The phenomenon of resistive switching (RS), which was initially linked to non-volatile resistive memory applications, has recently also been associated with the concept of memristors, whose adjustable multilevel resistance characteristics open up unforeseen perspectives in cognitive computing. Herein, we demonstrate that the resistance states of $\text{Li}_x\text{CoO}_2$ thin film-based metal-insulator-metal (MIM) solid-state cells can be tuned by sequential programming voltage pulses, and that these resistance states are dramatically dependent on the pulses input rate, hence emulating biological synapse plasticity. In addition, we identify the underlying electrochemical processes of RS in our MIM cells, which also reveal a nanobattery-like behavior, leading to the generation of electrical signals that bring an unprecedented new dimension to the connection between memristors and neuromorphic systems. Therefore, these $\text{Li}_x\text{CoO}_2$-based MIM devices allow for a combination of possibilities, offering new perspectives of usage in nanoelectronics and bio-inspired neuromorphic circuits.

The current interest in the field of resistive switching (RS) materials has recently been amplified largely by an enlightening re-investigation of TiO$_2$ film devices connecting RS to the concept of memory resistors (memristors). This remarkable connection has highlighted mainly the non-volatile adjustable (multilevel) resistance characteristics open up unforeseen perspectives in cognitive computing. Herein, we demonstrate that the resistance states of $\text{Li}_x\text{CoO}_2$ thin film-based metal-insulator-metal (MIM) solid-state cells can be tuned by sequential programming voltage pulses, and that these resistance states are dramatically dependent on the pulses input rate, hence emulating biological synapse plasticity. In addition, we identify the underlying electrochemical processes of RS in our MIM cells, which also reveal a nanobattery-like behavior, leading to the generation of electrical signals that bring an unprecedented new dimension to the connection between memristors and neuromorphic systems. Therefore, these $\text{Li}_x\text{CoO}_2$-based MIM devices allow for a combination of possibilities, offering new perspectives of usage in nanoelectronics and bio-inspired neuromorphic circuits.
and also an additional feature involving the occurrence of a significant electromotive force that results in the generation of electrical signals, which are more specific of a neuron. Remarkably, new insights into nanoionic-type memristive cells are coming into focus18.

**Results**

We have recently demonstrated15 the occurrence of large bipolar RS phenomena in MIM [Au/LixCoO2/doped-Si] devices, which however exhibited only two resistance states: ROFF (which corresponds to both the resistance of the pristine cell, and the highest resistance after voltage cycling) and RON (lowest resistance state), with a ROFF/ RON ratio in the range $10^4–10^5$. Here, we establish the multilevel character of this RS in MIM cells (schematic view illustrated in Fig. 1a) containing LixCoO2 thin films (whose structure is shown in Fig. 1b and 1c). Indeed, as an example shown in Fig. 1d, four well-separated stable resistance states are observed, thus clearly pointing out high multilevel resistance tuning possibilities for such devices.

Furthermore, due to their cumulative response to excitations7,8,14,19, memristive devices are promising candidates in the field of cognitive computation5,7, allowing learning rules such as Spike-Timing Dependent Plasticity (STDP). Such biological synapse-like behavior is of crucial importance towards the realization of neuromorphic systems11. In this respect, we first establish the MIM cells conductance evolution -reflecting the synaptic weight change- by sequential programming pulses. Below a negative threshold value (about $-3 \, \text{V}$), successive substrate/tip voltage pulses of negative polarity yield a several decades conductance increase with the number of pulses (red plots in Fig. 1e). Subsequent pulses of positive polarity yield back a conductance decrease (blue plots in Fig. 1e), thus highlighting the memristive additive behavior of the films. Then, in a second step, we investigated the synapses plasticity as a function of the stimulation rate. This is measured through the evolution of the current ratio $i_{\text{fin}}/i_{\text{ini}}$ between the current measured after $(i_{\text{fin}})$ and before $(i_{\text{ini}})$ twenty non-overlapping pulses, applied at different frequencies, $f$. Fig. 1f clearly shows a strong frequency-dependent behavior, with the $i_{\text{fin}}/i_{\text{ini}}$ ratio ranging from 2 up to $10^3$.

These observations and the importance of their potential application, require a better understanding of the underlying electrochemical mechanisms that govern such a behavior. In this respect, we first discuss the issue of filamentary vs homogeneous RS, which is very important, as a better downscaling may be achieved in the case of a homogeneous RS20,21. As Li$_x$CoO$_2$ is largely used in lithium ion batteries, an “homogeneous” switching would be likely. To demonstrate this point, we introduce a new original method of investigation that involves measuring the decrease in the MIM cells resistance from the

Figure 1 | Schematic diagram of a Li$_x$CoO$_2$-based MIM cell, structural characteristics of a Li$_x$CoO$_2$ film, and behavior of MIM cells under different kinds of action potentials. (a) Schematic diagram of a typical M/Li$_x$CoO$_2$/M cell (30 × 30 μm$^2$ for d, e and f). The probe/upper electrode contact resistance is in the $10^3–10^4$ Ω range, which is low, compared to the MIM resistance. (b) Bright-Field cross-section transmission electron microscopy (TEM) image of a Li$_x$CoO$_2$ film, exhibiting a mean c-axis direction nearly parallel to the substrate surface. (c) X-ray diffraction profile of the (003) reflection for a Li$_x$CoO$_2$ film. The c-parameter value derived from the peak position is 1.408 nm that points to a stoichiometry $x = 0.95$ (see Methods). (d) Lower/upper electrode successive I–V curves (0→$-6 \, \text{V}$→0 voltage ramps, 3 V.s$^{-1}$ sweeping rate); the first (in red) and the second (in green) curves include a 1 s waiting time period at $-6 \, \text{V}$; the third curve (in blue) includes a 2 s waiting time at $-6 \, \text{V}$. Four well-separated resistance states can be observed here. (e) The conductance of MIM cells (current measured at +1 V) increases after each consecutive set of 20 negative pulses of $-7 \, \text{V}$ ($\tau = 50 \, \text{ms}$, $T = 100 \, \text{ms}$, in red) and decreases after each consecutive set of 30 positive pulses of $+7 \, \text{V}$ ($\tau = 10 \, \text{ms}$, $T = 100 \, \text{ms}$, in blue) (f) the MIM conductance has been measured (at +1 V) before ($i_{\text{ini}}$) and after ($i_{\text{fin}}$) 20 non-overlapping pulses ($-7 \, \text{V}$, $\tau = 50 \, \text{ms}$); the corresponding ratio $i_{\text{fin}}/i_{\text{ini}}$ is plotted as a function of the pulse repetition frequency $f (=1/T)$, thus highlighting the strong influence of the pulse rate.
$R_{\text{OFF}}$ to the $R_{\text{ON}}$ state, as a function of the number of bias pulses applied, for different top electrode sizes. As illustrated in Figure 2, the number of pulses required for the resistance decrease depends dramatically on the top electrode surface area. The smallest MIM cells exhibit a higher rate of decrease in resistance—reflecting the reaction kinetics—than the largest cells. This indicates that some volume fraction is involved in the RS process. In addition, preliminary studies on 500 nm wide M/Li$_x$CoO$_2$/M cells show, after a very long bias application time, an increase in conductivity of the film surface surrounding the top electrodes (see Supplementary Information S1), which appears compatible with homogeneous RS.

The Au/Li$_x$CoO$_2$/Si configuration—not symmetric$^{22}$—of our cells involves Si as the bottom electrode: it corresponds to a solid state microbattery already reported by Ariel et al$^{15}$ for which, unlike the present study, no RS was observed, possibly due to their specific Li stoichiometry, x. In this case, when the bottom Si electrode is negatively polarized, Li$^+$ ions migrate towards the doped Si electrode, where they are reduced by forming Li$_x$Si complexes, thus yielding an electromotive force (EMF). The SiO$_2$ interface layer (thickness $\approx$ 9 nm, grown by thermal oxidation before Li$_x$CoO$_2$ deposition) behaves as a solid state electrolyte allowing Li$^+$ ion diffusion, while preventing electrical short circuit between the electrodes. While looking for the existence of such a SiO$_2$ electrolyte layer in our MIM cells, we found that just after the deposition of Li$_x$CoO$_2$ film on Si, the Li$_x$CoO$_2$/Si interface consists of a 2–3 nm thick native SiO$_2$ layer, which is considered to be too thin to avoid short circuiting. However, after the required post-annealing step (see Methods), we found that the SiO$_2$ thickness increased up to almost 17 nm, as confirmed by Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS) (see Supplementary Information S2 and S3).

In order to illustrate the occurrence of an EMF in our “nanobattery”, we applied a bias voltage on a MIM cell over a few minutes with the Si electrode being negatively polarized. This resulted, after bias removal, in an induced voltage, as evidenced by I–V curves using slow sweeping voltage rates (see Supplementary Information S4). Such a voltage is attributed to an EMF, and has been studied as a function of the applied bias duration. As illustrated in Fig. 3a, a negative bottom-top bias of $\sim$6 V leads first to a rapid decrease of the MIM cell resistance, corresponding to RS from $R_{\text{OFF}}$ to $R_{\text{ON}}$ (blue curve in Fig. 3a) and it is followed after several minutes, by a progressive increase of the EMF value, reaching about 400 mV after 30 minutes (red curve in Fig. 3a). Such a value, (independent of the top electrode area), is exceptionally high among EMF values reported for VCM cells$^{24}$. Interestingly for our Li$_x$CoO$_2$ MIM cells (involving alkali-metal ion redox reactions), the EMF is observed to arise after the $R_{\text{ON}}$ state is achieved, which underlines an opposite, complementary behavior, compared to electrochemical metallization memory (ECM) systems$^{25}$, or VCM systems involving oxygen ion related reactions$^{26}$. Furthermore, we observed that this EMF spontaneously decreases over a few minutes (see red curve in Fig. 3b), while the cell resistance remains surprisingly at its low resistance state $R_{\text{ON}}$ ($\approx 10^4$ $\Omega$, blue curve in Fig. 3b). Such a discharge time also confirms the electrochemical nature of the cell voltage. Indeed, the corresponding dielectric discharge time (which is roughly estimated in the 10$^{-5}$ s range) of the cell (with C in the 10$^{-9}$ F range) is seven orders of magnitude lower than the measured discharge time, ruling out any capacitive effects.

For the MIM cells, these observations lead us to propose a cobalt redox reaction involving lithium. For a negative silicon electrode polarization, cobalt is oxidized and lithium is reduced in silicon, as follows:

$$\text{Co}^{3+} \rightarrow \text{Co}^{4+} + e^{-} \quad (1)$$

$$\text{Li}^+ + e^{-} \rightarrow \text{Li} \quad (\text{Li}_x\text{Si complexes in Si}) \quad (2)$$

Although the whole phase diagram of the Li$_x$CoO$_2$ system is complex$^{25}$, the reported structure of Li$_x$CoO$_2$ in the field of batteries allows a qualitative insight on the RS of the MIM cells. For $x \approx 0.94$, Li$_x$CoO$_2$ is considered as a band insulator, whereas for $x \approx 0.75$, it is a metal. In between, the metallic and insulating phases coexist$^{26,27}$. This phase coexistence most likely occurs through the formation of puddles, like in another correlated oxide, such as V$_2$O$_3$ (ref. 28). A global x decrease is associated to the evolution of these coexisting phases: the metal-conducting phase ($x \approx 0.75$), progressively dominates over the insulating one ($x \approx 0.94$), corresponding to an insulator-to-metal transition. In our MIM cells, the pristine Li stoichiometry x of Li$_x$CoO$_2$ has been determined by X-ray Diffraction measurements to be $x \approx 0.95$ (with the Co$^{3+}$ concentration being almost constant throughout the film thickness, see Supplementary Information S5). A negative Si polarization leads to the oxidation of Co (which corresponds to equation (1)), and also to the migration of Li$^+$ ions into the Si electrode (where they are reduced, corresponding to equation (2)), with a consequent decrease of x in the film. The RS from $R_{\text{OFF}}$ to $R_{\text{ON}}$ (see blue curve in Fig. 3a) can thus be related to the growth of metal-like puddles in the film bulk, ultimately connecting the top and bottom surfaces of the film. It is noted that Ariel et al. did not observe RS in their batteries, which can be accounted for by their pristine stoichiometry $x = 0.7$. Further negative voltage application, during a much longer time (in the minutes range) yields a progressive occurrence of an EMF (red curve in Fig. 3a), which reflects the accumulation of Li in Si, and can be associated to a further x decrease in the Li$_x$CoO$_2$ film.

After bias voltage application removal, the EMF spontaneously completely discharges, which reflects Li reinsertion in the Li$_x$CoO$_2$ film and thus an x increase. However, this should lead to a recovery of the initial cell resistance. In contrast, at room temperature it remains at its $R_{\text{ON}}$ value ($\approx 10^4$ $\Omega$). In our case, switching from the $R_{\text{ON}}$ to the $R_{\text{OFF}}$ state can be, nevertheless, achieved by the application of a positive bottom-top bias ($\geq +2$ V) (ref 15). In addition, we have observed that this switching recovery from $R_{\text{ON}}$ to $R_{\text{OFF}}$ can also be induced by heating (see Supplementary Information S6). This $R_{\text{ON}}$ stability after the EMF discharge might be correlated to an electrochemical phenomenon already observed in Li$_x$CoO$_2$ electrochemical cells involving electrodes different from Si$^{26}$, which is attributed to the fact that it is difficult to re-intercalate all the extracted lithium ions$^{26}$. Another possibility, from a physical point

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**Figure 2** | MIM cell resistance as a function of the number of sequential applied voltage pulses, for different upper electrode surfaces. The MIM cell resistance is plotted as a function of the number of $-8$ V pulses ($\tau = 50$ ms, $T = 150$ ms), for various top electrode areas, from 500 × 500 $\mu$m$^2$ down to 10 × 10 $\mu$m$^2$ (dotted lines are a guide to the eye). The resistance compliance is low enough ($10^{4}$–$10^{0}$ $\Omega$) to avoid any capacitive effects.
of view, is that energy must be supplied to some Li\(^+\) ions which may be trapped in the SiO\(_2\) layer, to reinsert them all in the LixCoO\(_2\) film. On the other hand, our RS proposed mechanism leaves an open question about the pulse rate dependence, which cannot be linked to the onset of the EMF, since the time scales of the pulse frequency and the EMF are clearly different. This dynamic aspect of the involved process is being actively investigated.

In an effort to better understand the origin of the RS mechanism, we considered a CP-AFM/LixCoO\(_2\) direct nanometric contact, which enables us to focus on the changes in the LixCoO\(_2\) film alone. In contrast to the MIM cells, a direct [(CP)AFM tip/LixCoO\(_2\) surface] contact leads to opposite polarity modifications. For example, as shown in Fig. 4b, a sample-to-probe bias of \(-8\) V results in a large surface conductivity decrease, whereas a MIM cell, in its pristine state, switches to a state (R\(_{\text{ON}}\)) which is several orders of magnitude more conducting, for the same applied bias voltage (Fig. 4a).

Such opposite switching polarity behavior already suggests a different mechanism. Nevertheless, in order to gain further insight we shall try to identify the specific electrochemical processes involved. Therefore, we investigated the influence of the ambient water vapor pressure (P\(_{\text{H}_2\text{O}}\)) on the change of surface conductivity. In the tip-surface case, a water meniscus exists at the interface at ambient air. Its size, which strongly depends on the relative humidity (RH) and thus on the water vapor pressure P\(_{\text{H}_2\text{O}}\) (ref. 31), is critical for conducting-probe-mediated electrochemical reactions\(^{32}\). As shown in Fig. 5a, at P\(_{\text{H}_2\text{O}} = 4\) Torr, surface conductivity can be easily tuned: more (less) conducting areas are obtained after scanning rectangular regions at a +8 V (−8 V) sample-tip bias. Using the same procedure, a lower
PH$_2$O tuning again (Fig. 5d). Under ambient air (60% RH at 25°C), these results attest to the kind of involved reactions we previously suggested, i.e., local cobalt redox reaction, coupled to the meniscus water redox reaction (illustrated in Fig. 5e). The reactions can be written as follows, for a lower-electrode negative polarization:

$$\text{Co}^{4+} + e^- \rightarrow \text{Co}^{3+}$$  \hspace{1cm} (3)  \\
$$\text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^-$$  \hspace{1cm} (4)

At this point, it is worth noting that a tip-surface contact without water meniscus should yield similar results to MIM cells. However, we did not observe any resistance changes (see Fig. 5c) in this case. This underlines that a (CP) AFM tip cannot be considered as a simple electrochemical cell; assuming the lower Si electrode is negatively polarized, water is oxidized and cobalt is reduced, yielding a less conducting film surface.

Figure 5  |  Electrical images, showing the evolution of the surface-conductivity of Li$_x$CoO$_2$ films, as a function of the ambient water vapor pressure, and schematic diagram of the proposed electrochemical reactions occurring in a (CP) AFM probe/film contact. (a), (b), (c), (d) (CP) AFM images from a 10 × 10 μm$^2$ region recorded with +8 V after scanning an area of 4 × 2 μm$^2$ with two different sample-tip biases of +8 V and −8 V, resulting in surface-conductivity modifications of the Li$_x$CoO$_2$ film surface; the influence of the water vapor pressure $P_{\text{H}_2\text{O}}$ on the conductivity modifications is shown in (a, b and c). For $P_{\text{H}_2\text{O}} = 4 \times 10^{-2}$ Torr, almost no modification is distinguishable as shown in (c). When $P_{\text{H}_2\text{O}}$ is increased back to 4 Torr, the surface-conductivity can be tuned again as shown in (d). (e) Schematic diagram of the mechanism proposed for the tip-sample configuration. The condensation water capillary meniscus forms an electrochemical cell; assuming the lower Si electrode is negatively polarized, water is oxidized and cobalt is reduced, yielding a less conducting film surface.

$P_{\text{H}_2\text{O}}$ ($4.10^{-2}$ Torr) yields weaker modifications (Fig. 5b), and at $P_{\text{H}_2\text{O}} = 4 \times 10^{-3}$ Torr, no conductivity modulation can be achieved (Fig. 5d). Under ambient air (60% RH at 25°C, thus $P_{\text{H}_2\text{O}} = 14$ Torr), conductivity modifications even extend to a much larger area than the scanned area (see Supplementary Information S7). These results attest to the kind of involved reactions we previously suggested, i.e., local cobalt redox reaction, coupled to the meniscus water redox reaction (illustrated in Fig. 5e). The reactions can be written as follows, for a lower-electrode negative polarization:

$P_{\text{H}_2\text{O}}$ holds the metal-insulator transition, is coupled to the lithium intercalation/deintercalation in the conducting silicon electrode, whereas in the (CP) AFM probe-film case, it is coupled to the water redox reaction. Furthermore, we have observed a progressive occurrence of an EMF more specific of a neuron in MIM devices, which follows the switching from $R_{\text{OFF}}$ to $R_{\text{ON}}$ state, and disappears before the metal-to-insulator reverse transition. This latter transition is not spontaneous, but is induced by applying either voltage or heating. This specific behavior, observed for the first time in Li$_x$CoO$_2$ thin film-based MIM solid-state cells, brings together a new combination of possibilities with a potential easy integration on Si-based devices, hence offering exciting new perspectives in nanoelectronics and neuromorphic implementation.

### Methods

#### Samples.
Li$_x$CoO$_2$ thin films were deposited on degenerately doped p-type Si (111) wafers by RF magnetron reactive sputtering (Alcatel SCM 600 apparatus) using a stoichiometric (x = 1) Li$_x$CoO$_2$ target, with an applied RF power of 500 W. The films were grown in a 3/1 Ar/O$_2$ (2.2 Pa) atmosphere and a bias of ~50 V was applied to the substrate. The films (100 nm, as determined by a profilometer) were subsequently heated to 550 °C for 1 h in air in order to obtain the R-3m high-temperature (HT) Li$_x$CoO$_2$ phase.

Deposition of gold electrodes on Li$_x$CoO$_2$ films was performed by conventional Joule evaporation under secondary vacuum (10$^{-5}$ mbar). Nickel deposition masks, with various aperture sizes (≥10 μm) were used. For smaller electrodes (Supplementary information), electron-beam assisted deposition has been utilized (Au(40 nm)/Ti(10 nm)).

#### Measurements.

The Li$_x$CoO$_2$ stoichiometry x was determined by X-ray diffraction, using a MAR345 system mounted on a rotating anode generator (molybdenum target). The K$_\alpha$ radiation (0.0709 nm) is selected by a doubly curved multilayer optics that delivers a nearly parallel beam. The film surface is set perpendicular to the incident X-ray beam. In this geometry and due to the specific crystallographic texture of the film, the Bragg reflection onto the (003) planes of the crystallites is expected to appear as a homogeneous circle. The background originating from the diffraction by the rather thick silicon substrate is low enough to allow recording good quality data within a few hours exposure time. Quartz powder is further used to check precisely the sample to detector distance. The overall precision is estimated to ca. 1%.

Electrical characterizations and modifications of films were performed by (CP) AFM with a home-made system (Resiscope) for local contact resistances and current measurements, derived from a Multimode Nanoscope III AFM setup (Veeco) for ambient temperature measurements, and derived from an Envioscope AFM instrument (Veeco) for measurements under vacuum and under elevated tempera-
tutes (up to 190 °C). Pt-Si tips, as well as conducting diamond coated Si tips were used (spring constant ≈ 2 N/m).

Cross-sectional TEM studies at higher magnification were carried out on Li0.5CoO2 samples using a JEOL 2100 transmission electron microscope working at 200 kV. The samples were prepared by mechanical grinding, followed by ion milling using a GATAN Precision Ion Polishing system.

XPS measurements have been performed using a PHI 5000 Versaprobe spectrometer (Physical Electronics) operating at a base pressure of 1 × 10⁻⁹ Pa. A focused monochromatized Al Kα X-ray source (hv = 1486.6 eV) was used at 15 kV. High resolution core level spectra were acquired with a 23.5 eV pass energy, an energy step of 0.1 eV and a 50 ms dwell time. The spectrometer was calibrated with Cu 2p3/2 and Cu LMM of clean copper at 932.7 eV and 918.7 eV respectively. The Ar ion beam conditions for depth profiling were as follows: Ar ion source was operated at 2 kV and the raster area was 2 × 2 mm². Each sputter cycle was set to 30 s, which corresponds to a sputter depth of 2.6 nm in SiO2.

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Author contributions
R.S. synthesized the films; P.A.S., T.M., G.A. and R.W. fabricated the devices, V.H.M. performed the film modifications by (CP) AFM; J.G., C.N.M., C.M.O., E.S., A.B., C.B.L., P.A.A., K.W., F.J., D.A. and K.M. performed the film characterizations; All authors contributed to the writing of the paper.

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