Optical and electrical properties of BaTiO₃ thin films prepared by chemical solution deposition

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Abstract

Barium titanate sol was prepared using barium ethyl hexanoate and titanium isopropoxide. The sol was then spin coated on p-type single crystal silicon (100) wafers, stainless steel and fused silica substrates and annealed to give polycrystalline, transparent, and crack-free films. The surface morphology and structural properties of the films were studied using scanning electron microscopy and X-ray diffraction respectively. Crystalline phase could form only at a annealing temperature of 650°C and above. The effect of post deposition annealing on the optical and structural properties as well as on the band gap were analysed. Transmission spectra were recorded and from this, refractive index, extinction coefficient and thickness were calculated for films on fused silica annealed at different temperatures. The dispersion curve for the refractive index n of 650°C annealed film is fairly flat beyond 450 nm and rises sharply towards the shorter wavelength region, showing the typical shape of a dispersion curve near an interband transition. The present study indicates the validity of the DiDomenico model for the interband transition with a single electronic oscillator. The refractive indices lie in the range 1.75-2.5 for films annealed in the range 300-750°C. The electrical measurements were conducted on metal–ferroelectric–semiconductor (MFS) and metal–ferroelectric–metal (MFM) capacitors. The typical measured small signal dielectric constant was 66 and 140 at 1 MHz for the MFS and MFM capacitors respectively. Debye type dispersion was observed for films on stainless steel substrates with an activation energy of about 0.34 eV. The low field ac conduction was found primarily due to hopping of electrons through the trap centres. The L-V characteristics of the MFS capacitor were found to be ohmic at low fields and space charge limited at high fields. L-V characteristics of the MFM capacitor showed a strange behaviour, linear dependence of current on voltage up to 10³ V/m and V² dependence beyond 10⁵ V/m.

Keywords: Barium titanate; Chemical solution deposition; Optical properties; Electrical properties

1. Introduction

Ferroelectric (FE) materials are of interest for a number of applications, including non-volatile memories, dynamic random access memories, electro-optic switches, pyroelectric detectors, optical modulators, shutters, optical mixers, sensors, imagers and displays to name a few [1–5]. Recently high quality ferroelectric thin films (FETF) have been used for the development of advanced microwave signal processing devices [6]. Since in a FE material, the dielectric constant (ε′) can be varied by applying a d.c. electric field, it allows device characteristics to be ‘tuned’ in real time for particular application, e.g. resonators and delay lines. Thin films offer a unique advantage over bulk materials for these applications. Small, compact, low power microwave devices that can be fabricated from structures based on FE films include phase shifters, tunable filters, tunable resonators, phased array antennas and frequency agile microwave radio transceivers [6–10]. BaTiO₃ in thin film form promises to meet most, if not all, of these needs because of its special nature and unique combination of properties.

Barium titanate (BaTiO₃) in tetragonal form is a displacement type FE material for which the origin of ferroelectricity is derived from the displacement of ions relative to each other [11]. The most remarkable property of BaTiO₃ is its high permittivity. The room temperature dielectric constant of BaTiO₃ ceramics is known to be greater than 2000 [12]. But there are three major differences between the thin films and the bulk materials. First, the thin film dielectric constant is approximately a factor of five or more lower. Second, the temperature dependence of the dielectric constant is much broader. Finally, the Curie temperature, Tc, of the FE is
shifted. Most of the reported work, however, has failed to obtain BaTiO$_3$ thin films with high permittivity in comparison with BaTiO$_3$ ceramics. Recent success in depositing high quality BaTiO$_3$ thin films on insulating substrates has brought the photonic application of BaTiO$_3$ to reality [13]. However, for electronic applications, the deposition of BaTiO$_3$ thin films on conducting substrates has been used.

Realizing the technological importance, both in electronic and optical applications, it is important to understand the structural, electrical and optical properties of BaTiO$_3$ thin films. While there are problems with BaTiO$_3$ films such as leakage current, the electrical conduction mechanism in them is not yet very well understood despite extensive studies. The electrical properties of the films have been found to depend on the preparation technique, processing conditions and substrates used.

BaTiO$_3$ thin films have been prepared by methods such as hydrothermal [14], pulsed laser deposition [15], metalorganic chemical vapour deposition (MOCVD) [16], r.f. magnetron sputtering [17], argon ion beam sputtering [18], molecular beam epitaxy [19], excimer laser ablation [20], partially ionized beam technique [21], evaporation [22], electrochemical [23] and sol-gel [24]. Among these methods, sol-gel processing has the edge over other deposition techniques for good homogeneity, ease of chemical composition control, high purity, low temperature processing, and large area [5].

The typical problem in understanding BaTiO$_3$ thin films is the large variation (100 to 2500) in the reported values of the room temperature dielectric constant (Table 1). The anomaly in this large variation of room temperature dielectric constant, however, could not be clearly identified. The possible reasons may be due to the complex relation between processing techniques, substrates, deposition conditions, etc., on the grain size of the films and its growth characteristics. In this paper, we report the electrical and optical properties of BaTiO$_3$ thin films on different substrates namely stainless steel, silicon and fused silica.

2. Experimental details

Stoichiometric BaTiO$_3$ used in this study was prepared by using chemical solution deposition following Kamalasanan
et al. [24] as outlined in Fig. 1. For making BaTiO$_3$ thin films the sol was prepared in the following way. 4.23 g of barium 2-ethyl hexanoate was dissolved in 24 ml of methanol, 0.2 ml of water and 1 ml of acetyl acetone were added to this solution for hydrolysis and as a chelating agent respectively. The resulting solution was refluxed for 2 h. To this mixture 2.95 ml of titanium isopropoxide was added dropwise with constant stirring. The addition of chelating agent was found necessary to obtain a clear and stable sol. The precursor films were coated onto various substrates by spin coating using a photoresist spinner. The thickness of the film was controlled by adjusting the viscosity of the solution and the spinning speed. Various properties of the films were evaluated using a series of films deposited with a spinning speed of 3000 rev/min for 30 s on bare p-type silicon, stainless steel and fused silica. The effect of annealing temperature on the structure and optical properties of the films was evaluated for BaTiO$_3$ films on fused silica. In fact these studies were used to optimize annealing temperature and annealing time to obtain a fully crystalline film. The films on p-silicon were annealed at different temperatures and as will be explained later (SEM investigation), the films annealed at 700°C were found suitable for electrical studies. For films on stainless steel, post deposition rapid annealing was carried out at 750°C for 120 s. The object of this short processing time is to reduce the time-temperature product so that the desired physical and chemical processes are completed while unwanted processes such as impurity diffusion (e.g. Fe, Ni present in the stainless steel), interface reaction, decomposition, or evaporation etc. are minimized or suppressed [36]. Films produced in this way were polycrystalline and transparent without any cracks.

The structure of the films was analysed by X-ray diffraction (XRD). The XRD patterns were recorded in a Rigaku Geigerflex X-ray diffractometer (RU-200B) using Cu K$_\alpha$ radiation. The surface morphology of the films was analysed by scanning electron microscopy (SEM). The thickness of the films was measured from the SEM cross-section as well as from the transmission technique of Manifacier et al. [37]. Optical properties were measured on films grown on fused silica. Transmission spectra were recorded with a Perkin Elmer UV/VIS spectrophotometer. Refractive indices, extinction coefficient and band gap were calculated from the transmission spectra following a method given by Manifacier et al. [37]. Electrical properties were measured on films grown on stainless steel and p-silicon substrates. Several aluminium dots (diameter: 2 mm for MIM, 1 mm for MIS) were evaporated through a mask over an area of 1.5 cm by 1.5 cm on the films to form metal–Fe–metal (MFM) and metal–Fe–semiconductor (MPS) capacitors. In the case of MIS capacitors, electrical contact to the p-type silicon was formed by depositing aluminium film on the back of the wafer by thermal evaporation, followed by low temperature annealing (150°C) for a short duration (5 min). Aluminium was used to make the back contact due to the fact that Al can make p-type silicon even stronger p-type and thus reduce the barrier height for holes to surmount. This reduces the resistance for current flow in both directions. Again, to make proper ohmic contact, silicon wafers with rough back side were used. The rough region, which is electrically equivalent to a diffused generated layer, helps in achieving good ohmic contact [38]. Capacitance, $\tan \delta$ and $\omega$ conductivy were measured in the 20 Hz–1 MHz frequency range with a HP 4284 precision LCR meter. Leakage currents at different voltages were measured by means of a Keithly 617 programmable electrometer/source. C–V measurements were carried out on MFM and MFS configurations with a HP 4192 impedance analyser.

3. Results and discussion

3.1. Crystallinity

The crystallinity of the films was examined by X-ray diffraction. The pyrolysed films (400°C) were amorphous, and post deposition annealing was required to develop crystallinity. Annealing temperature effects were studied using a series of films deposited on fused silica. Fig. 2a shows the XRD patterns of the BaTiO$_3$ films on fused silica annealed at various temperatures. These films had the same number of coatings and were annealed for the same time (20 min). It was possible to obtain crystalline phase at an annealing
temperature of 650°C. As the annealing temperature was
increased the peaks in the XRD patterns became more
sharp and intense, indicating better crystallinity and an
increase in grain size. Similar observations have also been
reported earlier [39]. The polycrystalline nature and absence
of preferred orientation are evident from the X-ray diffrac-
tion patterns. Moreover, absence of unaccounted reflections
shows that no unwanted crystallites such as BaO, BaCO$_3$, are
present in the sample. The peaks in the XRD (Fig. 2a)
corresponding to (001) and (001) were not clearly resolved
to show the tetragonal structure and are broadened. The
broadening of the peak may be due to small grain size as
well as overlapping of (001) and (001) peaks arising due to
the high scan speed (10°/min) employed for taking the data.
To overcome this problem we recorded XRD spectra with a
slower scan speed (5°/min) for the 700°C annealed film on
fused silica substrate, shown in Fig. 2b. This XRD pattern
clearly exhibits the splitting corresponding to the tetragonal
structure and these data were used for the calculation of
lattice parameters. The calculated lattice constants are
\( a = b = 4.00 \, \text{Å} \) and \( c = 4.03 \, \text{Å} \), indicating that the films
were crystallized in the tetragonal phase. The \( c/a \) ratio of
\( \sim 1.01 \) is in good agreement with that reported by Joshy et
al [40]. Further, the observation of a butterfly loop in the \( C-
V \) curve and \( P-E \) hysteresis (Fig. 17, discussed later)
suggests the ferroelectricity and tetragonal structure of
BaTiO$_3$ film.

3.2. Morphology and microstructure

SEM photographs of the surface of the BaTiO$_3$ films on
silicon substrates annealed at different temperatures are
shown in Fig. 3. For films annealed at 600°C and 650°C
(Fig. 3a,b), the surface was continuous and without any
microcracks. But large particulates (<0.5 μm), whose
origin is poorly understood, were observed in these films
and grain size of the order of nanometres was also clearly
visible. Fig. 3c shows the surface morphology of the film
annealed at 700°C. These three SEM micrographs reveal the
increase in the grain size as the annealing temperature is
increased. The films annealed at 700°C did not show the
large particulates which were present in films annealed at
lower temperatures. Therefore films annealed at 700°C were
used for electrical measurements. The dark spots in these
SEM micrographs are pinholes which might have been
caused by the shrinkage of the film during crystallization.
Fig. 3d shows the typical cross-sectional view of the BaTiO$_3$
film on silicon annealed at 700°C. This reveals a dense
microstructure with uniform thickness. The thickness
observed was 1 μm for eight times spin coated film. This
cross-sectional view has also been used for the thickness
measurement of the film. The cross-sectional view exhibits
a well defined interface suggesting that no significant reac-
tion between BaTiO$_3$ film and silicon substrate has taken
place during annealing at the interface, confirming the
integrability of BaTiO$_3$ with silicon.

3.3. Optical properties

In the present work, the variation of refractive index \((n)\),
extinction coefficient \((k)\) and band gap \((E_g)\) with annealing
temperature have been investigated. The optical transmis-
sion spectra were recorded in the wavelength range 190-
900 nm for the BaTiO$_3$ films on fused silica because the
energy of optical absorption for fused silica is larger than
that of BaTiO$_3$. Fig. 4 shows the transmission spectra for
BaTiO$_3$ films thermally annealed at 600°C and 700°C for
20 min along with that of fused silica. The spectra show
strong attenuation in the short wavelength region. The aver-
age transmission in the visible range is \( \sim 75\% \) with strong
interference oscillations in the long wavelength region.
With the increase of annealing temperature, the absorption
dge of the film shifts to longer wavelengths and the trans-
mission spectra show more absorption. These results will be discussed later.

The optical band gap \( E_g \) for the film was calculated by considering a direct transition between the valence and conduction bands when a photon of energy, \( h\nu \), falls on the material. In this case, the absorption coefficient \( \alpha \) is related to the band gap \( E_g \) as \[ (a\nu)^2 = \text{Constant}(h\nu - E_g) \] (1) for the film was calculated by considering a direct transition between the valence and conduction bands when a photon of energy, \( h\nu \), falls on the material. In this case, the absorption coefficient \( \alpha \) is related to the band gap \( E_g \) as \[ (a\nu)^2 = \text{Constant}(h\nu - E_g) \] (1) for the film was calculated by considering a direct transition between the valence and conduction bands when a photon of energy, \( h\nu \), falls on the material. In this case, the absorption coefficient \( \alpha \) is related to the band gap \( E_g \) as

Exponential variation of \( T \) with absorption coefficient \( \alpha \) is more pronounced near the absorption edge, therefore, \( \alpha \) may be determined from the relation (41)\[ T = A \exp(-\alpha t) \] (2) where

\[ A = \frac{16n_0n_1(n^2 + k^2)}{[(n_0 + n)^2 + k^2][(n_1 + n)^2 + k^2]} \] (3) and \( n_0, n_1, n \) are the refractive indices of the film, air and the substrates respectively, \( k \) is the extinction coefficient of the film, and \( t \) is the thickness of the film. \( A \) is found to be unity at the absorption edge. \( E_g \) was determined for films annealed at different temperatures using Eq. (1). In the high energy region the factor \( (a\nu)^2 \) varied linearly with \( h\nu \). In the low energy region, the absorption spectrum deviated from the straight line as shown in Fig. 5a. This straight line behaviour in the high frequency region was taken as prime evidence for the direct band gap [32]. The optical band gap was determined by extrapolating the linear portion of the plot relating \( (a\nu)^2 \) versus \( h\nu \) to \( a^2 = 0 \). The band gaps thus obtained are shown in Fig. 5b as a function of annealing temperature. The
The band gap of the film varies between 4.38–4.31 eV for the annealing temperatures 400–600°C and decreases sharply from 4.31 to 3.75 eV when the annealing temperature is above 650°C. The corresponding transmission edge is clearly visible in Fig. 4. After the annealing temperature of 650°C the band gap settles at 3.7 eV. The sudden decrease in $E_g$ denotes the change in the structure. At 650°C, the film changes from the amorphous state to crystalline form and fully crystalline film is formed in the temperature range 650–750°C. XRD studies (Fig. 2a) also suggest such a structural transformation of BaTiO$_3$ thin films around an annealing temperature of 650°C. The value of $E_g$ (3.7 eV) obtained for the films investigated in the present study is higher compared to the band gap of 3.6 eV reported for single crystals [42]. This shift in $E_g$ to the higher side may be due to the stress-induced distortion of the band by lattice–film interaction, which depends on the processing parameters [36]. Similar change in the optical band gap was observed by Davis and Gower during the structural transformation of BaTiO$_3$ thin films deposited using excimer laser ablation [20].

One of the most direct applications of the interference fringes in the transmission spectra is in the estimation of film thickness [43]. The wavelengths at each peak and valley of the interference fringes were noted and corresponding $n$ values calculated from the envelop method [37]. Values of thickness from each pair of peaks and valleys were then calculated. Fig. 6 shows the variation of thickness with annealing temperature. Films showed a continued thickness reduction with annealing temperature up to 550°C (see Fig. 6) due to the shrinkage of the film. The film fabricated by CSD may shrink due to different chemical and physical changes taking place during the film formation process. They are (a) surface tensional forces exerted by the solid–liquid interface during solvent evaporation which occurs at room temperature, (b) removal of organics and subsequent collapse of pores during the pyrolysis of organics in the range 200–400°C, (c) bond formation between the metal atoms through oxygen atom due to the condensation of hydroxyl groups, (d) structural relaxation which is assisted by ionic movements at elevated temperature. It can be seen from the figure that thickness remains almost constant in the annealing temperature range 500–750°C. But the thickness increases for the films annealed above 750°C. This may be due to cracking of the film arising from the thermal mismatch of the film with the substrate but within the experimental error too much significance could not be attached to this behaviour.

Fig. 7a depicts the variation of refractive index with annealing temperature at different wavelengths. At 300°C the films have a refractive index of 1.75. It increases with annealing temperature and attains a maximum value 2.50.
around 750°C. The refractive index of thin film is proportional to its electronic polarization, which in turn is inversely proportional to the interatomic spacing [44]. Therefore, a reduction in the interatomic spacing resulting in the densification of the film (porosity reduction) will lead to an increase in the refractive index. Porosity may be the result of burn out of organic and volatile components beyond 350°C in chemically prepared films. This may result in lower density of film, which brings down the refractive index. But as the annealing temperature increases these pores will collapse due to viscous sintering and hence densification occurs leading to an enhanced refractive index. The important factors that contribute to densification of the film and hence the increased refractive index are (i) loss of organics, (ii) porosity reduction and (iii) structural transformation. The sharp increase in the refractive index for films annealed between 600–700°C is due to the crystallization of the perovskite phase.

The extinction coefficient $k$ also increases with annealing temperature (Fig. 7b). For films annealed at 700°C and above, $k$ shows a sharp increase in magnitude. This seems to originate from the fact that at high annealing temperature, the crystal size/grain size of the film increases. As per the nature of the Manifacier method, the calculated $k$ value actually includes the total optical losses caused by absorption and scattering [45]. At high annealing temperature, crystal size is large as compared to the wavelength; this would cause fairly strong scattering loss. This is accounted in the calculation of $k$, thus resulting in the high value of $k$ at high annealing temperatures.

Experimental data on the wavelength dependence of the refractive index of BaTiO$_3$ films at various annealing temperatures are plotted in Fig. 8a. The dispersion curves are nearly flat beyond 450 nm for the films annealed at lower temperatures. But for films annealed at 750°C this flat behaviour is only seen beyond 600 nm. These curves rise rapidly towards short wavelength, showing the typical shape of a dispersion curve near an electronic interband transition [46]. The observed increase in the refractive index with annealing temperature originates from the density and structural changes as already explained. An anomalous behaviour (sometimes a decrease of $n$) is observed in some of the films at shorter wavelengths. Similar observations have been reported by Manifacier et al. [37] and Pal et al. [47] for SnO$_2$ and ZnTe films, respectively.

Such behaviour can be attributed to the strong effect of the surface and volume imperfections on a microscopic scale. The optical dispersion behaviour was further analysed using Sellmeier dispersion formula for a single electronic oscillator. In the interband transition region, the optical data have most often been modelled with a single oscillator model, i.e., assuming that the medium contains elastically bound particles capable of vibrating with the same frequency of oscillation $\nu_0$. The Sellmeier dispersion formula is given by [46]

$$n^2(\lambda) - 1 = \frac{S_0\lambda_0^2}{(1 - (\lambda_0/\lambda)^2)}$$

where $S_0$ is an average oscillator strength and $\lambda_0$ is an average position of the oscillator. For analysing the above formula for the present case we have plotted the quantity $(1/(n^2 - 1))$ versus $1/\lambda^2$ for both the crystalline and amorphous films (Fig. 9). The data fits to a straight line indicating the applicability of Sellmeier’s dispersion formula for BaTiO$_3$ thin films. This behaviour also proves the validity of the DiDomenico [48] model for the interband transition with a single electronic oscillator. The values of $S_0$ and $\lambda_0$ were estimated from the slope ($-1/S_0$) and the infinite wavelength intercept ($1/S_0\lambda_0^2$) of the $(n^2 - 1)$ versus $\lambda^{-2}$ plot. The parameter $E_0$ can be associated with the energy of the oscillator given by $E_0 = h\nu_0/\lambda_0$ [49]. The values of $E_0$, energy dispersive parameter $E_i/S_0$, $S_0$ and $\lambda_0$ of amorphous and polycrystalline films are listed in Table 2 along with value of reported polycrystalline BaTiO$_3$ films.
these facts we qualitatively assign the variation of dispersion parameters to the effect of microstructure, grain size, density, and band gap difference in the three forms, amorphous film, crystalline film and the bulk BaTiO$_3$.

Fig. 8b shows the dispersion curve of extinction coefficients at different annealing temperatures. The values of $k$ for all the films are very small, which have allowed the light wave to traverse the sample several times and hence produced the interference fringes in the transmission curves (see Fig. 4). For 650°C and 750°C annealed films, the $k$ value increases very rapidly towards the short wavelengths. This may be attributed to scattering as already explained. At short wavelengths, the grain size is comparable with the wavelength causing excessive scattering. Since this has been treated as a loss, the calculated $k$ value is higher.

3.4. Electrical properties

3.4.1. BaTiO$_3$ films on silicon substrate

Besides studying dielectric properties, C-V and I-V measurements were also performed to investigate the possibility of using the sol-gel derived BaTiO$_3$ layer as an insulator gate in an MIS capacitor. C-V measurements were performed by applying an ac signal of 100 mV amplitude across the sample while a d.c. electric field was swept from negative to positive and back again. At 1 MHz, the C-D profile for the Al/BaTiO$_3$/Si structure is shown in Fig. 10. The characteristics exhibit clear regions of accumulation, depletion and inversion with a flat band voltage of about $-2$ V. The flat band voltage of $-2.0$ V indicates the presence of a depletion at zero bias condition. This caused a reduction in the measured capacitance to about 900 pF. The depletion layer capacitance ($C_d$) at zero bias has been calculated from the relation [52]

$$\frac{1}{C} = \frac{1}{C_{ave}} + \frac{1}{C_d}$$  (5)

The calculated values were in agreement with the values reported for other perovskites [50]. Some reports on the optical properties of BaTiO$_3$ films indicate a dependence of the parameters, $S_0$ and $E_0$ on the microstructure and band gap of the film [46]. $E_0$ was reported to be significantly higher ($-1$ eV) than the known bulk value and was explained due to the structure related increase in the optical band gap. In our case, the shift in the $E_0$ was largest in the amorphous films with low refractive index (about 1.80 or less), while in the crystalline films with higher refractive index, $E_0$ approaches the bulk value. The density of the film also plays a role in the variation of $E_0$. An increase in $E_0$ is reported with reduction in density of ceramic films [51]. Hence the higher value of $E_0$ in the case of amorphous films may be due to the reduced density and higher optical band gap as compared with the crystalline films and bulk BaTiO$_3$. In the case of thin crystalline films the grain size increases with increase in film thickness and the film with larger grain size gives $E_0$ near to the bulk value. Based on the

Fig. 8. Dispersion of the (a) refractive index and (b) extinction coefficient of BaTiO$_3$ film at different annealing temperature.

![Fig. 8](image-url)

Fig. 9. The single electronic oscillator model fit for amorphous and crystalline BaTiO$_3$ films.
and was found to be about 11.24 nF. The width of the depletion layer at zero bias condition has been determined to be about 70 Å using the relation

$$C_d = \frac{\varepsilon_r \varepsilon_0 A}{W}$$  \hspace{1cm} (6)

where \( \varepsilon_r \) is the dielectric constant of the semiconductor, \( A \) is the capacitor area, and \( W \) is the depletion layer width at zero bias condition. The thickness of the BaTiO_3 used for this study was 4800 Å. The dielectric constant obtained from the maximum capacitance under the accumulation condition [27] was \( \sim 66 \). The presence of small hysteresis observed during scanning between -10 to +10 V indicates the charge injection at the interface. No such hysteresis, however, was observed in the C-V behaviour for voltages larger than ±6 V. The absence of well-defined hysteresis reveals a good electronic Si/BaTiO_3 interface and establishes the possibility of integrating BaTiO_3 films directly onto bare Si substrates. It suggests that these capacitors can be used for charge storage in DRAMs. The dielectric constant (\( \varepsilon_r \sim 66 \)) for the annealed MIS capacitor is relatively small. A low dielectric constant SiO_2 layer forming in the MIS structure during high temperature annealing usually masks the dielectric constant of the insulating films [53]. But in the present case the SEM cross-sectional view of 700°C annealed film does not show an SiO_2 layer between the Si and the BaTiO_3 film. Yamanashi et al. [54] have observed an increase in dielectric constant of BaTiO_3 on silicon substrate with increased thickness and a maximum value has been observed for film with thickness \( \approx 2 \mu \text{m} \). The thickness of the film used in the present study was 4800 Å, so the observed low value may be due to the small grain size of the film as a result of reduced thickness. A thickness dependent grain size is also reported [13,55]. In addition to the small grain size, the coherent constraint between the film, and substrate creates strain in the film which substantially reduce the dielectric constant [12].

The leakage current measurement on the MIS structure is important for applications in devices such as DRAMs and non-volatile memories. A d.c. bias up to 15 V (positive potential to the gate electrode) was applied to the sample. Fig. 11a shows the I-V characteristics of 4800 Å thick polycrystalline BaTiO_3 thin film in the MIS configuration. The leakage current in the sample is of the order of nanoamperes, indicating good insulating behaviour.

The analysis of the conduction mechanism is now taken up which is important for electronic applications. Possible conduction mechanisms include (a) tunnelling, (b) Schottky effect, (c) Poole–Frenkel emission, and/or (d) space charge limited (SCL) current. As the thickness is well above 500 Å, tunnelling process is not expected for the present case.

Further we notice a small negative shift in the C-V curve (Fig. 10) which indicates the presence of positively charged trapping levels in the band gap of the insulator. Oxygen vacancies may be one of the charge traps in the specimen [56]. Other charge traps may include interface charges, fixed charges, polarization charges etc [56]. In the presence of positively charged traps one would expect Poole–Frenkel (PF) type conduction. Following Li et al. [57], for this kind of conduction mechanism log(I/V) versus V^{1/2} plot should be a straight line with a slope of \( \sim 2.86 \) and 0.769 respectively if one uses the optical dielectric constant (6.25) and static dielectric constant (66.00). The optical dielectric constant was obtained from the optical refractive index which was determined to be 2.31 at 600 nm from the transmission spectrum. The static dielectric constant used for calculating the slopes was measured independently using the C-V technique described above. But in Fig. 11b, the observed slope \( \sim 0.266 \) did not agree with either of these values, thus we can discount the PF mechanism. Enhanced Schottky (ES) conduction is the other conduction mechanism reported in this kind of film [57]. For this, the slopes of 1.43 and 0.384 are calculated theoretically using the expression given by Li et al. [57], respectively for the optical and static dielectric constant. When comparing with the slope of 0.384 obtained theoreti-
The conduction in the present case may arise due to space charge limited (SCL) current. The plot of \( \log(I) \) versus \( \log(V) \) (shown Fig. 11c) bears a striking resemblance to current-voltage characteristics of one carrier SCL injection controlled by trap levels distributed in energy, as described by Lampert and Mark [58]. The general feature of the \( I-V \) characteristics, namely a linear region followed by a superlinear, gives evidence of current injection which for a highly resistive material is space charge limited [55]. The following discussion is based on the work of Lampert and Mark. Here we are assuming non-blocking ‘ohmic’ contact for both the electrodes. According to Lampert and Mark, the current \( I \) in the low voltage region may be expressed as

\[
I = \left( \frac{2n_e \mu A}{d} \right) V
\]

where \( e \) is the electronic charge, \( d \) the film thickness, \( n_e \) the equilibrium carrier concentration, \( \mu \) the carrier mobility and \( A \) the area of the electrode. This is the regime where the equilibrium carrier concentration exceeds the injected carrier concentration. This ohmic region in the present case extends to low voltages up to 1 V. On the other hand, at high voltages, according to Lampert and Mark, current follows a square law dependence on voltage:

\[
I = \left( \frac{9 \varepsilon \sigma \mu}{8 d^2} \right) V^2
\]

where \( \varepsilon \) is the permittivity of the film. In this case the injected carrier concentration greatly exceeds the equilibrium carrier concentration. This \( I \) versus \( V \) dependence can be clearly seen in our case (Fig. 11c). For one carrier SCL current controlled by trap levels, the transition (Ohm’s law to square law) is supposedly characterized by a large increase in current over a small voltage region. This sharp crossover is not observed in our case. The lack of clearly defined crossover voltage, however, indicates the presence of traps distributed in energy [59]. This study thus confirms...
the dominance of space charge limited current controlled by
trap as the conduction mechanism in sol-gel derived
BaTiO$_3$ thin films on p-Si substrates.

3.4.2. BaTiO$_3$ films on stainless steel

The electrical properties of BaTiO$_3$ films deposited on
stainless steel substrates were measured. The top electrode
of the metal–insulator–metal (MIM) structure was vacuum
deposited aluminium dots and the oscillator level was
100 mV. The dielectric constant and dielectric loss are
shown in Fig. 12 as functions of frequency at different
temperatures. As the temperature increases, the peak in $\varepsilon''$
shifts to higher frequencies without much change in the
magnitude. There is also a corresponding dispersion in $\varepsilon'$. For any
dielectric material, the presence of an appreciable
resistance which may be arising from the intrinsic or extrinsic
sources, in series with film can effect the dielectric
response at higher frequencies. The existence of an interfacial barrier at one or both of the electrodes introduces
parasitic capacitance and resistance into the system which
causes the permittivity to decrease with frequency, as
observed in many oxide materials [38]. But in the present
case the peak position in the $\varepsilon'$ versus frequency curve is
shifted to higher frequency as the temperature is increased.
This behaviour seems to be due to reasons other than the
electrode effect. If the logarithm of the frequency corre-
sponding to the dielectric loss peak is plotted against the
reciprocal temperature a straight line results (Fig. 13). This
straight line behaviour can be expressed by the following
standard relation for the relaxation time $\tau$,

$$\tau = \tau_0 \exp \left( \frac{-E}{kT} \right)$$  (9)

The activation energy, $E$ and $\tau_0$ of the dispersion process
is given by the slope of the line and $Y$ intercept correspond-
ing to $1000/T = 0$. The calculated values of $E$ and $\tau_0$
were $0.34\ eV$ and $4.54 \times 10^{-7}\ s$ respectively. A fall in dielectric
constant taking place in conjunction with a peak in dielectric
loss resembles Debye-type relaxations. Also at higher
frequencies, the dielectric constant reduces to little less
than half of its value at low frequencies: This kind of relaxa-
tion in bulk BaTiO$_3$ is usually observed at the microwave
frequencies. So the observed dispersion in the case of
BaTiO$_3$ on stainless steel substrates seems to be due to
reasons other than the relaxation of orientation polarization.
Agar et al [60] observed this kind of dispersion in silicon
oxide and they attributed it to Debye type dispersion.
Mountwala [61] observed similar kind of dielectric beha-
vour on ultrathin BaTiO$_3$ and attributed the behaviour as the
consequence of surface moisture on the dielectric
properties. The MIM structure with considerable amount of space
charge polarization can lead to this kind of dielectric dispersion
and high loss tangent. The relaxation of space charge
polarization occurs at frequencies between 1 kHz and
100 kHz, which is also observed in the present case. We
believe that the space charge build up is due to the substrate
effect. Ichinose et al. [62] observed anomalous dielectric
behaviour in Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ ceramics and attributed it to
the space charge build up at the interface. They have
explained the space charge build up as due to the changes
in ionic valency from Fe$^{3+}$ to Fe$^{4+}$ in the B-site of the
perovskite structure. In the present case, at high annealing
temperatures the Fe present in the stainless steel may diffuse
into the insulating BaTiO$_3$ film. This Fe species can change
its ionic valency state from Fe$^{3+}$ to (Fe$^{3+}$-$e^-$), and thus may
cause the space charge build up at the grain boundary. The
diffusion of Fe causes a conductivity difference in the mate-
rial which results in space charge or interfacial polarization
along the boundary of the two regions having different
conductivities. The above view is supported by the fact
that we did not observe this type of dielectric behaviour
on BaTiO$_3$ film grown by the same technique on platinum
substrate [63]. These studies give an idea about the ineffec-

Fig. 14. Variation of dielectric constant and dielectric loss with tempera-
ture at different frequencies.
tiveness of stainless steel as substrate material for the preparation of crystalline BaTiO₃ films as far as the dielectric properties are concerned.

Fig. 14 indicates the variation of dielectric constant and dielectric loss with temperature at different frequencies. For all frequencies the ε' was essentially linear over the temperature range 50 to 125°C. No distinct peaking was detected at the ferroelectric transition temperature (120°C) of BaTiO₃, although a decline in dielectric constant (ε') and dielectric loss (ε'') appeared above 130°C. The observed dielectric constant was about 140 at 1 MHz. The dielectric constant of the film is lower than that of the bulk sample (ε' = 1800) which is attributed to the small grain size in the film. The observed value is still lower than the value reported for thin films (Table 1). This, perhaps, may be attributed to the substrate effect on the grain growth of the film. BaTiO₃ films on platinum substrate were having ε' of ~500 at 1 MHz [63]. While the exact cause of this low value in the present case is not known, a similar low value of ε' had been observed for SrTiO₃ thin film on stainless steel substrates as compared with films on platinumized silicon [39]. The major factors likely to contribute to this low value includes strain in the film induced by the substrate and the smaller grain size mentioned above. A substantial decrease in ε' for BaTiO₃ film due to strain has been reported [13]. The 'clamping' effect between neighbouring grains also gives rise to strain in the film [64].

The measurement of the ac conductivity (oscillator level 100 mV) for the film in the frequency range 10³–10⁶ Hz is shown in Figs. 15 and 16, respectively, as functions of frequency and reciprocal temperature. The plots of ac conductivity versus frequency display two regions (Fig. 15), one at low frequencies and the other at higher frequencies. At high frequencies, the curve exhibits an approximately square law dependence on frequency (σ ~ ω²). At low frequencies (≤3000 Hz), the graphs are still straight lines but their slopes are now much less than two (σ ~ ω⁰.⁵). The high frequency square law behaviour suggests the prevalence of an electronic hopping mechanism. But for this kind of conduction, a strong dispersion of ε' with frequency is not expected. In our case, the films showed dispersion in the dielectric constant at high frequencies. Hence, two-centre hopping is not the only mechanism for ac conduction in BaTiO₃ films on stainless steel. The departure from square law behaviour at lower frequencies is difficult to interpret unambiguously. This may be due to a multistage hopping process, which is plausible but no definite frequency dependence is predicted [60]. The average time the electron spends in each trap depends on the energy difference of the two states. An applied ac field will alter this energy difference and produce a net polarization which lags behind the applied field. Actually, the out of phase component of the polarization is the measure of ac conductivity. At high frequencies this out of phase component will increase and hence the σ ac will show a general increase with frequency. The temperature dependence of conductivity of sol-gel grown BaTiO₃ films was measured in the range 300–420 K. The results obtained are shown in Fig. 16, where σ is plotted as function of 1000/Τ(K) for various frequencies. The d.c. conductivity is a few orders of magnitude lower than the σ ac. This is expected because the electrons confined to traps cannot support a steady current, but it can contribute to alternating current. The curves representing σ ac remain temperature independent up to the temperature of 420 K (maximum temperature used) as expected for the hopping type conduction.

The effect of applied bias field on the capacitance of BaTiO₃ film on stainless steel is shown in Fig. 17a. The measurement was performed by superimposing an ac signal of amplitude 100 mV and frequency 1 MHz with d.c. bias on the film. The nature of the C-V loop indicates non-linear dielectric properties of BaTiO₃ film with applied bias field. It shows a typical butterfly loop which demonstrates the ferroelectric properties of the film [65]. Kamalasanan et

Fig. 15. Ac conductivity (σ ac) as a function of frequency at different temperatures.

Fig. 16. Variation of conductivity with 1000/T for various frequencies.
on stainless steel as found before for films on p-Si. The plot \( \log(I) \) versus \( \log(V) \) (Fig. 18b) also bears a striking resemblance to current–voltage characteristics of one carrier SCL injection controlled by trap levels as explained in the MIS case. In the present MIM case we also observed a low field ohmic region as in the case of film on p-Si. But the expected square law behaviour at high fields as observed in the MIS case was modified here. The current here exhibits the power law

\[ I \propto V^{\alpha} \quad (10) \]

Following Lampert and Mark, if the material has a different set of traps, an exponential distribution of traps comes into the picture. In this case, the concentration of the traps per unit energy decreases exponentially with energy away from the bottom of the conduction band edge. In this most general case, the voltage dependence is given by [58]

\[ I = e \mu N_c \left( \frac{e}{\epsilon \sigma k T} \right)^{1/2} V^{\alpha} \quad (11) \]

where \( N_c \) is the effective density of states in the conduction band, \( \epsilon \) Boltzmann’s constant, \( T \) a temperature parameter characterizing the trap distribution, and \( \alpha \) is a constant \( (\alpha = T_d/T, T \) is the lattice temperature). For \( \alpha < 1 \), the empty traps at the top of the distribution near the conduction band dominate and current \( I \propto V^{2} \) as in the MIS case explained before. If \( \alpha > 1 \), the deep levels also come to play an important role in the conduction; and current follows a power law \( (\alpha > 2) \) dependence on voltage. Based on the above discussion, the high field conductance in BaTiO\(_3\) thin films on stainless steel substrates may be attributed to the SCL current controlled by traps exponentially distributed in the band gap region.

4. Conclusion

In this work, we successfully deposited BaTiO\(_3\) thin films by CSD on different substrates. From the patterns of XRD, we confirmed the polycrystalline nature of BaTiO\(_3\) when annealed between 650 and 750°C. A better understanding has been achieved regarding the annealing temperature and crystallization through the optical properties. The optical band gap was found to be 3.75 eV for 650°C annealed film. The DrDomenico model for the interband transition with a single electronic oscillator was found valid. Optical characterization shows that scattering losses contribute to the total optical losses when grain growth occurs at elevated temperatures. Dielectric constant values of 66 and 140 were obtained at 1 MHz for films on p-silicon and stainless steel respectively. Debye extreme relaxation process was observed for films on stainless steel substrates with an activation energy of about 0.34 eV. The conduction mechanism of BaTiO\(_3\) films in MIS and MIM configurations was studied and was found due to space charge limited current. The current followed Ohm’s law in the low voltage region. At
high voltages, the MIS structure showed a square law dependence of current on voltage which is attributed to the SCL current controlled dominantly by the empty traps near the conduction band. But for the MIM structure the Voc dependence of the current suggests the involvement of deep trap levels in the conduction process, which is the result of a set of traps distributed exponentially from the bottom of the conduction band edge.

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