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Cluster beam synthesis of metal and metal-oxide nanoparticles for emerging memories

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ABSTRACT

In this work we present results concerning the cluster beam synthesis of metal and metal-oxide nanoparticles together with their applications in emerging memories like nanoparticle Flash memories and resistive switching memories. Regarding the former, very large memory windows of 7–8 V are presented at voltages below 10 V using Ni, Pt or Au nanoparticles. Regarding the latter, metal–insulator–metal devices based upon titanium oxide nanoparticle films show switching voltages well below 1 V with high-to-low resistance ratios as high as 1000. An in depth analysis of the physical and electrical properties of the titanium oxide nanoparticle films allows to shine light onto the physics behind the switching mechanism.

1. Introduction

Nanoparticles (NPs) are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. The interest in NPs with typical sizes in the range 1–100 nm is due to the fact that the magnetic, optical and electronic behaviour of bulk materials can be modified when they approach the nanometer scale. In the last 20 years, research has focused on understanding the origin of these new properties. There are two major phenomena that are responsible for these differences [1–3]. First, some interesting and sometimes unexpected properties of NPs are largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material. As the size of a crystal is reduced, the number of atoms at the surface of the crystal compared to the number of atoms in the crystal itself, increases. For example, a 4 nm diameter CdS nanoparticle has about 1500 atoms, of which about a third are on the surface. Properties, which are usually determined by the molecular structure of the bulk lattice, now become increasingly dominated by the defect structure of the surface. There are some properties that directly depend on the average coordination number of the participating atoms, such as the melting point or the solid–solid phase transition in a crystal. As a result of the reduction in the number of neighbouring atoms, surface atoms have narrower d-bands, so that the density of states can vary considerably. The second phenomenon occurs noticeably only in metals and semiconductors. It is called size quantization and arises because the size of a nanoparticle is comparable to the de Broglie wavelength of its charge carriers. Due to the spatial confinement of the charge carriers, the edge of the valence and conduction bands split into discrete, quantized, electronic levels. Thus, NPs lie in between the atomic and molecular limit of a discrete density of electronic states and the extended crystalline limit of continuous bands.

The focus of this work is the presentation of results concerning the use of NPs deposited using a novel room temperature cluster beam technique and the demonstration of their applications in two emerging non-volatile memory (NVM) technologies. The first one, initially proposed by Rana et al. [4], represents an evolution of the standard floating gate NVM (which is the building block of the Flash architecture) and consists in the replacement of the floating gate with a NP layer, namely Flash-like NP NVMs; the second relies on the resistive switching (RS) phenomenon of insulating and semiconducting materials but in our approach a NP film will be used rather than a conventional thin film, namely NP RS NVMs. This work, except of presenting new results, provides also a review and in depth insight into the main results obtained by the authors during the last years research on Flash-like NP NVMs [5–8] and more recently NP RS NVMs [9].

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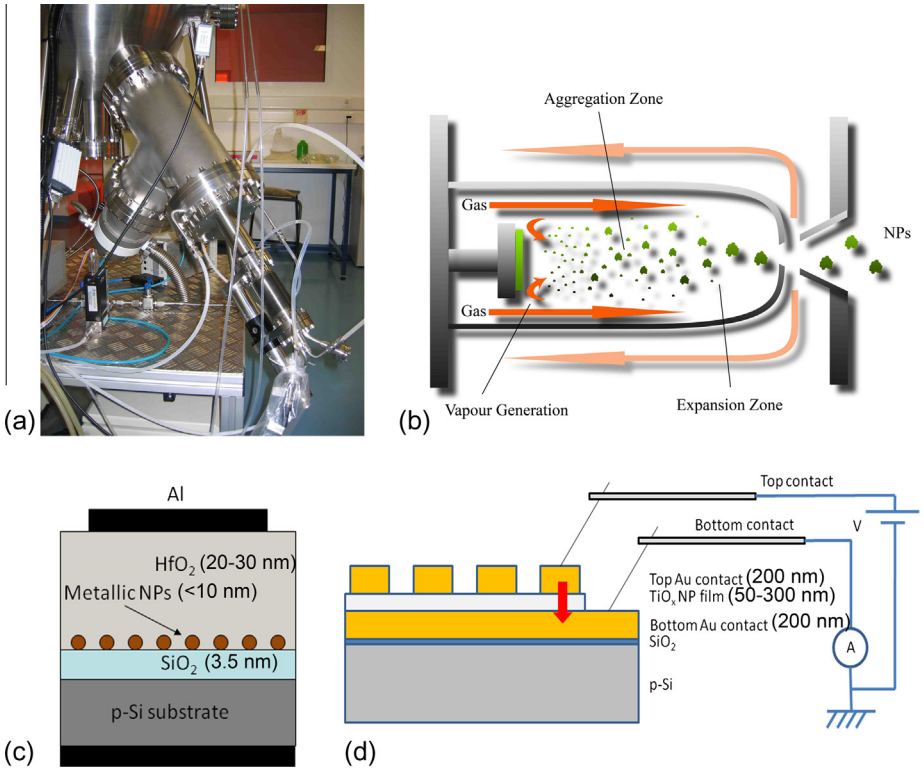

Fig. 1. (a) and (b) Picture and schematic of the cluster beam generator used in this work; (c) and (d) schematics of the devices presented in this work: the former is a Flash-like NP NVM and the latter is a crossbar RS NVM based on TiO NP films.

Concerning the Flash-like NPs NVMs, the use of metallic NPs represent an important advantage over Si NPs since the wide variety of materials available provide a variety of work functions that allows the engineering of the barrier seen by the charges stored into the NPs. On the other hand, the use of metal-oxide NPs in RS memories should provide the framework for creating multifunctional nanostructured films and easily tunable RS characteristics.

2. Experimental

The synthesis techniques of NPs, relevant for microelectronic applications, are basically three: colloidal, metal evaporation with subsequent thermal annealing, gas condensation. The preparation of NPs in colloidal systems is one of the most well-known methods for the synthesis of nanomaterials. Another well known technique is based on the evaporation of the thin metallic films on the substrate which drive to the formation of metallic islands [10]. In some cases the thermal annealing of the film helps in the formation of the NPs [11]. The drawback of this technique is the non-spherical shape of the NPs and the impossibility to perform size selection. The gas condensation technique is the one adopted in this work and is based on the nucleation and growth in flight of the metallic atoms from the gas phase. In this work the gas phase is realized by DC magnetron sputtering of the metallic target. This process takes place in a small chamber, NanoGen[1], attached through a small aperture (~5 mm) to the main one, where the samples are placed (Fig. 1a and b). As the sputtering goes on, the high pressure difference between the NanoGen and the main chamber (10^{-2} mbar and 10^{-4} mbar respectively) sweeps the atoms sputtered from the target material through the Nanogen toward the small aperture. During this phase, nucleation and growth of the NPs takes place until they reach the aperture and enter the main chamber to be soft landed on the sample's surface. The whole process takes place at room temperature and is schematically represented in Fig. 1b. It is clear that two are the main parameters governing the size and flux of the NPs: the gas pressure in the Nanogen, which depends mainly on the Ar flow and DC sputtering power, and the distance between the target and the final aperture. The latter can be varied from a minimum of ~10 cm (namely position 0) to a maximum of ~20 cm (namely position 100) and has direct effect onto the size of the generated NPs. The larger is the distance the bigger is the nanoparticle diameter. We should remind at this point that the detailed geometry of the system target-magnetron head also plays a role in defining the sputtering efficiency for a particular target. In particular, the target thickness and the way the target is mounted will contribute, together with the other parameters mentioned above, in defining the sputtering efficiency by defining the magnetic field strength and the Ar flux respectively. For this reason in the experiments presented here below we always kept the target thickness constant (a copper spacer was used when using thinner targets) to 3 mm and always mounted the targets in the same way in an attempt to minimize the effects of the above mentioned geometrical parameters and thus allow for a more reliable direct comparison of results obtained with different target materials. As is, this technique allows fabricating NPs with size distributions with standard deviations of 20–30% the mean size. Since the 80–90% of the NPs result to be charged with 1 electron, they can be manipulated in flight using appropriate electric fields [12,13]. The details of the physics governing this nanoparticle fabrication technique have been recently published by Quesnel et al. [14].

The samples discussed in this work are based on the deposition of NP films by DC sputtering of pure Ni, Pt, Au and Ti targets in our cluster beam generator. Ni, Pt and Au NPs were used in Flash-like NVMs while Ti NPs, upon in flight oxidation of the NPs before

[1] www.mantisdeposition.com.