Structural and electrical properties of the microwave irradiated and conventionally annealed TiO2 thin films derived from Sol-gel process

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Abstract

Two sets of TiO_2 thin films were prepared on p-type silicon substrates by sol-gel spin coating process. One set of TiO_2 films were conventionally annealed at 400^oC and 800^oC for three hours and the other set was exposed to microwave radiation at 540W and 900W for fifteen minutes. These films were characterized using XRD, SEM and AFM for structural, morphological and topographical information. XRD patterns revealed that the films showed polycrystalline behavior at and beyond 540W and 400^oC. Also the growth of the rutile phase was observed in films exposed to microwave irradiation at 900W. Metal Oxide Semiconductor (MOS) capacitors were fabricated using TiO_2 films with Al top electrode and their electrical properties such as C-V and I-V characteristics were investigated. From the C-V characteristics the dielectric constants were calculated. It was observed that the values of dielectric constants of microwave exposed films were less compared to the annealed films.

Keywords: Conventional annealing, Dielectric Constant, Microwave irradiation, Sol-gel technique, Thin films.

1. Introduction

A legion of attractive properties and possibilities of many applications has made extensive research on metal oxides an interesting endeavour. TiO_2 is one of the most explored materials due to its significant optical and electrical properties. TiO_2 is a n-type semiconductor with a wide band gap energy of 3.1eV and high refractive index of 2.6 [1]. It finds applications in various fields such as gas sensors [2, 3], dye sensitized solar cells [4], optical coatings [5], photocatalysts [6] and antimicrobial materials [7]. The quest for finding a metal oxide with high dielectric permittivity to replace amorphous SiO_2 in microelectronics has led to extensive research on materials like TiO_2, HfO_2 etc. TiO_2 thin films have proved to be one of the potential choices for the use as gate insulators in metal oxide semiconductor (MOS) capacitors due to their high dielectric constant and reduced leakage currents [8].

Several methods of deposition are in practice for the preparation of TiO_2 thin films like physical vapour deposition [9], metal organic chemical vapour deposition [10], DC reactive magnetron sputtering [11], pulsed laser deposition [12], electron beam evaporation method [13] and sol-gel method [14,15]. Among these processes, sol-gel method has several benefits over the other processes like low processing temperature, homogeneity of films, financial viability and possibility of coating large area substrates [14].

In the present work TiO_2 thin films were prepared by cost effective sol-gel technique and their structural and electrical properties have been investigated. There have been several studies on the structural and electrical properties of TiO_2 thin films. Li Ho chong et al have reported the structural and electrical properties of thermally grown TiO_2 thin films [16]. Marius Stamate et al have studied the dimensional effects on the electrical, dielectric and optical properties of TiO_2 thin films fabricated by DC magnetron sputtering [17]. Thilagam and co-researchers have carried out the first principal studies of the dielectric properties of TiO_2 polymorphs [18]. Jin Young Kim and group have reported their observations on the influence of anatase-rutile phase transformation on dielectric properties sol-gel derived TiO_2 thin films [19]. Pakama et al have studied the effect of repeated annealing temperature on the structural, electrical and optical properties of TiO_2 thin films prepared by dip-coating sol-gel method

[20]. Vitanov and group have investigated the structural and dielectric properties of TiO_2 thin films deposited by the sol-gel method on Si substrates [21]. Jyh Sheen and co-researchers have made measurements of dielectric properties of TiO_2 thin films at microwave frequencies using an extended cavity by perturbation technique [22].

Till date, to the best of our knowledge, there have not been any reports on the electrical properties of TiO_2 thin films irradiated by microwaves. In the present work, two sets of TiO_2 thin films prepared by sol-gel method have been subjected to two kinds of heat treatments namely, microwave irradiation at various powers for 15 minutes and conventional annealing at different temperatures for 3 hrs in air ambient. Both microwave exposed and conventionally annealed films have been characterized by XRD, SEM and AFM. The structural details of these films have been investigated. MOS capacitors have been fabricated by using these films as gate insulators and their electrical properties have been studied.

2. Experimental procedure

2.1 Synthesis

TiO_2 thin films were prepared by sol-gel spin coating technique. For the preparation of TiO_2 sol, Titanium Tetra Isopropoxide was used as the precursor. This was mixed with 2-methoxy ethanol, which is the solvent. The precursor to solvent ratio was maintained at 1:10. This mixture was stirred for an hour using a magnetic stirrer to facilitate the mixing. Then a few drops of catalyst, namely concentrated HCl was added to it. 3ml of Poly ethylene glycol was also added as the surfactant. The stirring was continued for 2 hrs. A few drops of a complexing and chelating agent was added to this solution. This mixture was allowed to stir for about 8hrs. Then it was aged for 24hrs in a airtight container. The resulting solution was the TiO_2 sol.

For the preparation of the TiO_2 thin films, a few drops of the TiO_2 sol was placed on the RCA cleaned p-type silicon substrate and was spun at a speed of 3000rpm for one minute. The films thus obtained were preheated at 60^{o}C for 10 minutes. This procedure was repeated five times to obtain desired thickness of the films. Two sets of as prepared TiO_2 films were taken for heat treatment. One set was exposed to 2.45GHz microwave irradiation at 540W and 900W for 15 minutes using a KORYO microwave oven (Model: KMG222). Another set was conventionally annealed at 400^{o}Cand 800^{o}C for 3hrs each. Both heat treatments were done at air ambient. These xerogel films were uniform.

2.2 Characterization

The thicknesses of both microwave exposed and conventionally annealed TiO_2 films were found using DEKTAK optical profilometer (Model:150). The structural confirmation was obtained by X-Ray Diffraction studies carried out using Bruker X-ray diffractometer by using Cu K_α radiation (λ=1.5406 A^o). The morphology of the films was analysed using scanning electron microscope (SEM- Sirion). The film roughness was determined using atomic force microscope (Model: A.P.E.Research A-100). The microwave exposed as well as the conventionally annealed films were used to fabricate MOS capacitors. Using a shadow mask, Aluminium electrodes of area 0.0206 X 10^{-6} m^2 were deposited on the films by thermal evaporation. On the rear side of silicon substrate Aluminium was deposited as the back metal contact. The C-V and I-V characteristics of MOS capacitors were studied using Impedance Analyzer (Model: Agilent 4294A with PM5) and Semiconductor Device Analyzer (Model: Agilent B1500A with PM5) respectively. From the C-V Characteristics dielectric constants were calculated.

3 Results and Discussions

3.1 Structural Properties

Fig.1 (a, b) shows the XRD patterns of Microwave irradiated TiO_2 films at 540W and 900W respectively. Fig. 1 (c, d) represent the XRD pattern of films conventionally annealed at 400^{o}C, and 800^{o}C for 3hrs respectively. The XRD plots of films microwave exposed at 540W and 900W show sharp and intense peaks at 2θ= 25.19°, 32.93°, 48.04° , 54.54° and 56.30° in the 2θ range from 20° to 60° showing crystallization. The peak positions match well with the JCPDS data. The conventionally annealed films at 400^{o}C and 800^{o}C also show sharp peaks at these 2θ values. From these XRD patterns, it is seen that increasing microwave power and annealing temperature lead to increased peak intensity implying improved crystallization. The peak at 32.93° corresponds to silicon. The peaks at 2θ=25.19° and 48.04° correspond to the anatase phase. It is also observed that in the films microwave exposed at 900W there is the growth of rutile phase which is confirmed by the peak at 2θ=27.4°. However the films conventionally annealed even at 800^{o}C for 3hrs do not exhibit the presence of rutile phase. Jim Young Kim et al have prepared the TiO_2 thin films by sol-gel spin coating method on platinized silicon substrate. They have observed that the crystallization commenced approximately at 450°C and the phase transformation from anatase to rutile occurred at 900°C based on the Differential Thermal Analysis (DTA) curve [19]. Vitanov et al have also have reported to have observed the rutile phase growth for films prepared by sol-gel method and annealed at 850^oC [21].

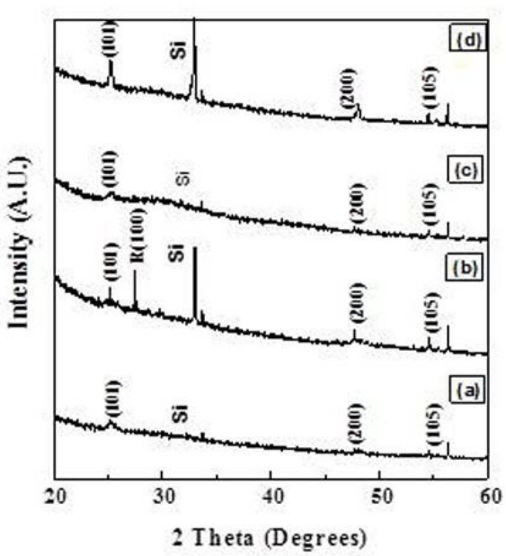

Fig. 1(a-d): XRD pattern of TiO_2 thin films microwaved at (a) 540w/15min (b) 900w/15min; annealed at (c) 400^oc/3hrs (d) 800^oc/3hrs.

3.2 Morphological Studies

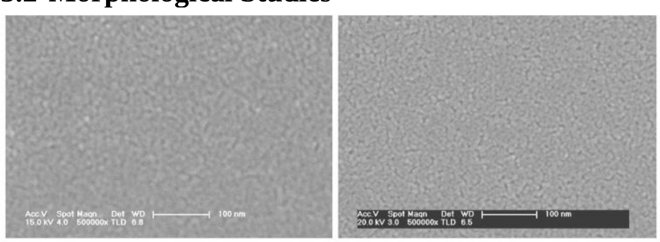

Fig.2 (a,b) : SEM micrographs of TiO_2 thin films (a) microwave exposed at 900W/15min (b) conventionally annealed at 800^oC/3hrs.

The SEM micrographs of TiO_2 films microwave exposed at 900W and conventionally annealed films at 800^oC are shown in Fig.2 (a ,b) respectively. The microwave exposed film at 900W shows somewhat elongated grains (elongation due to coalescing of individual grains) that are well connected through smaller but numerous voids of various sizes and shapes present between them. But the SEM micrograph of conventionally annealed films at 800^oC shows closely packed and somewhat spherical grains with slightly smaller voids in between. This film is denser and consists of small individual grains. It is difficult to recognize individual grains in the microwave irradiated film. A few cracks appeared in the microwave exposed films and these could be because of the rapid evaporation of the solvent, 2-methoxy ethanol.

The surface roughness of the microwave exposed films at 900W and conventionally annealed films at 800^oC determined by AFM are shown in Fig.3 (a, b) respectively. The scan area is 0.5µm X 0.5µm. The microwave exposed films exhibited lower surface roughness (R_a) of 0.35nm than the conventionally annealed films that exhibited a surface roughness of 3.12nm.

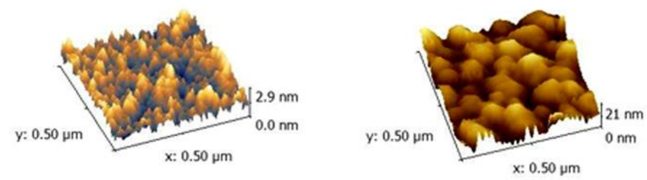

Fig.3 (a, b): AFM images of (a) microwave exposed TiO_2 films at 900W/15min (b) conventionally annealed films at 800^oC/3hrs.

3.3 Electrical Properties

3.3.1 C-V characteristics

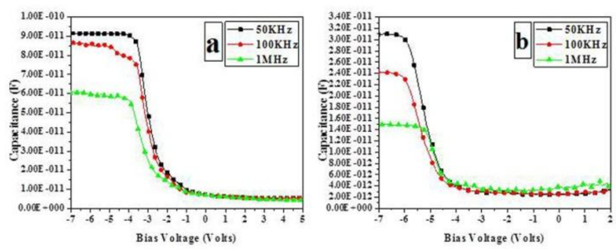

Fig.4 (a,b): C-V Charecteristics of microwave exposed films at (a) 540W (b) 900W.

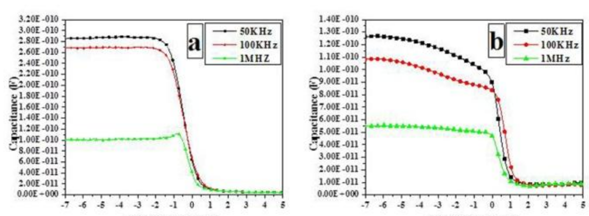

Fig.5 (a,b): C-V charecteristics of conventionally annealed TiO_2 films at (a) 400^oC (b) 800^oC.

Fig.4(a, b) and 5(a, b) show the C-V characteristics of MOS capacitors fabricated using the microwave exposed films at 540W and 900W for 15 minutes and conventionally annealed films at 400°C and 800°C for 3hrs respectively. The thickness of the microwave exposed films at 540W and 900W are 186nm and 177nm respectively. The thickness of the conventionally annealed films at 400°C and 800°C are

103nm and 87nm respectively. The oxide capacitances of the MOS capacitors at 50KHz, 100KHz and 1MHz and the dielectric constants calculated from the C-V plots are listed in Table.1. It is observed that for conventionally annealed films, the values of dielectric constant decreases with increase in annealing temperature. Even in the case of microwave irradiated films, the value of dielectric constant decreases with increase in microwave power. This could be due to the increase in the porosity of the films due to enhanced crystallization. The annealed films exhibit higher dielectric constants compared to the microwave exposed films. This may be attributed to the higher density of the annealed films.

Davinder Rathee et al have prepared TiO_2 thin films by sol-gel method and DC magnetron sputtering on Si wafer. They have reported the values of dielectric constant at 10KHz for the sol-gel film and the DC magnetron sputtering to be 73 and 18 respectively [23]. Vitanov et al have prepared the TiO_2 thin films on silicon substrates by sol-gel spin coating method. They have reported the values of dielectric constant for films annealed at 600°C/1hr and 850°C/15min in air ambient to be 20 and 20.4. The values of the dielectric constants of annealed films at 600°C/1hr and 850°C/15min determined by the quasi static C-V tests decrease with the increase in annealing temperature and their values are 24 and 20.4 respectively [21]. In the present work, the value of dielectric constant obtained for TiO_2 films annealed at 800°C matches closely with the value reported by Vitanov et al. At 1MHz, the dielectric constant of the microwave irradiated film at 540W is comparable to that of annealed films at 400^oC.

Table.1. Values of Oxide Capacitances and Dielectric constants for MOS capacitors using microwave exposed and conventionally annealed TiO_2 thin films.

TiO_2 Films heat treated		Oxide Capacitance (× 10^{-11}F)			Dielectric constant		
		50KHz	100KHz	1MHz	50KHz	100KHz	1MHz
annealed	400^0C	28.31	27.01	10.16	160.5	153.1	57.6
	800^0C	12.5	10.86	5.56	59.5	51.7	26.47
Microwave exposed	540W	9.16	8.62	6.03	93.55	88.03	61.63
	900W	3.1	2.406	1.496	30.14	23.39	14.5

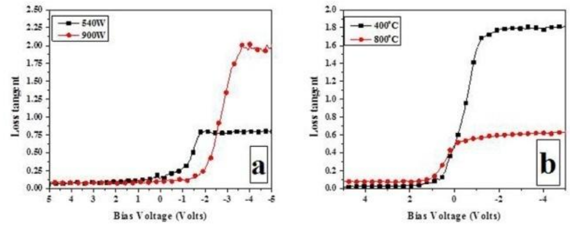

Fig.6 (a,b): Plot of Loss tangent Vs. bias voltage for TiO_2 thin films microwave exposed and conventionally annealed at 1MHz.

Fig.6 (a,b) shows the loss tangent at 1MHz for TiO_2 thin films microwave exposed at 540W and 900W and conventionally annealed films at 400°C and 800°C. From the Fig.6 (a) it is observed that the loss tangent increases with increase in microwave power in the accumulation region. This can be attributed to increased crystallization and higher leakage current. In the case of conventionally annealed films, in the accumulation region the loss tangent decreases with increase in annealing temperature. Linking-up of grains with increasing temperature may account for decreasing leakage current. At 4V the loss tangent for microwave exposed films at 540W and 900W show almost the same value 0.074. Conventionally annealed films at 400^oC and 800^oC, show loss tangent values 0.029 and 0.089 respectively at a gate voltage of 4V.

3.3.2 I-V characteristics

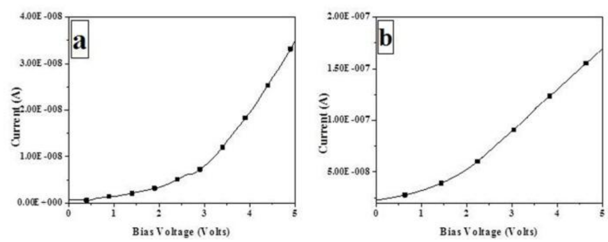

Fig.7 (a,b): I-V Characteristics of microwave exposed TiO_2 films at (a) 540W (b) 900W.

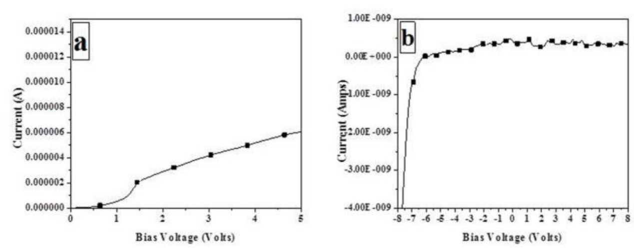

Fig.8(a,b): I-V Characteristics of conventionally annealed TiO_2 films at (a): 400°C (b) 800°C.

Fig.7 (a, b) and 8(a, b) show the I-V curves for MOS capacitors fabricated using microwave exposed and conventionally annealed films respectively. From the figure, it can be observed that for films exposed to microwaves and conventionally annealed at 400°C, the variation of leakage current is very small up to 0.5V.

Beyond 0.5V of bias voltage, the leakage current varies almost linearly. For the film conventionally annealed at 800°C, the leakage current increases rapidly up to -6V, and then almost becomes a constant. From the I-V plot, the resistivity and current density at a gate voltage of 4V have been calculated. The values for the microwave exposed films were found to be 2.22 X 10^7 Ωm and 96.6 X10^{-2} Am^{-2} (at 540W) and 3.5X 10^6 Ωm and 63.5 X10^{-2} Am^{-2} (at 900W). The values of resistivity and current density at 4V for conventionally annealed films are found to be 1.58 X 10^5 Ωm and 244.17Am^{-2} (at 400°C) and 2.25X10^9 Ωm and 204.2X10^{-4} Am^{-2} (at 800°C). The leakage current density decreases slightly with increase in microwave power and annealing temperature. The increased porosity of the films at higher power and at higher temperature could be causing this trend.

4 Conclusion

TiO_2 thin films were prepared by eco-friendly sol-gel spin coating technique. The resulting xerogel films were subjected to two kinds of heat treatments namely microwave irradiation at various powers and conventional annealing at different temperatures. It was observed from XRD data, while the TiO_2 films showed crystallization at 400°C, the microwave exposed films showed crystallization at 540W for a brief period of exposure of 15minutes. Even the phase transformation of the TiO_2 films from anatase to rutile materialized in microwave irradiated films at 900W. The morphological information from SEM revealed the formation of grains with voids in both sets of heat treated films. The AFM micrographs showed that the surface roughness of microwave exposed films was less compared to the conventionally annealed films. From the C-V characteristics of MOS capacitors fabricated using both sets of heat treated films, dielectric constants were calculated. It was observed that the value of dielectric constant decreased with the increase in microwave power and annealing temperature. The values of the dielectric constants of microwave exposed films were less compared to the annealed films.

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