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Review Article

Materials for Future Quantum Dot-Based Memories

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The present paper investigates the current status of the storage times in self-organized QDs, surveying a variety of heterostructures advantageous for strong electron and/or hole confinement. Experimental data for the electronic properties, such as localization energies and capture cross-sections, are listed. Based on the theory of thermal emission of carriers from QDs, we extrapolate the values for materials that would increase the storage time at room temperature to more than millions of years. For electron storage, GaSb/AlSb, GaN/AlN, and InAs/AlSb are proposed. For hole storage, GaSb/$Al_{0.9}Ga_{0.1}As$, GaSb/GaP, and GaSb/AlP are promising candidates.

1. Introduction

Current progress in the field of semiconductor memories is driven by the aggressive downscaling of the feature sizes of the building blocks of computers, such as logic nodes, memory nodes, and contact circuitry. However, as the feature sizes approach length scales in which the properties are governed by quantum mechanics, the downscaling approach will come to an end around the years 2020 to 2025. Then, the elements will just be a few nanometers in size, and interface roughness will lead to uncontrollable tunneling leakage. Hence, new ways must be found in order to still drive progress of semiconductor technology, a reason why the International Technology Roadmap for Semiconductors (ITRS) is calling for *new functionalities* to enhance current solutions [1].

Today's memory market is divided mainly between two semiconductor memories, the dynamic random access memory (DRAM) and the flash memory [2], both having their individual advantages and disadvantages. The DRAM is fast but volatile, which means that the information must be cyclically refreshed within some milliseconds. The flash on the other hand is nonvolatile with a storage time of more than ten years, but suffers from a slow write time of some microseconds. Consequently, the semiconductor memory community is seeking for replacements which could combine the advantages of both types. Different approaches toward that goal are studied at the moment, such as FeRAM, MRAM, or PCRAM to name just a few [3]. However, none of these memory types has yet hit the mass market due to various shortcomings concerning speed, endurance, and cost.

One potential candidate which could combine the advantages of a fast write speed and a long storage time is a memory based on self-organized quantum dots (QDs) [4, 5]. This memory would harvest the great potential provided by the large variety of different III–V materials, which can be combined to form nanometer-sized heterostructures acting as storage nodes. In addition to long storage times, a memory based on self-organized QDs could enable very fast write speeds, as the physical limit of the carrier capture time lies within the picoseconds range, being advantageous over another popular attempt: a memory based on metal nanocrystals. These nanocrystal memories suffer from the same shortcomings as the ordinary flash because the nanocrystals are still surrounded by an insulating dielectric which does not facilitate these fast write times.

The present paper investigates the current status of the storage times that can be achieved in self-organized QDs, surveying various materials for both electron and hole systems. Based on the theory of thermal emission, extrapolations are made, and various materials are proposed which eventually will yield nonvolatility.

2. A Memory Device Based on Self-Organized Quantum Dots

The basic structure of a QD-based memory is shown in Figure 1(a). It consists of a layer of self-organized QDs embedded into a modulation-doped field-effect transistor (MODFET) structure, which is made of a larger band gap material [6, 7]. The QDs are the storage node with charges used as information carriers, while the MODFET structure is used to perform the memory operations, such as writing, erasing, and reading-out of the information in the QDs.

The memory operations are shown schematically in Figures 1(b), 1(c), and 1(d) for a device using holes as information carriers. If a *logic 1* is stored in the QDs (here defined as full QDs), an emission barrier is needed in order to prevent the holes from leaving the QDs. The emission barrier is formed by the confining potential (i.e., the localization energy) of the QDs. In contrast, if a *logic 0* is stored, a capture barrier is needed in order to prevent holes from outside the QDs to enter the QDs. In order to charge the QDs in the writing operation, a gate bias is applied such that the energy levels of the QDs are completely above the Fermi level, and the holes get captured from the valence band continuum surrounding the QDs (Figure 1(c)). This capture process is extremely fast, potentially reaching down to some picoseconds at room temperature [8, 9]. For the erasing process, a gate bias in reverse direction is applied. This leads to an increased band bending around the QDs, making the emission barrier narrower. This increases the tunneling probability, and the holes inside the QDs tunnel out through the barrier into the valence band continuum. The read-out of the information in the QDs is done with a current measurement of the source-drain current. Carriers inside the QDs change the mobility and carrier concentration inside the channel, effects that are directly visible in the source-drain current.

3. Thermal Emission Rate and Storage Times in Quantum Dots

Storage of information is always a nonequilibrium situation, and all information will eventually be lost after a certain time, which is termed storage time or retention time. Hence, the storage time is an important figure of merit for a memory device. The QD-based memory should be designed in such a way, that the physical process limiting the storage time is thermal emission only. Then, the emission rate for electrons is equal to [10]

$$e_n = \gamma_n \sigma_\infty^n T^2 \exp\left(-\frac{E_{\text{loc}}}{kT}\right), \quad (1)$$

where γ_n is a temperature-independent constant, σ_∞^n is the electron capture cross-section of the dots, and E_{loc} is the localization energy for electrons. Similarly, the emission rate for holes is [10]

$$e_p = \gamma_p \sigma_\infty^p T^2 \exp\left(-\frac{E_{\text{loc}}}{kT}\right), \quad (2)$$

where γ_p is a temperature-independent constant, σ_∞^p is the hole capture cross-section of the dots, and E_{loc} is the localization energy for holes. Hence, as the storage time is the inverse of the emission rate, it is directly proportional to the inverse of the capture cross-section. The capture cross-section is a measure of how well the QDs couple to their surroundings in terms of energy exchange [11]. Using the laws of logarithm conversion, the contribution of the localization energy E_{loc} can be isolated [12]. When keeping the capture cross-section constant, the storage time will increase by one order of magnitude for every 60 meV additional localization energy. The storage times as a function of the localization energy for various capture cross-sections at room temperature are shown in Figure 2. From this graph, the localization energy required for nonvolatility can be extrapolated. For electrons, it lies between 1.1 and 1.4 eV, while for holes a slightly larger localization energy between 1.15 and 1.45 eV is required.

4. Experimental and Theoretical Storage Times in QDs

The electronic properties of QDs, such as the capture cross-section and the activation energy, can be determined using capacitance-voltage (C-V) spectroscopy, especially deep-level transient spectroscopy (DLTS) [13, 14]. To determine the localization energy, charge-selective DLTS is used, which enables the detection of carrier emission and capture with a much higher resolution, giving inside into the electronic structure of the QDs [15]. The activation energy of the ground state in the QDs is then the maximum confining potential of the QDs, and hence equal to the localization energy. Using these data, the storage time at room temperature can be extrapolated.

The experimental data for various material systems using electrons or holes as information carriers is listed in Table 1.

The experimental values for the localization energies of the QD ensembles are between 95 meV and 290 meV for electrons and between 337 meV and 800 meV for holes. The values for the capture cross-sections vary between $2{\cdot}10^{-14}$ cm^2 and $1{\cdot}10^{-10}$ cm^2 for electrons and between $4{\cdot}10^{-14}$ cm^2 and $5 \cdot 10^{-11}$ cm^2 for holes. Extrapolating the room temperature (300 K) storage time based on these values yields storage times up to 1.6 s. As the storage time is determined by the capture cross-section and the localization energy, this high value is mainly due to the small capture cross-section, which can be seen when comparing the material system InAs/$Al_{0.9}Ga_{0.1}$As with the Sb-based systems, in which a larger localization energy (800 meV) is reached, but also with a larger capture cross-section, leading to a smaller storage time of just 80 ms.

Table 1 also contains predicted values for the storage time based on localization energies which were calculated by 8-band-**k**·**p** theory [30, 31] or simply estimated by using the band offset between the materials if the heterostructure is unstrained [28]. The capture cross-sections are estimated based on the experimental results which we found so far for the QDs. As a result of the unknown capture cross-section, only a range of storage times can be given.

The experimental and theoretical results are shown in Figure 2, together with the theoretical values for the storage

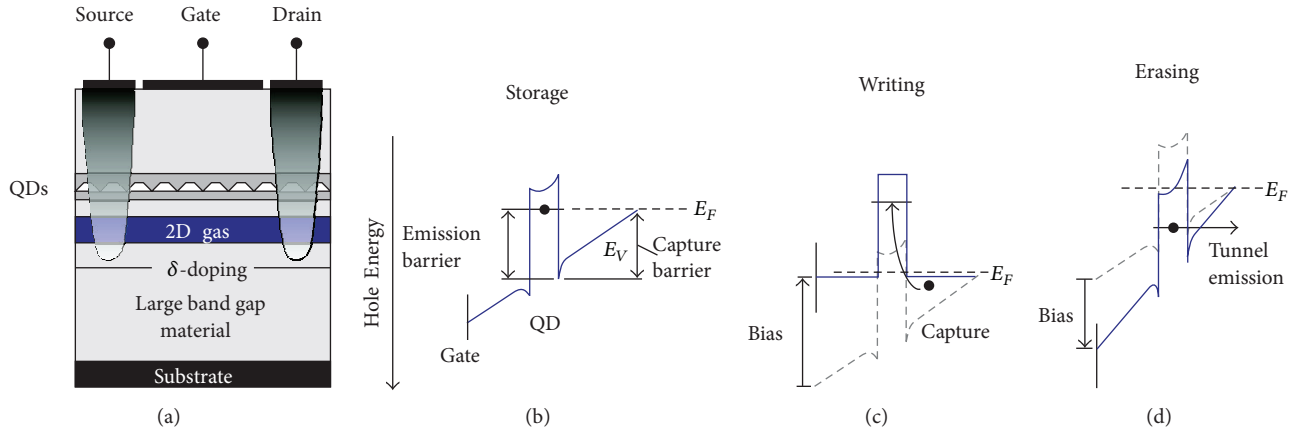

Figure 1: (a) Generic structure of a QD-based memory device, consisting of a layer of self-organized quantum dots embedded into an MODFET structure made of a large band gap material. (b) Storage of information requires an emission and a capture barrier. (c) Writing operation. (d) Erasing operation.

Table 1: Electronic properties and storage times at 300 K for various QD material systems. The bold entries are theoretical predictions based on 8-band-**k·p** calculations or estimations from the band offsets.

Material	Type	E_{loc} (meV)	σ_∞ (cm^2)	Storage time at (300 K)	Reference
Ge/Si	Hole	350*	$1{\cdot}10^{-13}$	0.1 μs	[16]
InAs/GaAs	Electron	95	$1{\cdot}10^{-11}$	0.4 ps	[17]
InAs/GaAs	Electron	160*	10^{-11} to 10^{-10}	0.1 ps	[18, 19]
InAs/GaAs	Electron	290	$2{\cdot}10^{-14}$	200 ns	[20]
InAs/GaAs	Hole	210	$7{\cdot}10^{-14}$	1 ns	[20]
InAs/$Al_{0.6}Ga_{0.4}As$	Hole	560	$7{\cdot}10^{-15}$	5 ms	[21]
InAs/$Al_{0.9}Ga_{0.1}As$	Hole	710	$4{\cdot}10^{-15}$	1.6 s	[22]
GaSb/GaAs	Hole	337	$1{\cdot}10^{-13}$	10 ns	[23]
GaSb/GaAs	Hole	450	$1{\cdot}10^{-12}$	1 μs	[15]
GaSb/GaAs	Hole	460	$7{\cdot}10^{-12}$	100 ns	[12]
GaSb/GaAs	Hole	760	$5{\cdot}10^{-11}$	2 ms	[12]
GaSb/$Al_{0.1}Ga_{0.9}As$	Hole	670	$1{\cdot}10^{-12}$	2 ms	[24]
GaSb/$Al_{0.3}Ga_{0.7}As$	Hole	800	$5{\cdot}10^{-12}$	80 ms	[12]
InP/$Ga_{0.5}In_{0.5}P$	Electron	220	$1{\cdot}10^{-8}$	0.04 ps	[25]
$In_{0.25}Ga_{0.75}As$/GaAs/GaP	Hole	489*	$2{\cdot}10^{-13}$	3 μs	[26]
GaSb/$Al_{0.9}Ga_{0.1}As$	**Hole**	**~1250**	**10^{-15}–10^{-10}**	**50 h to 100 yr**	**[12]**
GaSb/GaP	**Hole**	**~1400**	**10^{-15}–10^{-10}**	**1 yr to 100 k yr**	**[27]**
GaSb/AlP	**Hole**	**~1900**	**10^{-15}–10^{-10}**	**1 G yr to 100 T yr**	**[27, 28]**
GaSb/AlSb**	**Electron**	**~1200**	**10^{-15}–10^{-10}**	**36 h to 40 yr**	**[28]**
GaN/AlN	**Electron**	**~2000**	**10^{-15}–10^{-10}**	**10 G yr to 10 P yr**	**[29]**
InAs/AlSb**	**Electron**	**~2150**	**10^{-15}–10^{-10}**	**100 T yr to 1 E yr**	**[28]**

The values marked with an asterisk (*) are not localization energies but ensemble activation energies. (**) These heterostructures do not facilitate QDs, but they form unstrained ordinary quantum wells.

time. It is important to note that the theoretical extrapolations are only rough estimates, as the effective masses of different materials also differ, which affects the prefactor γ in the equations for the emission rates, such that the theoretical storage times shift slightly. It can be seen from Figure 2(a) that three material systems are potential candidates to facilitate electron storage times of much more than ten years at room temperature. GaSb/AlSb does not form quantum dots but could be exploited by using quantum wells with storage times up to 40 years. GaN/AlN could enable storage times above 10 billion years. InAs/AlSb also does not form quantum dots, but the quantum wells would show storage times beyond billions of years. In comparison with the electron systems, a massive body of experimental data is available for hole storage in QDs. Here, GaSb/$Al_xGa_{1-x}As$, a material system studied already with low Al content, could be further exploited if the Al content is increased. Nevertheless, storage times above ten years are only reached if a capture cross-section below

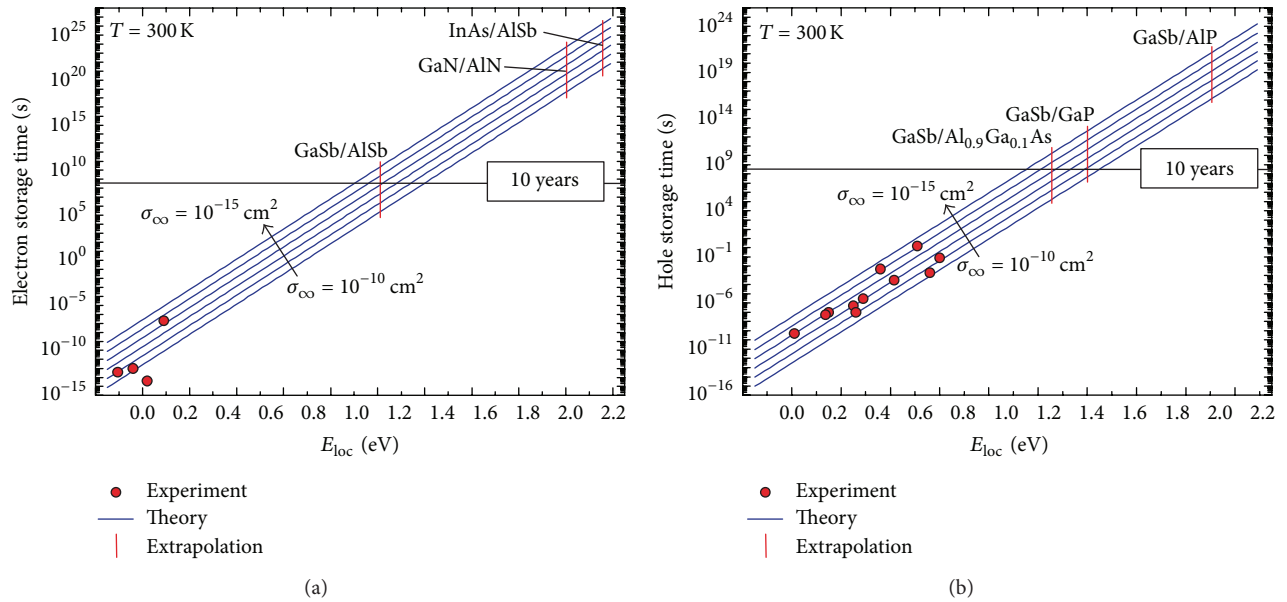

Figure 2: Experimental and theoretical storage times for the heterostructure materials listed in Table 1. (a) Electron storage. (b) Hole storage. Please note that the theoretical values (blue lines) are calculated for the effective electron and hole masses of GaAs. Hence, the extrapolated values for other materials might differ slightly.

10^{-13} cm^2 can be achieved. The experimental data for GaSb has shown, however, that the capture cross-section lies mainly above that value.

Another promising option is to use GaP as matrix material. Here, using a GaSb/GaP heterostructure, hole storage times above ten years can be reached if the capture cross-section is below 10^{-11} cm^2. A further increase to values in the range above billions of years is possible if GaP is replaced by AlP, which adds another 500 meV to the localization energy.

After listing all the potential materials which have been selected according to the rule that they must have a large band offset in the conduction or valence band, one has to take a look at the prospects of actually fabricating these materials. Quantum dots based on GaSb/$Al_{0.9}Ga_{0.1}As$ should pose no problem as $Al_{0.9}Ga_{0.1}As$ barriers are commonly used, and the technology of growing them is well established. Even if QD growth directly on $Al_{0.9}Ga_{0.1}As$ will be difficult, a thin interlayer of GaAs will allow the combination with GaSb. Growth of GaSb QDs on GaP has been demonstrated, although misfit dislocations induced by the large strain (~12%) are an issue [32]. To implement AlP instead of GaP, one has to use GaP substrates due to the lack of AlP substrates. Then, in addition to the challenges with GaP, background doping becomes an issue in AlP. GaN QDs embedded into AlN have already been grown successfully [33], but material quality is still an issue due to stacking faults and dislocations which are particularly adverse in electronic devices. GaSb/AlSb and InAs/AlSb quantum wells have been successfully grown repeatedly in the past and are used, for example, in high-mobility applications [34, 35].

Another potential option to increase the storage time in QDs might be the tailoring of the capture cross-section. As the transition probability from an initial state to a final state depends on the overlap of the wavefunctions, the size of the QDs is a key parameter. However, other effects, such as phonon coupling and Auger effects cannot be neglected. A detailed theoretical understanding of the capture cross-section, let alone the precise tailoring during QD growth, has yet to be achieved.

5. Conclusion

We have surveyed materials potentially available to fabricate a QD-based memory. Various materials are found for electrons and holes, with the majority of experimental data available for holes. As the storage time increases by about one order of magnitude for every additional 60 meV of localization energy added, the route to longer storage times is clear. Nevertheless, a second parameter, the capture cross-section of the QDs, also plays a key role for the storage time. The storage times of carriers in QDs span a range of 14 orders of magnitude, starting at a fraction of a picosecond and ending with seconds. A maximum storage time of 1.6 s was reached in InAs/$Al_{0.9}Ga_{0.1}As$ QDs. However, the maximum localization energy of 800 meV was reached in GaSb/$Al_{0.3}Ga_{0.7}As$ QDs, which have a storage time of just 80 ms due to the influence of the capture cross-section.

Based on 8-band-$\mathbf{k}\cdot\mathbf{p}$ calculations and simple band offset estimations, a handful of material systems was identified to increase the storage time of electrons and holes further, possibly up to millions and billions of years at room temperature. These are GaAs/AlSb, GaN/AlN, and InAs/AlSb for electron storage and GaSb/$Al_{0.9}Ga_{0.1}As$, GaSb/GaP, and GaSb/AlP for hole storage.

Hence, it can be concluded that although growth of the materials proposed will be challenging, a nonvolatile memory based on self-organized QDs is feasible.

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