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Fabricate and Characterization of SrTiO3-based MIM capacitors

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Abstract: The conventional method uses the stoichiometric mixture of metallic oxides to synthesize polycrystalline SrTiO3. The SrTiO3 was prepared by spin coating to fabricate Metal-Insulator-Matel (MIM) aluminum-SrTiO3 film-aluminum. The cubic structure of the prepared thin film of SrTiO3 was confirmed by X-ray diffraction analysis. Strontium Titanate was deposited on silicon substrates. Studying the effect of the film thickness on the structural and electrical properties. The surface morphology of deposited thin films was studied using a scanning electron microscope. Electrical properties for SrTiO3 films at constant frequency were measured. The electrical conductivity decreases with increasing thickness. The behavior of (capacitance- Frequency) at different thicknesses was discussed. It is noted that the dielectric constant decreases with increasing frequency for all films, and the dielectric constant increases as thickness increases.

Keywords: dielectric constant, C-V, capacitance-Frequency, conductivity.

1 Introduction

Ferroelectrics are materials that exhibit spontaneous polarization over a certain temperature range [1][2]. They are a special type of pyroelectrics belonging to piezoelectrics [3]. All these classes belong to the dielectric material. Ferroelectric materials possess spontaneous polarization, which can be reversed by applying an external electric field over a certain temperature range. Ferroelectric materials belong to special types of crystals (non-centrosymmetric structures) [4][5][6].

A ferroelectric crystal shows a hysteresis loop that can be observed in certain temperature regions and is also reversible spontaneous when the polarity voltage change [7]. Ferroelectric technologies have received extensive attention because of their ability to achieve desirable characteristics for applications due to the dependence of dielectric permittivity on the applied electric field [8][9]. The dielectric constant of the ferroelectric bulk materials and thin films changes with the electric field [10][7][11].

“Because some factors, such as deposition methods, condition deposition, large defects, mechanical stress during film growth, annealing, substrate types, substrate temperature, and other parameters, impact the properties of thin films” [12][2]. The resulting properties, which may differ for thin film and bulk ferroelectrics, are permittivity, losses, and temperature-dependent bulk materials of ferroelectric materials, especially ceramics. Single crystals had more commercial because thin film for ferroelectric materials has only recently years used [3][13][7].

The ferroelectric film is used as capacitance due to the small dimensions desired in Dynamic Random Access Memories (DRAM) [14]. Due to the large storage capacity per unit area then, ferroelectric materials are either used or are promising candidates [15]. High tunability and low dielectric loss are critical parameters for optimum frequency performance [16].

“At room temperature, $SrTiO_3$ crystallizes in the ABO_3 cubic perovskite structure (space group Pm3m) with a lattice parameter of 0.3905 nm and a density of 5.12 g/cm3, as shown in Fig.1” [17][18].

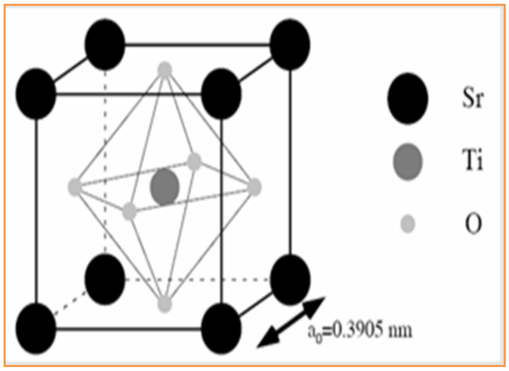

Fig. 0: Atomic structure of $SrTiO_3$ at R.T.

“The basic principle of chemical solution deposition is to prepare a solution of elements of the desired compound in a

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solvent, then coat this solution to a substrate, let the solution polymerize to form a gel, and then fire this gel to obtain an inorganic oxide” [19]. Sol-gel method has an advantage when used to deposit thin films, such as more easily achieved homogeneity and composition control [20][21][6]. It does not need to vacuum high, so it is more economical. Sol-gel is the simplest thin film coating technique involving the hydrolysis and polycondensation of relevant molecular precursors. The spin coating does not need to heat the substrate compared with other techniques during deposition [22][15][23].

The industrial application of ferroelectrics at that time includes Multi-layer Ceramics Capacitors (MLCCS), transducers, and actuators [24]. Perovskite ferroelectric nanomaterials are attractive and show potential applications in different fields, including solar energy conversion and storage memory [25][26]. Since piezoelectric, pyroelectric, and ferroelectric have nonlinear properties, widely investigated perovskite materials such as BaSrTiO3, BaTiO3, SrTiO3, CaTiO3, along with suitable dopants. One of the promising applications of ferroelectric bypass capacitors for 2.3 GHz operation in mobile digital telephones is the product with digital telephones [27].

2 Experimental details:

Sol-gel is the simplest thin film coating technique involving the hydrolysis and polycondensation of relevant molecular precursors. The synthesized solution is spun onto a substrate to obtain a thin film and then subjected to heating treatment. The important feature of the sol-gel method is that it is prepared thin films with composition control.

The raw materials used to prepare SrTiO start from TiCl4 to prepare Ti(O.H). “The hydrolysis of TiCl4 and TiO(NO3)2 was obtained by dissolving Ti(OH)4 in nitric acid”.

Firstly, citric acid and Sr(NO3)2 were dissolved by continuous stirring in deionized water to form a solution. Next, the previous O3)2 solutions. After that, the solution was heated at 100-110ºC under vigorous stirring until a gel formed, then the gel was dried in the oven as the dried-gel. Additionally, the residue solid was washed thoroughly with one mol/l HNO_3 solution and deionized water to remove impurities (such as SrCO3). The former solution adds by using a burette slowly drop by drop to later solation and reflexed at 110ºC (2hrs) after adjusting between (3-5) P.H. “Thin films were prepared by spin-coating the above solution with different speeds depending on the thickness of the thin film” [14].

Before the deposition of the films, the substrates were cleaned by adopting a standard chemical procedure. The solution at 2000 rpm was spun on a cleaning substrate. The substrate was fixed at the center of the rotating. Spin coating is commonly used to produce thin layers on flat substrates. An excess of the solution is dripped on the top of the substrate. After being fixed on the spinner plate, the substrate is rotated at (2000 rpm) for (30 s). This rotation continues until the fluid is spanned off the edge of the substrate and the required thickness is reached. Then, the hotplate heated the substrate at 150ºC (10 min) for each deposited layer. Substrates for all samples were annealed in a furnace depending on the substrate, such as Si substrate annealed at 700ºC for 15 min. The process is repeated with one and more layers to obtain desired film thickness. “The samples were fabricated as Electrode-Ferroelectric (Insulator)-Electrode (MIM), aluminum electrodes fixed by silver past on two faces of SrTio3 thin film” [12]. The characteristic measurements which were done to investigate the structural features of the films were X-ray diffraction (XRD) and topography using Scanning electron microscopy.

3 Theoretical part

3.1 Electrical Properties

The resistivity (ρ) of a film is calculated by applying ohm’s law;

$$relation\ \rho = \frac{RA}{L} \tag{1}$$

“Where R is the resistance, A is the area of the film in a planar geometry, which is given by the product of the film thickness and film width, and L is the spacing between the electrodes. The conductivity of the films is determined from the relation” [28]:

$$\sigma_{d.c} = \frac{1}{\rho} \tag{2}$$

The activation energy (E_a) is :

$$ln\frac{\sigma}{\sigma_o} = \frac{E}{K_B\, T} \tag{3}$$

“By drawing the relation of $ln\sigma_{d.c}$.vs. 1000/T. The activation energy (E_a) is calculated from the production of the slope using Boltzmann constant (k_B) by (eV) units as in the following equation”[29]

$$E_a = 0.08625 * slope \tag{4}$$

Where (0.08625) resulted from the transition (kB) to(eV/K) units.

The value of dielectric constant or relative permittivity ε_r is given:

$$\varepsilon_r = \frac{cd}{\varepsilon_o\, A} \tag{5}$$

“Where d = the thickness of the sample (m). C = the capacitance (Farad). A = cross-section area (m^2)”. “ε_o = space permittivity, equal to 8.854×10-12 (F/m). ε_r = the relative permittivity of the material” [30].

The dielectric loss (tan δ) of thin films is calculated according to the:

$$tan\delta = \frac{\varepsilon''}{\varepsilon} \tag{6}$$

The film thickness (t) was measured using the optical interferometer method; this method was based on interference of light beam reflected from the thin film surface and substrate bottom. He-Ne laser of wavelength (632.8nm) was used, and the thickness was determined using the formula[31].

$$t = \frac{\Delta x}{x}\frac{\lambda}{2} \qquad (7)$$

“Where x is fringe width, Δx is the distance between two fringes, and λ is the wavelength of laser light”.

4 Results & discussion:

SrTiO3 thin films prepared in this work by sol-gel technique were also examined by x-ray diffraction pattern at 2θ from 20° to 80°, d-spacing can be determined using the Scherrer equation. In the prepared $SrTiO_3$ powder, as shown in Fig. 2., the peaks have low crystallinity at room temperature; in other words, the intensity of these peaks reflected from the planes is very low. The XRD pattern of SrTiO3 film is shown in Fig. 3. The analysis demonstrates that the reflection planes are (100), (110), (111), (200), (210), (211), (220), and (301). The Crystallographic data of card No.96-151-2125.

The major peak (110) has the highest degree of crystallinity. The intensity of the peaks increases with the increasing thickness of the film. The effect of changing thickness was very important to obtain a polycrystalline cubic $SrTiO_3$ structure thin film.

The FWHM of those peak decreases with the increase in the change in thickness of films. Low FWHM means a large grain size of the film. The diffraction peaks refer to the cubic phase of $SrTiO_3$ with a=b=c= a= 3.89900 Å. The absence of impurity peaks suggests the high purity of the SrTiO3 films. The average crystalline size was calculated using the Scherer formula. The grain size increased with the thickness of the films, as shown in Fig. 3.

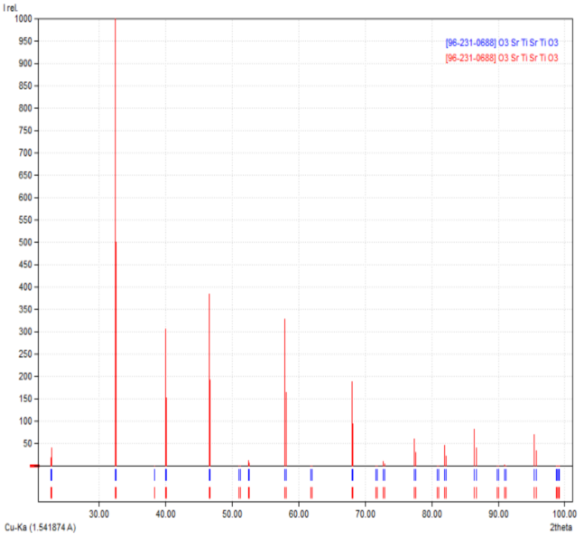


Fig. 2: XRD pattern for SrTiO3 powder

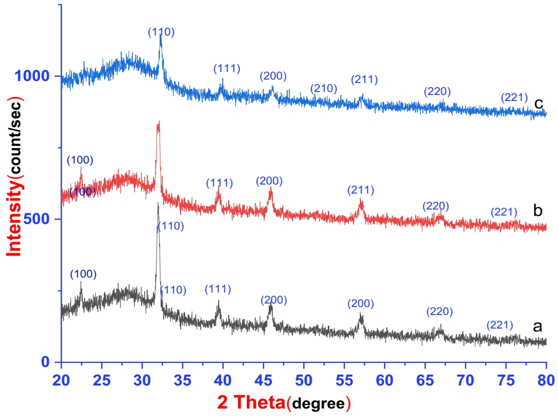
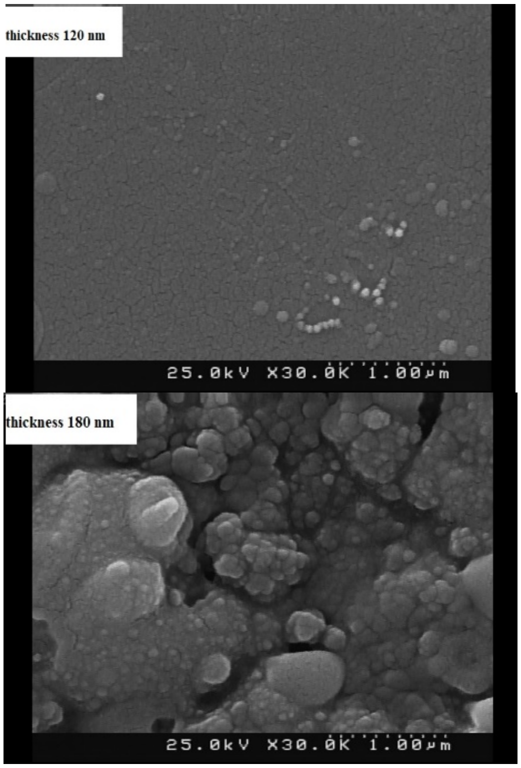


Fig. 3: XRD pattern of SrTiO3 film with different thicknesses of film annealing at 773 K.

Fig. 4 shows SrTiO3/silicone substrate films of different thicknesses deposited at constant annealing temperature (T=773K). It is found that the grain size increases with increasing film thickness. The micro stresses and the dislocation density in the film decrease with increasing thickness. This result is in agreement with Ref. (4)

The release of the stress built up in the films reduces interplanar spacing, thus minimizing the stacking fault probability in the films. The surface roughness increases with increasing thickness, as shown in Fig. 3. This result indicates that the growth of larger grains with increasing thickness increases surface roughness.



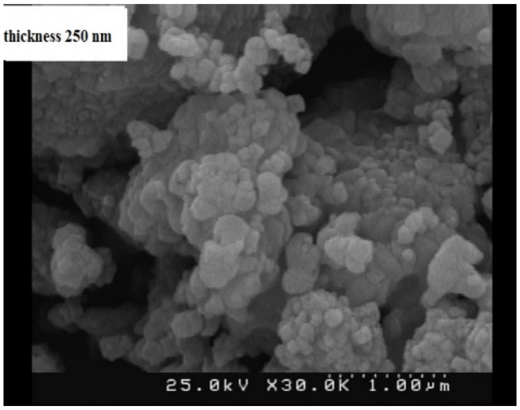


Fig. 4: SEM images for SrTiO3 film with different thicknesses (120,180, and 250 nm)

Electrical measurements of SrTiO3 films deposited by the spin coating technique on the silicon substrate were done at an annealing temperature of 773 K and with different film thicknesses.

A digital electrometer (Keithely 616) was used to measure the electrical properties of SrTiO3 thin films, which were deposited on silicon substrates at an annealing temperature of 773 K and different thicknesses. D.C. electrical conductivity was measured as a function of temperature for SrTiO3 films. It was done by putting the films in an electrical furnace. The electrical conductivity was calculated from equation (2), and the activation energy from equation (3).

Dielectric measurements were carried out for the prepared films at an annealing temperature (773k) for different thicknesses (120, 180, 250) nm. The SrTiO3 thin film samples were prepared in the sandwich of Metal- Insulator-Metal configuration (MIM), where the metal was an (Al) electrode of (200 nm thickness and 1cm diameter) which acts as electrodes. The dielectric studies for these samples were carried out using LCR meter (model 4194A made in Japan). The capacitance and dielectric loss factor (20 kHz-100 kHz) were found in the frequency range. The value of the dielectric constant or relative permittivity (ε_r) was calculated from equation (5). The value of the dispersion factor or loss factor of test samples is given by equation (6).

D.C Conductivity ($\sigma_{d.c}$)

The conduction mechanism of the SrTiO3 films is believed to be related to the concentration of the electrical carriers, which is the oxygen vacancy in the structure. The change of conductivity with thickness indicates that all the film samples have a negative temperature coefficient of resistivity which suggests their nature. In the conductivity mechanism study, it is convenient to plot the logarithm of conductivity (Ln σ) as a function of 1000/T for SrTiO3 films, as shown in Fig. 5 . It is noticed that conductivity displays two mechanisms of charge carriers transport, yielding two activation energies at two thermal ranges. In the range of (303-333) K the activation energy E_{a1} is produced due to the hopping of charge carriers between localized states inside the energy gap. In the range of (343-403) K, the activation energy E_{a2} is produced due to the transfer of charge carriers to a farther distance from the extended state by thermal excitation. From Fig. 5 , σRT is found to decrease with increasing thickness; it decreases from (9×10-7-6.19×10-7) (Ω.cm)-1. The conductivity of SrTiO3 films decreases with the increase in film thickness, which is related to the decrease in carrier concentration. The activation energy decreased with increased temperatures.

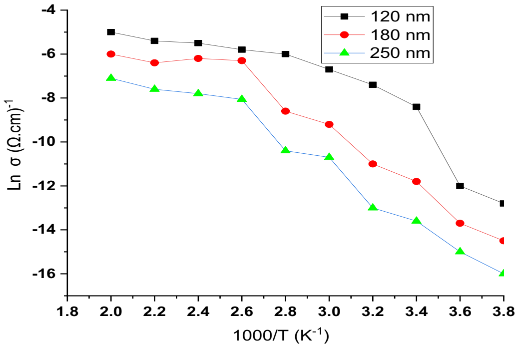


Fig. 5: the relation between σ vs. temperatures for (MIM) $SrTiO_3$ thin films

The prepared SrTiO3 thin films were annealed at the temperature (of 773k) with different thicknesses (180, 190, and 250) nm and were measured at room temperature. Fig. 6 shows that the dielectric constant has a high value at a low frequency. It decreases sharply at (25kHz) and remains almost constant above this frequency. This result agrees with the results Ref. [9]. The high dielectric constant value at low frequencies is believed in the interfacial polarization of space charges, a highly resistive interfacial layer, or a high-density distribution of interface states. From the same figure, the decrease of the dielectric constant ε_r with the frequency increase can also be noticed. Fig. 6 shows loss factor (tan δ) variation with frequency for all prepared films at room temperature, similar to the observed dielectric constant. The thickest film has the lowest dielectric loss; this means that the point defect density decreases with increasing film thickness and indicates again that growth improves with increasing thickness.

The fact that the dielectric constant tends to decrease due to the frequency of steps indicates that there may be more than one polarization mechanism in the structure. There are four possible polarization mechanisms depending on the investigated frequency and temperature. “The dielectric constant at low frequencies indicates the presence of space-charge polarization or electrode polarization. This behavior indicates that the polarization in the structure is temperature dependent. Given the molecular structure of the studied sample, the high dielectric constant at low frequencies” [32].

When the dielectric constant is investigated depending on the film thickness, it is observed that the dielectric constant decreases with decreasing film thickness, as shown in Fig. 6.

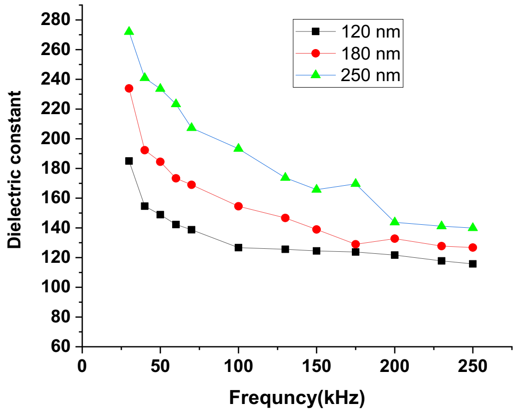


Fig. 6: The Variation of Dielectric Constant with Frequency for (MIM) SrTiO3 Films at Different Thickness.

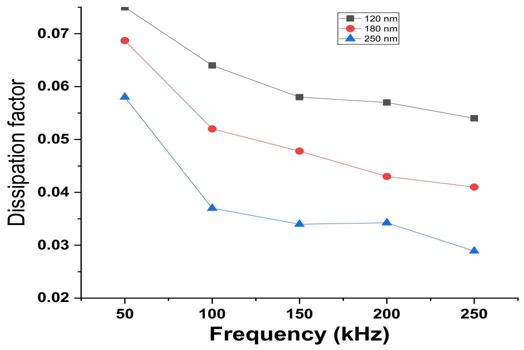


Fig. 7: The Variation of dielectric loss with frequency for (MIM)SrTiO3 Films at Different Thickness.

C-V Measurement

We have fabricated high-quality ceramic-based metal/insulator/semiconductor i.e. Al/SrTiO3/Si (110) structures by spin coating technique. The dielectric properties of SrTiO3 were investigated from C–V characteristics curves which were measured at a frequency of 1 MHz. The C–V curves measured with increasing bias voltage from (0.1-1) volt showed very small variation in each curve. Fig. 8 shows capacitance vs. applied voltage of 200 kHz frequency for the SrTiO3 films at different thicknesses (120, 180, and 250 nm) with a constant annealing temperature of 773k. The figure indicates that the capacitance is independent of the bias voltage. However, for the SrTiO3 film of 250nm thickness, the C–V curve shows a small variation in capacitance as a function of the applied field. The films were found to have paraelectric properties from the capacitance-voltage characteristics. These results suggest that the SrTiO3 films can be used as insulator layers in dynamic random-access memories or cladding layers in electroluminescent devices. The relative dielectric constant, estimated from the maximum value of capacitance, was found to be (13, 25, and 67 pf) for films grown at (120,180, and 250 nm), respectively. This result shows that the relative dielectric constant increases with film thickness.

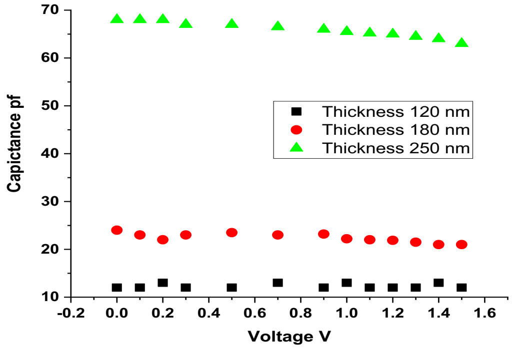


Fig. 8: The Variation of Capacitance with Applied Voltage for the MIM Structures with Different Thickness.

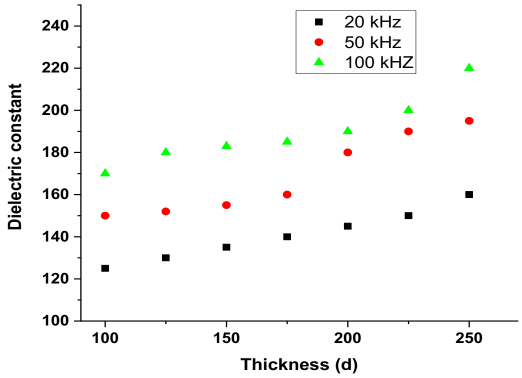


Fig. 9: The dielectric constant with applied voltage for the MIM Structures with Different Thicknesses

Conclusion

The SrTIO3 film was prepared by spin coating technique. The XRD pattern exhibited a cubic phase for thin film. The SEM images revealed the roughness of the film increased with the increased thickness of the film. The d.c conductivity and activation energies for all films decrease with increasing film thickness. The charge carriers have two transport mechanisms over the range of (303-473) K for the deposited film. The dielectric properties behaviour shows that the dielectric constant increased with film thickness. The Capacitance-voltage measurements at a frequency of 200 kHz of all films (M-SrTiO3/M) refer to the paraelectric properties of STO films. They are suitable for applications as insulator layers in dynamic random-access memories or as cladding layers in electroluminescent devices.

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Conflict of Interest

The initiative has no funding, and the authors declare no competing financial interests.

Availability of data materials:

Data will not be shared because these data help study the correct form for suitable applications.

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