Dielectric Properties of Ultrathin CaF₂ Ionic Crystals

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Mechanically exfoliated 2D hexagonal boron nitride (h-BN) is currently the preferred dielectric material to interact with graphene and 2D transition metal dichalcogenides in nanoelectronic devices, as they form a clean van der Waals interface. However, h-BN has a low dielectric constant (~3.9), which in ultrascaled devices results in high leakage current and premature dielectric breakdown. Furthermore, the synthesis of h-BN using scalable methods, such as chemical vapor deposition, requires very high temperatures (>900 °C), and the resulting h-BN stacks contain abundant few-atoms-wide amorphous regions that decrease its homogeneity and dielectric strength. Here it is shown that ultrathin calcium fluoride (CaF₂) ionic crystals could be an excellent solution to mitigate these problems. By applying >3000 ramped voltage stresses and several current maps at different locations of the samples via conductive atomic force microscopy, it is statistically demonstrated that ultrathin CaF₂ shows much better dielectric performance (i.e., homogeneity, leakage current, and dielectric strength) than SiO₂, TiO₂, and h-BN. The main reason behind this behavior is that the cubic crystalline structure of CaF₂ is continuous and free of defects over large regions, which prevents the formation of electrically weak spots.

The integration of 2D materials in solid-state electronic devices and circuits may allow developing advanced applications with superior performance. However, the interaction of 2D materials like graphene and 2D transition-metal dichalcogenides (TMDs) with adjacent 3D dielectrics in electronic devices (normally SiO₂ or metal oxides) has been shown to be very problematic, as the 2D/3D interface usually contains a large number of defective bonds.[3] This promotes uncontrollable charge trapping and de-trapping, which creates unwanted deviations of several parameters of the devices (i.e., hysteresis and threshold voltage in transistors), and results in a faster device degradation.[2] To solve this problem, one common strategy is to use multilayer hexagonal boron nitride (h-BN) as substrate and/or dielectric.[3,4] However, so far h-BN dielectrics only work reliably when synthesized by (non-scalable) mechanical exfoliation, which results in a considerably lower amount of defects.[4] When the h-BN is synthesized using scalable methods, such as chemical vapor deposition (CVD), it contains abundant lattice distortions that propagate vertically from one layer to another, leading to few-atoms-wide amorphous regions with weaker dielectric strength (see Figure S1, Supporting Information).[5,6] When integrated as dielectric in a device, the presence of these defective regions decreases the homogeneity of the leakage current (see Figure S2a, Supporting Information), and reduces the lifetime of the device due to the stochastic nature of the dielectric breakdown (DB) process.[7] Moreover, the dielectric constant of h-BN is only ~3.9, which in ultra-scaled devices results in high leakage current and premature DB.[8,9] Furthermore, the synthesis of high-quality layered h-BN by CVD requires high temperatures >900 °C,[10,11] which impedes its direct growth on patterned wafers. Consequently, finding insulating materials with a high dielectric constant that are compatible with graphene and other 2D materials is of paramount importance for the construction of advanced solid-state 2D materials based electronic devices and circuits.

CaF₂ is a dielectric material with a band gap of ~12.1 eV and a dielectric constant of ~8.4 that can be grown on a large-scale at low temperatures (~250 °C) using molecular beam epitaxy (MBE).[12] Thick (>100 nm) stacks of CaF₂ have been used for more than 30 years in optoelectronics to fabricate windows, lenses, and lasers (among others) due to their excellent chemical stability when exposed to moisture and high relative humidities.[13] A recent report has demonstrated the use of ultra-thin (~2 nm) CaF₂ (III) films as gate dielectric in field-effect transistors (FETs) with bilayer molybdenum disulfide (MoS₂) channels, and presented high on/off current ratios up to 10⁷ and small hysteresis.[14] As the surface of the CaF₂ (III) film is terminated with inert fluorine atoms, this material does not present dangling bonds and it can form a van der Waals...
interface with adjacent 2D layered materials, making it one of the most promising dielectrics for future 2D materials based electronic devices and circuits. However, the density and type of defects in ultrathin CaF$_2$ films, as well as their effect on the dielectric performance of this material have never been analyzed in depth. In this investigation, we use characterization tools with sub-nanometer resolution to analyze the crystallographic structure, types of defects, and electrical properties of ultrathin CaF$_2$ films, and demonstrate that this material exhibits very high homogeneity, ultralow leakage current, and high dielectric strength. These observations are related to the absence of amorphous defective paths across the ultrathin CaF$_2$ film, as its cubic crystalline structure is continuous over long areas, something that so far has never been achieved in 2D layered dielectrics like multilayer h-BN.

High-quality ultrathin CaF$_2$ films were grown on a Si (111) surface by MBE at 250 $^\circ$C (see Experimental Section). We collected >56 consecutive cross-sectional high-resolution transmission electron microscopy (TEM) images with sub-nanometer resolution, and at some locations also conducted energy-dispersive X-ray spectroscopy (EDX) as well as electron energy loss spectroscopy (EELS) to analyze the local chemical composition (see Experimental Section). As Figure 1 shows, the cubic crystalline structure of the CaF$_2$ film follows different patterns in the TEM images, including 2D layered pattern with an interlayer distance of $\approx 0.32$ nm (Figure 1d), hexagonal pattern (Figure 1e), cubic pattern (Figure 1f), and point-like pattern (Figure 1g). This observation is related to the angle of the different orientations of the cubic CaF$_2$ crystal with respect to the electron beam of the TEM (see Figure S3, Supporting Information). More importantly, these patterns merge into one another very smoothly and without any visible defect (see Figure 1a–c and Figure S4, Supporting Information). This observation is fundamentally different to what has been often reported for CVD grown multilayer h-BN, which shows a layered structure with abundant few-atoms-wide amorphous regions embedded every < 10 nm (see Figures S1 and S2, Supporting Information). In contrast, for ultrathin CaF$_2$ films we never observed amorphous defective regions similar to those observed in multilayer h-BN. The high-resolution TEM images also reveal that the thickness of the CaF$_2$ film is $\approx 2.5$ nm, and that it shows minimal thickness fluctuations (<0.32 nm). This observation is further confirmed by topographic maps collected via atomic force microscopy (AFM), which shows that the surface of the CaF$_2$ sample is atomically flat (see Figure S5, Supporting Information), with a root mean square (RMS) roughness of only 54 pm, similar to that of industrial Si wafers. The correct chemical composition of the samples was confirmed by analyzing the concentration of Ca, F, and Si at multiple locations of the sample using EDX and EELS (see Figures S6

![Figure 1](https://www.advancedsciencenews.com)
and S7, Supporting Information); the concentration of parasitic elements like Cr (from the protective coating) and O (from the environment) was also mapped. Both tests clearly showed that the Ca and F signals overlap, and that they are sandwiched by Cr and Si. The O and Cr signals overlap due to the partial oxidation of the Cr film during the sputtering process, as expected.[16]

The electrical properties of the ultrathin CaF2 films have been characterized at the nanoscale using a conductive atomic force microscope (CAFM) working in high-vacuum (≈10⁻⁶ Torr) and provided with solid Pt tips. Ramped voltage stresses (RVS) have been collected at >280 different randomly selected locations of the CaF2 sample (see Experimental Section and Figure S8, Supporting Information), and the results have been compared to those obtained on industrial SiO2 (≈4.7 nm thick) grown by thermal oxidation on n⁺Si, TiO2/1.5 nm SiOx, and ≈6 nm h-BN by applying RVS from 0 to 10 V. Each plot shows >300 I–V curves collected at different locations. The mean value (μ) and standard deviation (σ) of VON is indicated. b) Current maps collected on each sample by applying the minimum voltage needed to observe current above the noise level, which was 7 V for CaF2, 8.5 V for SiO2, 1.5 V for TiO2, and 5 V for h-BN. Scale bars in (b), 30 nm for CaF2 and 100 nm for SiO2, TiO2, and h-BN. c) Statistical analysis of the size of the conductive spots observed in each map of panel (b).

Figure 2. Nanoscale electrical homogeneity of CaF2, SiO2, TiO2, and h-BN observed via CAFM. a) I–V curves collected on the surface of ≈2.5 nm CaF2, 4.7 nm SiO2, 2 nm TiO2/1.5 nm SiOx, and ≈6 nm h-BN by applying RVS from 0 to 10 V. Each plot shows >300 I–V curves collected at different locations. The mean value (μ) and standard deviation (σ) of VON is indicated. b) Current maps collected on each sample by applying the minimum voltage needed to observe current above the noise level, which was 7 V for CaF2, 8.5 V for SiO2, 1.5 V for TiO2, and 5 V for h-BN. Scale bars in (b), 30 nm for CaF2 and 100 nm for SiO2, TiO2, and h-BN. c) Statistical analysis of the size of the conductive spots observed in each map of panel (b).
spots detected was always the smallest. More specifically, the mean radius of the weak spots in CaF$_2$ is only $\approx 3.7$ nm, which is remarkably smaller than in SiO$_2$ ($\approx 8.87$ nm), TiO$_2$ ($\approx 7.24$ nm), and h-BN ($\approx 14.48$ nm), as shown in Figure 2c. See additional explanations in Note S1 (Supporting Information).

Another important observation in Figure 2a is that the value of $V_{ON}$ for the $I$–$V$ curves collected on $\approx 2.5$ nm CaF$_2$ is close to that of the $I$–$V$ curves collected on $\approx 4.7$ nm SiO$_2$ and $\approx 6$ nm h-BN, and much higher than that observed on $\approx 3.5$ nm TiO$_2$/SiO$_X$ (where $X$ is a very important property that can be exploited to improve the reliability and time-dependent variability of electronic devices.

In addition, from Figure 3 the dielectric strength of both CaF$_2$ and SiO$_2$ can be calculated dividing the DB voltage by the thickness of each insulating material, resulting in values of $\approx 278 \pm 1.7$ MV cm$^{-1}$ and $20.3 \pm 0.9$ MV cm$^{-1}$. It is worth noting that the dielectric strength of the SiO$_2$ sample is consistent with that previously observed in other industrial SiO$_2$ samples, indicating the high quality of the thermal SiO$_2$ and the validity of the characterization method employed. Note that this value is higher than those previously reported for TiO$_2$ ($\approx 3$ MV cm$^{-1}$) and mechanically exfoliated h-BN ($\approx 12.0$ MV cm$^{-1}$) via CAFM. Additional discussion about the calculation and meaning of dielectric strength can be found in Note S3 (Supporting Information). This observation further indicates the extraordinary potential of ultrathin CaF$_2$ films to serve as dielectric in nanoelectronic devices.

Figure 3. Analysis of leakage current and dielectric strength in CaF$_2$ and SiO$_2$. $I$–$V$ curves collected on the surface of $\approx 2.5$ nm CaF$_2$ and $\approx 4.7$ nm SiO$_2$ samples by applying RVS from 0 to 10 V, using a logarithmic current-to-voltage preamplifier. For CaF$_2$ and SiO$_2$ a total of 43 and 58 locations have been analyzed. The dielectric strength of CaF$_2$ is $27.8 \pm 1.7$ MV cm$^{-1}$, and the dielectric strength of SiO$_2$ is $20.3 \pm 0.9$ MV cm$^{-1}$. The leakage current across the CaF$_2$ film is so low that it cannot be detected with the CAFM.
Future studies on CaF$_2$ dielectrics should include the characterization of other intrinsic dielectric properties, such as capacitance, dielectric constant, and time and frequency-dependent stability. Furthermore, the synthesis of high-quality CaF$_2$ on other substrates different than Si (111) may be necessary in order to facilitate its integration on 2D materials based solid-state electronic devices. Finally, carrying out electrical reliability analyses on test structures with areas similar to that of the channel of state-of-the-art FETs would be very useful to further understand the performance of CaF$_2$ at the device level. We are aware that developing such studies in a statistical and reliable manner would require substantial amount of work that would deserve one/few independent publication/s, and for that reason such tasks are out of the scope here.

In conclusion, we have demonstrated that ultrathin (=2.5 nm) CaF$_2$ films show outstanding performance as dielectric when exposed to electrical stresses. By applying RVS with the tip of a CAFM at multiple locations, we have statistically demonstrated that CaF$_2$ is more homogeneous and has a higher dielectric strength (=278 MV cm$^{-1}$) than SiO$_2$ (=203 MV cm$^{-1}$), TiO$_2$ (=3 MV cm$^{-1}$) and h-BN (=12.0 MV cm$^{-1}$), and that the leakage current across CaF$_2$ is orders of magnitude smaller than in nearly twice as thick SiO$_2$. Cross-sectional high-resolution TEM images demonstrate that the main reason behind this enhanced dielectric performance is that the cubic crystalline structure of the ultrathin CaF$_2$ film is continuous and defect-free over large regions, which prevents the formation of electrically weak spots.

**Experimental Section**

**Calcium Fluoride Growth:** Ultrathin CaF$_2$ layers were grown by MBE on weakly doped single-crystal n-Si (111) substrates with $N_D = 10^{15}$ cm$^{-3}$ and a misorientation of 5–10 angular min. Before the growth process, a protective oxide layer was formed after chemical treatment.[28] This layer was removed by annealing for 2 min at 1200 °C under ultrahigh-vacuum conditions (10$^{-6}$–10$^{-7}$ Pa). This allowed to obtain an atomically clean 7 × 7 Si (111) surface. The CaF$_2$ film was grown on this surface by MBE at 250 °C, which is known to be the optimum temperature to produce pinhole-free homogeneous CaF$_2$ layers.[29] The deposition rate of CaF$_2$ measured by a quartz oscillator was ~1.3 nm min$^{-1}$. The growth processes and crystalline quality of the CaF$_2$ layers were monitored using reflection high-energy electron diffraction, with an electron energy of 15 keV.

**Preparation of the SiO$_2$, TiO$_2$, and h-BN Samples:** The ultrathin SiO$_2$ films with a thickness of ~4.7 nm were grown by thermal oxidation of n$'$-Si (1 0 0) wafers with a resistivity of 0.002–0.003 Ω cm at the laboratories of Infineon Technologies. Note that this company has been growing SiO$_2$ of outstanding quality (i.e., low amount of defects and ultraflat surface) for more than 30 years. The ~2 nm TiO$_2$ films were grown on n-type Si wafers, with a resistivity ranging between 0.008 and 0.02 Ω cm, using a plasma-enhanced ALD system from Cambridge Nanotech. These wafers had a 1.5 nm native oxide on top, leading to a ~2 nm TiO$_2$/1.5 nm SiO$_2$/n$'$-Si structure. The Ti and O sources used were tetraethyl(dimethyl amido) titanium (Ti(NMe$_2$)$_4$) and oxygen inductively coupled discharge, respectively. The exposure time to Ti(NMe$_2$)$_4$ during one ALD cycle was 0.1 s, and the interval time between two exposures was 10 s, resulting in a growth rate of 0.51 Å per cycle. The ~6 nm h-BN samples were grown by CVD on Cu substrates at 1000 °C using ammonia borane as precursor.[30] The quality of these samples represented state-of-the-art, as confirmed by the low amount of defects detected via TEM and the minimal thickness fluctuations proved by AFM. The ~2 nm SiO$_2$ grown by thermal oxidation on p-type Si (with $N_A = 5 \times 10^{16}$ cm$^{-3}$), used only in

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.
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2D materials, calcium fluoride, dielectric strength, van der Waals interfaces

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