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Review

Modern chemical synthesis methods towards low-dimensional phase change structures in the Ge–Sb–Te material system

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Abstract

This report centers on different modern chemical synthesis methods suitable for production with which low-dimensional crystalline structures are attainable in the Ge–Sb–Te material system. The general characteristics of the methods are described first. The special challenges are discussed for the Ge–Sb–Te material system. Growth optimization is studied, and the resulting nanostructures are presented. At last a comparison of the methods is given with respect to research scale vapor transport approach on the one hand and the potential described for future application in technology on the other hand.

Keywords: nanostructures; self-assembly; data storage; epitaxy.

1. Introduction

Phase change (PC) materials are well known for their unique characteristic that physical properties such as reflectivity and resistivity change by orders of magnitude when their state of aggregation is altered from amorphous to crystalline and vice versa [1,2]. The resistance changes exhibit a hysteretic signature so that the property is labeled memristive [3]. These characteristics are found in the higher chalcogenides, i.e. in tellurides such as germanium antimony telluride (GST) of various compositions and silver indium antimony telluride (AIST) as well as in a few selenides. The materials have attracted a lot of attention not only due to a fundamental interest in the origin of the property change but also due to the development of applications which take advantage of these changes. The application of data storage is especially of extreme importance for modern information technology. The reflectivity change has already been exploited industrially in optical data storage devices such as in CDs, DVDs and Blu-ray Discs [2]. The resistivity change is to be employed for next generation electronic non-volatile data storage. Until resistive memories can become commercially available on a large scale, however, a number of issues regarding reliability, lifetime, sustainability and integration density need to be addressed. Furthermore, possibilities for a functionality expansion may additionally come into focus. The key to these challenges will lie in the reduction of PC material dimensionality. One of

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the most intensively studied materials for phase change memory (PCM) cells based on conventional thin films is $Ge_2Sb_2Te_5$ (GST), leading to a programming current of the order of a few 100 μA [4]. It has been shown that the use of GST-based nanostructures allows the exploitation of the scaling properties of a PCM device, along with the advantage of low-manufacturing costs and a reduction of the power consumption. In particular, GST nanowires (NWs), acting as self-heating resistors, offer promising perspectives. An overview of their fabrication and characterization techniques can be found in Reference 5. The basic idea to downscale the phase change materials is related to the reduction of the programming volume, which in turn reduces the required energy (set and reset currents, necessary to crystallize and melt the GST, respectively) for the amorphous-to-crystalline and crystalline-to-amorphous phase transitions, thus the power consumption. On top, a crucial factor in reducing the programming current is given by the contact area between the phase change material and the electrodes [4]. Heat localization plays a crucial role for an optimized PCM switching process, along with the absence of thermal cross talk among adjacent cells. From this point of view, chalcogenide nanowires are promising, since they have shown a reduced thermal conductivity and a reduced proximity disturbance; last, different size effects contribute to the advantages of nanostructures [6] such as the reduction of the set currents with NW dimensions and power consumption [7]. The nanowires themselves additionally help shed light on the fundamental mechanisms of phase switch. In particular, Y. Jung et al. and S. Nam et al. [8,9] examined single GST NWs with HR-TEM observations and could reveal the structural and electrical modifications during the phase change. A recrystallization mechanism dominated by nucleation was confirmed and a transformation to the amorphous phase was ascribed to the formation, oriented motion and clustering of dislocations driven by electrical wind forces. All in all the reduced dimensionality will further help elucidate the characteristics of structures and help nurture the further improvement of the materials on the one hand. Low dimensional structures inherently possess the prospect of ultra-high integration, higher switching speed and lower power consumption of the developed devices on the other hand. Progress in their development is not only economically driven, but essential to green information technology. In the past, PC materials were predominantly deposited as thin films by physical vapor deposition (PVD) techniques such as sputtering, laser ablation and evaporation and are amorphous. Low dimensional structures of these thin films can only be realized by lithographical structuring techniques followed by reactive ion etching (RIE). However, RIE is most likely to produce damage in the material during etching, especially since the bond strengths in the higher chalcogenides are weak. Unfortunately, an assessment of material properties with respect to their dimensionality then becomes questionable. Therefore conventional deposition techniques have reached their limit. To enter the next development stage and also to help surpass the limits of functionality [10], modern nanotechnology methods are called for which can produce the low-dimensional structures directly using self-assembly processes. Standard nanotechnological methods need to be applied to the deposition of phase change materials. They are based on the growth of *crystals* in the desired habitus and size. In contrast to as deposited amorphous materials, which become polycrystalline and form grain boundaries upon crystallization that may affect their properties, the methods discussed here inherently allow the formation of highly perfect monocrystalline material.

Even though monocrystalline nanostructures have already been produced to a high degree of perfection by a vapor transport technique [11–14], this approach is only useful for research scale nanostructure synthesis but not suitable for industrial application. In this paper at first 3 different chemical synthesis techniques were chosen, which are used in modern synthesis for the formation of crystalline nanostructures, and will be introduced: the vapor liquid solid/particle assisted growth (VLS-MOVPE) method and the selective area growth method both using metalorganic vapor phase epitaxy (SA-MOVPE) and solvothermal synthesis. Schematics of the synthesis methods under discussion are presented in Fig. 1. The first two methods are carried out in the gas phase, whereas the latter deals with synthesis in the fluid or liquid phase. The methods will then be applied to the synthesis of crystalline nanoscale phase change materials in the Ge–Sb–Te material system structures. Since for any device application, position control is mandatory, a short survey on nanostructure positioning methodology is given. At last the nanostructure synthesis methods will be compared and assessed with respect to the vapor transport approach on the one hand and to their application for future data storage devices based on resistive switching on the other hand.