Towards High-density Non-volatile Solid State Memories

We want the electronic gadgets of tomorrow to be smaller and lighter, but also faster and more powerful: Whether MP3 players, camera mobile phones, navigation systems or notebooks, all have to be compact but also able to store increasingly large amounts of music, images, films or maps, and process them quickly. Innovative new solid state memories would contribute greatly towards making electronics smaller and more powerful, especially if they were able to save information permanently, even without being connected to an electric power source, but still process data as quickly as the working memories of present-day computers.

To realize such advanced solid state memories, new concepts are being developed worldwide, among them magnetic (MRAM), phase-change (PCRAM) and ferroelectric (FRAM) random access memories. The latter have attained a clear advantage - they already achieved the state of commercial products, however, so far only with a rather low memory density of, e.g., 64 Mbit. This is not sufficient for present-day working memories of PCs, which require memory densities in the Gbit/inch$^2$ or even Tbit/inch$^2$ range. On the other hand, the target is worth the efforts: A notebook with a non-volatile FRAM as high-density, quick working memory would work without the slow and heavy harddisk, and the annoying booting procedure would become a matter of the past, too. Physicists and material researchers worldwide work hard to overcome the present limits of ferroelectric memories [1]. Problems which need to be solved are both material- and process-related. Among the ferroelectric materials under study are complex oxides like PbZr$_{0.2}$Ti$_{0.8}$O$_3$ (PZT) or BaTiO$_3$. Chemical stability, oxygen stoichiometry, and processibility are matters of concern. To achieve a memory density in the range of 100 Mbit/inch$^2$ by help of an array of ferroelectric "dots", i.e. small features consisting of a ferroelectric material, the lateral repeat distance - the pitch - of the dots needs to be smaller than 100 nm, which requires each dot to be even smaller in lateral size. Ferroelectricity being a collective phenomenon, a certain minimum number of unit cells is required to be involved.
It was not clear from the beginning whether a ferroelectric dot of far less than 100 nm size has enough unit cells and thus would still show the required ferroelectric properties, or not. Another problem is related to the surfaces and interfaces: In a small object with a volume of, say, 0.0001 µm³, a considerable part of the atoms are close to the surface or the interfaces with other materials. These atoms may behave differently from those in the bulk, thus affecting the properties. Moreover, the quality of the surface is also related to the preparation and processing methods which have been used to obtain the small ferroelectric object: If they include harsh steps, like mechanical (imprinting) or chemical (etching) removal of the material around, the surface of the remaining small ferroelectric object may be damaged, which may result in considerably degraded properties.

We have been working on these problems using different approaches during recent years [2]. Recently we found a method to prepare arrays of ferroelectric dots of PZT which are embedded between bottom and top platinum electrodes, thus forming tiny capacitors [3]. Each of the capacitors has a lateral size below 100 nm, even going down to 40 nm. In the latter case the pitch is as small as 60 nm, which is equivalent to a memory density of 176 Gbit/inch². In spite of these small sizes, the PZT material still preserves its ferroelectric properties, and thus the array of nano-capacitors can be used as a solid state memory. Due to the small sizes of our nano-capacitors, various microscopies had to be applied in order to look into the details of structure and properties, viz. scanning (SEM) and transmission electron microscopy (TEM), and scanning force microscopy both in tapping mode (AFM) and in the so-called piezoresponse mode (PFM).

The performance of our arrays of nano-capacitors is a result of the principle on which they are based. In the ferroelectric material PZT, all unit cells have permanent electrical dipoles. The positive and negative poles of a permanent electrical dipole can be interchanged quickly. Cooperating with colleagues from
Max Born Institute Berlin, we were recently able to show that this process requires an intrinsic time as small as one picosecond [4]. PZT can therefore save data permanently like a hard drive, but process it as quickly as an advanced present-day working memory.

Figure 1 shows a scheme of the process. A thin perforated mask made of anodic aluminum oxide (AAO) is being prepared, which contains an ordered array of small holes with sub-100 nm diameter. This mask is obtained by electrochemically oxidizing an aluminum surface, a method known as the eloxal process. A basic version of the latter has been used for decades to provide aluminum components with a protective coating and to give aluminum tableware a matt-metallic sheen. In the basic version of this process, pores generally eat into the aluminum oxide in a random pattern. However, by carefully selecting the temperature, pH level and chemical composition during oxidation, in our case the pores were forced into a hexagonal arrangement where each pore is surrounded by six others [5]. The mask was then placed on a single crystalline magnesium oxide (MgO) plate heated to 650°C. This plate is coated with an epitaxial platinum layer which serves as support, and later as bottom electrode. The material PZT is deposited through the holes of the mask onto the platinized MgO plate by a process called pulsed laser deposition (PLD) [6, 7], thus obtaining small PZT dots with a thickness of, say, 70 nm. A thin platinum cover completes the capacitors, in which now the platinum layers serve as electrodes, and the PZT is the dielectric. Finally the thin alumina mask is removed, leaving the array of ferroelectric nano-capacitors easily accessible.

Figure 2 shows (a) an SEM image of part of the AAO mask and the prepared PZT dot array, (b) a TEM cross section image of part of the MgO plate carrying the Pt bottom electrode which in turn carries the PZT nano-capacitors of 40 nm diameter, and (c) a higher magnified TEM cross section image showing four nano-capacitors of 80 nm diameter after removal of the mask. Perfectly ordered arrays can be achieved using an imprint technique to even better control the anodization [8]. Figure 3 shows (a) a characteristic curve, the so-called piezoelectric hysteresis curve, which has been recorded by PFM. It demonstrates the memory properties of a single nano-capacitor: At zero bias, there are two possible stable conditions of the capacitor at ± 90 pm/V, which serve as the positive and negative memory signal. In the right part of the figure a switching experiment is shown: Part (b) shows the AFM topography image of a number of nano-capacitors, whereas (c-e) are PFM images, where the negative memory state is coded in dark, and the positive memory state in bright. In (c), all the visible capacitors have been switched into the negative state (dark color), in (d) two capacitors (left from the label "PFM") have been
switched into the positive state (bright color), and in (e) the left of these two capacitors has been switched back into the negative state (dark color). Switching is performed by applying a voltage of 3 V of respective sign to the conducting tip of an AFM, which touches a single capacitor, as schematically shown in the inset of (a). As can be seen from these images, switching is possible without cross talk. This and more results have shown that the arrays of nano-capacitors can effectively be used as model memories [3]. More investigations will concentrate on further reducing the pitch of the arrays, down to a Tbit/inch$^2$ memory density.

References

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