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Structural and Dielectric Studies of Ni doped TiO 2 Thin Films for Electro-Optic Devices

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Abstract

Index terms—

1 I. INTRODUCTION

In the few recent years experimental investigation on the electronic transport properties of semiconducting oxides in thin films have been much intensified. Titanium oxide thin films have attracted much attention because of their applications in microelectronics devices, optical thin film devices, gas sensors etc. The structural and semiconducting properties of TiO 2 films can be strongly modified by doping with impurities like In, Cr, Cd, Ce, and Fe or by different processing parameters [1].

Evaluation of electrical properties is important in understanding the conduction mechanism. Critical evaluation of these properties is necessary to produce reproducibly good quality films. Electrical properties of transparent conducting TiO 2 thin films derived from methods other than sol-gel, have been investigated extensively and literature survey indicates a lot of scatter in experimental data due to variations in mobility and carrier concentration, arising as a consequence of variations in stoichiometry and dopant concentration (both intentional and unintentional). These two quantities are strongly dependent on the choice of processing method and the processing conditions. The development of methods for modification of dielectric and electrical properties of thin films of oxides is of great interest. Further studies have shown that ions of different transition and noble metals incorporated into titanium oxide as matrix could modify its optical and electrical properties [2]. The dielectric constant reported for TiO 2 thin films are scattered over a large range dependent on deposition methods, film thickness and process parameters. Various methods or techniques such as London Journal of Research in Science: Natural and Formal electro deposition technique [3], Molecular chemical vapor deposition [4], Magnetron sputtering [5], Chemical spray pyrolysis [6], Sol-gel spin coating [7] technique are used to prepare these thin films. Each technique has its own advantages. We have used sol gel dip coating technique to prepare samples as this technique is cheaper and better uniformity is obtained by this technique.

Various authors study on the metal doped TiO 2 thin films, Cu doped TiO 2 thin films [8], Al doped TiO 2 thin films [9], Mn doped TiO 2 thin films, [10]. These pure and metal doped TiO 2 thin films have different types of applications i.e. in the manufacturing of LED [11], fabrication of capacitors in microelectronics [12], switching devices [13], integrated circuits (ICs) and field effect transistors (FETs) [14][15]. Modern technology demands scaling down the thickness of the material in order to increase the stability, performance and compact size of the electronic devices in accordance with the Moore law and quantum well effect [16]. Also the research work on dielectric response of TiO 2 doped by different percentage of Ta, and Ca or Nb, Ba has been carried out in literature [17][18][19] Materials having dielectric constant in the range between 10-15 for frequencies above 1 GHz are practically utilized in treating biomedical modeling problems related to electromagnetic radiation scattering in the human organs such as liver, kidney, brain and tissues like fat and skin [20] In this work we have investigated the dielectric properties of pure and Ni doped TiO 2 thin films, as doping modifies the electronic structure and dielectric properties of the material. Ni doped TiO 2 have shown several interesting properties like photocatalytic, hydrophilicity, optical and electrical properties. But the information and study about dielectric properties is limited.

2 II. EXPERIMENTAL

Partially hydrolyzed 0.5 molar solution of TiO 2 was prepared in isopropyl alcohol by adding equimolar ratios of titanium tetra butoxide and water. Nitric acid was used as a catalyst. Solution was refluxed for two hours and pure TiO 2 film was fabricated from this solution by sol-gel dip coating technique at a lifting speed of 24 mm/sec. To prepare Ni doped TiO 2 films a stock solution of the Ni acetylacetonate prepared in isopropyl alcohol . The calculated quantities of the stock solution were added to the undoped TiO 2 solution. The solution was stirred vigorously by magnetic stirrer using Teflon coated bit [21]. Identical processing parameters were maintained for all doped TiO 2 thin films.

All the films were fabricated on ITO coated glass in vertical lifting geometry under tight control relative humidity and temperature maintained between 40-50% and 25-30 o C respectively. Dopant concentration was varied from 2 to 10 mol% for Ni doped TiO 2 thin films. Coated substrates were hanging in the vertical position for one minute to allow the excess solution at the bottom edge of the substrate to drip the solution. These samples were subsequently dried at the 100 o C for half an hour before sintering and then sintered at 500 o C for 1 hour.

To study dielectric properties Al/TiO 2 /ITO the heterostructure is prepared on the ITO coated glass. The top Al (aluminum) electrode is prepared by electron deposition technique and bottom ITO (indium tin oxide) electrode prepared by photolithography technique. The thickness of top Al electrode is 300 nm and the thickness of bottom ITO electrode is 500 nm as measured by thickness profilometer. Copper wires connected to top and bottom electrodes with the help of silver paste for dielectric measurements.

3 Characterization Techniques

X-ray photoelectron spectroscopy of the samples was conducted using Perkin Elmer 1257 with a hemispherical analyzer. The resolution of the instrument is 0.1 MeV. Accelerating voltage used for the analysis was 15 KV. It can detect all the elements except H and He. Dielectric measurements were London Journal of Research in Science: Natural and Formal carried out in an electrically shielded plate condenser using HP 4192 A IMPEDANCE ANALYSER in the frequency range 20 Hz to 10 MHz. at room temperature.

4 III. RESULTS AND DISCUSSION

All the Ni doped TiO 2 films are highly stable and scotch resistant under investigations by scotch tape test and mechanically rubbing with cotton cloth using detergents. They were also found to be stable under harsh environments (containing vapors of different gases, acid fumes etc.) and under open environment (under sun) kept continuously for six months. Not even a single pin hole or scotch was developed in the films and they again passed scotch tape test after this treatment.

5 XRD studies

All the Ni doped TiO 2 films sintered at 500 o C for 1 hour exist in anatase phase as already reported [21] by Davinder et.al. The particle size goes on decreasing with increase in Ni content. The particle size decreased from 40 nm in case of 2 mol% Ni doped TiO 2 film to 20 nm in case of 10 mol % Ni doped TiO 2 thin film. The reason for this decrease in particle size is due to the introduction of Ni +2 ions which change the surface charge of TiO 2 solution particles and the distances from each other. In this way The TiO 2 particles are most likely formed in the smaller size [22]. These results are in good agreement with the results reported in literature [23]

6 XPS Studies

XPS analysis of all the samples carried out on thin film samples coated on glass substrates by irradiating the samples with MgK?-X rays (1253.6 eV). Typical wide scan XPS spectra for the samples are shown in figure numbers 1(a), 1(b), 1 (c), 1(d), 1(e) and 1(f). In this study, the positions of binding energy corresponding to Ti 2p 3/2 and Ti 2p 1/2 lines for pure TiO 2 films were found at 457.95 eV and 463.6 eV; these indicate the presence of Ti 4+ in TiO 2 film. The binding energies of Ti 2p for the Ni-doped samples were almost the same as those for pure TiO 2 film, except that the XPS peaks slightly broadened in doped films containing more than 4 mol% nickel oxide. Titanium also in the Ti 4+ oxidation state in all the doped TiO 2 films. Oxygen in the films was in the form of O 2- in TiO 2 and NiO. The O 1s peak, which broadened to a higher binding energy position associated with the surface hydroxide, could be seen in films 2 mol% Ni doped TiO 2 and 6 mol% Ni doped TiO 2 with the small amounts of nickel. The redox potential for photo-generated holes is +2.53 V versus the standard hydrogen electrode (SHE) [24] after reaction with the hydroxide; these holes can produce hydroxyl radicals (?OH) whose redox potential is only slightly decreased.

London Journal of Research in Science: Natural and Formal The presence of NiO characterized by high-intensity satellites at the binding energy 9 eV higher than the main Ni 2p 3/2 and Ni 2p 1/2 . In samples c and d with higher Ni concentration, the Ni 2p peaks and their satellites had high intensity, indicating the existence of fully oxidized nickel oxide in the films [25]. Although the intensities of Ni 2p peaks were low because of the small amount of Ni, the shake-up satellites peaks with comparably high intensity could clearly be seen in the spectra. To a great extent, the final composition of the films depends not only on the chemical composition of the solution, but also on their intensity of hydrolysis and polycondensation processes, as well as on the substrate [26]. Fig. 1(e) and 1 (f) show the peak positions of Titanium and oxygen respectively.

7 Dielectric constant of Ni doped TiO_2 films

There are two modes of measurements i.e series mode and parallel mode [27]. These curves closely resemble those predicted by the Debey's relaxation model for orientation polarization [28]. A saturation effect is observed In high frequency region, electric capacitance & dielectric constant are no longer frequency dependent. Dielectric constant depends upon various factors such as temperature, frequency of electric field, humidity, radiation effect, mechanical stress. The variation of dielectric constant with crystallite size may be expressed as follows. The defect sites in the TiO_2 lattice can induce defect oriented polarization to the neighboring defect free cells in the crystal lattice. This defect oriented polarization possesses short range ordering inside the lattice contributing to the total polarization of the TiO_2 lattice and therefore the total dielectric constant of the TiO_2 [29]. The growth of the microscopic Polar regions will be restricted due to the constraints for small crystallite sizes. As the crystallite size increases it enhances the growth of microscopic polar regions inside the crystallite and hence the dielectric constant with further increase of crystallite size the relative number of microscopic polar regions may be reduced due to larger crystallite sizes or it may be due to the loss of short range ordering due to larger crystallite sizes. An increase in frequency of the AC applied voltage decreases the value of dielectric constant of non linear dielectrics. The high dielectric constant at low frequency could be due to the presence of defective species such as Ti^{+3} , electrode polarization or space charge injection [30][31] The very low value of dielectric constant at high frequencies is important for the fabrication of materials towards ferroelectric, photonics and electro-optic devices [32]. The behavior observed in dielectric loss with increasing frequency could be explained due to Maxwell-Wagner effect. Various factors such as thickness of the film, applied electric field, frequency of measurement, temperature affect the value of dielectric constant as well as d.loss. Oxygen vacancies distort the main structure unit of TiO_2 crystal, causing the appearance of additional electric dipole moments [33]. Dielectric loss occurs due to the heating effect of the dielectric material. D.loss in real materials the polarization does not respond instantaneously to an applied field. This causes d.loss. The origin of d.losses is the time delay between electric field and electric displacement values. D.losses increase with increase in number of grain boundaries per unit volume in new crystalline materials because grain boundaries are defective regions and suppress the harmonic oscillations of dipolar under an electric field.

8 Dielectric Loss

The dielectric loss of any material describes qualitatively dissipation of electrical energy due to different processes i.e. 1) Dielectric conduction, 2) Dielectric resonance, 3) losses from non linear processes. Also the dielectric loss of various types are ion migration losses, DC conduction losses, ion jump and deformation losses ion vibration and electron polarization losses. Higher conductivity also favors the d.loss.

9 Density of interfacial states

We have calculated the number of interfacial states of pure and Ni doped TiO_2 thin films by using the formula [34] given by equation number (1) by taking capacitance at Hz and 10 MHz. In this Ni doped TiO_2 films the numbers of interfacial density of states with increase in Ni content are given in table **??**. The decrease in dielectric constant and dielectric loss with increase in frequency is due to decrease in particle size. Dielectric constant of the materials is the basic property which gives detailed information about polarization mechanisms. The very low value of the dielectric constant at higher frequencies is important for fabrication of materials towards ferroelectric, photonics and electro optics devices. [1,2,3]

1527

Figure 1: 15 27 ©

1


Figure 2: Fig. 1 .

1


Figure 3: Fig. 1 .

Figure 4:

2

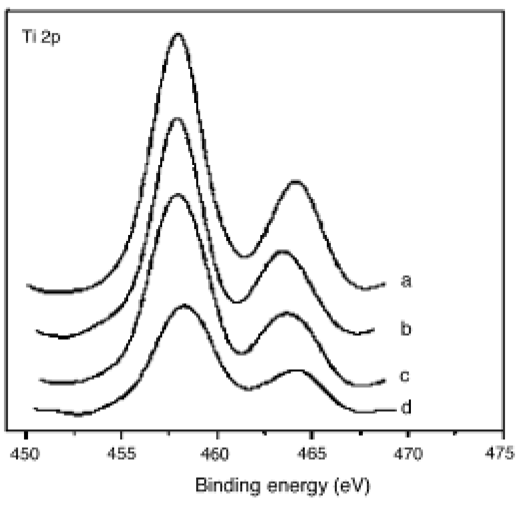
Figure 5: Fig. 2 :

29

Figure 6: Fig. 29 ©

3

Figure 7: Fig. 3 :



1

Figure 8: (1)

I

Sample	Number of interfacial states(cm -2	eV -1)
2 mol % Ni/TiO 2 film	0.749959X10 11	
4 mol % Ni/TiO 2 film	2.180125X10 11	
6 mol % Ni/TiO 2 film	1.33971875X10 11	
8 mol % Ni/TiO 2 film	3.5105625X10 11	
10 mol % Ni/TiO 2 film	1.582275X10 10	
	IV. DISCUSSION	

Figure 9: Table I :

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[2] Volume 23 | Issue 9 | Compilation 1.0 © 2023 Great Britain Journal Press Structural and Dielectric Studies of Ni doped TiO2 Thin Films for Electro-Optic Devices

[3] Volume 23 | Issue 9 | Compilation 1.0 © 2023 Great Britain Journal Press Structural and Dielectric Studies of Ni doped TiO2 Thin Films for Electro-Optic Devices

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