

Ageing of GeTe nanowires

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Summary

In this paper we report a TEM study on the ageing of GeTe nanowires, for scaled phase memory devices application, when exposed to normal atmospheric conditions. Selective oxidation of Ge occurs, leading to the formation of a Ge oxide amorphous shell around the wire, with GeTe₄ nanocrystals embedded within. The oxidation process takes place in a few weeks after the sample preparation, seriously endangering the device integrity and correct functioning.

Key words: TEM; Phase change memory; nanowires; ageing.

Introduction

Phase change memories (PCMs) are an innovative class of memory devices whose working principle relies on peculiar properties of chalcogenide materials. The active region of the memory cell can be written by inducing a phase change between the amorphous and crystalline phases using ns long current pulses. The phase transition is very fast, as it is achieved on the time scale of the tens of ns, and reversible, meaning this that the stored information can be written and erased at will. The stored information is then read measuring the cell resistance: low resistance, i.e. the active region is in its crystalline phase, translate as a binary "1" while the high resistance state, amorphous phase, translate as a binary "0". Therefore, as long as the state of the active region does not undergoes any phase transformation the information is safely stored inside it. PCMs offer the potential for better endurance, data retention, speed and scalability with respect to the current Flash memories. (Raoux et al., 2010; Lacaíta and Wouters, 2008)

The most studied chalcogenide phase change alloys are Ge₂Sb₂Te₅ and GeTe. The latter, in particular, is the system of choice for fundamental studies owing to its well-understood atomic structure and simple binary chemical composition, which allows for an easier result interpretation in comparison with other Ge–Sb–Te ternary alloys. Self-assembled GeTe

nanowires (NWs) received a great interest in the field of PCM applications, because of their potential to allow a defect-free scaling down in the fabrication of high performing, highly integrated, and low-power memory devices (Raoux, 2009; Yu *et al.*, 2008; Lee *et al.*, 2008; Longo, 2014). Reducing the size of the PCM cells to the nano-scale reduces the active material volumes to be programmed, so that shorter and less intense current pulses are required, as already demonstrated in previous studies (Jung *et al.*, 2008; Lee *et al.*, 2008; Jung *et al.*, 2009; Lee *et al.*, 2006; Meister *et al.*, 2006; Jennings *et al.*, 2009).

Besides these positive effects, as the device sizes continuously scale down, insufficiency in the material properties gradually emerged. One of the most important figures of merits that characterize the PCMs quality is the data retention time: namely how long the information can be stored before spontaneous phenomena modify the active region resistivity (Raoux *et al.*, 2010).

The main failure mechanism of PCMs is the recrystallization of the amorphous phase that decreases its resistivity and destroys the stored information. Under normal working condition, the process takes several years to be completed. However, under harsh conditions, such as high temperature/high power (automotive) applications, it speeds up notably (Gleixner *et al.*, 2007). Moreover, highly integrated devices fail more quickly than low integrated ones, indicating a reduced stability of the amorphous

phase at smaller dimensions, as suggested by experiments on the recrystallization time of amorphized nanowires (Lee *et al.*, 2008).

In this paper, we report on the ageing effect that turns the GeTe NWs crystalline phase into an amorphous one, induced by a selective surface oxidation of the Ge, that results in the assembling of Te-rich nanocrystals. The phenomenon happens on a shorter time scale than the recrystallization and has dramatic effects on both the structure and morphology of the NWs under investigation, being potentially able to destroy the memory cell itself in a few weeks. We constantly followed the NWs ageing for several weeks after the NWs synthesis, enabling a deeper understanding and description of the chemical and structural transformations involved.

Methods

The self-assembled growth of GeTe NWs was performed in an MOCVD AIX 200/4 reactor on Si(100)/SiO₂ (50 nm thick, thermally grown) substrates. The substrates were preliminarily loaded into an evaporator, where an Au metal catalyst layer with nominal thickness of 2 nm was deposited by e-beam evaporation at a low deposition rate of 0.1 nm/s. The MOCVD self assembly of the studied NWs was carried out at the temperature of 400°C and pressure of 50 mbar; more details are contained in Longo *et al.*, 2011. The NWs ageing proceeded under normal atmospheric conditions, by keeping them in the laboratory without any particular precaution. In order to assess the chemical and structural transformations undergone by the sample, High Resolution and Analytical TEM investigations were performed on the NWs dispersed on holey-carbon grids, by means of a JEOL 2200FS Field Emission microscope, operating at 200 kV, and equipped with in-column Ω -filter, X-ray energy dispersive (EDX) Spectroscopy and two high angle annular dark field (HAADF) detectors.

Results and discussion

The as-grown NWs (Figure 1) crystallize in the high-temperature stable, rock salt β -GeTe phase (Rabe and Joannopoulos, 1987). They present good crystalline quality and no extended defects are visible, as confirmed by the electron diffraction pattern of Figure 1b): it shows six equivalent reflections having lattice parameters $d=0.212$ nm consistently with

the [111] zone axis. The ageing effects are already visible on the sample after a few days from the synthesis, even if the oxidation process is in its early stage. A close inspection at the High Resolution (HR) TEM image, reported in Figure 1a), reveals that a thin native oxide layer, less than 5 nm thick, is already present on the NW sidewalls. Moreover, the NWs surface itself is not smooth and in some points it appears to be distorted, as within the highlighted white circles.

The amorphous shell is very thin and it is difficult to characterize its nature, the same goes for the surface distortions. However, at this stage, it will not affect the correct device functioning.

TEM observations are repeated on the same sample six weeks after the growth and the results are summarized in Figure 2.

The situation is now completely different: the oxide layer, which has progressively grown on the surface at the expenses of the wire, has doubled its thickness (around 10 nm thick). The distortions observed at the NWs surface have evolved into clear Moirè fringes (circled in red), suggesting the presence of crystal grains at the surface, as a result of a non-complete oxidation of the wire.

The diffraction pattern of the NW is reported in Figure 2b). Here two sets of diffraction spots appear.

The first set, composed by the six outer and brighter spots, corresponds to the (220) reflections family of the β -GeTe. The six less intense and inner spots (red circled in Figure 2b) correspond to a plain spacing $d = 0.38$ nm, which is not compatible with any crystalline phase of the GeTe. Instead, in the literature, the lattice parameter matches with a Te rich Ge-Te phase, namely the GeTe₄ (JCPDS PDF-33-0585).

Close to the outer set of GeTe reflections there are other six spots corresponding to a slightly larger d -spacing than that of the GeTe ($d=0.226$ nm). These are the (422) diffraction spots of the GeTe₄. They appear to have a ring-like displacements due to the presence of satellites spots produced by dynamical scattering (multiple diffraction).

Interestingly, the diffraction spots coming from nanometric crystalline grains randomly located along the NW are sharp, indicating a strong epitaxial relationship with the underlying GeTe NW core.

Further insight on the crystal grains comes from the HAADF-STEM image reported in Figure 3a). They appear as the brighter spots decorating the surface of the wire. The observed contrast is consistent with the chemical composition of the grains, because

the GeTe_4 has a higher density than GeTe .

In Figure 3b the EDX map of the same region depicted in Figure 3a is reported. Even if it is not possible to spot the GeTe_4 crystal on the map, interesting information on the chemistry of the NWs surface arises: the outermost region of the NWs contains only Ge.

This can be clearly observed in the intensity line profiles of the Ge and Te signals across the wire, reported in Figure 3c). In between the red lines taken as a reference on the images, Ge and Te are uniformly distributed, while only the Ge signal extends outside the red lines. This observation implies that the amorphous shell surrounding the NWs is mainly composed by Ge-oxide.

The effect of the selective Ge oxidation keeps increasing over time, as reported in Figure 4. After twelve weeks from the growth, the thickness of the oxide amorphous layer further increases, reaching an average thickness of 20 nm. The amount of GeTe_4 nanocrystals also increased and now they completely cover the whole surface of the NWs. Most of the grains are entirely embedded in the thick amorphous shell which covers the NWs, but they still retain a good epitaxial relationship with the GeTe core, as confirmed by the Fast Fourier Transform (FFT) reported as inset.

A computer algorithm offers the possibility to obtain a distribution map of the intensity exhibited by each spatial frequency present in a HRTEM image. It has been applied to the image in Figure 4a to obtain the map reported in Figure 4b.

The map has been colour-coded, according to the circles on the FFT inset: the intensity of the lattice fringes with the spatial frequency pertinent to the GeTe is shown in green, while for the GeTe_4 clusters the red colour has been used.

Interestingly the two signals are well separated, in perfect agreement with the results discussed so far. The GeTe lattice is present only in the core region of the NW, while the GeTe_4 nanocrystals are embedded in the amorphous oxide shell.

In the light of the results gathered during the different investigations, we are allowed to suggest the following mechanism for the ageing process. It is graphically summarized in Figure 5.

Due to the air exposure, preferential oxidation of the Ge occurs at the surface of the NWs. The Ge oxide forms the outer amorphous shell, which keeps growing over time. Simultaneously, the excess Te aggregates forming the GeTe_4 nanocrystals. Because both the GeTe and GeTe_4 belong to the cubic system, the latter can easily form an epitaxial relationship with the GeTe it originated from.

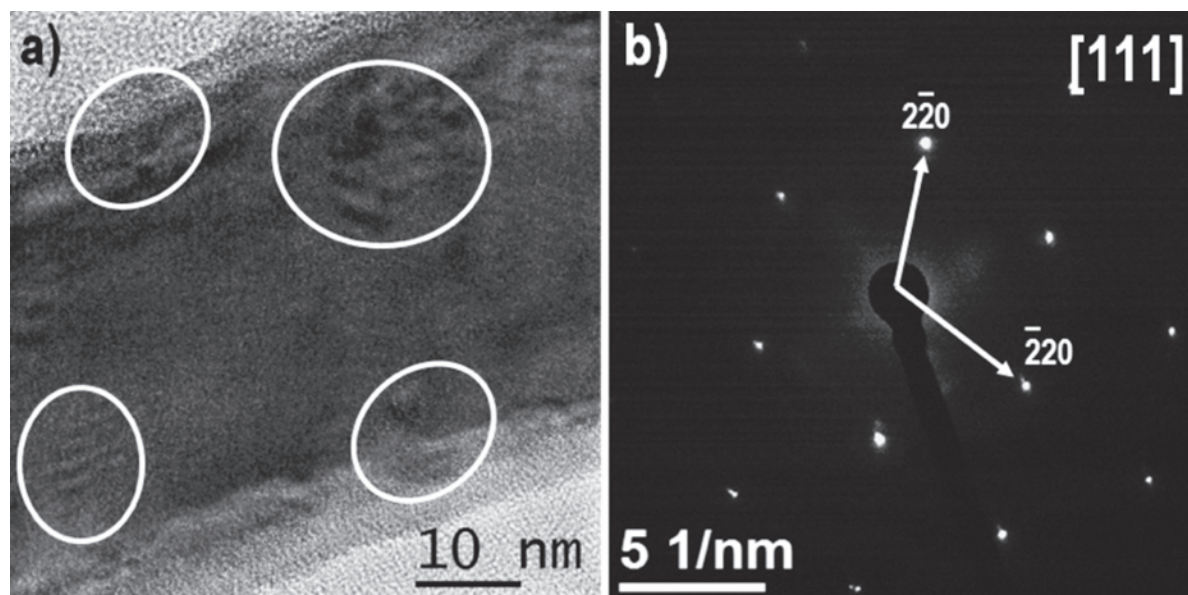


Figure 1. a) TEM image of an as-grown NW exhibiting the rock salt $\beta\text{-GeTe}$ phase and b) its electron diffraction pattern recorded along the $[111]$ zone axis.

As the Ge oxidation precedes and the shell thickness increases, the nanocrystals are eventually embedded into the oxide layer.

We can further argue that the selective oxidation of Ge that we observe is a peculiar behaviour of the GeTe NWs. In fact, similar studies on bulk material indicate a congruent oxidation of both the atomic species and the formation of a GeO_2 and TeO_2 mixture (Yashina *et al.*, 2008).

Conclusion

In this paper we bring compelling evidence of a selective Ge oxidation at the surface of GeTe NWs. The excess Te self-assembles forming GeTe_4 nanocrystals. As the oxidation continues, the thickness of the amorphous shell surrounding the NWs embeds those crystals.

The process is very fast: we observed the forma-

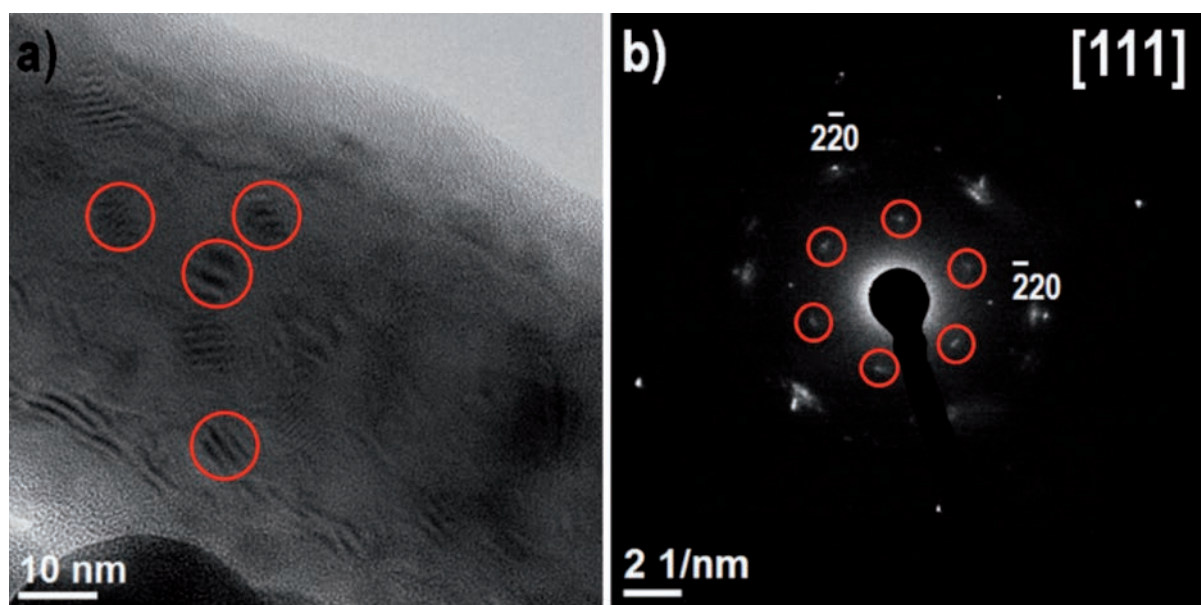


Figure 2: a) TEM image of a GeTe NW after six weeks from the synthesis and b) its electron diffraction pattern recorded along the [111] zone axis. The six inner spots (red circles) come from the nanosized grains circled in a) and correspond to the (220) reflection of the GeTe_4 .

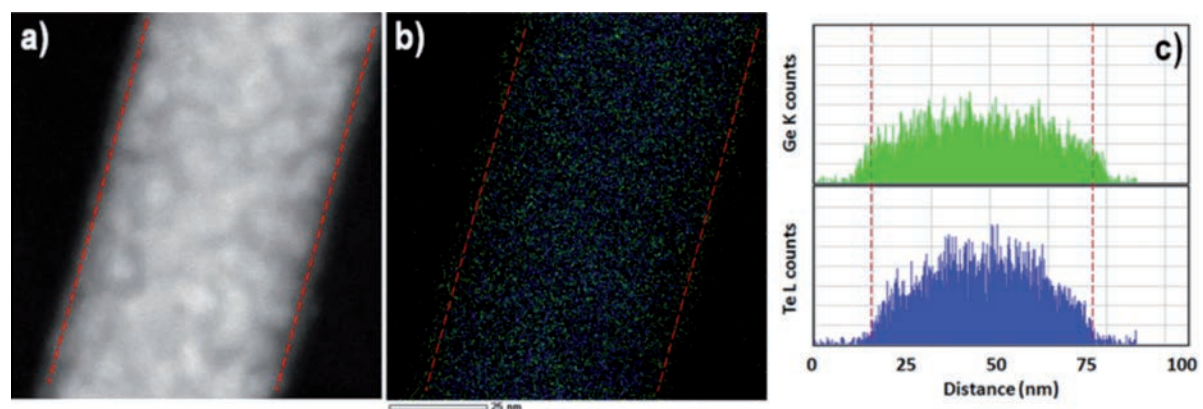


Figure 3: a) STEM-HAADF image of a six weeks aged NW. b) EDX map of the elemental distribution of Ge (green) and Te (blue) and c) intensity line profiles across the NW diameter.

tion of a 20 nm thick amorphous shell, corresponding to a consistent part of the overall NWs diameter, in less than three months, starting from the NWs synthesis.

The presence of an amorphous shell is certainly able to alter the electrical properties of the NWs, and consequently, of the device: the electrically insulat-

ing oxide shell prevents any further writing or reading of the memory cell basically destroying it. Considering the velocity of the process, that largely exceeds the commonly studied device failure mechanism, our results will help designing future PCMs devices.

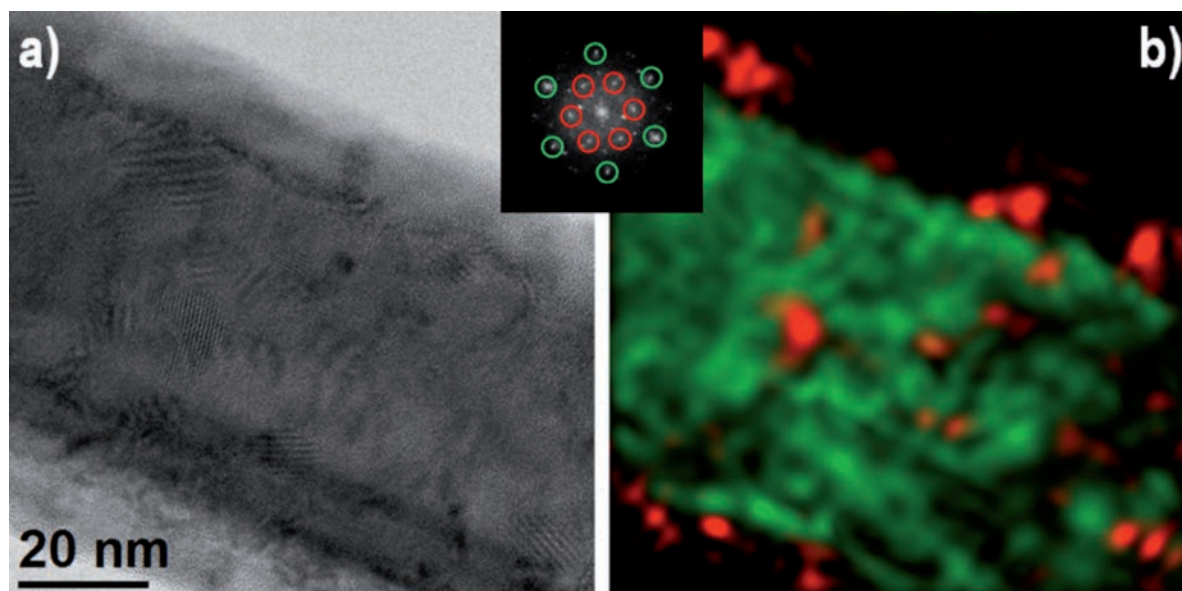


Figure 4: a) TEM image of a twelve weeks aged NW. b) Map representing, in false colors, the region where the GeTe (green) and GeTe₄ (red) atomic structures are observed. The map is color-coded according to the FFT reported as inset.

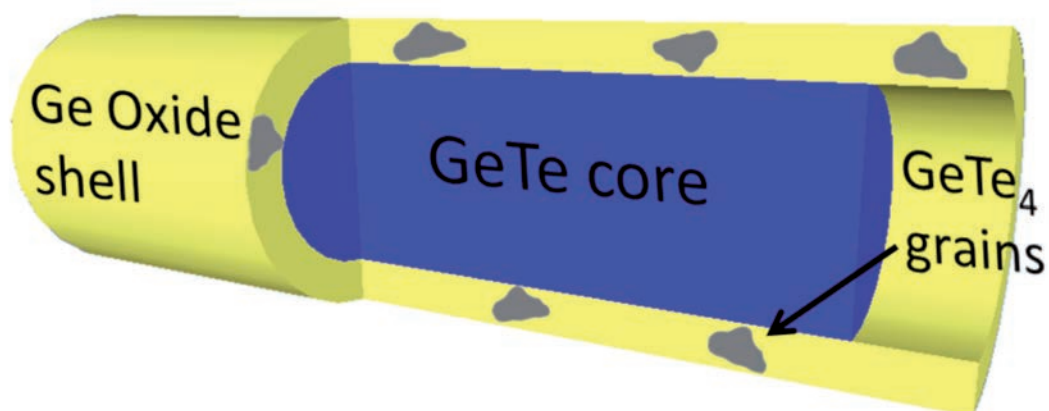


Figure 5. A graphical representation of the ageing process.

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