
21 films grown on the HfO₂ layers have excellent structure and interface with the HfO₂ layers.

Figure 3. SEM top view for different diamond films on Si substrates with different oxides layers on the surface. (a) UNCD film on SiO₂ surface layer, (b) UNCD film on WO_x surface layer, (c) UNCD film on TiAlO_x (TAO) layer on Si; (d), (e), and (f) show UNCD, NCD, and MCD films' surface morphology, respectively, grown on HfO₂ surface layers. Notice the fully dense coverage of the UNCD film on the HfO₂ layer, as opposed to on the surface of the other oxides.

Figure 4. SEM cross section for different diamond films on Si substrates with different oxides layers on the surface. (a) UNCD (160 nm thick) film on SiO₂ (400 nm thick) surface layer, (b) UNCD (200 nm thick) film on WO_x (90 nm thick) surface layer, (c) UNCD film (~200 nm thick) on a TiAlO_x (TAO) layer (~170 nm thick); (d), (e) and (f) show UNCD (145 nm thick), NCD (420 nm thick), and MCD (1.8 μm thick) films, grown on 100, 30 and 30 nm HfO₂ layers on Si substrates, respectively.

A great advantage of using the HfO₂ layer as a template layer to grow polycrystalline diamond films on top is that the HfO₂ film can be grown with extreme conformality on 3-D geometries with high aspect ratio surface topography, providing a platform for growing also extremely conformal UNCD film. As an example, **Figure 5 (a) to (e)** show SEM images of UNCD films grown very conformally on the vertical walls of 3-D cylindrical structures fabricated on Si substrate by photolithography and reactive ion etching (RIE). The UNCD films were grown on a 20 nm thick HfO₂ layer grown by ALD.

Figure 5. (a, b, c) Low magnification SEM image of UNCD film grown on 3-D Si pillar array of pillars with 10 μm diameter, 5 μm high, and 10 μm spacing among them. Higher resolution cross sectional SEM images of (d) top part of a Si pillar, and (e) bottom corner of the same Si pillar, shown in the lower resolution SEM images in (a), (b), and (c).

An initial demonstration of the technological applications of diamond films grown on HfO_2 template layer is provided by the measurement of the intrinsic electrical properties of a UNCD film grown on a HfO_2 layer on a Si substrate. Hall measurements were performed using a LakeShore 8400 series instrument and employing the Van der Pauw method applying a magnetic field (1.7 Tesla) and electrical current in different directions and magnitude with an amplified AC mounted signal in order to remove noise and increase the accuracy of the measurement. Results

shown in **Table 1**, reveal p-type behavior on the surface conductivity of the polycrystalline films grown on the HfO₂ layer. The type of carriers were determined by the hall voltage through all the contact configuration measurements with the electrical current and magnetic field positive and negative, respectively. All samples consisted of HfO₂ films with different thicknesses and the same area (1 cm²), grown on Si substrates. The structures for Hall measurements were triangular with gold (200 nm thick) triangle contact layers on the corners (see Fig. attached to Table 1. These measurements were focused on sheet resistance only, since it is very well known that electrical conductivity through diamond films is controlled extensively by the grain boundaries [32, 33], due to dangling bonds, and over the surface by quantum states of holes accumulated on the 2D surface layer formed on the hydrogenated air-exposed top-surface region of diamond. [34, 35] Hall measurements show a mobility increase as a function of grain size increase from UNCD to MCD, and a reduction in carrier concentration from UNCD to MCD. Further research is underway to determine what combined carrier mobility/concentration is more appropriate for the performance of these diamond films as semiconductors, working simultaneously as active layer and heat sink for TFTs devices. [36]

	UNCD	NCD	MCD
Hall mobility [cm ² /V·s]	2.54	36.59	210.66
Carrier type	P	P	P
Sheet carrier concentration [1/cm ²]	2.91E16	5.56E13	6.55E13
Sheet Hall coefficient [cm ² /C]	214.3931	13.47	95301.51
Sheet resistivity [Ω/□]	84.38	3067.95	452.4
Hall voltage [V]	0.000375	0.000103	0.1667

Table 1. Hall measurement results from UNCD, NCD and MCD films grown on top of HfO₂ surface layer on Si substrates. Side Figure: Schematic of Hall measurement approach.

On the other hand, one of the challenges is to produce high resistivity diamond films with high dielectric level to be able to encapsulate electronic devices and avoid electrical shortcuts between contacts or to encapsulate complete Si-based microchips with a corrosion resistant coatings for use of microchips in harsh environments. In this respect, Prior R&D performed by Auciello's group, demonstrated that Si microchips can be encapsulated by insulating/corrosion resistant UNCD films to enable implantation of the Si chip inside the eye,^[7] as the main component of an artificial retina (microchip), implantable inside the eye to receive images from an external CCD camera and process it to inject electrical uses into the brain, through the optical nerve, to restore partial vision to people blind by genetically-induced degeneration of the retina photoreceptors. UNCD-encapsulated Si microchips were implanted for up to two to three years in rabbit's eyes, performing exceptionally well^[7] as insulating/extremely corrosion resistant encapsulating coating to enable Si-based microchip implantation inside eyes, which without the UNCD coating is destroyed by chemical corrosion induced by the eye saline.^[7] In addition, UNCD films were grown, as dielectric layers with fast charging/discharging (microsecond range) behavior, on top of bottom electrodes of RF MEMS switches controlled by integrated CMOS devices for operating phase array antennas for radars and mobile communication devices.^[37, 38] The insulating UNCD dielectric films eliminated the failure of the conventional RF MEMS switches observed when using SiO₂ or Si₃N₄ dielectric films on the bottom electrodes, which exhibited fast charging (microseconds) but very slow discharging (100s microseconds) leading to the switch getting stacked in the close position. The reason UNCD films were used in both applications described above, as an insulating protective layer, is because UNCD films grown

1 using the patented Ar(99%)/CH₄(1%) gas mixture^[1, 39] can be grown at 350-400 °C, within the
2 thermal budget of Si-based CMOS devices, while the MCD films grown with the conventional
3 H(99%)/CH₄(1%) cannot be grown at such a low temperature, thus resulting in the destruction of
4 the Si-based CMOS devices.

5 The demonstration that diamond films can be grown on HfO₂ layers, can make a positive
6 impact in the applications of diamond films described above, and they will be investigated.

7 **4. Conclusions**

8 In conclusion, it has been demonstrated that UNCD, NCD and MCD film can be grown on
9 an HfO₂ template layer. The demonstration of the feasibility of growing polycrystalline diamond
10 films on HfO₂ template layer may open the pathway for integration of diamond films on Si-based
11 micro- and nano-electronic devices, since HfO₂ is widely used in the microelectronic industry as
12 the main gate dielectric layer in the new generation of CMOS devices. The formation of a nm
13 thick HfC interface layer on the surface of the HfO₂ film appears to be a key step in the
14 nucleation and growth of diamond films on a HfO₂ layer, as demonstrated by the work described
15 in this paper. The HfO₂ layer grown by ALD provides an **outstanding** process to grow UNCD
16 films with extreme conformality on 3-D structures, opening the pathway to new micro and
17 nanodevices using the electrical conductivity demonstrated for N-UNCD films with nitrogen
18 incorporation into grain boundaries or boron doping in the grains (B-UNCD). On the other hand,
19 the demonstration of high thermal conductivity MCD film growth on HfO₂ layer, which is the
20 main dielectric layer in the new generation of CMOS devices, may provide the pathway for using
21 MCD films as heat dissipation layers for those devices, since MCD exhibits the highest thermal
22 transport in both the perpendicular and parallel directions to the surface, after single crystal
23 diamond, which can not be grown on large areas (up to 300 mm in diameter) Si wafers currently

1 used for manufacturing integrated circuits. Based on the information presented in this paper, the
2 integration of diamond films on HfO₂ template layers may provide the bases for transformational
3 technologies involving the integration of oxide and diamond films.

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References

- [1] O. Auciello and A.V. Sumant, *Diam. and Related Mater.*, **2010**, 19(7–9), 699.
- [2] R. Radhika, N Kumar, K J Sankaran, R. Dumpala, S Dash, M S Ramachandra Rao, D Arivuoli, A K Tyagi, N H Tai and I-Nan Lin, *J. of Phys. D: Appl. Phys.*, **2013**, 46(42), 425304.
- [3] Y.C. Lin, K.J. Sankaran, Y.C. Chen, C.Y. Lee, H.C. Chen, I.N. Lin, N.H. Tai, *Diam. and Related Mater.*, **2011**, 20(2), 191.
- [4] F.A.M. Koeck and R.J. Nemanich, *Diam. and Related Mater.*, **2009**, 18(2–3), 232.
- [5] P.M. Koinkar, S.S. Pati, T-G. Kim, D. Yonekura, M.A. More, D.S. Joag, R-ichi Murakami, *Appl. Surf. Sci.*, **2011**, 257(6), 1854.
- [6] R.N. Arenal, Ch. 4, in *Ultananocrystalline Diamond (Second Edition)*, O.A.S.M. Gruen (Editor) (William Andrew Publishing: Oxford, **2012**, p. 103.
- [7] X. Xiao, J. Wang, J. A. Carlisle, B. Mech, R. Greenberg, R. Freda, M. S. Humayun, J. Weiland, and O. Auciello, *J. Biomedical Materials*, **2006**, 77B (2), 273.
- [8] P. Bajaj, D. Akin, A. Gupta, D. Sherman, B. Shi, O. Auciello, R. Bashir, *Biomedical Microdevices*, **2007**, 9 (6), 787.
- [9] A.R. Krauss, O. Auciello, D.M. Gruen, A. Jayatissa, A. Sumant, J. Tucek, D. Mancini, N. Moldovan, A. Erdemir, D. Ersoy, M.N. Gardos, H.G. Busmann, E.M. Meyer, M.Q. Ding, *Diam. and Related Mater.*, **2001**, 10(11), 1952.
- [10] V.P. Adiga, A. V. Sumant, S. Suresh, C. Gudeman, O. Auciello, J. A. Carlisle, R. W. Carpick, *Phys. Rev. B*, **2009**, 79(24), 245403.
- [11] A.V. Sumant, O. Auciello, R. W. Carpick, S. Srinivasan, and J. E. Butler, *MRS Bulletin*, **2010**, 35(04), 281.
- [12] S. Wang, V.M. Swope, J.E. Buttler, T. Feygelson, and G.M. Swain, *Diam and Related Mater.*, **2009**, 18(4), 669.

- 1 [13] O. Auciello, P. Gurman, M. B. Guglielmotti, D.G. Olmedo, A. Berra and M. J. Saravia,
2 MRS Bulletin, **2014**, 39 (07), 621.
- 3 [14] J. Robertson, Eur. Phys., J. Appl. Phys. **2004**, 28, 265.
- 4 [15] X. Xiao, J. Birrell, J.E. Gerbi, O. Auciello and J.A. Carlisle, *J. of Appl. Phys.*, **2004**, 96(4),
5 2232.
- 6 [16] E.M.A. Fuentes-Fernandez, J. J. Alcantar-Peña, G. Lee, A. Boulom, H. Phan, B. Smith,
7 T. Nguyen, S. Sahoo, F. Ruiz-Zepeda, M. J. Arellano-Jimenez, C.A. Martinez-Perez,
8 M. J. Yacaman, R.S. Katiyar, O. Auciello, Thin Solid Films **2016**, 603, 62.
- 9 [17] V.I. Merkulov, J.S. Lanni, C.H. Munro, S.A. Asher, V.S. Veerasamy, and W.I. Milne,
10 *Phys. Rev. Lett.*, **1997**, 78(25), 4869.
- 11 [18] J. Robertson and E.P. O'Reilly, *Phys. Rev. B*, **1987**, 35(6), 2946.
- 12 [19] F. Klauser, D. Steinmüller-Nethl, R. Kaindl, E. Bertel, and N. Memmel, *Chem. Vapor*
13 *Deposit.*, **2010**, 16(4-6), 127.
- 14 [20] A.C. Ferrari and J. Robertson, *Phys. Rev. B*, **2000**, 61(20), 14095.
- 15 [21] S. Praver and R.J. Nemanich, *Philosophical Transactions of the Royal Society of London.*
16 *Series A: Mathematical, Physical and Engineering Sciences*, **2004**, 362(1824), 2537.
- 17 [22] A.C. Ferrari and J. Robertson, *Philosophical Transactions of the Royal Society of*
18 *London. Series A: Mathematical, Physical and Engineering Sciences*, **2004**, 362(1824),
19 2477.
- 20 [23] A.C. Ferrari and J. Robertson, *Phys. Rev. B*, **2001**, 63(12), 121405.
- 21 [24] D.C. Barbosa, F.A. Almeida, R.F. Silva, N.G. Ferreira, V.J. Trava-Airoldi, and
22 E.J. Corat *Diam. and Related Mater.*, **2009**, 18(10), 1283.
- 23 [25] D.C. Barbosa, L.L. Melo, V.J. Trava-Airoldi, and E.J. Corat, *J. Nanosci. Nanotech.*,
24 **2009**, 9(6), 3944.
- 25 [26] P. Špatenka, H. Shur, G. Erker, and M. Rump, *Appl. Phys. A*, **1995**, 60(3) 285.
- 26
27
28
29

- [27] L. Ramqvist, K. Hamrin, G. Johansson, A. Fahlman, and C. Nordling, *J. of Phys. and Chem. of Solids*, **1969**, 30(7), 1835.
- [28] N.N. Naguib, J. W. Elam, J. Birrell, J. Wang, D. S. Grierson, B. Kabius, J. M. Hiller, A. V. Sumant, R. W. Carpick, O. Auciello, J. A. Carlisle, *Chem. Phys. Lett.*, **2006**, 430(4–6), 345.
- [29] A. Hirata, H. Zheng, and M. Yoshikawa, *Diam. and Related Mater.*, **1998**, 7(11–12), 1669.
- [30] P.W. May, K.N. Rosser, N.A. Fox, C.M. Younes, and G. Beardmore, *Diam. and Related Mater.*, **1997**, 6(2–4), 450.
- [31] W. S. Lee, H. J. Lee, Y. J. Baik and J. K. Park, *U.S. Patent 2013/0260157*, issued Mar. 13, 2013.
- [32] L. Wang, Q. Zeng, J. Huang, R. Xu, K. Tang, J. Zhang, Y. Xia, *Thin Solid Films*, **520**(2) (2011) 717.
- [33] L. Gan, A. Bolker, C. Saguy, R. Kalish, D.L. Tan, B.K. Tay, D. M. Gruen, P. Bruno, *Diamond and Related Materials*, **18**(9) (2009) 1118.
- [34] L. Gan, E. Baskin, C. Saguy, and R. Kalish, *Phys. Rev. Lett.*, **96**(19) (2006) 196808.
- [35] C.E. Nebel, B. Rezek, and A. Zrenner, *Diamond and Related Materials*, **13**(11–12) (2004) 2031.
- [36] H. Kozak, A. Kromka, O. Babchenko, and B. Rezek, *Sensor Letters*, 2010. **8**(3): p. 482-487.
- [37] O. Auciello, A. V. Sumant, C. Goldsmith, S. O’Brien, S. Sampath, C. Gudeman, W. Wang, J. C. M. Hwang, J. Swonger, J. A. Carlisle, S. Balachandran, D. C. Mancini, *Micro-and nanotechnology Sensors, Systems, and Applications-II*, edited by Thomas George, Saif Islam, Achyut Dutta, *Proc. SPIE*. 7679, (2010) 76791K-1.

- 1 [38] O. Auciello, S. Pacheco, A.V. Sumant, C. Gudeman, S. Sampath, A. Datta, R.W. Carpick,
2 V.P. Adiga, P. Zurcher, Z. Ma, H.C. Yuan, J.A. Carlisle, B. Kabius, J. Hiller. *Are*
3 *Diamonds a MEMS Best Friend?*, IEEE Microwave Magazine, vol. 8, (2008) 61-75.
4
5 [39] N. Naguib, J. Birrell, J. Elam, J.A. Carlisle, O. Auciello, “A Method to Grow Carbon Thin
6 Films Consisting Entirely of Diamond Grains 3-5 nm in Size and High-Energy Grain
7 Boundaries”, US Patent #7,128,889, October 31, 2006.

Science and Technology of Diamond Films Grown on HfO_2 Interface Layer for Transformational Technologies

LMTEM of UNCD film on $\text{HfO}_2/\text{SiO}_2/\text{Si}$

HRTEM of UNCD film

TEM-EELS elemental profile of UNCD/ $\text{HfO}_2/\text{SiO}_2$ heterostructure

HRTEM of UNCD film on $\text{HfO}_2/\text{SiO}_2/\text{Si}$