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An overview of MgTiO3 thin films: Deposition Techniques and Properties

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Abstract: The purpose of this work is to present an overview of different methods used for fabrication of MgTiO3 thin films and the influence of deposition methods on the properties of the films. The nature and quality of the film change with deposition method, resulting in a variation in the internal properties of the film. Some of the popular deposition techniques used to fabricate MgTiO3 films are described in this report. The structural, optical and electrical properties of MgTiO3 thin films obtained by various research groups are reported here along with the characterization techniques. The information about the substrate used to deposit MgTiO3 films are stated. Furthermore, the effect of different doping in A and B site of MgTiO3 films as well as their applications in different fields are reported.

Keywords: Ceramics; Deposition techniques; Dielectric; Integrated circuits; Thin Film

1. Introduction

MgTiO3 (MTO) is one of the most versatile ceramics used in the field of dielectric resonators, optoelectronics and microwave integrated circuits. MTO shows excellent dielectric properties, microwave properties and thermal stability in the bulk and thin film form (Zheng et al, 2007; Sebastian et al, 2008; Anjana et al, 2009, Pamu et al, 2009). Thin films are gaining huge attention from the worldwide scientist and researchers due to their smaller size along with their outstanding properties suitable for integrated circuit design. The development of new technologies, techniques in integrated circuit industry demand high quality thin films for different applications. As the thin film technology is emerging in the race of miniaturization of devices and creating new opportunities for researchers to expand the utility, we have chosen the MTO thin film to study.

The properties of thin films are very sensitive to the structure and thickness of the film. Various types of methods are introduced for fabrication of the films. Further, researchers are always looking for new materials to produce thin films for different functions. Among them, MTO thin films are very popular due to their excellent optical and dielectric properties even in microwave frequency range. The properties exhibited by the MTO films are suitable for optoelectronics and telecommunication industry (Ferraris et al 2000; Pamu et al, 2007; Pamu et al, 2009). In this w ork, we will discuss the different deposition techniques and progress in MTO thin films in terms of nature, function and properties.

DEPOSITION TECHNIQUES OF MGTIO3 THIN FILMS:

The deposition technique of thin film refers the process of fabrication of film onto a substrate material. The structural properties of thin films including thickness, surface roughness and purity of the films are highly influenced by deposition techniques (Chaudhari et al, 2021). The source material and substrate used for deposition also plays a crucial role to choose a technique for thin film deposition. Various techniques are reported to create MTO films based on the application of the films. In this work, we will discuss some of the popular deposition techniques used by scientific community till now.

1. **Metalorganic Chemical Vapor Deposition:** The Chemical Vapor Deposition is a widely used method for thin film fabrication. In this method, vapor phase of the material to be deposited flows into a reaction chamber containing a substrate. Through a thermal process the vapor reacts with the substrate to form a solid thin film. By varying the deposition time and vapor concentration the thickness of the film can be controlled. The thin films fabricated using CVD technique are highly conformal. The high cost of CVD equipment and complexity of the process are the main drawback of this techniques.

2. **Sol-gel Methods:** Sol-gel process is a wet chemical method to synthesis nano particles as well as to produce thin films.

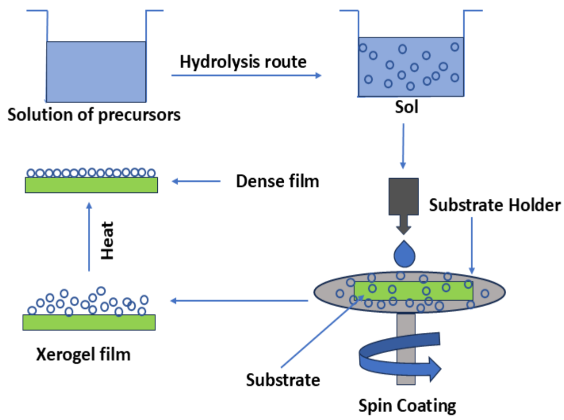

Fig 1: Steps for preparation of thin film by the Sol-gel process.

This process involves gel formation from colloidal substance by hydrolysis route. Based on the composition and synthesis route different types of gel including xerogel, ambigel, cryogel, aerogel can be formed. The obtained gel is deposited onto substrate mainly by spin coating and dip coating technique, and after heat treatment required film can be obtained. The steps for preparation of thin film by the Sol-gel process are shown in Fig 1. The main drawbacks of this process are volume shrinkage and occurrence of pores due to the evaporation of unwanted residual during heat treatment.

3. **Aerosol Deposition Techniques:** Aerosol deposition (AD) technique is a form of spray coating process to grown good quality thin film. By using this process thin film can be produced directly from initial bulk powder of material on almost any substrate even at room temperature. A schematic diagram of AD technique is shown in Fig 2. The technique contains an aerosol generator unit where aerosol is created by mixing initial powder to be deposited and gas. The generated aerosols are accelerated to the low-pressure deposition chamber by de Laval type nozzle to supersonic velocities forming an aerosol jet at outlet. These aerosols made fall on substrate at high speed by creating pressure difference between aerosol generator and deposition chamber.

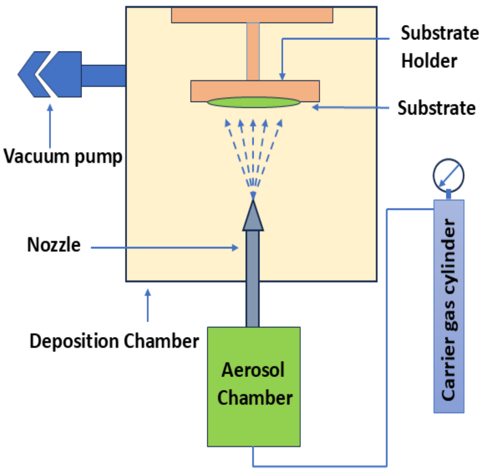

Fig 2: Schematic diagram of Aerosol Deposition Technique.

4. **Electron Beam Evaporation:** In Electron beam evaporation method, a tungsten filament is heated by high voltage current to eject highly charged electron by thermionic process. By using electromagnetic field, the ejected high energetic electrons are directed towards the target material placed in a cooled crucible. The electron beam bombarded the target material and evaporate the material. The evaporated material is then deposit on the substrate. The whole process is performed within a vacuum environment. By using this method very pure film can be grown in a less time, but the complexity and high cost limited the use of this method. Fig 3 shows the schematic diagram of Electron Beam Evaporation.

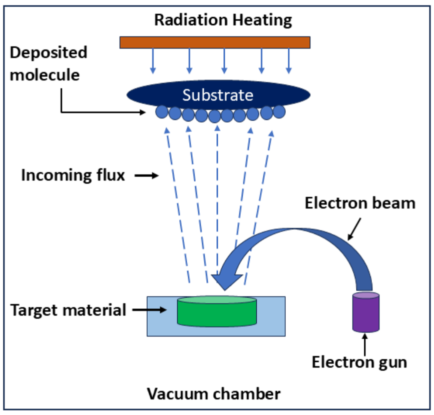

Fig 3: Schematic diagram of Electron Beam Evaporation.

5. **Pulse Laser Deposition:** In this process laser pulses are used to deposit thin film, therefore the process is named as pulsed laser deposition. This is one form of physical vapor deposition. During the process a laser beam is used to evaporate the target material, then deposited on the substrate. The laser wavelength, energy, pulsed duration, ambient gas pressure, target to the substrate distance are the main parameters to influence the quality of the deposited film. Depending upon the nature of target material these parameters should be optimised to get a good quality thin film. The schematic diagram of Pulsed Laser Deposition is shown in Fig 4.

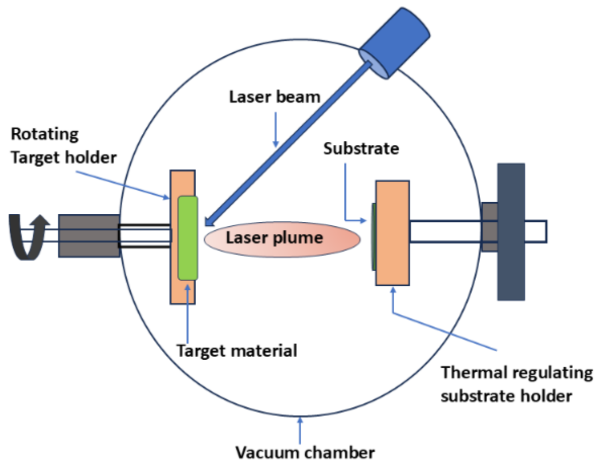

Fig 4: Schematic diagram of Pulsed Laser Deposition.

6. **RF Sputtering:** RF sputtering technique is used for deposition of insulating/dielectric thin film. Generally, RF frequency of 13.56 MHz is applied to cathode via impedance matching network inside the deposition chamber containing inert gas to create plasma. Magnetron sputtering enhances plasma confinement and boosts ionization efficiency, resulting in high deposition rates onto the substrate.

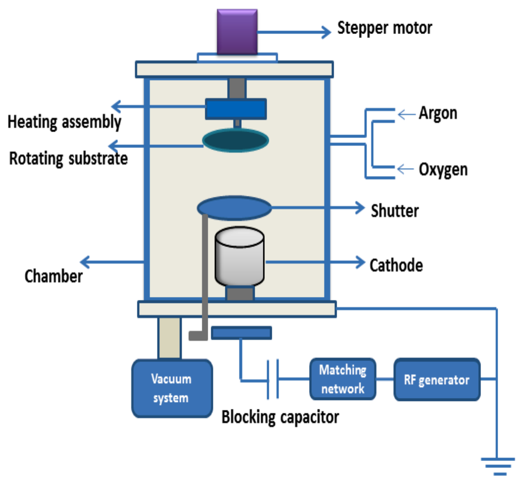

Fig 5: Block diagram of simple RF sputtering system (Gogoi, 2019).

This technique employs a magnetic field is produced parallel to the cathode surface to trap the emitted electrons and enhance the deposition rate. In reactive magnetron sputtering, reactive gases are added to inert gas (Ar) to react with sputtering material. This process impacts the deposition rate and quality of the film. Several key parameters can be adjusted in RF sputtering to control films properties. The RF power, substrate-target distance, amount of deposition gas, time, and base pressure can be optimized to get desired film thickness and characteristics. Fig 5 shows the block diagram of simple RF magnetron sputtering system.

PROGRESS IN MGTIO3 THIN FILMS:

In 1997, J. Zeng et. al reported for the first time, MgTiO3 thin films prepared by metalorganic CVD techniques. Si and SrTiO3 substrates were used for the film deposition. They obtained single phase randomly oriented MgTiO3 on Si substrate and only a (012) orientation on SrTiO3 substate at 650oC. The film thickness was around 1.26 micrometer (Zeng et al,1997). Y.H. Choi et. al. used Metalorganic solution deposition method to fabricate MTO thin films on aplane Al_2O_3 substrate. The obtained epitaxial MTO films showed a fine feature in surface microstructure and roughness with thickness of around 300 nm. They reported the dielectric constant of 21 and dielectric loss 2% at 100 kHz of the MTO film (Choi et al, 2001). J. Lee used Sol-gel process to deposit MTO thin film on a sapphire crystal. The epitaxially grown films had grain size of 10-20 nm and refractive index of 2.305 (Lee, 1999). K.P. Surendran et. al. developed MTO films by sol gel synthesis and studied the dielectric properties. They obtained a dielectric constant of 16.3 and dielectric loss of 0.0021 at 1 MHz for the films annealed at 700oC (Surendran et al, 2008). In 2010, K.P. Surendran again reported Ni and Zn doped $MgTiO_3$ film using Sol-Gel technique and analysed the effect of doping in dielectric response and temperature stability of the film. They used Platinum coated Si Substrate [(111)Pt/TiO_2/SiO_2/(100)] for the film deposition and obtained 500 nm crystalline thick films after annealing at 650oC for 1 hr (Surendran et al, 2010). C.F. Tseng et al fabricated $Mg(Zr_{0.05}Ti_{0.95})O_3$ thin film by Sol-Gel method on n-type Si(100) substrate obtained about 140 nm thick films. They reported the effect of annealing temperature on the optical and electrical properties of the films (Tseng et al, 2011). Y.C. Wu used Aerosol deposition method to deposit MTO films at room temperature and studied the effect of different gases and flux on the prepared MTO film (Wu et al, 2012). Electron beam evaporation method was used by C.H. Lee to deposit MTO film on Si(100) substrate. Their aim was to use the MTO film as buffer layer for the improvement of adhesion properties between Platinum film and Si substrate for integrated device application. They obtained densely packed $MgTi_2O_5$ and $MgTiO_3$ film on Si(100) substrate at 650oC (Lee et al. 2003). S. Kang et. al tried to grow $MgTiO_3$ thin film on Sapphire (C-plane Al_2O_3), SiO_2/Si and Platinized Silicon (Pt/Ti/SiO_2/Si) substrates to study the microwave dielectric and optical properties. The film deposited on Platinized Silicon (Pt/Ti/SiO_2/Si) substrate exhibited dielectric constant of 24 and dielectric loss of 1.5% at 1 MHz (Kang et al, 2000).

$MgTiO_3$ thin films were grown by C.L. Huang et. al using RF sputtering temperature. They used n-type Si(100) substrate for the film deposition and kept the substrate temperature of 400oC. Different RF powers (100 to 400 W) were applied for film deposition and effect of RF power on film microstructures were studied. Metal-insulator-semiconductor (MIS) capacitor structure was formed to analysed the electrical properties of the films. They reported dielectric constant of 16.2 at 10 MHz, leakage current density of 2.03x10-9 A/mn2 and dissipation factor of 0.641 for the MTO film deposited under RF power of 400 W (Huang et al, 2005; Huang et al, 2006). Y.B. Chen used different Ar/O2 ratios, substrate temperature (200-400oC) and deposition time for deposition of MTO using RF Sputtering and observed significate effect of deposition parameters on the film microstructure and properties. The optimum dielectric properties were obtained for the film deposited at RF power 400 W, substrate temperature of 400oC for deposition time 3 hr (Chen et al, 2005). Y.B. Chen et. al. again reported the effect of O2/Ar ratio and annealing temperature on the MTO film grown by RF Sputtering. They observed strong dependence of electrical properties of the film on the sputtering gas (Chen et al, 2006). We also prepared phase pure nanocrystalline MTO thin films using suitable dopants Ni, Co and Zr by using RF magnetron sputtering technique. The effect of processing parameters such as oxygen mixing percentage (OMP), annealing temperature on the crystal orientation, optical, electrical and dielectric properties of MTO thin films were studied thoroughly. The microwave dielectric properties are reported for Ni doped MTO films by using Split Post Dielectric Resonator method (Santhosh et al, 2014; Santhosh et al, 2015; Gogoi et al, 2015; Gogoi et al, 2016).

In 2021, Negishi M et al. used pulsed laser deposition technique and obtained single crystal MTO thin film on Al_2O_3(001) substrate. They varied the oxygen pressure during deposition and got (0001) oriented MTO thin film at 10-5 Torr. The films exhibited optical bandgap of 4.4 eV indicating a transparent insulator. A detail study on crystal structure was carried out and concluded that the obtained films can be used in optical devices (Negishi M, Fujiwara K et al, 2021). To examine the photoluminescence behaviour of MTO film Negi D et al. tried Li ion implantation into RF sputtered MTO films. They observed significate changes in the properties of the film and found out reduction in crystallinity and generation of defects in the film with ion implantation. The reduction of average decay lifetime of MTO films with Li ion implantation was reported (Negi D et al, 2023). Nedi D et al. again reported Co ion implanted RF sputtered MTO thin films. They observed that the PL emission intensity is quenched upon Co ion implantation (Negi D et al, 2023).

CONCLUSION:

The process of depositing thin films and finding new materials to create thin film has been developing over the last 200 years. In this work, we discussed some of the popular fabrication techniques of $MgTiO_3$ thin films and remarkable findings till now. This study reveals that choosing a proper deposition technique is one of the main criteria to get good quality thin film. In case of MTO films, among all the mentioned techniques RF Sputtering has garnered significant attention due to its unique combination of advantages including low crystalline temperature, uniform surface, higher deposition rate, precise control over stoichiometry, and cost-effectiveness.

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