

ULTRARAM™: a low-energy, high-endurance, compound-semiconductor memory on silicon

Peter Hodgson

Lancaster University <https://orcid.org/0000-0001-5813-8772>

Dominic Lane

Lancaster University

Peter Carrington

Department of Engineering, Lancaster University, Lancaster, LA1 4YW, United Kingdom

<https://orcid.org/0000-0003-2107-5602>

Evangelia Delli

Lancaster University

Richard Beanland

University of Warwick <https://orcid.org/0000-0003-1749-4134>

Manus Hayne (✉ m.hayne@lancaster.ac.uk)

Lancaster University <https://orcid.org/0000-0001-5224-9156>

Article

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1 **ULTRARAM™: a low-energy, high-endurance, compound-**
2 **semiconductor memory on silicon**

3 Peter D. Hodgson,¹ Dominic Lane,¹ Peter J. Carrington,² Evangelia Delli,² Richard
4 Beanland³ and Manus Hayne^{1*}

5 ¹ Department of Physics, Lancaster University, Lancaster LA1 4YB, United Kingdom

6 ² Department of Engineering, Lancaster University, Lancaster LA1 4YW, United Kingdom

7 ³ Department of Physics, University of Warwick, Coventry, CV4 7AL, United Kingdom

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9 *Corresponding author: Manus Hayne m.hayne@lancaster.ac.uk

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ULTRARAM™ is a non-volatile memory with the potential to achieve fast, ultra-low-energy electron storage in a floating gate accessed through a triple-barrier resonant tunnelling heterostructure. Here we report the implementation of ULTRARAM™ on a Si substrate; a vital step towards cost-effective mass production. Sample growth was carried out using molecular beam epitaxy, by first depositing an AlSb nucleation layer to seed the growth of a GaSb buffer layer, followed by the III-V memory epilayers. Fabricated single-cell memories show clear 0/1 logic-state contrast after ≤ 10 -ms duration program/erase pulses of ~ 2.5 V, a remarkably fast switching speed for 10- and 20- μm devices. Furthermore, the combination of low voltage and small device capacitance per unit area results in a switching energy that is orders of magnitude lower than dynamic random access memory and flash, for a given cell size. Extended testing of the devices revealed retention in excess of 1000 years and degradation-free endurance of over 10^7 program/erase cycles, exceeding very recent results for similar devices on GaAs substrates.

24 A memory that is fast and non-volatile, with high endurance and low-energy logic-state switching, *i.e.*
25 a so-called universal memory, has long been dismissed as unachievable due to the apparently
26 contradictory physical properties such a device would require¹. Conventionally, a fast, high-endurance
27 memory seemingly necessitates a frail logic state that is easily lost, even requiring constant refreshing;
28 for example, dynamic random access memory (DRAM). In contrast, a robust, non-volatile logic state
29 ostensibly requires large amounts of energy to switch, which (gradually) damages the memory
30 structure, reducing endurance; for example, flash. The detrimental aspects of these two conventional
31 memories have stimulated research into a range of emerging memory technologies, such as resistive
32 RAM², magnetoresistive RAM³ and phase-change memory⁴. Significant progress has been made, with
33 emerging memory products in small- or large-scale commercial production, but, as with conventional
34 memories, the trade-off between logic state stability and switching energy remains. **ULTRARAM™**
35 breaks this paradigm via the exploitation of InAs quantum wells and AlSb barriers to create a triple-
36 barrier resonant-tunnelling (TBRT) structure. The 2.1-eV conduction band offset of AlSb with respect
37 to the InAs that forms the floating gate (FG) and channel, provides a barrier to the passage of electrons
38 that is comparable to the SiO₂ dielectric used in flash. However, inclusion of two InAs quantum wells
39 (of different thicknesses) within the TBRT structure, as shown in Fig. 1, allows it to become transparent
40 to electrons when a low voltage (~2.5 V) is applied, due to resonant tunnelling. By using the TBRT
41 heterostructure as the barrier between FG and channel, rather than the usual monolithic material, a
42 charge-based memory with extraordinary properties can be achieved.

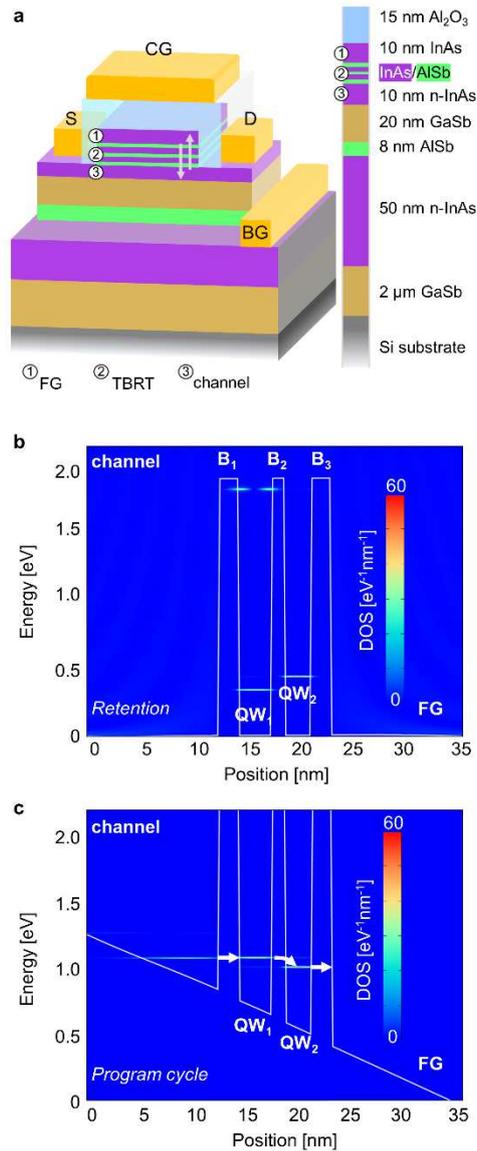
43 Incorporation of **ULTRARAM™** onto Si substrates is a vital step towards realising low-cost, high-volume
44 production. Si substrates offer several advantages over III-Vs, including mechanical strength and large
45 wafer sizes, thereby allowing fabrication of more devices in parallel and reducing production cost.
46 Moreover, Si is the preferred material for digital logic and has a highly mature fabrication route.
47 Integration of the complementary technologies of III-Vs and Si has historically been carried out by
48 wafer bonding techniques, but such approaches have drawbacks such as added complexity of
49 fabrication and differences of wafer size, often resulting in inefficient use of substrate material⁵. More

50 recently, heterogeneous epitaxy has offered a promising route towards the efficient co-integration of
51 III-Vs and Si. However, direct epitaxial deposition is challenging due to the polar (III-Vs) to non-polar
52 (Si) interface, lattice mismatch and differences in thermal expansion coefficients⁶⁻⁹. In order to prevent
53 defect formation and realise practical, high-performance, integrated, III-V devices on Si substrates,
54 careful consideration must be given to mitigate these challenges.

55 Here we report on the epitaxial incorporation of ULTRARAM™ heterostructures onto Si substrates,
56 their fabrication into devices and testing. Results show non-volatile, high-endurance operation that
57 exceeds recently reported results on GaAs substrates¹⁰.

58 **Memory concept**

59 ULTRARAM™ is a charge-based memory where the logic state is determined by the presence or
60 absence of electrons in a FG. As can be seen in Fig. 1, the FG is electrically isolated from the control
61 gate (CG) by Al₂O₃ dielectric, and from the underlying channel by the InAs/AlSb TBRT heterostructure.
62 The presence of electrons in the FG (defining a logic 0 state) depletes carriers in the underlying n-type
63 InAs channel, reducing its conductance. Thus, the charge state of the FG and, therefore, the logic state
64 of the memory is read non-destructively by measuring the current through the channel when a voltage
65 is applied between the source (S) and drain (D) contacts. The final component of the memory is the
66 InAs back-gate (BG), which allows voltages to be applied vertically across the gate stack for various
67 operations.



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69 **Fig. 1 | ULTRARAM™ device concept.** **a**, Schematic cross-section of an ULTRARAM™
 70 device with corresponding material layers. The floating gate (FG), triple-barrier
 71 resonant-tunnelling structure (TBRT) and readout channel are highlighted. Arrows
 72 indicate the direction of electron flow during program/erase operations. **b**, and **c**, Non-
 73 equilibrium Green's functions (NEGF) calculations of density of states alongside
 74 conduction band diagrams for no applied bias (*i.e.* retention) and program-cycle bias
 75 respectively. B_1 , B_2 and B_3 are the AlSb barrier layers. QW_1 and QW_2 are the InAs
 76 quantum wells in the TBRT.

77 The novel component of this memory is the TBRT structure¹¹, which, unlike single layer barriers, can
78 be switched from a highly electrically-resistive state to a highly conductive state by the application of
79 just ± 2.5 V. This is achieved by careful design of the thicknesses of the AlSb barriers and InAs quantum
80 well (QW) layers¹². When the memory is in the retention state (Fig. 1b), *i.e.* when no voltage is applied
81 to the device, the electron ground states in the TBRT QWs are misaligned with each other and are
82 energetically well above the 300-K electron populations of the InAs FG and channel layers. Indeed, the
83 non-volatility is strengthened by the QW ground states residing at an unusually high energy for a
84 resonant-tunnelling structure. This is due to a combination of the ultrathin QWs and the
85 extraordinarily low electron effective mass in InAs¹³. In this state, the TBRT provides a large barrier
86 that prevents electron transfer into or out of the FG. However, the application of a suitable bias across
87 the device tilts the conduction band such that the TBRT QW ground states align with occupied electron
88 states in the channel (during the program operation, Fig. 1c) or the FG (during the erase operation).
89 This allows electrons to move rapidly across the TBRT region in the intended direction by the
90 inherently-fast quantum-mechanical process of resonant tunnelling. Due to the low voltages required
91 and the extremely low capacitance per unit area of the device, ultra-low logical state switching
92 energies of 10^{-17} J are predicted for 20-nm feature size ULTRARAM™ memories^{12,14}, which is two and
93 three orders of magnitude lower than DRAM and flash respectively^{12,15}. ULTRARAM™ prototype
94 devices grown on GaAs substrates have previously exhibited non-volatile retention of 10^5 s and an
95 endurance of 10^6 program-erase cycles.¹⁰ Thus, the demonstration of devices grown on Si substrates
96 with similar or improved performance would be a major step towards commercialisation.

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98 **Epitaxy of III-Vs on Si and sample characterisation**

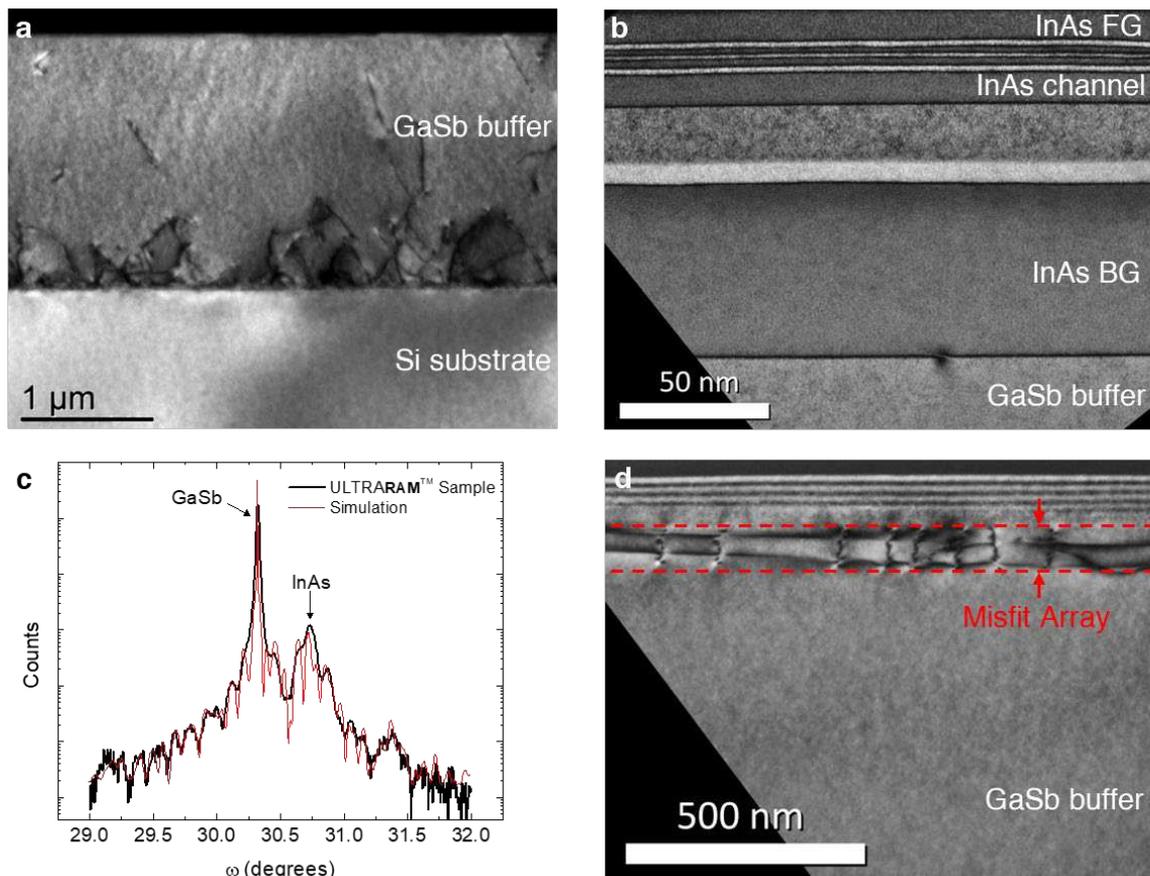
99 Sample growth on 3" n-type Si substrates was carried out by molecular beam epitaxy (MBE) on a Veeco
100 GENxplor system. The substrates have a 4° offcut towards the [0-11] crystal direction, creating
101 diatomic steps on the non-polar Si surface, which inhibits the formation of anti-phase domains (APDs)

102 during growth of polar III-V materials⁵. Prior to the growth of a complete structure with the
103 ULTRARAM™ memory layers, a GaSb buffer growth procedure was developed to provide a high-
104 quality III-V surface. To achieve this, *in-situ* thermal desorption of the Si wafer's native oxide was
105 followed by deposition a 17-monolayer AlSb nucleation layer, which forms into three-dimensional
106 islands¹⁶. These islands reduce the diffusion length of Ga atoms during the initial growth of the
107 subsequent 2- μm GaSb buffer, helping to promote two-dimensional epitaxy and preventing the
108 formation of planar twinning defects^{8,9,17}. The large lattice mismatch between the Si substrate and the
109 GaSb buffer of 12.3% is relieved by a periodic array of 90° interface misfit dislocations propagating
110 laterally along the Si-III/V interface¹⁸. A two-temperature-step GaSb growth method¹⁹ was used to
111 reduce the density of vertically propagating threading dislocations (see Methods section for more
112 details). Using this approach, a GaSb/Si buffer layer was obtained with a surface defect density of
113 $(2.5 \pm 0.1) \times 10^8 \text{ cm}^{-2}$, as measured by electron channelling contrast imaging (ECCI), and a root-mean-
114 square surface roughness of $1.9 \pm 0.2 \text{ nm}$, as measured by atomic force microscopy (AFM) by taking
115 the average of three $100 \mu\text{m}^2$ scans. High-resolution X-ray diffraction (XRD) measurements further
116 confirmed the high quality of the buffer layer. A rocking curve measurement of the GaSb (004) plane
117 revealed an extremely narrow peak with a full-width at half maximum of 172 arcsec. In addition, XRD
118 pole-figure measurements of the GaSb (111) plane indicate that the buffer is either free from, or has
119 an extremely low density of, planar twins¹⁷. Cross-sectional transmission electron microscope (TEM)
120 images, such as Fig. 2a, show that the buffer layer is APD free, and that the majority of threading
121 dislocations are confined to the first 500 nm of GaSb.

122 These results demonstrate that the GaSb buffer layer on Si is of high quality, and suitable for
123 deposition of the ULTRARAM™ memory layers. The first epilayers grown on such a buffer are the 50-
124 nm InAs n-type BG and 8-nm AlSb barrier, which separates the BG from the active parts of the device,
125 as shown in Fig. 1a and Fig. 2b. Next, a 20-nm GaSb spacer was deposited, followed by a 10-nm InAs
126 n-type layer (channel) and the InAs/AlSb TBRT. The nominal TBRT layer thicknesses are 1.8 nm of AlSb,

127 3.0 nm of InAs, 1.2 nm of AlSb, 2.4 nm of InAs and 1.8 nm of AlSb. Finally, a 10-nm InAs FG completes
128 the structure. More information on the MBE growth of the sample is given in the Methods section.

129 The ECCI-measured surface defect density in the ULTRARAM™ sample was found to be
130 $(2.1 \pm 0.1) \times 10^8 \text{ cm}^{-2}$, which is slightly lower than that observed for the buffer. This is not surprising,
131 since interfaces with misfit strain, such as the GaSb/InAs/AlSb layers used here, are known to
132 encourage the recombination and termination of threading dislocations and are routinely used as
133 dislocation filters²⁰⁻²². A high-resolution XRD ω -2 θ scan of the memory sample, which displays clear
134 satellite peaks from the memory epilayers, is shown in Fig. 2c. Optimal fitting to the data is achieved
135 assuming 15% misfit strain relaxation in the InAs BG. Further investigation by TEM revealed the
136 presence of a misfit dislocation array at the interface between the GaSb buffer and InAs BG layer (Fig.
137 **2d**), which are responsible for this relaxation. These misfit dislocations do not propagate into the GaSb
138 layer above, and act as a threading dislocation filter. Remnant threading dislocations in the BG are not
139 expected to significantly influence device performance as this layer is only used as a ground contact
140 when biasing the CG.



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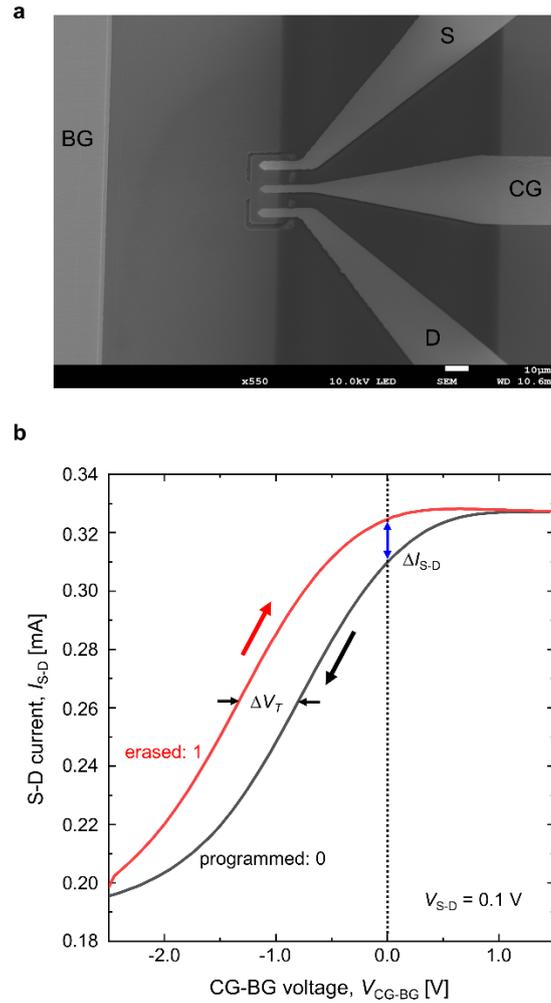
Fig. 2 | III-V on Si Material characterisation. **a**, Dark-field $g = 220$ transmission electron microscope (TEM) image of a GaSb/Si buffer layer. **b**, Dark-field $g = 002$ TEM image of the ULTRARAM™ sample. Only the memory layers and the top of the GaSb buffer are visible in this image. A single 60° misfit dislocation is visible in the InAs/GaSb buffer interface. **c**, Experimental and simulated ω - 2θ high-resolution X-ray diffraction scan of the ULTRARAM™ sample. The Si substrate's diffraction peak occurs at a larger angle and is not shown in this scan. **d**, Dark-field $g = 220$ TEM image of the upper part of the structure. The specimen tilt of $\sim 20^\circ$ allows the misfit dislocation array in the InAs back gate (BG) / buffer layer interface to be seen. The lower and upper dashed lines indicate the intersection of this interface with the specimen surfaces.

154 **Basic memory operations**

155 Single bit ULTRARAM™ memory cells on Si substrates were fabricated at gate lengths of 10- and 20-
156 μm . Fig. 1a shows a schematic cross-section of a fabricated memory cell. A scanning electron
157 microscope image of a fabricated 10- μm gate-length device is shown in Fig. 3a with device terminals
158 labelled. Here, we define a charged FG as logic 0, and the absence of charge as logic 1. Program and
159 erase cycles, to charge and discharge the FG respectively, use voltage pulses of $\leq \pm 2.55$ V on the CG.

160 The memory's readout logic is demonstrated in Fig. 3b. A 4-terminal measurement is used, where the
161 CG to BG voltage ($V_{\text{CG-BG}}$) is varied whilst measuring the current from S to D under a constant 0.1 V S-
162 D bias ($V_{\text{S-D}}$). A negative $V_{\text{CG-BG}}$ bias produces carrier depletion of the channel layer, similar to that
163 observed in an n-type metal-oxide field-effect transistor, resulting in an observable increase in
164 resistance with increasing negative bias. When the device is in a programmed state (0), the negative
165 charge on the FG enhances the CG bias such that depletion of the channel occurs at a lower $V_{\text{CG-BG}}$.
166 The difference between the two states allows a 0.5 V threshold-shift (ΔV_{T}) to be observed, centred at
167 a $V_{\text{CG-BG}}$ of approximately -1.25 V, as shown in Fig. 3b. By increasing $V_{\text{CG-BG}}$ to ± 2.5 V the memory can
168 be programmed/erased, creating the hysteresis seen in the data. Note that the joining of the states at
169 > 0.8 V positive CG bias does not indicate program and erase operations: the memory window cannot
170 be observed under high positive gate bias due to saturation of the carrier population in the channel.

171 These results demonstrate that the FG logic state can be read non-destructively. Furthermore, the
172 program/erase voltage is around 10 times lower than that of flash memories^{15,23}, corresponding to a
173 switching energy per unit area that is lower than DRAM and flash by factors of 100 and 1000
174 respectively^{12,15}.



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Fig. 3 | Memory device and basic operation. **a**, Scanning electron microscope image of a fabricated ULTRARAM™ device of 10- μm gate length. **b**, S-D current measurement at constant S-D voltage, $V_{S-D} = 0.1$ V, during a voltage sweep across the CG-BG (V_{CG-BG}) from +2.5 V to -2.5 V (black line) and -2.5 V to +2.5 V (red line), representing the program and erase cycles respectively. The hysteresis indicates a threshold voltage shift for the memory (ΔV_T) of 0.5 V.

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In this work, an n-type InAs, normally-on, channel layer was chosen for simplicity, as the primary objective was to demonstrate single-cell ULTRARAM™ operation on Si substrates. Whilst this channel design is sufficient for that purpose, it results in a low current contrast between logic states, labelled as ΔI_{S-D} in Fig. 3b. It is important to emphasise that this is a consequence of the simplicity of the channel and not a result of insufficient contrast in the programmed and erased state of the FG, as proven by

187 the 0.5 V threshold window in Fig. 3b. Indeed, the implementation of a normally-off channel should
188 allow a similar readout mechanism to flash, in which the application of a reference gate voltage only
189 induces conduction in the channel in the absence of charge in the FG (erased state), thereby greatly
190 increasing 0/1 current contrast for the same ΔV_T memory window^{12,24}. Such an improvement of the
191 0/1 contrast through careful modification of the channel design will allow memory arrays to be built
192 with a novel high-density RAM architecture^{10,12}. Furthermore, the inclusion of the gate dielectric
193 provides flexibility to significantly increase ΔV_T by increasing the gate dielectric capacitance: this can
194 be achieved by thinning the layer or by using higher-k dielectric materials.

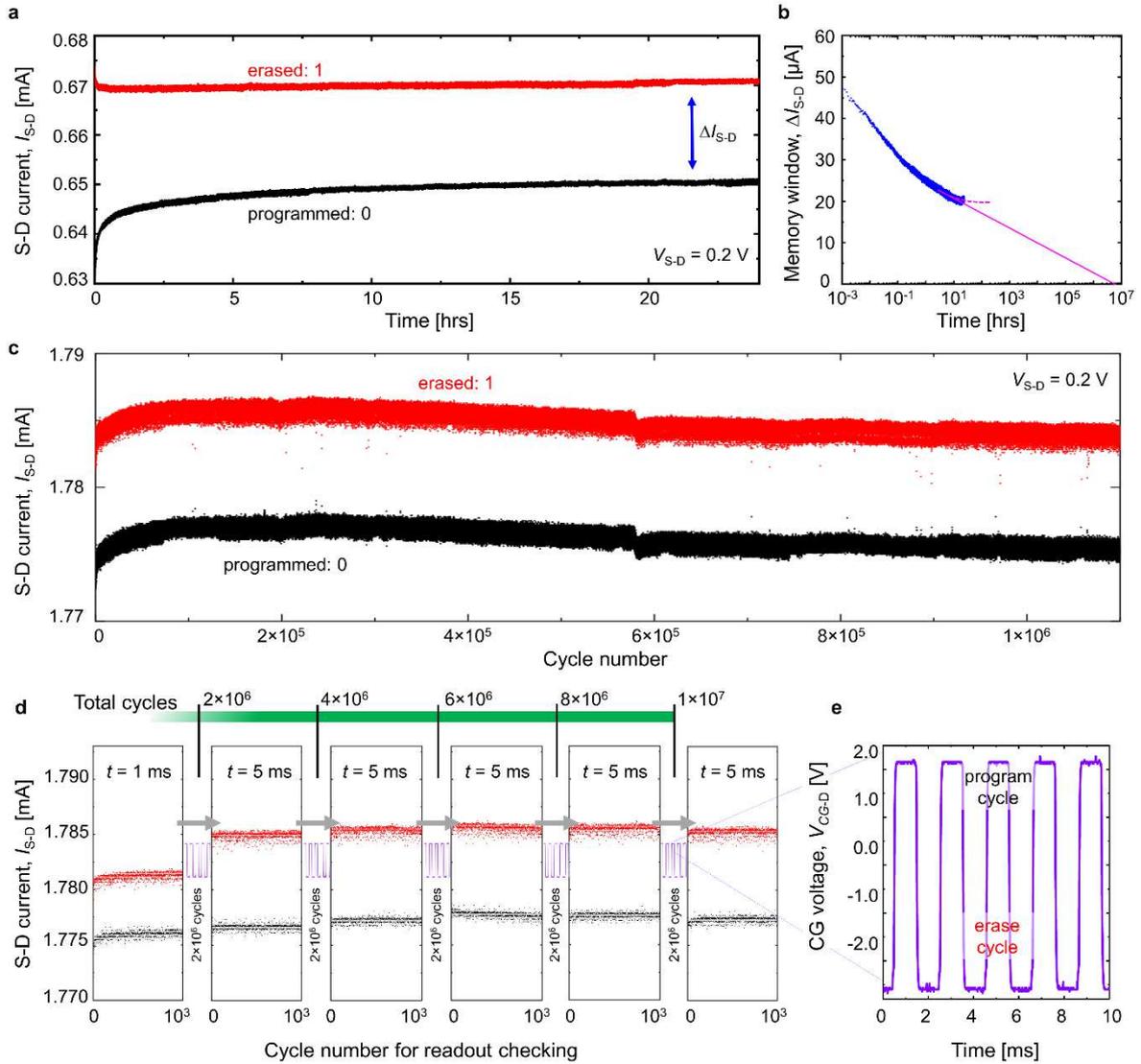
195 **Retention, endurance and speed testing**

196 Retention testing of the memory state was carried out at room temperature on a 20- μm -gate-length
197 device by repeatedly measuring I_{S-D} under a V_{S-D} bias of 0.2 V, but in the absence of V_{CG-BG} bias: a simple
198 readout scheme made possible by the n-doped InAs, normally-on channel. Memory retention was
199 confirmed for >24 hours for both program and erase states using $>10^6$ readout operations, limited
200 only by the length of the experiment (Fig. 4a). There is an initial decay in the I_{S-D} contrast between the
201 two logic states (*i.e.* the memory window, ΔI_{S-D}), before it plateaus at around 22 μA after roughly 14
202 hours. To investigate the memory's retention further, ΔI_{S-D} was plotted on a log-scale and different
203 fittings were made to the data, as shown in Fig. 4b. By extrapolating these fitted lines to the point at
204 which $\Delta I_{S-D} = 0$, *i.e.* when the memory window closes, the retention time of the memory can be
205 estimated. The plateauing of the memory window after 14 hours makes determination of the
206 retention time difficult, as shown by the dashed line in Fig. 4b, which extends to infinity. Therefore, a
207 second fitting is shown (solid line in Fig 4b), which follows the decay of the memory states, prior to
208 the final 10 hours of data. This provides an extremely conservative lower limit for the memory's
209 retention of at least 10^7 hours, which is more than 1000 years.

210 A similar, but more prominent, initial state decay was previously observed in the first prototype
211 ULTRARAM™ devices on GaAs substrates¹⁴, and was subsequently eliminated with improved material

212 quality.¹⁰ The return of the partial state decay for these first devices on Si substrates corroborates this
213 correlation with material quality, where the most likely candidate is charge trapping at defect sites on
214 the heterojunction interfaces. Thus, we predict a similar elimination of the state decay on Si substrates
215 with continued development of the material epitaxy. Nevertheless, the 0/1 contrast throughout the
216 24-hour test and the extremely long predicted retention times clearly demonstrate the non-volatility
217 of the logic states.

218 Endurance testing was carried out at room temperature by program-read-erase-read cycling on a
219 second 20- μm device using 5-ms-duration $V_{\text{CG-D}}$ pulses of +2.1 V and -2.55 V respectively, with $I_{\text{S-D}}$
220 readout measurements at $V_{\text{S-D}} = 0.2$ V in the absence of gate bias. The memory cell successfully
221 underwent 10^6 program-read-erase-read cycles with a stable memory window and without
222 degradation as shown in Fig. 4c. Moreover, the cell had zero cycle failures and <50 partial switches
223 during the 10^6 cycles. Of particular note is the reproducible nature of the I_{SD} values for programmed
224 and erased states, with neither the pronounced drift observed in the first prototypes¹⁴, nor the large
225 fluctuations in I_{SD} seen in more recent devices¹⁰. The latter was attributed to non-optimal etching of
226 the channel during device fabrication, and has been almost completely eliminated due to an improved
227 process (see Methods section for details). In Ref. 14 the drift in I_{SD} was attributed to an asymmetry in
228 the program/erase process. This was later shown by quantum transport simulations to be the result
229 of the asymmetry of the TBRT structure, allowing resonant tunnelling to occur at a lower voltage for
230 the program cycle than for the erase cycle¹². As a result, the use of symmetric voltages, such as ± 2.5
231 V, results in over-programming, such that more electrons are added in a program cycle than are
232 removed in by an erase, producing a current drift with each cycle. Fortunately, the state will quickly
233 stabilise with repeated cycling once the correct voltages are identified. The remaining small drift of
234 the I_{SD} window observed in Fig. 4c over many thousands of cycles is likely to become inconsequential
235 with the implementation of the normally-off channel readout scheme.



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Fig. 4 | Retention and endurance characteristics. **a**, Retention data for a 20- μ m-gate-length cell. Program and erase cycles consisted of 10-ms duration pulses at +2.5 V and -2.5 V respectively. Readout is performed at an S-D bias of 0.2 V, and in the absence of gate bias. **b**, S-D current difference (ΔI_{S-D}) for the >24 hour retention plotted on a log scale. The continuous magenta line indicates the least generous interpretation of the decay data, whereas the dashed magenta line follows the stabilisation of the memory window. **c**, Endurance data for continuous program-read-erase-read cycling (5-ms pulses) on a second 20- μ m-gate-length cell demonstrating a clear 0/1 contrast exceeding 10^6 cycles. **d**, Extended endurance to $>10^7$ cycles using continuous pulse trains

246 of 2×10^6 program-erase cycles repeated five times separated by 1000 program-read-
247 erase-read cycles to confirm memory operation persists. The program and erase pulse
248 duration, t , was 1 ms in the absence of read, and 5 ms with the read, except for the first
249 set of 1000 program-read-erase-read cycles, where it was also 1 ms. The data is
250 presented chronologically from left to right with the total cycles counted by the green
251 bar. e, Oscilloscope trace showing the applied gate bias for a section of the pulse train
252 during $t = 1$ ms program-erase endurance cycling.

253 The endurance testing on this device was then extended by a further order of magnitude using a
254 slightly modified methodology to increase the cycling speed by substantially reducing the number of
255 read operations; these take significantly longer than program and erase due to testing equipment
256 limitations. Firstly, an initial set of 1000 program-read-erase-read cycles was applied to the device to
257 confirm correct operation, followed by a pulse train of 2×10^6 program-erase cycles without any read,
258 in both cases with program/erase pulse durations of 1 ms. The 2×10^6 , 1-ms program-erase pulses were
259 then repeated multiple times, an example section of which is shown in Fig. 4e. In each case, these
260 were followed by 1000 program-read-erase-read cycles, but with program/erase pulses of 5 ms
261 duration to increase the width of the ΔI_{S-D} memory window, making it easier to detect any potential
262 degradation. The process was repeated five times, resulting in a little over 10^7 program/erase cycles
263 applied to the device. As can be clearly seen in Fig. 4d, there is no degradation of the ΔI_{S-D} window
264 throughout these tests, meaning that the endurance is at least 10^7 . This therefore represents an
265 endurance capability that is at least two to three orders of magnitude better than flash^{15,23}.

266 In all of the above tests, the program and erase states were set using between 1- and 10-ms voltage
267 pulses, two times longer than the switching times used in our recent report of ULTRARAM™ on GaAs
268 substrates¹⁰. In both cases, the devices operate at a remarkably high speed for their large (20 μm)
269 feature size. Assuming ideal capacitive scaling²⁵ down to state-of-the-art feature sizes, the switching
270 performance would be faster than DRAM, although testing on smaller feature size devices is required

271 to confirm this. The small loss in performance when switching from GaAs to Si substrate may be a
272 result of charge trapping at defect sites contributing to the RC-delay and program/erase voltage
273 screening. However, note that the switching speed for the present devices on Si is 1000 times faster
274 than the first devices on GaAs substrates, suggesting only a modest change in material quality on Si
275 compared to the more mature GaAs substrate growth method^{10,14}.

276 Finally, regarding reproducibility, the majority of devices with 10- and 20- μm gate length on the chip
277 exhibited memory characteristics. However, there was significant device-to-device variation in
278 absolute channel current, memory window size and state decay during retention. The difference in S-
279 D current ($I_{\text{S-D}}$) between the device data presented in Fig. 4a and c shows this clearly, and is the most
280 extreme example to be found on the chip. It is believed to be caused by S-D to BG current leakage due
281 to etch pitting of defects during fabrication, which creates an alternative conducting path from S to D.
282 Whilst the TEM image in Fig. 2d shows the movement of threading defects to produce a misfit
283 dislocation array at the bottom of the BG, threading defects are not eliminated and etch pitting
284 suggests that a small number may continue into the overlying channel. Work is ongoing to reduce this
285 device-to-device variation with further development of material epitaxy and fabrication processes.

286 **Conclusions**

287 We have demonstrated ULTRARAM™ compound-semiconductor, floating-gate memory cells on Si
288 substrates. A high-quality GaSb buffer on Si was developed, onto which the memory layers were
289 successfully implemented. TEM and XRD scans revealed the presence of threading defects in the InAs
290 BG, which likely slightly impinge on device performance due to varying levels of S-D to BG current
291 leakage. However, the remaining memory epilayers exhibit excellent quality with abrupt material
292 interfaces and a low surface defect density of $(2.1 \pm 0.1) \times 10^8 \text{ cm}^{-2}$. Testing of the fabricated single cell
293 memory devices shows strong potential, with devices demonstrating a clear memory window during
294 ≤ 10 -ms program/erase operations, which is remarkably fast for 10- and 20- μm gate-length devices.
295 The ~ 2.5 V program/erase voltage and low device-areal-capacitance results in a switching energy per

296 unit area that is 100 and 1000 times lower than DRAM and flash respectively. Extrapolated retention
297 times in excess of 1000 years and degradation-free endurance tests of over 10^7 program-erase cycles
298 prove that these memories are non-volatile and have high endurance. Further work to improve
299 epitaxial quality, fine-tune the fabrication process, implement a normally-off channel design and scale
300 the devices is ongoing.

301 **Methods**

302 **Non-equilibrium Green's function calculations.** The quantum transport of electrons through the
303 resonant tunnelling structure was calculated with the nextnano.MSB software package, which uses
304 the non-equilibrium Green's function framework. This method also generalizes the so-called Büttiker
305 probe model and takes into account all relevant individual scattering mechanisms to accurately
306 model the tunnelling structure. Further details of the method can be found elsewhere^{12,26,27}.

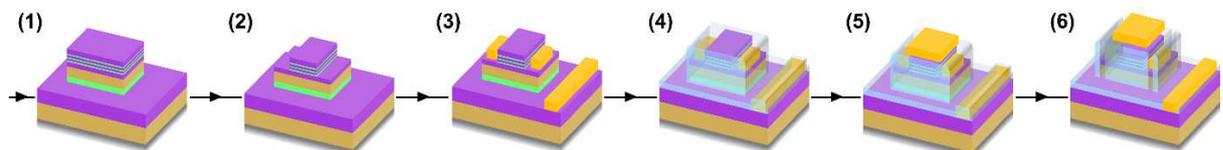
307 **Molecular beam epitaxy.** Samples were grown using a solid source Veeco GENxplor MBE system
308 equipped with As and Sb valved cracker cells. Epilayers were deposited on 3" Si n-type (100)
309 substrates with a 4° offcut towards [0-11]. The substrate's native oxide was thermally desorbed in
310 the MBE growth chamber at a temperature of approximately 1000 °C. The substrate was then cooled
311 to 490 °C, and was exposed to a Sb flux for 5 minutes. A 17-monolayer (ML) AlSb nucleation layer
312 was then deposited at a growth rate of 0.36 ML/s. Next, a 2- μm -thick GaSb layer was deposited at a
313 growth rate of 0.66 ML/s, using a two-step temperature technique¹⁹ where the substrate
314 temperature was increased to 515 °C after 1.5 μm of GaSb had been deposited. The substrate was
315 then cooled to 435 °C and the 50-nm InAs BG was deposited at a growth rate of 0.4 ML/s, followed
316 by a 8-nm-thick AlSb barrier at a growth rate of 0.1 ML/s. Next, the substrate was heated to 515 °C
317 for the deposition of a 20-nm GaSb layer at 0.66 ML/s. The substrate was then cooled back to 435 °C
318 for the remainder of the growth, starting with a 10-nm InAs channel, with n-type doping by Si to a
319 nominal carrier density of $1 \times 10^{18} \text{ cm}^{-3}$. This was followed by the TBRT layers, which consist of 1.8 nm
320 of AlSb, 3.0 nm of InAs, 1.2 nm of AlSb, 2.4 nm of InAs and 1.8 nm of AlSb. Finally, a 10-nm thick InAs

321 FG layer completed the structure. The growth rates of the InAs and AlSb in the TBRT and FG were 0.2
322 ML/s and 0.1 ML/s respectively.

323 **X-ray diffraction.** High-resolution X-ray diffraction measurements were carried out on a Bruker D8
324 Discover system. The copper K- α X-ray beam was conditioned by a two-bounce Ge crystal and
325 collimating optics. The diffracted signal was collected using a scintillation counter with a one-bounce
326 Ge crystal at its entry slit. Fitting of ω - 2θ data was carried out using RADS Mercury software.

327 **Transmission electron microscopy.** TEM specimens were prepared using standard techniques,
328 *i.e.* grinding, polishing and ion milling to electron transparency using 6-kV Ar⁺ ions. A final low-
329 energy (0.5 kV) ion mill was used to reduce surface damage. Samples were examined in a JEOL 2100
330 LaB₆ transmission electron microscope (TEM) operating at 200 kV.

331 **Electron-channelling-contrast imaging.** Electron-channelling-contrast images were collected
332 using a Zeiss Gemini scanning electron microscope with a solid-state backscatter detector operating
333 at 20 kV.



334

335 **Fig. 5 | Process flow diagram for the fabrication of ULTRARAM™ memory cells.** The
336 process progresses from left to right as labelled. **(1)** Inductively-coupled etch to the BG
337 layer to form device mesas. **(2)** Alternating wet etch with citric and buffered oxide
338 etchant to form S-D regions. **(3)** Ti-Au metallisation for S-D and BG. **(4)** Al₂O₃ gate
339 dielectric deposition via atomic layer deposition. **(5)** Ti-Au metallisation for the CG
340 terminal. **(6)** SiO₂ deposition for further passivation. In the final stage a buffered oxide
341 etch is carried out in square photoresist windows within the S-D region: the slit structure
342 here is presented to observe the etch within the schematic.

343 **Device fabrication.** A top-down processing procedure was employed to fabricate memory devices
344 with gate lengths of 10 and 20 μm . Fig. 5 demonstrates the general process flow, in which a memory
345 cell is formed via numerous steps. Separate ultraviolet (UV) lithography stages were used to pattern
346 the BG, device mesa and source/drain areas. For the device mesa and BG, excess material was dry
347 etched with an Oxford Instruments Plasma Lab 100 inductively-coupled plasma (ICP) machine. The
348 etching process was carried out using a Cl_2/Ar (2.5/5 sccm) gas mixture and a chamber pressure of
349 10 mTorr, with an ICP power of 120 W and an RF power of 18 W. Removal of material to define the S
350 and D areas was achieved by successive, alternating, selective wet-etching to remove the FG and
351 TBRT layers of the heterostructure. A solution of citric acid, hydrogen peroxide and de-ionised water
352 in 1:3:1 volumetric ratio was used to selectively etch InAs over AlSb, whilst buffered oxide etchant
353 (BOE) at 10:1 was used to selectively etch AlSb over InAs. The use of BOE significantly improves etch
354 uniformity compared to tetramethylammonium hydroxide-based etchant used previously¹⁰, due to
355 increased selectivity with the underlying GaSb layer, minimising damage by chemical contact
356 through etch pits in the thin InAs channel layer. Thermally evaporated Ti-Au contact terminals were
357 then added to the InAs channel layer (S and D), which was pre-treated by the HF from the prior etch
358 step²⁸. The Al_2O_3 gate dielectric is added via thermal atomic layer deposition using a Veeco Savannah
359 S100 system. The deposition was carried out at 200 °C and consisted of 10 trimethylaluminum
360 (TMA)-only pulses to ensure TMA self-cleaning (AsO_x removal) of the InAs FG²⁹, followed by 150
361 cycles of TMA and H_2O pulses, leading to an Al_2O_3 layer thickness of about 15 nm. Ti-Au CG contacts
362 were deposited on top of the gate dielectric via thermal evaporation, followed by further passivation
363 consisting of 120 nm of SiO_2 deposited using an Oxford Instruments plasma-enhanced chemical
364 vapour deposition machine. Access to all device terminals was obtained by chemical etching of the
365 oxide layers of SiO_2 and Al_2O_3 in the S, D and BG regions and SiO_2 and Ti in the CG region (using BOE,
366 10:1) through openings in the photoresist provided by UV lithography. A hard-baked, positive
367 photoresist, lifting layer was then patterned on one edge of the devices by UV lithography, enabling

368 continuous contacts to access the device terminals. Lastly, final contacts for device probing and
369 bonding were added by another Ti-Au thermal evaporation process.

370 **Device Testing.** Electrical characterisation was performed using a Keithley 2634B dual-channel
371 source measure unit (SMU) controlled using dedicated LabVIEW programs. All tests were performed
372 at room temperature and pressure. Remarkably, shielding the devices from varying ambient (room)
373 light levels was found to be unnecessary. Device terminals were contacted using a Wentworth
374 Laboratories probe station with triaxial probe connections. Endurance cycling (program-read-erase-
375 read) was performed in pulsed-mode at around ~500 cycles per minute, where each of the program-
376 read-erase-read pulses are separated by ~50 ms as a result of the pulse initiation delay of the SMU.
377 Current measurements for the retention test were taken at 0.2 V S-D voltage at a rate of ~500 cycles
378 per minute. The retention data was gathered under the same readout conditions as above in a single
379 continuous run for the E state immediately after a 5-ms -2.5-V E-cycle (CG-D pulse), and similarly for
380 P retention monitoring, which followed a +2.5-V pulse across the CG-D of the device of 5 ms
381 duration.

382

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