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Growth and self-assembly of $BaTiO_3$ nanocubes for resistive switching memory cells

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ABSTRACT

In this work, the self-assembled $BaTiO_3$ nanocubes based resistive switching memory capacitors are fabricated with hydrothermal and drop-coating approaches. The device exhibits excellent bipolar resistance switching characteristics with ON/OFF ratio of 58–70, better reliability and stability over various polycrystalline $BaTiO_3$ nanostructures. It is believed that the inter cube junctions is responsible for such a switching behaviour and it can be described by the filament model. The effect of film thickness on switching ratio (ON/OFF) was also investigated in details.

1. Introduction

Resistive random access memory (RRAM) is a feasible next generation, non-volatile memory technology that utilizes two bi-stable resistances, such as high resistance states (HRS) and low resistance states (LRS). One bit of a RRAM device can be composed of one transistor and one RRAM capacitor. In contrast to a dynamic random access memory capacitor (DRAM) [1,2], a RRAM capacitor exhibits two resistances states of HRS and LRS that can be switched by an external bias or preserved as information. In comparison with current non-volatile random access memory (NVRAM), RRAM has unique advantages, such as a smaller bit cell size, and lower operating voltages. In addition, the resistive transition induced by electric pulses with opposite polarities can be achieved within tenths of nanoseconds at room temperature and the resultant resistance states can be retained for 10 years [3]. Thus, RRAM is expected to be widely utilized as the future nanoscale memory devices.

The key component of RRAM devices are capacitors that consist of an insulating layer (metal oxides) sandwiched by two electrodes, and exhibit reversible electrical field induced resistive switching. The switching processes in metal oxides capacitors seem to be limited to a small region near the interfaces between the electrodes and the metal oxide layer [4–6] in vertical directions, which makes the use of nanometer scale metal oxide films highly desirable. However, cost and complication are the drawback of current optics-based lithography technology for making nanoscale features. As a result, nanometer scale metal oxide based resistive devices were seldom reported [7]. To fabricate RRAM devices in a nanometer scale, it is necessary to construct well defined nanocapacitors for memory cells.

For the design of nanocapacitors, the synthesis of metal oxide nanostructures with well-controlled shapes is of great interest because the size and shape largely determine the resistive switching properties [10–12]. Moreover, the self-assembly of metal oxide nanostructures into tailored nanocapacitor arrays with the enhanced properties is a promising strategy for potential RRAM device applications. For the first issue, the formation of perovskite oxide nanostructures with a wide variety of shapes, including rods, spheres, cubes, and many other exotic shapes has been reported via vapor and solution based methods. Among these shapes, cubic structures are the ideal building blocks because their unique structure usually results in the formation of highly coordinated square arrays that are important for high density information storage. The distinct geometry of nanocubes would leads to an excellent non-volatile behaviour with a narrow dispersion of the on/off ratio because of the formation of straight and extensible conducting filaments along the direction of each vertically aligned nanocube. Furthermore, the bottom-up approach using self-assembled perovskite oxide nanocubes will offer a platform to directly characterize the nanoscale conduction paths by confining the resistive switching area and identifying the location of conduction paths. Therefore, the self-assembly of perovskite oxide nanocubes with ideal nanocapacitor arrays would have great potential for fundamental research and next generation RRAM applications.

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In this paper, well-defined $BaTiO_3$ nanocubes with a good size distribution were prepared and continuous thin films were obtained with self-assembly technique. The electrical properties of self-assembled $BaTiO_3$ nanocubes were measured and they show promising resistive switching properties. A conducting filament model based on oxygen ions/vacancies was suggested to explain resistive switching properties.

2. Experimental section

Chemicals, such as Barium hydroxide octahydrate (Sigma-Aldrich, $Ba(OH)_2 \cdot 8H_2O$, $\geq 98\%$ purity), Bis (ammonium lactate) titanium dihydroxide (Sigma-Aldrich, $C_6H_{18}N_2O_8Ti$, 50 wt% in H_2O), Sodium hydroxide (Sigma-Aldrich, NaOH, $\geq 98\%$ purity), oleic acid(Fluka, $C_{18}H_{34}O_2$, $\geq 99.0\%$ purity), and *tert*-butylamine (Aldrich, $C_4H_{11}N$, $\geq 99.5\%$ purity) were used without further purification.

In a typical synthesis, the Barium hydroxide octahydrate and bis(ammonium lactate) titanium dihydroxide (TALH, Molar ratio = 1: 1) were mixed into aqueous solutions. 5 M of sodium hydroxide solutions was added into aqueous solutions. The solutions then were transferred into a 50 ml vessel and *t*-butylamine and oleic acid were added in to the solution. The ratios of Ba, oleic acid and *t*-butylamine were varied, such as ratio of 1:8:8 was used in the synthesis. The total volume of final solution was 30 ml. Then the vessel was placed into autoclave and heated up to 200 °C for 72 h with stirring. After 72 h, the precipitate was centrifugally separated and washed by ethanol twice for dispersion preparation. The precipitate was then dispersed into 3 ml of toluene. After that, the dispersed solution was drop coated three times to get self-assembled $BaTiO_3$ thin films. The film was treated with ultraviolet (UV) after every drop coating to eliminate all organics.

The phase composition of the samples was determined by X-ray powder diffraction (PANalytical Empyrean with Cu*K*α). The morphologies and microstructure of the samples were characterized by scanning electron microscopy (Nova Nano SEM 230) and transmission electron microscopy (Philips CM200), respectively. To measure the electrical properties (resistive switching characteristics) of the films, Au top electrodes (250 μm in diameter) were patterned and deposited by sputtering using a metal shadow mask. Voltage–current curves of the films were measured using an Autolab 302N electrochemical workstation controlled with Nova software. In the measurement, the working electrode and sensor electrode were connected to the gold (Au) top electrode, while the reference and counter electrodes were connected to the bottom electrode, which is illustrated in Fig. 1.

3. Results and discussion

Fig. 2 shows the TEM images of the particles synthesized at fundamental reaction conditions (200 °C, 72 h). An ordered arrangement of $BaTiO_3$ nanocubes with well-defined cubic morphology ranging from 15 to 30 nm was obtained. The HRTEM image of the nanocube showed that it was highly crystalline, and the single crystalline nature of an individual $BaTiO_3$ nanocube can be confirmed by the uniform crystal lattice fringes of the whole nanocube. The distance between the lattice fringes was 0.403 nm, corresponding to the (1 0 0) planes of cubic $BaTiO_3$, suggesting that the as-prepared $BaTiO_3$ nanocubes are exposed with (1 0 0) facets.

The TEM specimen was actually prepared from the suspension that was simply made from dissolving the dried $BaTiO_3$ powders into toluene. Apparently, this method may cause the random aggregation of nanocubes and a disordered array would be expected to see. However, a small area of self-assembly can be observed in Fig. 2b. This phenomenon can be explained as the strong repulsive forces, which are attributed to the interactions

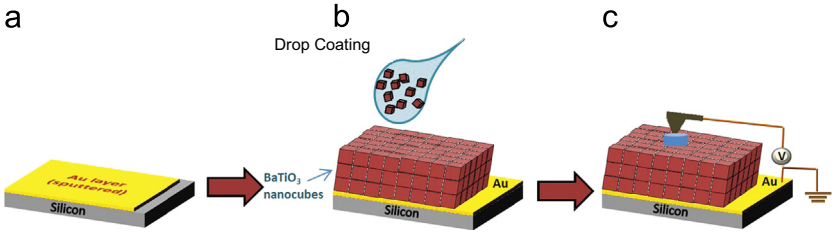

Fig. 1. Schematic diagram for the sample preparation and measurement processes.

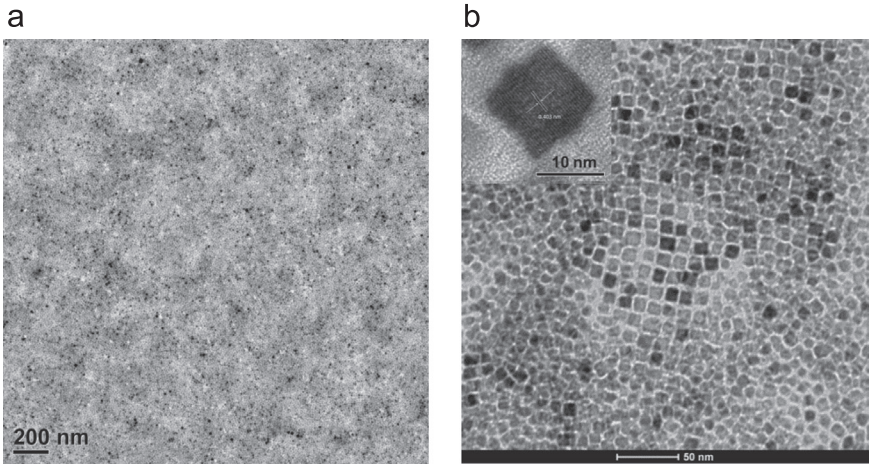

Fig. 2. TEM and HRTEM images of $BaTiO_3$ nanocubes.