Characterization of Physical and Electrical Properties of BaTiO₃ Films Deposited on p-Si by Modified Polymeric Precursors

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Highly uniform BaTiO₃ (BTO) films with thickness well below 100 nm were deposited on p-Si by spin coating using a modified polymeric precursor method. The polymeric precursor gel was redissolved into glacial acetic acid to improve the wetting property of the spinning solution to the Si substrates (2.5-in. diameter). The morphology, composition, thickness, and refractive index of the films were investigated using x-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), and ellipsometry. The films are found to be polycrystalline. They exhibit uniformity over the whole wafer in regard to thickness, composition, and absence of surface features. The capacitors constructed with the BTO films on Si were further investigated by electrical characterizations. Current-voltage (I-V) measurements reveal a leakage current due to a Poole–Frenkel mechanism. The energy gap is evaluated to be 3.95 eV. A metal-insulator-semiconductor (MIS) behavior is observed through capacitance-conductance-voltage (C-G-V) measurements. The interface state density (Dᵢ) at the BTO/p-Si interface is estimated to be of the order of 10¹² eV⁻¹ cm⁻².

Key words: High-k dielectrics, metal-oxide-semiconductor (MOS) capacitors, electrical characterization, interface states, polymeric precursor method, barium titanate

INTRODUCTION

Alternative high-k dielectrics to SiO₂ have recently attracted great attention for applications in electronic devices.¹⁻³ One promising class of materials is ferroelectrics, such as SrTiO₃ (STO), BaTiO₃ (BTO), and (Ba₁₋ₓSrₓ)TiO₃ (BST).¹⁻⁴ Barium titanate (BaTiO₃) and the other perovskite-type materials are being extensively studied for their potential commercial applications in metal-oxide-semiconductor (MOS) capacitors due to their desirable dielectric properties.³⁻⁸ Many methods, such as sputtering,⁹ laser ablation,¹⁰ metalorganic chemical vapor deposition (MOCVD),¹¹ and sol-gel¹² techniques, have been used to grow thin films; however, most of these methods are expensive and require complex equipment. The polymeric precursor method¹³⁻¹⁶ is a chemical technique that offers several advantages, such as low cost, good compositional homogeneity, high purity, relatively low processing temperatures, and the ability to coat large substrate areas. In this technique, the desired metal cations are chelated in a solution using a hydroxycarboxylic acid as the chelating agent. The solution is mixed with a polyhydroxyalcohol and heated to promote esterification reactions in the solution, while the metals remain homogeneously distributed in the polymeric network. However, we found it problematic to obtain uniform films by spin coating the aqueous polymeric precursor solution directly on Si, probably due to the poor wettability of the aqueous solution to the hydrophobic Si surface. The problem of uniformity can be alleviated by using concentrated aqueous solution, but this will
typically result in films with thickness well above 100 nm by only one spin of the solution, which is undesirable for use as dielectrics in MOS devices. In this study, we have modified the polymeric precursor method by redissolving the polymeric precursor gel into glacial acetic acid, and have for the first time, to the best of our knowledge, succeeded in obtaining highly uniform BTO films directly on Si substrates with thickness well below 100 nm.

Metal-oxide-semiconductor capacitors (MOSCAP) with BST, BTO, and STO films as the dielectric, as in metal-insulator-semiconductor (MIS) structures, have been reported and analysed. In all cases, reliability issues have risen due to process related defects, leakage currents, or abnormal behavior of the dielectric. These issues have been reported and analysed concerning different materials and deposition techniques while recent reports indicate that degradation mechanisms need to be addressed in more detail if more complex systems are to be built. In this paper, we will report the electrical properties of MOSCAPs constructed with the BTO films deposited on p-Si using our modified polymeric precursor method. The aim is to study the electrical properties, identify possible defects, and compare the results to those recently published on similar capacitors built with sputtered films deposited at low temperature. Issues such as the leakage current and its origin, as well as the capacitive and conductive response of the MOSCAPs are examined.

EXPERIMENTAL PROCEDURE

The BTO films were prepared by a modified polymeric precursor method. Initially, Ti (IV) isopropanoxide was added into a citric acid solution (60–70°C) to form titanium citrate. After homogenization of the Ti-citrate solution, a stoichiometric amount of BaCO₃ was slowly added under stirring. Ammonium hydroxide was also added to promote the complete dissolution of BaCO₃ (the final pH of the solution was 7–8). After homogenization of the solution, ethylene glycol was added to promote citrate polymerization by polyesterification reactions. The molar ratio of Ba/Ti was 1:1, the citric acid/Ba molar ratio was fixed at 1.00, and the citric acid/ethylene glycol ratio was fixed at 60/40 (mass ratio). Polymerization was performed at 90°C for 12 h in an open-mouthed 500 mL beaker (evaporated water was compensated for periodically). At the final stage, more water was not added so that the polymeric precursor solution became a highly viscous gel. A solution for spin coating was prepared by redissolving 0.25 g of the gel with 10 mL of glacial acetic acid. Polished Si (100) wafers (p-type, 2.5 in.) were freshly treated with HF solution before use as substrates. The solution was deposited onto the Si substrates by spinning at 3000 rpm for a period of 30 sec. An atmosphere of acetic acid was created over the spinning substrate by forming a pool of acetic acid underneath the spinning stage and covering up the system with an inverted cup. After deposition, the films were dried on a hot plate at ~150°C for 2 min to remove residual solvents. Heat treatment was carried out in a furnace under air at atmospheric pressure with a preset temperature and all samples were treated at 450°C for 2 h.

The thickness and refractive index of the BTO films on Si were measured with an ellipsometer (Rudolph Research Auto-El III, at λ = 632.8 nm) and were averaged over 3–5 different measuring points.

X-ray diffraction spectra were recorded using a Philips Goniometer PW1050-25, with the CuKα line. Analysis with scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS) was carried out on a JSM-6300 scanning electron microscope equipped with the EDS detector 6699 (window ATW2). The atomic analysis was performed with the program Link-ISIS.

The resistivity of the Si substrates was in the range of 100–500 ohm cm. Construction of effective electronic devices was made possible by the evaporative deposition of Al metal electrodes on the back of the Si substrate in order to form an ohmic contact and on top of the BTO films via a mask allowing the creation of 1-mm, 2-mm, and 3-mm dots. Thus, devices with the structure of Al/BTO/p-Si were prepared.

For the electrical measurements, the samples were kept in a cryostat under a controlled reduced He atmosphere. The temperature was controlled using an Oxford ITC503 Temperature Controller with a resolution of ±0.01 K.

The current-voltage (I-V) curves were taken using a Keithley 617 programmable electrometer connected with an Oltronix power supply, in the temperature range from 213 K to 333 K.

The dielectric response measurements, C-V, G-V, and admittance spectroscopy Y-ω were performed using a Novocontrol Alpha-N Dielectric Response Analyzer suitably controlled by the WinData software package at room temperature.

RESULTS AND DISCUSSION

The BTO films on Si deposited with our modified polymeric precursor method look to the naked eyes very uniform over a whole silicon wafer (2.5-in. diameter), free of striations and interference color. This is in agreement with the ellipsometry measurements, which show that the film thickness and refractive index are consistently 57.1 nm (±0.3 nm) and 1.802 (±0.003), respectively, measured on 3–5 points well separated over the whole film surface. The crystallinity of the BTO thin films was investigated by x-ray diffraction (XRD). Figure 1 depicts the XRD spectrum of a 570 Å film. Three peaks are present, which correspond to the BTO cubic structure. An additional peak present corresponds to the Al contacts used as electrodes. Therefore, the thin films under investigation are of a polycrystalline nature.