Giant energy storage effect in nanolayer capacitors charged by the field emission tunneling

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Abstract

We fabricate nanolayer alumina capacitor and apply high electric fields, close to 1 GV m$^{-1}$, to inject charges in the dielectric. Asymmetric charge distributions have been achieved due to the selectivity of the quantum tunneling process. Namely, the electrons near the Fermi level cannot tunnel into regions near the cathode, where the total energy would be less than the potential energy. This mechanism exhibits a strong tendency to populate charge traps located near the anode, i.e. the regions where their potential energy is the lowest. Such spatially selective charging of the dielectric allows a permanent bulk charge storage in the dielectric layer, even if the capacitor plates are short-circuited, provided that the temperature is sufficiently low so that the conductivity of the dielectric is negligible. The stored charge can be recovered if the temperature is increased above ~250 K for the dielectric tested, i.e. Al$_2$O$_3$. In our experiments, the total charge stored in the dielectric was up to seven and a half times higher than the charge stored on the capacitor plates. Also, measurements of the breakdown voltage show that the breakdown electric field, i.e. the dielectric strength, is independent of the thickness of the dielectric.

Keywords: dielectric absorption, soakage, battery action, dielectric relaxation, charge storage

(Some figures may appear in colour only in the online journal)

1. Introduction

The energy storage problem is of great importance now since the continuous usage of traditional energy carriers leads to their depletion. The environmental burden of the fossil fuels utilization is also very strong [1]. Many alternative methods of energy generation typically have highly varied production rates, e.g. changing from maximum generation capacity to zero within 12 h in case of the solar energy. Such methods of energy generation become economically viable only if sufficiently efficient methods of storing the energy can be found. The existing rechargeable batteries are mostly based on ionic effects, and by their nature have severe limitations on physically implementable charging/discharging rates, as well as growing costs of production due to the use of rare and difficult to produce chemical elements in many types of more efficient batteries. On the other hand, creation of all-electronic energy storage mechanisms would provide a valuable alternative.

The only known mechanism of the energy storage based on electrons is the usual capacitor, made of two metallic plates separated by a dielectric. There are two limiting factors
in such systems, namely the dielectric strength and the leakage [2–6], which, taken together, greatly restrict the possibility of employing capacitors as a replacement for common electrochemical energy storage systems.

Recently there has been a resurgence of interest in a potential role of electronic capacitors as energy storage devices [7–10]. Of particular interest is the possible increase of the energy density resulting from the reduction of spacing between the capacitor plates down to the nanometer scale. In such nanolayer capacitors, in which the thickness of the dielectric layer is on the order of a few nanometers, the dielectric strength was demonstrated to increase significantly [11–13]. Consequently, these nanocapacitors can tolerate substantially higher electric fields before a breakdown damaging of the dielectric layer would finally occur. We demonstrate here yet another important phenomenon occurring in nanolayer capacitors: the dielectric layer can be asymmetrically charged so that the amount of charge stored inside the dielectric can be many times higher than the charge accumulated on the capacitor plates. One of the most suitable, easily accessible, and actively researched materials for the dielectric layer of nanolayer capacitors is the aluminum oxide, which can be deposited using commercial atomic layer deposition machines [14–16]. This dielectric compound (Al2O3) typically exhibits low leakage currents, which is an important advantage in energy storage applications [13, 17, 18]. Since Al is a good conductor and Al2O3 is a good insulator, and both are relatively inexpensive, they can be a material of choice for building energy storage facilities. As of now, aluminum oxide finds applications in pulsed sources of power [9, 10, 15, 19].

Here we discover that the electrons can be effectively injected into the dielectric using the field emission effect. The electrons, when injected, become trapped because the amorphous alumina has a substantial density of the electronic traps. If the temperature is sufficiently low, the injected electrons remain stable. If the temperature is increased to the point when the electrons begin to diffuse through the dielectric then the trapped charge is released to the plates of the capacitor and a battery action is observed, since the electrons mostly diffuse to the nearest capacitor plate, which is the anode. Similar effects have been considered theoretically [20, 21] and now we provide an experimental evidence, obtained on capacitors with nanoscale dielectric layers. The most significant result is that the energy stored can be much greater (7.5 greater in the best case obtained so far) than the charge stored on the plates of the capacitor. The successful charge storage in the dielectric requires an asymmetric electronic density distribution. If the distribution is symmetric than the amount of charge flowing to the cathode and anode would be the same. Yet, if the distribution is asymmetric then one of the electrodes will get more charges, which leads to a significant discharge current, i.e. a release of energy. We demonstrate that such asymmetric charge distributions can be created by means of the field emission.

2. Experimental details

We fabricate and study Al nanolayer capacitors of the type Al/Al2O3/Al (samples S_1, S_2, S_3). In addition to those, for comparison, we have fabricated and studied Cr/Al2O3/Cr capacitors (sample S_b) as well. The Al and Cr top (25 nm) and bottom (25 nm) plates were produced by thermal evaporation onto a glass substrate in a vacuum of \(10^{-5}\) Torr. The alumina \((d = 10 \text{ nm for samples S_1, S_2, S_3, and } 9 \text{ nm for S_b})\) was deposited using trimethylaluminum/H2O-based ALD deposition at 80°C. The surface of the sample S_1 was \(A = 1 \text{ mm}^2\), with the capacitance \(C = 8 \text{nF}\). For samples S_2, S_3, and S_b these parameters were \(A = 2.25 \text{ mm}^2, 2.25 \text{ mm}^2, 1.21 \text{ mm}^2\) and \(C = 12 \text{nF}, 11.43 \text{nF}, 7 \text{nF}\) correspondingly. Measurements at cryogenic temperatures were performed using a sample-in-vacuum dipstick \(10^{-5}\) Torr, immersed in liquid N2. To shield the samples from external electromagnetic noises the samples were placed into a Faraday cage, located inside the dipstick.

Electrical measurements were performed with Keithley 6517B electrometer. The output voltage, \(V\), of this device was applied to the capacitor through a calibrated series resistor, \(R_{\text{d}} = 1 \text{ G}\Omega\). The current in the circuit, \(I\), was also measured by Keithley 6517B. The voltage on the sample (the tested capacitor), \(V_S\), was computed by the formula \(V_S = V - IR_{\text{d}}\). The 'high' voltage terminal was always connected with the top plate of the capacitors, which means that the positive voltage corresponds to the positive potential on the top plate.

The experiment was carried out in several successive phases: #1 charging the capacitor at \(T = 77 \text{ K}\), for the time duration of \(t_{\text{ch}}\), which was a few hours, at a fixed voltage on the sample \(V_S\), typically a few volts; #2 discharging through a series standard resistor \(R_{\text{d}} = 1 \text{ G}\Omega\) for a duration of 5 min, followed by a conformational discharging with the plates being short-circuited (without any resistor but through a copper wire) for 50 min, to further ensure that the plates of the capacitor are fully discharged; #3 warming up to room temperature, while the applied voltage was zero.

To obtain the current–voltage dependence ('I–V curve') and to measure the breakdown voltage, the voltage was applied in small discrete steps of \(\sim 0.1 \text{ V}\). The time delay between the voltage steps was 300 s for the capacitors with 20, 25, 30, 50 and 100 nm alumina thicknesses, and 100 s for the 7, 10 and 15 nm alumina thickness. The time delay is needed to achieve the true equilibrium value of the current for the set voltage. The measurements of the current in the circuit were performed using Keithley 6517B. This device is equipped with an adjustable voltage source, which also provides a voltage biasing. In case of the breakdown voltage measurement, the voltage was increased step by step up to the breakdown of the capacitor, which appeared as a sharp increase of the current. The breakdown electric field is calculated as \(E_{\text{br}} = V_{\text{br}}/d\), where \(V_{\text{br}}\) is breakdown voltage, \(d\) is a dielectric thickness.
The typical time dependence of the charging current for a full experimental cycle is shown in Figure 1(a) (insert) is that the charging current drops slowly at long times. The charging curve exhibits a plateau, which indicates that the current flowing into the capacitor is larger than the one expected for an ideal capacitor. We explain this current by the charge penetration in the dielectric, which is also known as soakage as well as dielectric absorption [17, 22, 23].

To better understand the charge storage in the capacitor, including its dielectric layer, we first integrate the discharge current and find the total charge exiting the capacitor. The integral charge (stage #2) was \( Q_P = \int i dt \approx 51.87 \text{nC} \), which correspond well to the charge stored on the capacitor plates estimated by the capacitor charge formula \( Q_P = C_{77} V_S = 52.36 \text{nC} \). Subsequent heating of the previously discharged capacitor exhibits a much larger integral charge, which is a highly surprising result. Namely, the total charge released due to the heating of the capacitor was evaluated at \( Q_D = \int i dt \approx 346 \text{nC} \), based on the time dependence plot for the discharge current \( i(t) \) (Figure 1(a)). Here the subscript \( \ll D \) implies that this charge was stored in the dielectric and was released during the heating stage. Not that the discharge current occurs only as the temperature reaches \( \sim 225 \text{K} \) and most of it is released at \( \sim 250 \text{K} \). An important observation here is that the direction of the heat-induced current matches the direction of the initial charging current (as measured in stage #1).

In Figure 2 the total charge, \( Q_D \), released during the stage #3 (warming up) is shown, normalized by the calculated charge stored on the capacitor plates in the fully charged states, \( Q_P = C_{77} V_S \), where \( V_S \) is the voltage on the capacitor, corresponding to the charging cycle (stage #1). The charge stored in the dielectric, \( Q_D \), is obtained, as explained above, by the integration of the current flowing out of the capacitor during the warming up (stage #3). As is illustrated in Figure 2, the dielectric-stored charge depends strongly on the charging voltage. At voltages \( V_S < 4 \text{V} \) for \( \text{Al}/\text{Al}_2\text{O}_3/\text{Al} \) and \( V_S < 4.7 \text{V} \) for \( \text{Cr}/\text{Al}_2\text{O}_3/\text{Cr} \) the stored charge is near zero. As we increase the charging voltage to the level at which the field emission leakage current becomes significant (Figure 2 insert), we observe a strong increase of the stored charge \( Q_D \). The normalized charge reaches its maximum value of \( Q_D/Q_P = 6.6 \) (corresponding to the charging voltage \( V_S = 4.8 \text{V} \) and the electric field of \( 0.48 \text{GV/m} \), which is \( \sim 25\% \) lower than the breakdown voltage (see below) measured for \( \text{Al}/\text{Al}_2\text{O}_3/\text{Al} \) nanolayer capacitors. Thus, we discover that the charge stored in the dielectric can be much larger than the charge stored on the capacitor plates. The results on a Cr film capacitor confirmed the finding: The maximum normalized charge was \( Q_D/Q_P = 6.9 \) (corresponding to the charging voltage \( V_S = 5.1 \text{V} \)). Further increase of the charging voltage leads to a steep drop of the stored charge \( Q_D \).

The voltage–current dependence of two typical nanolayer capacitors is shown in Figure 2(insert). At low temperature (\( T = 77 \text{K} \) and low voltages, the leakage current is so low that it is undetectable. Yet, at \( T = 295 \text{K} \) the leakage is visible
even at low voltages, at which the field emission effect is negligible. As the voltage exceeds some threshold, \( V_\text{th} \), we detect the field emission current, which increases roughly exponentially with the voltage on the capacitor, \( V_S \). At \( T = 77 \text{ K} \), the \( V-I \) curves show some hysteresis, but only during the first cycle of the sweeping voltage. If the voltage is increased to the maximum and decreased to zero and then the \( V-I \) curve is measured again then the hysteresis does not occur (at \( T = 77 \text{ K} \)). We explain this fact by the conjecture that the electrons enter the dielectric in the first charge cycle, get trapped by the dielectric and do not move away as the voltage is reduced to zero. The circles on the figure 2(insert) correspond to a \( V-I \) curve measured after the sample was warmed up to the room temperature and then cooled again to 77 K. This curve shows that the effect is reproducible, and the charges can indeed be removed from the dielectric if the temperature is increased to room temperature. Additional confirmation to this conclusion comes from the \( T = 295 \text{ K} \) curve (the curve #1 in figure 2(insert)). At this high temperature the charges cannot get trapped because the charges are mobile. This fact is clearly illustrated by the corresponding \( V-I \) curve, which exhibits a significant leakage current even at low voltages. Correspondingly, the \( V-I \) curve always shows the same amount of hysteresis, even if the voltage is cycled many times.
There is an increased of $Q_D$ as the time is increased up to $\sim 10-20$ h. In this respect such nanolayer capacitors resemble rechargeable batteries which require a long time to be charged.

We also performed experiments to establish stability of the stored charge. The sample S_3 was charged at a voltage $V_S = 4.82$ V, discharged for 5 min with the resistor and discharged for 50 min with short-circuited plates, at 77 K. Then the stored charge was measured giving us $Q_D = 275$ nC. In the subsequent experiment all steps were the same but the discharge with shorted plates continued for 136 h. The resulting charge was $Q_D = 214$ nC. Thus, we demonstrate that the charge is quite stable even if the plates are short-circuited for a long time.

The maximum efficiency observed in our experiments was 7.5, in the sense that the charge stored in the dielectric was 7.5 times higher than the charge stored on the capacitor plates during the charging. To our knowledge this is much larger than any value reported previously [24–26]. We also estimated the energy density. The total energy was $W_D = Q_D/2C \approx 5.2 \, \mu J$. The volume of the dielectric and the mass of the dielectric have been evaluated using standard table value. Then the resulting energy density is $w = W_D/(Ad) = 520 \, J \cdot cm^{-3}$. The results are shown in figure 4. An important finding there is that, to achieve high energy density, the charging voltage needs to be precisely tuned and the charging time needs to be sufficiently long. This is higher than $\sim 307 \, J \cdot cm^{-3}$, which is the highest value we are aware of, achieved previously in Au/SrTiO$_3$/$La_{0.67}Sr_{0.33}$MnO$_3$ capacitors [27]. If expressed per unit mass the energy density is $\sim 200 \, J \cdot g^{-1}$, assuming the density [28] of the alumina 2.6 g · cm$^{-3}$.

4. Discussion

The observed current produced upon the heating of the capacitor is entirely due to release of the charge previously accumulated in the dielectric layer [22, 23, 29]. Furthermore, the direction of this additional current demonstrates that it cannot be attributed to dielectric polarization from hindered movement of dipoles, which constitutes one of the two main mechanisms of dielectric response [30]. A discharge current from this type of polarization flows in the same direction as the conventional discharge current from the capacitor plates, i.e. in the opposite direction of the charging current. Yet, the discharge current we measure as we increase the temperature flows in the same direction as the charging current. We suggest that the secondary discharge current results from the other type of dielectric response, involving the charge accumulation due to tunneling and subsequent trapping of electrons at localized sites in the dielectric layer. This process leads to the formation of localized trapped charge in the dielectric, which cannot be dissipated by thermal fluctuations at cryogenic temperatures even when the applied voltage is reduced to zero.

The main factor determining the filling of localized electron traps appears to be the charging voltage. At low charging voltages $V < V_{th}$ there is no leakage current through the capacitor, and the electron traps in the dielectric layer primarily remain unoccupied (figure 5(a)). Here, $V_{th}$ is the threshold voltage at which the field emission leakage current through the capacitor begins (figure 2, insert). The filling of traps starts at $V > V_{th}$, at the onset of the field emission. Note that the average energy of the charge traps located near the anode is lower since the electrons are attracted to the anode. At charging voltages exceeding $V_{th}$ electrons can tunnel into localized trap sites with the energy below the Fermi level, i.e. only those which are located close to the anode [31, 32] (figure 5(b)). Thus, the field emission effect produces a strongly nonuniform distribution: more charges are injected
into the region near the anode while the region near the cathode is completely depleted of extra electrons since the electrons cannot tunnel in the traps in that region, since the energy of such traps is higher. The resulting trapped charge distribution in the dielectric layer is substantially inhomogeneous, with a progressively larger concentration of trapped electrons closer to the anode.

If the capacitor is discharged at low temperature, the majority of trapped electrons remain in the dielectric layer, since the thermal fluctuations are insufficient for the electrons to escape from the trapping sites. This is clear also from the fact that at low temperature the measured diffusive electronic conductivity is undetectable (i.e. the conductivity occurring at low bias).

When the temperature is increased in the later stage of the experiment, the energy of thermal fluctuations becomes sufficient for freeing electrons from the trapping sites. Therefore, this stage of the experiment essentially represents a thermal spectroscopy analysis (see figure 6) of electron traps: At any given temperature the electrons leaving the dielectric layer are such that are trapped at sites with the trapping energy of the order of $k_B T$. Therefore, at a sufficiently high temperature many electrons regain mobility and move towards the nearest electrode. Since the concentration of trapped charges was larger close to the anode, we observe the asymmetric discharge current, matching the direction of the charging current (figure 1(a)). In this thermal escape process the electrons diffuse to the anode since it is the closest electrode to the majority of them.

To confirm the fact that the electron mobility is high at room temperature compared to the cryogenic temperatures, we present a measurement of the leakage current at $T = 295$ K, shown in figure 2 (insert). In this figure the low-voltage leakage is visible on the room temperature curve. This leakage is below the noise level at $T = 77$ K. This fact explains the need of low temperatures to operate the charge storage function of the dielectric layer in the capacitor.

Figure 5. Schematic representation of the suggested mechanism: Charge injection into the dielectric region adjacent to the anode, by the field emission mechanism. The gray lines represent empty traps, and the blue lines represent the filled traps. Electrons can only fill up the traps which are lower in energy compared to the Fermi level.

Figure 6. Discharge current versus temperature, at zero applied voltage. The plots show the thermal escape of electrons from their traps. The curves represent a form of thermal spectroscopy. The time (19, 24 and 29 h) indicated is the charging time, while the charging voltage was $V_S = 5.1$ V. (Insert) The breakdown electric field (i.e. the dielectric strength) as a function of the dielectric film thickness, obtained on capacitors with Al electrodes. The dielectric strength appears independent of the film thickness at the scale between 7 and 100 nm.

If the charging voltage greatly exceeds $V_{th}$, electrons tunneling from the cathode can access traps with higher energy (figure 5(c)), i.e. those near the cathode. This leads to a more homogenous charge distribution in the dielectric layer. As a result, the difference between the numbers of electrons freed from traps closer to the anode and from those closer to the cathode upon heating of the capacitor is reduced (figure 2). For a certain value of the charging voltage, the charge reaching both electrodes upon the thermal discharge becomes identical, and we no longer observe a discharge current.

It should be noted that the efficiency of a capacitor to store energy is also limited by its dielectric strength. Yet, we
have observed (figure 6, insert) that the strength of the electric field at which the breakdown occurs is considerably larger than the field needed to charge the dielectric and it is independent of the thickness (figure 6, insert) of the dielectric. Thus, employing nanolayer dielectrics, needed for an efficient field emission charging, does not negatively impact the capacitor performance.

To analyze the effect of field emission on the measured current we analyze the current versus voltage dependence. The expression for the field emission current density is:

\[ J = e^3 E^2 / (8\pi \hbar e \phi_b) \cdot \exp[-8\pi (2m^* / h)^{1/2} / \phi_b^{3/2} / 3hE] \]

where \( J \) is the current density, \( e \) is the electronic charge, \( h \) is the Planck’s constant, \( \phi_b \) is metal-insulator energy barrier height, \( m^* \) is effective electron mass in the insulator. For the sake of the analysis, we will use voltage \( V \), which is related to the electric field \( E \) as \( V = Ed \), where \( d \) is a dielectric thickness. The current density \( J \) is calculated as \( J = I/A \), where \( A \) is the area of the capacitor and \( I \) is the measured current. Then, the equation for the field emission current become:

\[ I = e^3 A V^2 / (8\pi \hbar e \phi_b^3) \cdot \exp[-8\pi (2m^* / h)^{1/2} / \phi_b^{3/2} / 3hV_s]. \]

According to the equation, it is useful to plot the logarithm of the current divided by the voltage squared, \( \ln(I/V_s^2) \), versus the inverse voltage, \( 1/V_s \). The results are shown in figure 7. In the first plot (a) the initial dependence is shown, while the second plot (b) represents the dependence taken in the second sweep, when the dielectric was charged. The dependence is expected to be linear in these coordinates. The linear fits show good agreement with the data. Thus, the field emission effect is confirmed. It is interesting to note that in the second measurement the barrier height is almost twice larger. We take this fact as evidence confirming the trapping of additional charges in the dielectric.

5. Conclusions

We fabricate and study Al/Al₂O₃/Al and Cr/Al₂O₃/Cr nanolayer capacitors to optimize the process of the energy storage by purely electronic mechanisms (without involvement of ionic effects). It is found that the field emission process is able to selectively charge the layer of the dielectric close to the anode, which can be referred to as spatially selective dielectric soaking. The charge can be reliably stored in the dielectric layer and remains intact even if the capacitor plates are short-circuited, provided that the temperature is sufficiently low, i.e. lower than \(~200 \text{ K}\) in the considered cases. The stored charge can be released into the capacitor plates by heating the system to room temperature, or at least up to \(~225 \text{ K}\). We discover that the charge stored in the dielectric exceeds strongly the charge stored on the plates of the capacitor. The largest ration observed, between the charge stored on the dielectric and the charge stored on the capacitor plates, was \(~7.5\). The total charge stored in the dielectric corresponds to the energy density \(~520 \text{ J} \cdot \text{cm}^{-3}\). Also, the nanolayer capacitors show excellent thermal stability as their capacitance does not change with temperature. The ratio of the capacitances of the capacitor at liquid nitrogen temperature to room temperature was in the range between 0.93 and 0.97.

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