Combinatorial synthesis and evaluation of epitaxial ferroelectric device libraries

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Combinatorial libraries of parallel-plate capacitors, consisting of Pt and La_{0.5}Sr_{0.5}CoO_{3} electrodes and a doped Ba_{x}Sr_{1-x}TiO_{3} dielectric layer, have been fabricated and analyzed to systematically study the effects of dopants on device performance. Epitaxial heterostructure libraries with sharp interfaces were generated from amorphous layers on LaAlO_{3} substrates. Two hundred and forty different host/dopant combinations were synthesized on a 1/2 in. by 1/2 in. substrate, with 23 capacitors for each combination. Addition of 1.5 mol % W was found to increase the figure of merit ($e/I_{\text{leak}}$) 220-fold and reduce the high-frequency (MHz and GHz) loss tangent by fourfold. © 1998 American Institute of Physics. [S0003-6951(98)00533-6]

Because performance of electronic devices can depend heavily on interactions between different constituent materials, it is often desirable to evaluate materials properties in a device format. The analysis and optimization of the effects of adjacent materials and interfaces on the performance of a multilayer device can be quite complex, and often involve a highly empirical, iterative experimental approach. A combinatorial approach, in which many different devices are fabricated and rapidly analyzed, may help to directly solve materials issues related to device performance. There are many multilayer device applications ranging from spin-valve magnetic recording heads to electroluminescent devices that could immediately benefit from such an “integrated device chip” approach. The ability to generate and analyze device libraries would significantly expand the scope of materials issues subject to combinatorial approaches. Here, we report the fabrication and analysis of combinatorial libraries of parallel-plate capacitors, in which thin-film dielectrics with different compositions are directly incorporated into arrays of epitaxial multilayer device structures.

A pressing materials issue in the development of the next generation of integrated capacitors and dynamic random access memories (DRAMs) is the identification of the optimum dielectric material. A useful figure of merit for evaluating charge storage capacitors in DRAMs made of high dielectric constant materials, where excessive leakage rather than avalanche breakdown limits performance, is the time constant for charge storage, $RC$ (where $C$ is the capacitance, and $R$ is the effective resistance defined as the operating voltage divided by the leakage current). In turn, the ratio of the effective dielectric constant and leakage current density, $e/I_{\text{leak}}$, can be used to evaluate dielectric performance. Because of its large dielectric constant, Ba_{x}Sr_{1-x}TiO_{3} (BST) is a leading candidate material.

One strategy that has been used to lower leakage current in devices made of this material involves engineering Schottky barriers at the interfaces between both electrodes and the dielectric material. Schottky barriers have been shown to reduce device leakage current to a level of $10^{-8}$ A/cm$^2$. This low leakage current results not from the intrinsic properties of BST, but instead mainly from the Schottky barriers. Formation of good barriers often requires careful heat treatment of the completed device in different atmospheres at high temperatures. An alternative approach for reducing leakage current is to directly reduce conduction in the dielectric material itself, eliminating the need for interfacial Schottky barriers. Here, we show that combinatorial methods can be used to systematically investigate the properties of devices made from the host BST containing a large number of different metal dopants. Our results show that 1.5 mol % of added with W can significantly reduce the conduction (leakage current and loss tangent) of BST and improve its $e/I_{\text{leak}}$ ratio 220-fold.

The epitaxial growth of heterostructures in combinatorial thin-film device libraries is necessary in order to explore the intrinsic effects of compositional variations in the absence of polycrystalline microstructural effects, which can provide sites for charge traps and other defects. However, because the conventional techniques of high-temperature in situ epitaxial thin-film growth cannot be used for combinatorial synthesis, we have developed synthesis methods to form epitaxial multilayers from amorphous layers deposited at room temperature.

To construct a capacitor library, a 100–200 nm thick amorphous layer of La_{0.5}Sr_{0.5}CoO_{3} (LSCO) was deposited from a stoichiometric target on a LaAlO_{3} (100) substrate at room temperature using a pulsed laser deposition (PLD) system. The substrate was then annealed $ex situ$ at 850 °C for 1.5 h to form an epitaxial LSCO bottom electrode. The substrate was then mounted back in the PLD chamber and different combinations of the host and dopant were deposited at different sites on the substrate using two-dimensional high-precision shutters. In the $x$ direction, the substrate is divided into three different host regions, BaTiO_{3}, Ba_{0.7}Sr_{0.3}TiO_{3}, and...
Ba₀.₅Sr₀.₅TiO₃, each deposited from stoichiometric targets. In the y direction, the substrate typically is divided into separate dopant regions (up to 4), each containing 0–3 mol % dopant added as a gradient to each host (Fig. 1). The stoichiometry is controlled by moving the shutters at a controlled speed during deposition. Metal oxide dopants (WO₃, Fe₂O₃, MgO, Y₂O₃, CeO₂, La₂O₃, and Mn₃O₄) were used since they have higher deposition rates for PLD than the corresponding metals. In order to assure uniform diffusion, the dopant layers are sandwiched between two identical host layers; the total thickness of the doped BST samples ranged from 300 to 350 nm. With the automated multitarget carousel and shutters in our PLD system, the host/dopant layers can be deposited in a single experiment, typically, in less than 3 h. The library is then annealed ex situ in two steps to ensure interdiffusion of dopants and epitaxial crystal growth. Typical annealing conditions involve treatment at 400 °C for 24 h followed by 850 °C for 1.5 h in flowing oxygen.

The x-ray diffraction patterns of a control sample of Ba₀.₅Sr₀.₅TiO₃ (300 nm) deposited on top of a LSCO (100 nm) electrode, which was grown on a LaAlO₃ (100) substrate, are illustrated in Fig. 2. The sample was prepared in the multilayer format described above and processed concurrently with the library chip. The θ–2θ scan shows (001) peaks of BST, indicating formation of a single phase [Fig. 2(a)]. The ϕ scan of the (101) planes of both the BST layer (top) and LaAlO₃ substrate (bottom) indicate epitaxial growth of both the electrode (LSCO peaks are coincident with the LaAlO₃ peaks) and the dielectric layer [Fig. 2(b)]. Rutherford backscattering spectroscopy (RBS) was used to analyze the composition and verify the extent of interdiffusion in our samples. The RBS spectrum of another sample in which W (20 nm) was sandwiched into BaTiO₃ (250 nm) deposited on a LSCO (100 nm) electrode on MgO (100) substrate (and again processed concurrently with the library) is shown in Fig. 2(c). The fit and the measured spectrum indicate that diffusion of the dopant is highly uniform: the ratio of the elements present at different depths in the BST film is 5:5:1 for Ba: Sr: W, which corresponds to the intended composition of this sample. Similar results were obtained with other dopants. The fit also verifies that the interface between the BST layer and the bottom LSCO electrode is extremely sharp with undetectable interdiffusion. This result indicates that diffusion takes place readily before phase nucleation, but once a crystal structure has formed, it is difficult to induce interdiffusion between the layers. Thus, epitaxial heterostructures, with sharp interfaces and uniformly doped functional layers, can be grown from amorphous layers in a library format.

To complete the device structure, individual Pt electrodes (50 nm) were deposited with a photolithographic mask. The compositional map and a photograph of one such library on a 1/2 in. × 1/2 in. substrate are shown in Fig. 1. Approximately 5500 capacitors, each 50 μm × 50 μm in size, are formed with 240 different host/dopant concentration combinations. This affords about 23 capacitors for each host/dopant concentration, providing a test of the reproducibility of each device.

Both the dielectric constant (εr) and IV characteristics of the individual capacitors in the libraries were measured. The dielectric constant was measured at 1 MHz and is plotted as a function of the mol % of added Y, La, or W dopants for the individual capacitors in the libraries.
In titanate compounds, it is well known that existence of oxygen vacancies provides the primary means of hopping conduction that results in Poole–Frenkel leakage currents and resistance degradation. Oxygen vacancies arise from different mechanisms such as low oxygen partial pressure during material synthesis at high temperatures or the existence of acceptor impurities. W\(^{1,6}\) is expected to substitute into Ti\(^{4+}\) sites as a donor and suppress the formation of oxygen vacancies during the crystallization process at high temperature.\(^5\) Our observation of a large reduction in the Poole–Frenkel leakage current is consistent with this picture. The residual leakage current in W-doped BST [Fig. 3(b)] shows much less voltage dependence, and probably arises largely from extrinsic origins. Other high valence donor dopants may display similar effects, such as those observed in Nb-doped BST films.\(^5\) Mn\(^{3+}\) is expected to substitute into Ti\(^{4+}\) sites as an acceptor. The leakage reduction mechanism in this case may arise from the pinning of free-electron charges released from the oxygen traps.

The effects of dopants on similarly fabricated individual BST films were also probed with other measurements. At 1 GHz, incorporation of up to 3 mol % of W was found to reduce the loss tangent in BaTiO\(_3\) (BTO) films by as much as fourfold, as measured by a scanning-tip microwave near-field microscope.\(^7\) At 1 MHz (measured with interdigital electrodes), the same dopant was found to reduce the loss tangent in BTO films by about the same factor. These measurements further confirm the device results and suggest that doping with W reduces the conductivity of the material. The finding of a large reduction in Poole–Frenkel leakage current by addition of W demonstrates that significant improvements in device performance can result from optimizing materials in a device library format.

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**FIG. 3.** (a) Dielectric constant vs dopant concentration for various dopants in Ba\(_{0.5}\)Sr\(_{0.5}\)TiO\(_3\) (330 nm thick) capacitors measured at 1 MHz using a HP4280A; (b) current–voltage characteristics of W-doped Ba\(_{0.5}\)Sr\(_{0.5}\)TiO\(_3\) (330 nm); and (c) of Mn-doped Ba\(_{0.5}\)Sr\(_{0.5}\)TiO\(_3\) (330 nm thick) capacitors. The data points are averaged over values obtained from several capacitors with the same dopant concentration. Not all the duplicate capacitors within each composition were measured. In order to minimize the effect of relaxation currents, for each measurement, voltage is first applied for 0.5 s, and then current is measured in the next 0.2 s.

Ba\(_{0.5}\)Sr\(_{0.5}\)TiO\(_3\) in Fig. 3(a). The variation in \(\epsilon_r\) for adjacent rows of capacitors with identical host/dopant combinations is, typically, within 5% of an average value. All dopants used were found to reduce \(\epsilon_r\) of BST.

The voltage-dependent leakage current for capacitors doped with W and Mn is shown in Fig. 3(b). The observed voltage dependence of leakage currents for both doped and undoped BST is apparently dominated by Poole–Frenkel emission.\(^4\) The values of the Poole–Frenkel leakage current densities for undoped BST observed here are similar or better than those commonly observed.\(^4\) Although the data show no clear Schottky barrier breakdown threshold behavior, a weak bias–polarity dependence in the leakage current was observed, indicative of the presence of a weak barrier (most likely at Pt/BTO interfaces). It was found that the W- and Mn-doped capacitors display significant reductions in the Poole–Frenkel leakage current in all three hosts, while the capacitors doped with other metals did not show any noticeable change in leakage current. The leakage current density reduces to 1.5 × 10\(^{-6}\) A/cm\(^2\) at 5 V for capacitors doped with 1.5% W [Fig. 3(b)]. Although, doping reduces the dielectric constant slightly (from ~600 to ~400), the more dramatic effect on leakage current results in a significant improvement in the \(\epsilon/\epsilon_{\text{leak}}\) ratio: \(\epsilon/\epsilon_{\text{leak}}\) for 1.5% W-doped BST is improved ~220-fold over pure BST.

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