Negative Capacitance for Electrostatic Supercapacitors

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The increasing demand for efficient storage of electrical energy is one of the main challenges in the transformation toward a carbon neutral society. While electrostatic capacitors can achieve much higher power densities compared to other storage technologies like batteries, their energy densities are comparatively low. Here, it is proposed and demonstrated that negative capacitance, which is present in ferroelectric materials, can be used to improve the energy storage of capacitors beyond fundamental limits. While negative capacitance was previously mainly considered for low power electronics, it is shown that ferroelectric/dielectric capacitors using negative capacitance are promising for energy storage applications. Compared to earlier results using (anti)ferroelectric materials for electrostatic energy storage, much higher efficiencies of more than 95% even for ultrahigh energy densities beyond 100 J cm$^{-3}$ are demonstrated using nonepitaxial thin films suitable for integration on 3D substrates. Stable operation up to 150 °C and $10^8$ charging/discharging cycles is further demonstrated.

1. Introduction

The storage of electrical energy has only been possible since the invention of the capacitor in 1745.[1] When a voltage is applied to a capacitor, energy is stored in the electric field in the dielectric material which separates the two conducting electrodes. The major advantages of the energy storage in capacitors are a high energy storage efficiency, temperature, and cycling stability as well as high power densities. On the other hand, regular dielectric capacitors cannot compete with the orders of magnitude higher energy storage densities of, e.g., batteries or fuel cells.[2] However, so-called supercapacitors, which combine the high power density of capacitors with much higher energy densities, are ideal for applications where a large amount of energy has to be stored and released in a relatively short time.[3–6] Currently, high energy density electrochemical supercapacitors, which are mostly based on the double-layer capacitance and pseudocapacitance effects, are used, e.g., to stabilize the power grid, recover braking energy in electric vehicles or provide a backup power supply for critical electrical systems.[3,7] Recently, there has been increasing interest in purely electrostatic solid state supercapacitors based on highly polarizable materials, e.g., ferroelectrics and antiferroelectrics.[8–11] Here, we propose and demonstrate a new way to increase the energy density of electrostatic capacitors by using negative capacitance (NC), which was recently observed in ferroelectric materials.[12–18] However, the concept should be applicable to other materials and structures exhibiting positive feedback mechanisms, which were proposed as the origin of NC.[19] In contrast to previous research on NC, which was focused on reducing the switching energy of nanoscale transistors,[19] we first propose to use NC to increase the energy stored in capacitors beyond conventional limits. This can be achieved by combining a ferroelectric material, which exhibits NC, with a regular dielectric material, which has a positive capacitance, in a capacitor structure with fixed charges at the interface between both layers. The resulting nonlinear charge–voltage characteristics of this ferroelectric/dielectric capacitor improves the stored energy at a fixed voltage compared to the dielectric layer alone, which would be impossible with only positive capacitance materials. Moreover, our approach highlights a more general pathway toward improved energy storage systems by utilizing materials with other “negative” properties, e.g., negative stiffness materials[20] for mechanical energy storage systems.

2. Energy Storage in Nonlinear Capacitors

In general, the electrostatic energy density in a dielectric material is given by

$$w = \int_0^D E(D) \, dD$$

(1)

where $E$ is the electric field and $D$ is the electric displacement field. Note that the relationship between $E$ and $D$ can be nonlinear. Similarly, when describing the total electrostatic...
energy stored in a capacitor (neglecting fringing fields), we can write

\[ W = \int_0^Q V(Q) dQ \]  \hspace{1cm} (2)

where \( V \) is the applied voltage and \( Q \) is the charge on the electrodes. Graphically, the stored energy (density) therefore coincides with the area above the \( Q-V \) (\( D-E \)) curve as shown in **Figure 1a** for a linear positive capacitor with constant capacitance \( C = Q/V \). Since in a linear dielectric \( D = \varepsilon E \), where \( \varepsilon \) is the permittivity, it follows that \( Q = CV \) and we obtain the well-known expressions \( w = \varepsilon E^2/2 \) and \( W = CV^2/2 \). In such regular capacitors, the maximum stored energy is limited by the breakdown field strength and permittivity of the dielectric. When thinking about an NC material, the relationship between \( Q \) and \( V \) (or \( D \) and \( E \)) cannot be linear for all applied voltages, since such a capacitor would be able to supply infinite amounts of energy. However, materials which show a differential negative permittivity \( (dD/dE < 0) \) or capacitance \( (dQ/dV < 0) \) can indeed exist if this NC region is bounded by regions of positive capacitance as shown exemplarily in **Figure 1b**. The simplest way to describe the behavior in **Figure 1b** is by using a 3rd order polynomial, which is shifted along the \( Q \)-axis as described by

\[ V = a(Q - \Delta Q) + b(Q - \Delta Q)^3 \]  \hspace{1cm} (3)

where \( a < 0, b > 0 \) and \( \Delta Q = (-a/b)^{1/3} \) is the remanent charge. Note that the bias point in **Figure 1b** (red dot), where \( dQ/dV < 0 \), would be unstable in an isolated capacitor. The material would quickly relax to the positive capacitance regions, which would lead to a hysteresis when trying to measure the \( Q-V \) curve by forcing a voltage as indicated by the dashed blue arrows. This inherent \( Q-V \) hysteresis caused by the unstable NC region is undesirable for energy storage applications, since the area inside the hysteresis loop corresponds to the dissipated energy \( W_{\text{loss}} \) as shown in **Figure 1b**. In this case, the energy recovered during discharging of the capacitor \( W_d \) will be lower than the energy supplied during charging \( W_c \). Therefore, we can define the hysteresis loss as

\[ W_{\text{loss}} = W_c - W_d = \int_0^Q V(Q) dQ - \int_0^0 V(Q) dQ \]  \hspace{1cm} (4)

The average energy densities \( \langle w_{\text{loss}} \rangle \), \( \langle w_c \rangle \), and \( \langle w_d \rangle \) can be obtained by dividing \( W_{\text{loss}} \), \( W_c \), and \( W_d \) by the capacitor volume. The energy storage efficiency \( \eta \) of the capacitor is then defined as

\[ \eta = \frac{\langle w_d \rangle}{\langle w_c \rangle + \langle w_d \rangle} \]  \hspace{1cm} (5)

As can be seen from Equations (4) and (5), if there is no \( Q-V \) hysteresis, the energy storage efficiency of a capacitor is \( \eta = 1 \) since \( W_c = W_d = W \).

3. Proposal of a Negative Capacitance Super capacitor

In the following we will describe a way to create a supercapacitor using NC, but without reducing the storage efficiency due to hysteresis. If we combine a positive capacitance material \( (V = Q/C) \) with an NC material described by Equation (3) in series (see **Figure 1c**), we obtain the following \( Q-V \) relation of the total capacitor

\[ V = \left( \frac{1}{C} + a \right) Q - aQ^3 + bQ^4 \]  \hspace{1cm} (6)

Since the combined supercapacitor should ideally have no \( Q-V \) hysteresis to achieve \( \eta = 1 \), the condition \( 1/C > -a \) must be satisfied, which was originally proposed for hysteresis-free NC transistors by Salahu-din and Datta. An exemplary \( Q-V \) curve of such an NC supercapacitor can be seen in the right panel of **Figure 1c**. Due to the positive curvature of the nonlinear \( Q-V \) curve, \( W \) can be significantly increased compared to the linear capacitor in **Figure 1a**, even at identical voltage \( V \) and stored charge \( Q \). Using Equations (2) and (6), the energy stored in such a capacitor is given by

\[ W = \left( \frac{1}{2C} + a \right) Q^2 - bQ^3 + \frac{b}{4} Q^4 \]  \hspace{1cm} (7)
To determine the maximum energy storage enhancement compared to the same capacitor without NC layer, we investigate the case where $1/C = -a$, which corresponds to the optimal capacitance matching condition of both layers. After normalizing $W$ to the energy of the capacitor $C$, at the same voltage, which is $W_0 = CV^2/2$, we obtain a maximum energy storage enhancement $W/W_0$ at the voltage $V = V_{\text{max}}$ (see Supporting Information for a detailed derivation). In a first order approximation we can write

$$\frac{W}{W_0} \bigg| _{V=V_{\text{max}}} = 1 - aC$$

(8)

which surprisingly is independent of $b$ and only depends on the product $aC$. In the case of perfect capacitance matching ($aC = -1$), the enhancement is roughly two, which means that the energy stored at identical voltage is doubled. The voltage $V_{\text{max}}$, where this maximum enhancement is observed can be obtained from

$$V_{\text{max}} \approx \left(\frac{4}{3C} + \frac{1}{a}\right)\Delta Q$$

(9)

It should be noted, that both $a$ and $1/C$ are proportional to the thickness of the NC layer and dielectric, respectively. For energy storage applications, the NC supercapacitor should be designed such that it operates around the voltage $V_{\text{max}}$. This enhancement of the stored energy at identical voltage due to positive $Q-V$ curvature is the one of the main advantages of the proposed NC supercapacitor. Furthermore, the overall leakage current through the capacitor will be reduced, and the breakdown voltage will be improved by adding the NC layer. Therefore, it should be possible to apply much higher voltages to the NC supercapacitor compared to the same capacitor without NC layer, leading to significantly higher energy densities. Lastly, as shown above, with the hysteresis-free condition $1/C > -a$, the theoretical storage efficiency will be $\eta = 1$. Note that when combining two positive capacitance layers, $W/W_0$ is always smaller than one.

4. Ferroelectric/Dielectric NC Supercapacitors

As mentioned earlier, a hysteretic $Q-V$ behavior as shown in Figure 1b is well known from ferroelectric materials, which possess a spontaneous electric polarization $P_S$ whose direction can be reversed by the application of an electric field $E$. Due to the inherent $P-E$ hysteresis of ferroelectric materials, a lot of previous work has been focused on nonvolatile memory devices. However, in recent years it was argued that ferroelectric materials could also exhibit an NC without the typical $P-E$ hysteresis, if coupled to a material with positive capacitance. Growing experimental evidence suggests that this is indeed possible.

To qualitatively understand how NC in ferroelectric materials can be used to build a supercapacitor, it is useful to examine the basic physical characteristics of dielectric and ferroelectric capacitors. Figure 2a,b shows the free energy–displacement field ($F-D$), displacement field–electric field ($D-E$) and capacitance–displacement field ($C-D$) relationships of a short-circuited dielectric capacitor and a ferroelectric capacitor. For the latter case, the displacement field $D_f$ is approximately identical to the ferroelectric polarization $P_f$. The blue circles indicate the equilibrium state of each capacitor. For the dielectric capacitor in Figure 2a, the free energy $F_d$ is identical to the electrostatic energy $w_d = D_d^2/2\varepsilon_d$, where $\varepsilon_d$ is the dielectric permittivity. Since $\varepsilon_d$ is constant, the electric field in the dielectric $E_d$ is proportional to the displacement field $D_d$. Therefore, the capacitance of the dielectric capacitor $C_d$ is also constant. When no voltage is applied to such a dielectric capacitor, there is no charge $Q$ on the electrodes, because $E_f = 0$ and thus $D_d = 0$. On the other hand, for a shorted ferroelectric capacitor as shown in Figure 2b, the equilibrium state is characterized by a spontaneous polarization $\pm P_S$, which correspond to one of the degenerate energy minima in the double well free energy landscape $F_f$. The model for the ferroelectric is based on Landau–Ginzburg–Devonshire theory assuming a homogeneous ferroelectric polarization $P_f$. The polarization charges $P_f$ are completely compensated by the charges $+Q$ and $-Q$ on the electrodes. In this simple picture of homogeneous $P_f$, the relationship between $P_f$ and the electric field in the ferroelectric $E_f$ has an “S”-shape. Since the ferroelectric capacitance $C_f$ is proportional to the slope $dP_f/dE_f$, $C_f$ is negative in the region of smaller $P_f$. This NC region of $dP_f/dE_f < 0$ coincides with the free energy barrier where $d^2P_f/dE_f^2 < 0$. However, the capacitance $C_f$ in the equilibrium state (around $P_f = \pm P_S$) is always positive. This can also be seen from the dependency of the inverse capacitance $1/C_f$ on $P_f$, which is shown on the right-hand side of Figure 2a.

To create an NC supercapacitor with a ferroelectric/dielectric stack as shown in Figure 1c, we first need to ensure that the ferroelectric is in one of its spontaneous polarization states when no external voltage $V$ is applied. This can be achieved, e.g., by introducing a sufficiently large fixed charge $\sigma_f$ at the ferroelectric/dielectric interface as indicated in Figure 2c. Such a fixed charge is typically observed at the interface between different dielectrics and can be engineered, e.g., by changing the dielectric material or thickness in a stack consisting of two or more layers. Besides this, $\sigma_f$ might originate from electrons trapped at deep interface states. The charge $\sigma_f$ plays the same role as the $\Delta Q$ introduced in Equation (3) and effectively shifts the $Q-V$ curve upward. See the Supporting Information for a detailed derivation of the theory for the ferroelectric/dielectric NC supercapacitor. In the example given in Figure 2c, $\sigma_f = -|P_S|$, which results in a complete compensation of $P_f$ at the ferroelectric/dielectric interface if $P_f = -P_S$, leading to $D_d = 0$ and $E_f = 0$. If there would be no charge $\sigma_f$, the uncompensated charge $P_f$ at the ferroelectric/dielectric interface would result in a large depolarization field in the ferroelectric, making the spontaneous polarization state unstable when $V = 0$. This would be detrimental for the performance of the NC supercapacitor. Notice that in Figure 2c, the total free energy $F$ has no negative curvature and the $Q-V$ curve has a positive slope, which corresponds to a strictly positive total capacitance $C = dQ/dV$ in the entire voltage range. This can be achieved by matching the capacitances of the ferroelectric and the dielectric layers as discussed in Section 3.
By applying a positive voltage $V_1$ to the NC supercapacitor as shown in Figure 2d, at first $P_f$ increases only slightly in the positive capacitance regime of the ferroelectric which leads to a small increase of the stored charge $Q$ and energy $W$ (green area) with increasing voltage. Notice that in this bias region, the electric fields in the ferroelectric $E_f$ is still increasing with increasing $V$. However, by further increasing the voltage toward $V_{\text{max}} > V_1$ as shown in Figure 2e, the ferroelectric enters the NC region of the “S”-shaped $P_f$–$E_f$ curve, where the field in the dielectric $E_d$ is amplified due to the decreasing field in the ferroelectric $E_f$. In this case, the total differential capacitance will be larger than that of the dielectric alone.$^{[15,16,18]}$ In this region, a small change in external voltage leads to a large increase in $Q$ and thus also in $W$. By increasing the voltage further beyond $V \gg V_{\text{max}}$ the storage enhancement $W/W_0$ will be reduced and the ferroelectric will enter its second positive capacitance region. Therefore, operating the capacitor at $V = V_{\text{max}}$ is desirable for energy storage applications.

5. Experimental Demonstration

To test our proposed NC supercapacitor design, we fabricated ferroelectric/dielectric capacitors using ferroelectric Hf$_{0.5}$Zr$_{0.5}$O$_2$ (HZO) and dielectric Al$_2$O$_3$ or Ta$_2$O$_5$ thin films as described in the Experimental Section. HZO was chosen,
because it is a lead-free ferroelectric material with a wide process window and a large electronic band gap, which can be deposited conformally on 3D substrates by atomic layer deposition. Al2O3 and Ta2O5 were selected for their high breakdown field strength, relatively high permittivity and low leakage currents in their amorphous form. The stabilization of the ferroelectric orthorhombic phase in the HZO layers was confirmed by grazing-incidence X-ray diffraction measurements, which can be found in the Supporting Information. Furthermore, the morphology and thickness of the individual layers was investigated by transmission electron microscopy (TEM), which can also be found in the Supporting Information. The TEM results show that the HZO films are polycrystalline with a lateral grain size of 10–20 nm, while the Al2O3 and Ta2O5 layers are amorphous.

Figure 3 shows experimental data for a TiN/HZO/Ta2O5/TiN capacitor using a pulsed electrical measurement technique as reported recently. The layer thicknesses of 11.5 and 13.5 nm for HZO and Ta2O5, respectively, were determined by TEM. The integrated charges during charging (Q) and discharging (Qd) as well as their difference (Qint) are shown as a function of the applied voltage in Figure 3b. By integrating the area above the Q–V curve according to Equation (2), we obtain \( \langle w_0 \rangle, \langle w_c \rangle, \langle w_d \rangle \) and \( \eta \), which are shown in Figure 3c. When examining \( \eta \) as a function of \( \langle w_c \rangle \) as shown in Figure 3d, even for ultra-high energy densities above 100 J cm\(^{-3}\), we can obtain efficiencies of more than 95%. It should be noted that since \( \langle w_0 \rangle \) is the average energy density of the total capacitor and most of the energy is stored in the dielectric, the actual energy density in the dielectric is much higher (up to \( \approx 200 \) J cm\(^{-3}\), see Supporting Information for details). By dividing \( \langle w_c \rangle \) by the discharging time (\( \approx 400 \) ns) we can calculate a maximum power density of 272.5 MW cm\(^{-2}\). The integral capacitance \( C_{int} = Q/V \) at maximum power density is 1.56 \( \mu \)F cm\(^{-2}\). In Figure 3e, we compare the discharged energy density per area for the HZO/Ta2O5 supercapacitor (W) and the expected one for the Ta2O5 without HZO (\( w_0 \)) based on the measured permittivity of a TiN/Ta2O5/TiN capacitor, which is \( \approx 23.5 \). As can be seen from the energy storage enhancement \( W/W_0 \) in Figure 3f, the simple theory for the NC supercapacitor (Equation (55), Supporting Information) agrees well with the experimental data when using the extracted parameters (a and b) from ref. [18].

An important prerequisite for reliable supercapacitor operation is temperature, cycling, and frequency stability. In Figure 4a, the small-signal capacitance per area and the loss factor are shown as a function of frequency. In the low frequency regime at zero bias, \( \tan(\delta) \) is in the range of 0.6% while the capacitance density is about 1.3 \( \mu \)F cm\(^{-2}\). The stability with charging/discharging cycles can be inferred from the data in Figure 4b. Up to \( 10^8 \) cycles, \( \langle w_0 \rangle \) remains roughly constant at about 38 J cm\(^{-3}\) at an applied maximum voltage of 10.6 V. During further cycling up to \( 10^8 \) times, \( \langle w_0 \rangle \) begins to decrease to about 31 J cm\(^{-3}\), while \( \eta \) remains high at about 99%. This decrease in \( \langle w_0 \rangle \) might be related to the pinning of ferroelectric domains, which then do not contribute to the NC effect anymore. Furthermore, in Figure 4c, it can be seen that \( \langle w_0 \rangle \) is nearly independent of the measurement frequency across a broad frequency range. While some ferroelectric materials exhibit a strong dependence of their properties on temperature, this does not seem to be the case for the HZO films used here,

as shown in Figure 4d, where the high \( \langle w_d \rangle \) and efficiency are unaffected by an increase in temperature up to 150 °C.[9] These characteristics indicate that reliable supercapacitor operation should be feasible using our proposed capacitor design.

5.1. Changing the Dielectric and Layer Thicknesses

For the HZO/Ta2O5 capacitor shown in Figure 3, the maximum energy storage enhancement \( W/W_0 \) is only \( \approx 1.1 \) which is far from the theoretical maximum \( \approx 2 \), since the capacitance matching \( aC = −0.16 \) was not ideal. To improve the maximum \( W/W_0 \), we fabricated similar capacitors using Al2O3 instead of Ta2O5 (see the Experimental Section).[16] With the additional advantage that Al2O3 has an even higher breakdown field strength than Ta2O5.[32–34] Furthermore, we varied the thickness of both the Al2O3 and the HZO layer to investigate the effect on the energy storage properties. Figure 5a depicts the \( \eta \) versus \( \langle w_0 \rangle \) curves for an HZO thickness of 7.7 nm and varying Al2O3 thicknesses from 1.5 to 4 nm. It is apparent that an increase in the Al2O3 thickness both increases the maximum obtainable \( \langle w_0 \rangle \) as well as the overall efficiency. The increase in \( \eta \) for thicker Al2O3 seems to be directly related to the decreased probability of electron tunneling through the layer.[15,16] The injection of electrons into the ferroelectric/dielectric interface can lead to hysteretic switching,[15,16,18] which will strongly degrade \( \eta \). This also explains the even higher observed efficiency for the much thicker Ta2O5 film shown in Figures 3 and 4. The increase of \( \langle w_0 \rangle \) for thicker Al2O3 layers on the other hand can be explained by the increased volume fraction of the dielectric material compared to the combined volume of the ferroelectric and the dielectric. Since the electric field in the dielectric is typically much higher compared to the ferroelectric in the NC region, most of the energy in the capacitor is stored in the dielectric and not in the ferroelectric layer. Therefore, decreasing the volume fraction of the ferroelectric layer should increase the overall energy density (see Supporting Information for a detailed derivation).

A similar behavior can be observed in Figure 5b, where the HZO thickness was changed, but the Al2O3 thickness was fixed at 4 nm. The highest maximum \( \langle w_0 \rangle = 121 \) J cm\(^{-3}\) is achieved for 7.7 nm HZO and 4 nm Al2O3. This corresponds to a maximum power density of 302.5 MW cm\(^{-2}\) and \( C_{int} = 2.2 \) \( \mu \)F cm\(^{-2}\). However, for the actual \( w_0 \) inside the Al2O3 layer, much higher values can be estimated (see the Supporting Information). While the overall trend of the efficiency is almost identical for both HZO thicknesses (mostly related to the properties of the dielectric), \( \langle w_d \rangle \) for the thinner HZO seems to be roughly scaled by a factor close to the ratio of the total thicknesses (15.3 nm/11.7 nm = 1.31). Therefore, increasing the ratio of dielectric to ferroelectric thickness without degrading the ferroelectric properties might be useful way to improve the overall \( \langle w_0 \rangle \) of the capacitor further. However, one should keep in mind that this might degrade the matching of the dielectric capacitance to the ferroelectric NC region, thus reducing the voltage gain. Therefore, an optimum in between too thick and too thin dielectric layers can be expected. In the Supporting Information it is shown that for good capacitance matching and a small ratio of ferroelectric to dielectric thickness, dielectrics with higher permittivity, and ferroelectrics
with a smaller negative permittivity are preferable. In Figure 5c, the charge–voltage curves for the best layer combination of 4 nm Al₂O₃ and 7.7 nm HZO can be seen, where a strong increase in the differential capacitance is visible in the NC regime. The corresponding energy storage enhancement in Figure 5d shows a higher maximum of ≈1.5 compared to the HZO/Ta₂O₅ sample due to the much better capacitance matching (ΔC ≈ −0.58).

5.2. Comparison to Previous Supercapacitor Results

Figure 6 shows a comparison of reported highest ⟨w_d⟩ and corresponding efficiencies η for solid state supercapacitors using nonepitaxial materials.⁹,³⁵–⁴³ As can be seen, the first NC supercapacitors demonstrated in this work have roughly twice the maximum ⟨w_d⟩ while at the same time improving the efficiency.
above 85%. At comparable energy densities as reported in literature (\(\langle w_d \rangle \approx 40–60 \text{ J cm}^{-3}\)), our NC supercapacitors have much higher efficiencies above 97%. Considering that this is the first experimental demonstration of the NC supercapacitor concept, these values are already very encouraging and there should be plenty of room for further improvement. While other groups have reported capacitors with even higher maximum \(\langle w_d \rangle\) (up to 307 J cm\(^{-3}\)), these results were all obtained by using epitaxially fabricated ferroelectrics\[^{11,44–47}\] which limits these materials to applications in planar capacitors on flat and lattice-matched substrates. By contrast, by using only polycrystalline\[^{48}\] and amorphous materials, which can be deposited via atomic layer deposition as shown here, almost arbitrary substrates with complex 3D surfaces can be used to achieve much higher energy densities per projected substrate area as experimentally shown before\[^{36,43}\]. In this way, the effective energy density per projected substrate area can be easily improved by a factor of 30 or higher, depending on the aspect ratio and density of the 3D structures (e.g., density of capacitor trenches). This makes polycrystalline materials much more promising for applications compared to epitaxial ones. While the capacitors used in this work have a rather small area, other authors have recently demonstrated that much larger energy storage capacitors based on similar HfO\(_2\) based antiferroelectric materials are feasible\[^{43}\].

6. Conclusion

We have proposed that by combining an NC layer (e.g., a ferroelectric) with a regular positive capacitance layer (e.g., a dielectric), it is possible to build an NC supercapacitor, which can store large amounts of electric energy with high efficiency. For an optimal NC supercapacitor design, the capacitances of both layers should be closely matched (\(aC \approx -1\), and the NC layer should be in a positive capacitance state when no voltage is applied (\(\Delta Q\)-shift). Furthermore, the capacitor should be operated close to \(V_{\text{max}}\), to obtain the highest benefit due to the NC effect.

This new concept has three main advantages: (1) By engineering a nonlinear \(Q-V\) curve with positive curvature, the stored energy can be increased compared to a regular capacitor even at identical voltage. (2) The breakdown voltage and leakage currents of the capacitor are improved by the addition of the NC layer, thus enabling much higher energy storage densities. (3) Since there is no hysteresis, the theoretical efficiency is 100%.

Furthermore, we have first experimentally demonstrated this concept by using ferroelectric/dielectric capacitors with different layer thicknesses and materials (HZO and Al\(_2\)O\(_3\) or Ta\(_2\)O\(_5\)). Since only polycrystalline and amorphous materials...
were used, integration on 3D substrates is promising for high storage density applications. Maximum discharged energy densities above 100 J cm\(^{-3}\) were achieved at efficiencies higher than 95%. Stable operation was shown in a broad frequency and temperature range (up to 150 °C) as well as for up to 10⁸ charging/discharging cycles. Lastly, it was shown that increasing the ratio of dielectric to ferroelectric thickness can improve both maximum energy density as well as efficiency, since most of the energy is stored in the dielectric layer. For improving the capacitance matching and reducing the volume fraction of the ferroelectric layer at the same time, dielectric materials with larger permittivity and ferroelectrics with smaller negative permittivity were shown to be advantageous. In conclusion, our results pave the way for next-generation solid state supercapacitor technologies for highly efficient short-term storage of electrical energy.

7. Experimental Section

**Sample Fabrication:** Metal–ferroelectric–dielectric–metal capacitors were fabricated on Si (100) substrates with a native SiO\(_2\) layer. Bottom TiN electrodes of 12 nm thickness were reactively sputtered in a BESTEC and an Alliance Concept physical vapor deposition tool at room temperature. Subsequently, Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) (HZO) films were grown by atomic layer deposition (ALD) in an Oxford Instruments OpAL ALD tool at 260 °C using the precursors TEMA-Hf, and TEMA-Zr with water as the oxygen source. Alternating ALD cycles of TEMA-Hf and TEMA-Zr were applied to achieve a homogeneous distribution of Hf and Zr in the films. For samples using Al\(_2\)O\(_3\) as the dielectric layer, ALD was carried out directly after HZO deposition without breaking vacuum using TMA.
and water as precursors at 260 °C. The film thicknesses were adjusted by the total number of ALD cycles. On the other hand, samples with Ta2O5 as the dielectric layer were fabricated by reactive sputtering of Ta2O5 at room temperature after ALD of HZO. Top TiN electrodes were then deposited in the same way as the bottom electrodes. After top electrode deposition, crystallization of the HZO layers was achieved by annealing the samples at 500 and 600 °C for 20 s in nitrogen atmosphere for Ta2O5 and Al2O3 samples, respectively. To define circular capacitor areas (A ≈ 8000 μm2), 10 nm Ti and 50 nm Pt were evaporated through a shadow mask. These evaporated Pt dots served as a hard mask during the subsequent wet etch (NH4OH, H2O2, and H2O solution) of the TiN top electrode. Reference capacitors of TiN/Ta2O5/TiN and TiN/Al2O3/TiN were fabricated in the same way as described above, just omitting the HZO ALD step, to obtain the permittivity of Ta2O5 and Al2O3.

Characterization: Grazing-incidence X-ray diffraction measurements were carried out on a Bruker D8 Discover (Cu-Kα radiation, λ = 0.154 nm) for structural analysis of the samples. The microstructural investigations of the samples containing Ta2O5 were performed by TEM using a JEM ARM 200F high resolution electron microscope operated at 200 kV. TEM analysis of the samples containing Al2O3 was carried out on a Zeiss Libra 200 TEM. Electrical measurements were carried out on a Cascade Microtech RF Probe Station with a Keithley 4200 SCS with a 4225-PMU and RPM remote amplifier, an HP 8110A pulse generator and a Tektronix TDS7154B digital oscilloscope. For pulsed charge–voltage measurements, capacitors were connected to the pulse generator while measuring the current and voltage via the oscilloscope with a 50 Ω and 1 MΩ input impedance, respectively. Rise and fall times of the voltage pulses were fixed to 150 ns each. If not stated otherwise, the duration of each individual pulse was set to 400 ns. Using small-signal capacitance measurements, the relative permittivity of the Al2O3 and Ta2O5 layers were determined to be 8 and 23.48, respectively.

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.

Keywords

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[1] J. Ho, T. R. Jow, S. Boggs, IEEE Electr. Insul. Mag. 2010, 26, 20.
[2] A. Evans, V. Strezov, T. J. Evans, Renewable Sustainable Energy Rev. 2012, 16, 4141.
[3] R. F. Ribeiro, B. K. Johnson, M. L. Crow, A. Arsoy, Y. Liu, Proc. IEEE 2001, 89, 1744.
[4] Q. Zhang, X. Wang, Z. Pan, J. Sun, J. Zhao, J. Zhang, C. Zhang, L. Tang, J. Luo, B. Song, Z. Zhang, W. Lu, Q. Li, Y. Zhang, Y. Yao, Nano Lett. 2017, 17, 2719.
[5] Q. Zhang, W. Xu, J. Sun, Z. Pan, J. Zhao, X. Wang, J. Zhang, P. Man, J. Guo, Z. Zhou, B. He, Z. Zhang, Q. Li, Y. Zhang, L. Xu, Y. Yao, Nano Lett. 2017, 17, 7552.
[6] Q. Zhang, J. Sun, Z. Pan, J. Zhang, J. Zhao, X. Wang, C. Zhang, Y. Yao, W. Lu, Q. Li, Y. Zhang, Z. Zhang, Nano Energy 2017, 39, 219.
[7] A. González, E. Goikolea, J. A. Barrena, R. Mysyk, Renewable Sustainable Energy Rev. 2016, 58, 1189.
[8] K. Yao, S. Chen, M. Rahimabady, M. S. Mirshekarloo, S. Yu, F. E. H. Tay, T. Sritharan, L. Lu, IEEE Trans. Ultrason., Ferroelectr.,Freq. Control 2011, 58, 1968.
[9] M. H. Park, H. J. Kim, Y. J. Kim, T. Moon, K. D. Kim, C. S. Hwang, Adv. Energy Mater. 2014, 4, 1400610.
[10] A. Chauhan, S. Patel, R. Vaiash, C. R. Bowen, Materials 2015, 8, 8009.
[11] B. Peng, Q. Zhang, X. Li, T. Sun, H. Fan, S. Ke, M. Ye, Y. Wang, W. Lu, H. Niu, J. F. Scott, X. Zeng, H. Huang, Adv. Electron. Mater. 2015, 1, 1500052.
[12] A. I. Khan, K. Chatterjee, B. Wang, S. Drapcho, L. You, C. Serraio, S. R. Bakaui, R. Ramesh, S. Salahuddin, Nat. Mater. 2015, 14, 182.
[13] A. I. Khan, D. Bhowmik, P. Yu, J. S. Kim, X. Pan, R. Ramesh, S. Salahuddin, Appl. Phys. Lett. 2011, 99, 113501.
[14] P. Zubko, J. C. Woidel, M. Hadjimichael, S. Fernandez-Pena, A. Sené, I. Luk’yanchuk, J.-M. Triscone, I. Šikhusev, Nature 2016, 534, 524.
[15] J. Y. Kim, H. Hamada, T. Moon, Y. J. Kwon, C. H. An, H. J. Kim, K. D. Kim, Y. H. Lee, S. D. Hyun, M. H. Park, C. S. Hwang, Nano Lett. 2016, 16, 4375.
[16] M. Hoffmann, B. Max, T. Mittmann, U. Schroeder, S. Slesazeck, T. Mikolajick, 2018 IEEE Int. Electron Devices Meeting (IEDM), IEEE, San Francisco, CA, USA 2018.
[17] A. K. Yadav, K. X. Nguyen, Z. Hong, P. García-Fernández, P. Aguado-Puente, C. T. Nelson, S. Das, B. Prasad, D. Kwon, S. Cheema, A. I. Khan, C. H. Ju, J. Ighilier, J. Junquera, L. Q. Chen, S. A. Muller, R. Ramesh, S. Salahuddin, Nature 2019, 565, 468.
[18] M. Hoffmann, F. P. G. Fengler, M. Herzig, T. Mittmann, B. Max, U. Schroeder, R. Negrea, P. Lucian, S. Slesazeck, T. Mikolajick, Nature 2019, 565, 464.
[19] S. Salahuddin, S. Datta, Nano Lett. 2008, 8, 405.
[20] T. Jagliński, D. Kochmann, D. Stone, R. S. Lakes, Science 2007, 315, 620.
[21] A. I. Khan, M. Hoffmann, K. Chatterjee, Z. Lu, R. Xu, C. Serraio, S. Smith, L. W. Martin, C. H. Ju, R. Ramesh, S. Salahuddin, Appl. Phys. Lett. 2017, 111, 253501.
[22] M. Hoffmann, A. I. Khan, C. Serraio, Z. Lu, S. Salahuddin, M. Pešić, S. Slesazeck, U. Schroeder, T. Mikolajick, J. Appl. Phys. 2018, 123, 184101.
[23] M. Hoffmann, M. Pešić, S. Slesazeck, U. Schroeder, T. Mikolajick, Nanoscale 2018, 10, 10891.
[24] M. McMillen, A. M. Douglas, T. M. Correia, P. M. Weaver, M. G. Cain, J. M. Gregg, Appl. Phys. Lett. 2012, 101, 242909.
[25] M. E. Lines, A. M. Glass, Principles and Applications of Ferroelectrics and Related Materials, Oxford University Press, Oxford, UK 2001.
[26] J. F. Scott, C. A. Paz de Araujo, Science 1989, 246, 1400.
[27] M. Hoffmann, M. Pešić, K. Chatterjee, A. I. Khan, S. Salahuddin, S. Slesazeck, U. Schroeder, T. Mikolajick, Adv. Funct. Mater. 2016, 26, 8643.
[28] V. L. Ginzburg, Zh. Eksp. Teor. Fiz. 1945, 15, 739.
[29] A. F. Devonshire, London, Edinburgh, Dublin Philos. Mag. J. Sci. 1949, 40, 1040.
[30] D. K. Simon, P. M. Jordan, T. Mikolajick, I. Dinsteiner, ACS Appl. Mater. Interfaces 2015, 7, 28215.
[31] M. Pešić, T. Li, V. De Lecce, M. Hoffmann, M. Materano, C. Richter, B. Max, S. Slesazeck, U. Schroeder, L. Larcher, T. Mikolajick, IEEE J. Electron Devices Soc. 2018, 6, 1019.

[32] S. Ezhilvalavan, T. Y. Tseng, J. Mater. Sci.: Mater. Electron. 1999, 10, 9.

[33] H. C. Lin, P. D. Ye, G. D. Wilk, Appl. Phys. Lett. 2005, 87, 182904.

[34] Y. Q. Wu, H. C. Lin, P. D. Ye, G. D. Wilk, Appl. Phys. Lett. 2007, 90, 072105.

[35] M. Hoffmann, U. Schroeder, C. Künneth, A. Kersch, S. Starschich, U. Böttger, T. Mikolajick, Nano Energy 2015, 18, 154.

[36] M. Pešić, M. Hoffmann, C. Richter, T. Mikolajick, U. Schroeder, Adv. Funct. Mater. 2016, 26, 7486.

[37] F. Ali, X. Liu, D. Zhou, X. Yang, J. Xu, T. Schenk, J. Müller, U. Schroeder, F. Cao, X. Dong, J. Appl. Phys. 2017, 122, 144105.

[38] P. D. Lomenzo, C.-C. Chung, C. Zhou, J. L. Jones, T. Nishida, Appl. Phys. Lett. 2017, 110, 232904.

[39] K. D. Kim, Y. H. Lee, T. Gwon, Y. J. Kim, H. J. Kim, T. Moon, S. D. Hyun, H. W. Park, M. H. Park, C. S. Hwang, Nano Energy 2017, 39, 390.

[40] B. B. Yang, M. Y. Guo, D. P. Song, X. W. Tang, R. H. Wei, L. Hu, J. Yang, W. H. Song, J. M. Dai, X. J. Lou, X. B. Zhu, Y. P. Sun, Appl. Phys. Lett. 2018, 113, 183902.

[41] J. Chen, Z. Tang, B. Yang, S. Zhao, Appl. Phys. Lett. 2018, 113, 153904.

[42] M. G. Kozodaev, A. G. Chernikova, R. R. Khakimov, M. H. Park, A. M. Markeev, C. S. Hwang, Appl. Phys. Lett. 2018, 113, 123902.

[43] K. Kühnel, M. Czernohorsky, C. Mart, W. Weinreich, J. Vacuum Sci. Technol., B 2019, 37, 021401.

[44] H. Cheng, J. Ouyang, Y.-X. Zhang, D. Ascienzo, Y. Li, Y.-Y. Zhao, Y. Ren, Nat. Commun. 2017, 8, 1999.

[45] A. A. Instan, S. P. Pavuny, M. K. Bhattarai, R. S. Katiyar, Appl. Phys. Lett. 2017, 111, 142903.

[46] C. Hou, W. Huang, W. Zhao, D. Zhang, Y. Yin, X. Li, ACS Appl. Mater. Interfaces 2017, 9, 20484.

[47] H. Pan, J. Ma, Q. Zhang, X. Liu, B. Guan, L. Gu, X. Zhang, Y.-J. Zhang, L. Li, Y. Shen, Y.-H. Lin, C.-W. Nan, Nat. Commun. 2018, 9, 1813.

[48] J. Müller, T. S. Böscke, U. Schröder, S. Mueller, D. Bräuhaus, U. Böttger, L. Frey, T. Mikolajick, Nano Lett. 2012, 12, 4318.