# Crystalline Calcium Fluoride: A Record-Thin Insulator for Nanoscale 2D Electronics

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**Introduction:** Two-dimensional (2D) electronics can enable FETs down to a few nanometers. However, these devices require scalable insulators which should form high-quality interfaces with 2D channels and maintain low gate leakage currents for sub-1 nm equivalent oxide thickness (EOT). Previously used amorphous oxides result in poor interfaces with 2D materials, while hBN has mediocre dielectric properties ($\varepsilon < 5$, $E_g = 6$ eV) [1]. As a promising alternative, we suggest the use of the crystalline ionic insulator $CaF_2$ ($\varepsilon = 8.43$, $E_g = 12.1$ eV) which forms van der Waals interfaces with 2D semiconductors [2]. At the moment, $CaF_2$ can be grown by molecular-beam epitaxy (MBE) down to a few nanometers thickness [3] and appears promising for chemical vapour deposition (CVD) [4] and atomic-layer deposition (ALD) [5]. Here we discuss our recent progress [3, 6, 7] on ultra-thin $CaF_2$ which presents a universal platform for 2D devices. In particular, we demonstrate nanoscale $MoS_2$ FETs with $L$ =50-60 nm and a record-thin ~2 nm $CaF_2$ insulator (EOT ~ 0.9 nm) which exhibits near-ideal subthreshold swing (SS).

**Growth and structure of $CaF_2$ films:** MBE of $CaF_2$ on Si(111) has been known for over three decades [8]. However, previously used high-temperature growth (up to 800°C), which targeted high crystallinity, results in the formation of triangular pinholes [9]. To address this problem, we have succeeded in growing $CaF_2$ at 250°C [6] after careful cleaning of Si(111) substrates [10]. This allowed us to obtain pinhole-free homogeneous $CaF_2$ films with 1−2 nm thickness. For instance, the atomic-force microscopy (AFM) image in Fig.1a shows that the surface of $CaF_2$ is flat with clearly visible atomic steps, and the transmission electron microscopy (TEM) images from Fig.1b,c confirm that the 2 nm thick $CaF_2$ film consists of triple F-Ca-F monolayers (1 ML = 0.315 nm, Fig.1c). Despite low-temperature MBE growth, reflection high energy electron diffraction (RHEED) patterns (Fig.2) contain distinct streaks which indicates high crystallinity of our $CaF_2$ films grown on atomically clean Si(111).

**High-quality $CaF_2$ for device applications:** An important advantage of $CaF_2$ is its inert (111) surface which forms well-defined interfaces with 2D materials [2] (Fig.3a). This is in contrast to amorphous oxides like $HfO_2$ which contain dangling bonds (Fig.3b). Also, $CaF_2$ has a reasonably high permittivity ($\varepsilon = 8.43$), an extremely wide bandgap ($E_g = 12.1$ eV) and forms high band offsets with Si and 2D semiconductors (Fig.3c). Thus, predicted leakage currents through $CaF_2$ are lower [11] than those through $HfO_2$, hBN and $SiO_2$ (Fig.3d), and fit the end-of-roadmap requirement.

To understand leakage mechanisms through $CaF_2$, we measured the $I-V$ curves of Au/$CaF_2$/Si(111) diodes [3,6,12]. We found that the results can be reproduced with theoretical tunneling models considering thickness fluctuations [3] and transverse momentum conservation [12] (Fig.3e). The latter becomes important because of the (111) orientation and further suppresses tunneling through $CaF_2$ [12]. Next we analyzed the light emission of hot electrons which are injected through $CaF_2$ to p-Si under accummulation ($V_{Si} > 0$) and can be involved in recombination (RR), intra-band (IB) and intra-band direct (IB-d) radiative transitions (Fig.4a) [3, 13]. We found that activation thresholds measured for different photon energies $\hbar\omega$ are close to their estimated values (Fig.4b) and concluded that carrier injection through $CaF_2$ is elastic, i.e. takes place without energy dissipations. This means that our $CaF_2$ layers are mostly defect-free and thus perfectly suited for device applications.

**$MoS_2$ FETs with 2 nm $CaF_2$:** Fig.5 demonstrates the use of Si(111)/$CaF_2$ substrates for $MoS_2$ FETs [7]. Devices have been produced by transferring bilayer CVD-grown $MoS_2$ films onto $CaF_2$ and shaping Ti/Au electrodes with e-beam lithography. First we fabricated hundreds of large-area ($L$ = 400 - 800 nm) $MoS_2$ FETs with 2 nm thick $CaF_2$ [7] and confirmed the device structure using scanning electron microscopy (SEM, Fig.5a) and TEM (Fig.5b). Then we found that the best devices exhibit SS down to 90 mV/dec and record-high on/off current ratios up to $10^7$ for 2 nm thick insulators (Fig.5c). Finally, we extended the source Ti/Au area and shaped nanoscale $CaF_2$/$MoS_2$ FETs with $L$ =50-60 nm (Fig.6). These devices exhibit excellent drain current control by the gate bias $V_G$ and near-ideal SS down to 60 mV/dec, which slightly degrades at larger $V_D$ where the device reaches the full on state.

**Conclusions:** We fabricated high-quality crystalline 1−2 nm $CaF_2$ films and successfully used them for $MoS_2$ FETs with record-thin gate insulators. For the first time we demonstrated $MoS_2$ FETs with simultaneously sub-1 nm EOT insulators and sub-100 nm channel length and found that these devices can exhibit near-ideal SS. Our results suggest that Si(111)/$CaF_2$ substrates provide a universal platform for future 2D nanoelectronics, which has enormous potential due to the possibility of direct growth of 2D semiconductors on $CaF_2$ [14].

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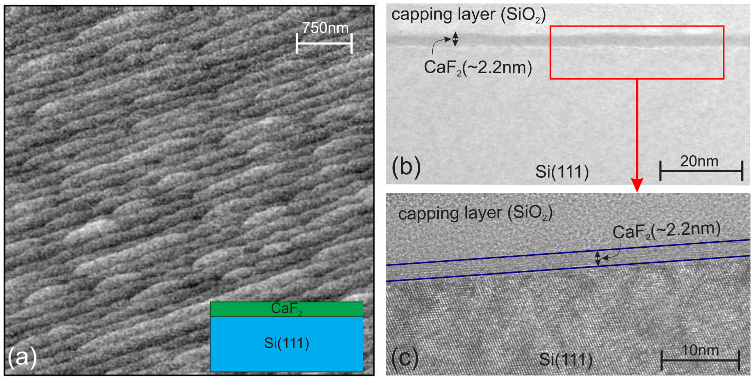


Fig. 1: (a) Typical surface relief of our ultra-thin $CaF_2$ films grown by MBE on Si(111) at 250°C. Low (b) and high (c) resolution TEM images of the $CaF_2$(2 nm)/Si(111) samples confirm the nominal thickness of $CaF_2$ of about 2 nm. Atomic layers of $CaF_2$ are visible in (c).

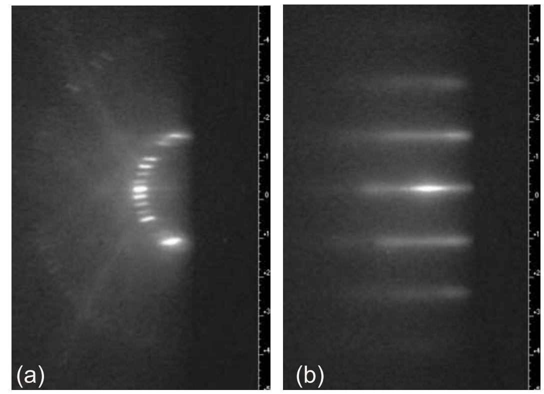


Fig. 2: RHEED patterns of the Si(111) surface showing the $7\times7$ superstructure (a) and a 2 nm thick $CaF_2$ grown on Si(111) at 250°C (b). Distinct reflections confirm the high crystalline quality of $CaF_2$.

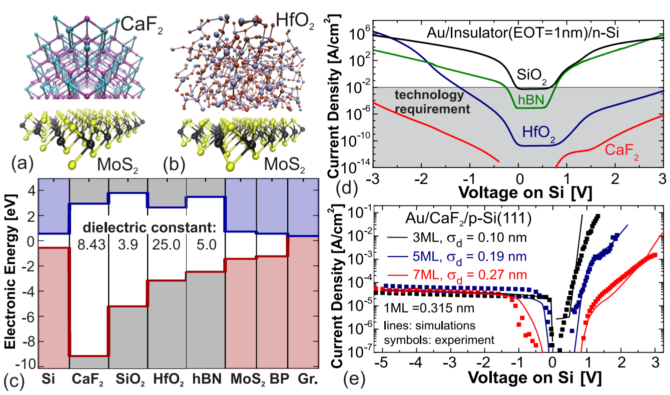


Fig. 3: Schematic $MoS_2/CaF_2$ (a) and $MoS_2/HfO_2$ (b) interfaces. (c) Band diagram showing the relative matching of $CaF_2$ and other insulators to 2D semiconductors. (d) Theoretical leakage currents through the tunnel diodes with these insulators for EOT = 1 nm. $CaF_2$ is expected to satisfy the technology requirements. (e) Leakage currents through Au/$CaF_2$(3−7 ML)/p-Si(111) structures can be well fitted with the tunnel model considering transverse momentum conservation and thickness fluctuations measured with AFM.

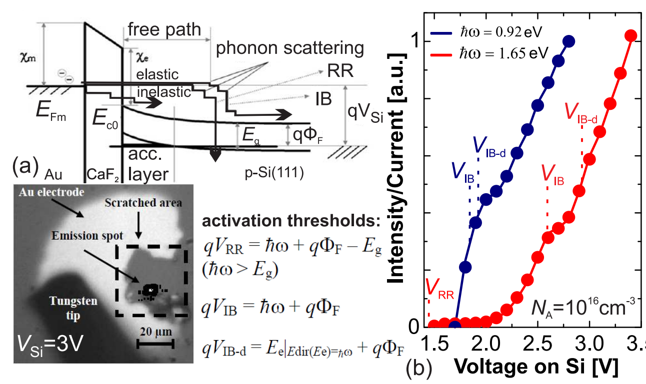


Fig. 4: (a) Band diagram of Au/$CaF_2$/p-Si structure explaining the origin of injection-related light emission in accummulated p-Si (top), photon emission spot overlaid on the optical image of scratched Au electrode and the formulas used to estimate RR, IB and IB-d activation thresholds (bottom). (b) Voltage dependences of the intensity of light emission measured for two different photon energies. Activation thresholds are close to estimated values (marked), which confirms elastic electron injection through $CaF_2$.

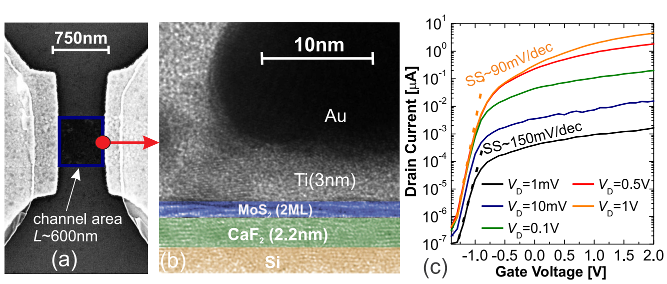


Fig. 5: (a) SEM image of the channel area of our large-area $CaF_2/MoS_2$ FET. (b) TEM image obtained near Ti/Au electrode confirms the device structure with bilayer CVD-$MoS_2$ on top of ~2 nm thick $CaF_2$. (c) The best devices exhibits an on/off current ratio up to $10^7$ and SS down to 90 mV/dec.

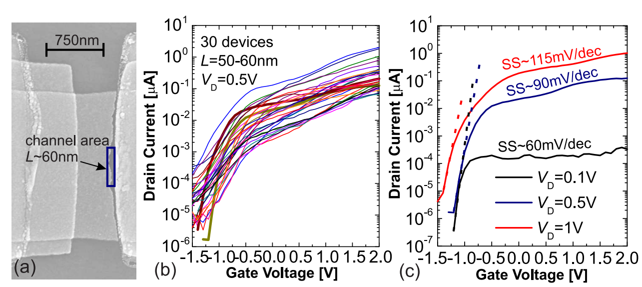


Fig. 6: (a) SEM image of our nanoscale $CaF_2/MoS_2$ FET. The channel length is about 60 nm. (b) $I_D$-$V_G$ characteristics of 30 nanoscale $CaF_2/MoS_2$ FETs. (c) The best device (same as used for SEM in (a)) exhibit SS down to 60 mV/dec and an on/off current ratio up to $10^5$.

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