Dielectric Thin Film from Barium Titanate Nanopowders

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Abstract. BaTiO₃ nanopowders prepared by using organic acid precursor method were thermally grown onto steel under a vacuum of 10⁻⁵ torr, using an Edwards E-306 coating unit. Reflection measurements of coated steel, in the spectral range 200-1100 nm, were carried out using a double beam spectrophotometer. Characterizations of the deposited layer such as adhesion, hardness, dielectric properties and corrosion resistance have been investigated. Surface morphology of fabricated thin film using scanning electron microscope (SEM) reveal that adhered, dense and void free deposited film enables the coated steel to exhibit high corrosion resistance. The microhardness is improved from 116 HV for uncoated steel to 464 HV for coated ones. Dielectric properties were investigated for coated and pure steel samples. The impedance and phase were found to increase with frequency for the as-deposited samples.

1. Introduction

The use of ferroelectrics in thin film form has many general advantages in reduced size and weight. Ferroelectric thin films are very promising for a wide range of application such high dielectric capacitors, insulating surface layer, non-volatile memories with low switching voltage, infrared sensors and electro-optics devices. Due to high dielectric constant, low dielectric loss, low leakage current, low temperature coefficient of dielectric constant, and the composition dependent Curie temperature, pervoskite BaTiO₃ family ceramic thin films, the most popular dielectric materials, are receiving extensive investigation as the charge-storage dielectric for G-bit dynamic random access memory (DRAM), other on-chip components such as de-coupling capacitors and positive temperature coefficient of resistance (PTCR) thermistors [1]. Due to the desirable properties and applications, over the last few decades, synthesis of BaTiO₃ nanopowder and thin film has attracted great attention. Various chemical methods could be employed for the production of these fine particles like sol-gel techniques [2], co-precipitation, alkoxide hydrolysis [3], metal-organic processing [4], hydrothermal treatment [5] and mechanochemical synthesis [6]. Organic acid precursor method is a promising technique that offers relative low cost, uniform size, homogenous powder and high purity of the ceramics. In addition, different techniques have been also applied to prepare thin film of barium

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titanate such as r.f. - sputtering [7], pulsed laser ablation [8] and metal-organic chemical vapor deposition [9]. Recently, Dent A. H. et al [10] have successfully optimized High velocity oxy-fuel (HVOF) spraying for the deposing of barium titanate as dense thick dielectric layer (25-150 μm) and compared the dielectric constant (k) values of these deposits with those (k) values of BaTiO₃ layers produced by plasma spraying. The maximum dielectric constant values achieved by HVOF method for deposition are in the range 70-115. Plasma spraying of these materials has produced layers with k values close to 200. However, considerable success has been achieved for both processes, through particular problems inherent in each type of deposition are still to be overcome.

Despite that several techniques have been explored to deposit thin film of BaTiO₃, less attention has been devoted to thermal evaporation. In this paper, we have reported about the applying of thermal evaporation technique for thin film fabrication of BaTiO₃ nanopowder prepared by using organic acid precursor method using titanium dioxide TiO₂ as a source of titanium and oxalic acid as organic acid. The adhesion characteristics and corrosion properties of thin film have been studied. The reflection and dielectric measurements have been determined. Microstructure and surface morphology of fabricated thin film have been investigated.

2. Experimental

2.1. BaTiO₃ nanopowder preparation
BaTiO₃ nanopowders were prepared using organic acid precursor method. The starting materials used were barium chloride BaCl₂.2H₂O from (Fluka AG CH-9470 Buchs, Switzerland), TiO₂ powders from (ADWIC, El-Nasr Pharmaceutical Chemical Co.) and oxalic acid (ADWIC 99.5 %). A solution of Ba: Ti: oxalic acid mole ratio 1:1:1 was stirred and evaporated at 80 °C till a clear, viscous resin was obtained, then dried at 110 °C for 24 hrs. The precursor formed was heated at 1000 °C for 2 hrs to form BaTiO₃ nanopowders (100 nm). The XRD patterns of the resulting products were characterized by a Brucker D8-advance X-ray powder diffractometer with Cu Kα radiation (λ = 1.5418 Å). The micrograph of BaTiO₃ was examined by direct observation via scanning electron microscope (SEM) model (JSM-5400).

2.2. BaTiO₃ thin film preparation
Thin films were thermally grown onto steel sheet substrates under a vacuum of 10⁻⁵torr, using an Edwards E-306 coating unit. The growth rate and thickness were measured during growth using a crystal oscillator thickness monitor. The growth rate was adjusted to be as low as 10 nm/second to avoid the differential evaporation of elements constituting the alloy. Optical measurements, in the spectral range 200-1100 nm, were carried out using a double beam spectrophotometer type Shimadzu UV-VIS-160A

2.3. Characterization of BaTiO₃ thin film
Electrochemical tests were carried out in a 3.5% NaCl aerated aqueous solution using a classic three-electrode cell with a Pt-wire as counter electrode and an Ag/AgCl electrode as a reference electrode. The exposed area is 1 cm². Potentiodynamic tests were carried out with a scan rate of 0.2 mV/s, using an AUTOLAB PG STAT 30 Potentiostat. From E vs. log I curves, the corrosion potential (Ecorr) & corrosion current densities (Icorr) were obtained using the tafel extrapolation method. Corrosion rate is calculated from the following equation:

\[ \text{Corrosion rate (m/year)} = 0.13 \frac{I_{\text{corr}} \times (E_W)}{d} \]  

where Icorr is the corrosion current density as μA/cm², E_W is the equivalent weight and d is the density in g/cm³. Adhesion characterizations of the deposited layer have been carried out using the scratch test method. In this method, six parallel cuts were made on the test panel by a cutting tool (Multi-blade) with 6 cutting edges spaced 1 or 2 mm apart. Adhesion tape (AME Ricav Tape) was applied firmly to the cut area and then removed rapidly by pulling at right angles to the test panel. According to international standards ISO 2409, the coating adhesion was classified to 6 classes. Surface morphology
of fabricated thin film has been investigated using scanning electron microscope (SEM) model (JSM-5400). The Vickers hardness of pure steel and titanate-coated steel were determined by using a 100 g load with diamond pyramid indenter technique (Tukon Series B200 Microhardness Tester). The result was the average of five measurements. The Dielectric measurements were carried out using HIOKI 3532 LCR HiTester which is an impedance meter with test frequency ranges from 42 Hz to 5 MHz. The measurements were carried out at room temperature. The substrate was steel sheet with a thin film of BaTiO₃ thermally evaporated on one surface of the sheet.

3. Results & discussions

3.1. Characterization of nanopowder

Organic acid precursor method was applied to prepare BaTiO₃ powder in nanosize. Figure 1 shows XRD patterns of precursor sample produced from solution mixture of barium chloride, titanium dioxide and oxalic acid mole ratio 1:1:1 evaporated at 80 °C and thermally treated at 1000 °C to a well crystalline barium titanate BaTiO₃ phase (JCPDS Card # 79-2263). The crystallite size of BaTiO₃ for the most intense peak determines from the X-ray diffraction data using the Debye-Scherrer formula:

\[ d_{RX} = \frac{k \lambda}{\beta \cos \theta} \]

where \( d_{RX} \) is the crystallite size, \( k = 0.9 \) is a correction factor to account for particle shapes, \( \beta \) is the full width at half maximum (FWHM) of the most intense diffraction peak (311) plane, \( \lambda \) is the wavelength of Cu target = 1.5406 Å, and \( \theta \) is the Bragg angle. The average crystallite size of the produced BaTiO₃ powders is 100 nm.

Scanning electron microscope photomicrographs of precursor sample is shown in figure 2. The samples are uniform in shape, have a perovskite cubic phase ABO₃ and the crystallite size of the sample corresponded well to their X-ray diffraction calculation size.

![Figure 1. XRD patterns of BaTiO₃ powder](image)

![Figure 2. SEM of prepared BaTiO₃ powder](image)

It is worth to mention that the organic acid precursor method is a successful and low cost method for preparation of nanopowder of cubic phase BaTiO₃ since it depends on commercial chemicals such as oxalic acid, TiO₂ and BaCl₂, which are available.

3.2. Characterization of BaTiO₃ thin film

The adhesion of BaTiO₃ coating to the steel base depends to a great extent on surface pretreatment condition before coating process. It was found that BaTiO₃ coating layer proceed high adhesion strength. It was found that the coated layer has high adhesion strength and classified according to ISO classification in class (0).

The microhardness measurements using 100gf load showed increasing of the microhardness from 116 HV for uncoated steel to 464 HV for coated samples. The improvements in the microhardness of the coated steel samples can be attributed to the presence of hard BaTiO₃ film in the outer surface with finer grain size, which obstruct the movement of dislocation and resist plastic flow and may be also due to the induced thermal effect during the deposition process. The surface morphology of coated
steel was investigated using SEM. It can be seen from figure 3 that the evaporated particles are of cubic uniform shape with average size 100 nm and corresponding well to the prepared powder. Beside, good distribution and complete surface coverage of steel by evaporated particles confirmed that dense and void free deposit is produced by thermal evaporation of titanate powder.

**Figure 3.** SEM of coated BaTiO₃ film

**Figure 4.** Polarization curves of pure and coated steels

Potentiodynamic polarization measurements as given in figure 4 showed that values of anodic current density of steel/BaTiO₃ samples are lower than uncoated steel samples over the scanning potential range. Table 1 lists the corrosion potential, polarization resistance \( R_p \) at corrosion potential \( E_{corr} \) and the calculated corrosion current density \( I_{corr} \) and corrosion rate \( CR \). Pure steel has been found to possess corrosion current densities of 380 \( \mu A/cm^2 \) while BaTiO₃ films have smaller corrosion current densities of 2.5 \( \mu A/cm^2 \). The percent protection efficiency \( E \% \) and total porosity \( P \) in BaTiO₃ films were estimated using below equations in accordance to Juzeliunas [11]:

\[
E\% = \frac{R_p^{-1} \text{ (uncoated)}}{R_p^{-1} \text{ (coated)}} \times 100
\]

\[
P = \frac{R_p \text{ (uncoated)}}{R_p \text{ (coated)}}  \times 10^{(-\Delta E_{corr} / \beta_a)}
\]

where \( \Delta E_{corr} \) is the difference between corrosion potentials and \( \beta_a \) is anodic tafel slope for steel substrates that was obtained from the polarization curves (figure 4). It was about 0.160 V/dec. The BaTiO₃ films showed high protection efficiency (96%) and very low porosity (0.02).

**Table 1.** Corrosion characteristics of steel and titanate coated samples in 3.5 % NaCl solution

| Sample        | \( R_p \), Ohm/ cm² | \( E_{corr} \), mV | \( I_{corr} \), \( \mu A/cm^2 \) | CR, mpy | E, % |
|---------------|---------------------|---------------------|----------------------------------|---------|------|
| Steel         | 68                  | -660                | 380                              | 113     | -    |
| Steel-BaTiO₃ | 1800                | -619                | 2.5                              | 6.3     | 96   |

The mechanism of the electrochemical process or corrosion reaction involves two half reactions as follow:

\[ \text{Fe} \rightarrow \text{Fe}^{+2} + 2e \] (anodic) \hspace{2cm} (5)
\[ \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e \rightarrow 2\text{OH}^- \] (cathodic) \hspace{2cm} (6)

These reactions must be caused by ion diffusion process taking place through the pores of BaTiO₃ coating on the metal surface. Since BaTiO₃ film has low porosity as calculated above (0.02), the film is characterized by lower conductivity or higher film resistance (1800Ω). Hence, the formation of titanate thin film with low porosity significantly improves the corrosion resistance of steel.

An RCL Bridge of the type given above in the experimental part was used to measure the AC conductivity of the BaTiO₃ coated steel substrate. The BaTiO₃ film was sandwiched between the steel substrate as lower electrode and a silver paste surface electrode as upper electrode. Figure 5 shows the variation of impedance and phase of the BaTiO₃ film with frequency. The BaTiO₃ film shows low impedance that increases with frequency due to the small thickness of the film. It is well known that the dielectric properties of BaTiO₃ are very much dependent on the grain size [12]. The low thickness of the BaTiO₃ film will only show the trend of variation of some parameters such as the impedance...
and phase with frequency. The impedance and phase increase with frequency for the as-deposited samples.

Figure 6 shows the reflectance spectra of both uncoated blank and BaTiO$_3$ coated steel substrates measured at room temperature. No interference fringes were observed in the obtained spectra. This can be attributed to the poor quality of the surface of the used steel substrates as well as some inhomogeneities in the thickness of the BaTiO$_3$ films [13]. It can be noticed from the figure that the reflectance of both samples increase with the increase of the wavelength of the incident radiation. This observation draws attention to the fact that these samples are more reflective on going towards the infrared region of spectrum. It is also clear from figure 6 that the BaTiO$_3$ coated steel substrates are less reflective than the blank ones.

4. Conclusions
Organic acid precursor method is successfully applied to prepare the nanopowder of BaTiO$_3$. Thin films of BaTiO$_3$ could be deposited on steel surface by thermal evaporation of titanate nanopowder under vacuum. The BaTiO$_3$ thin films exhibited high adhesion toward substrate, low porosity and consequently high corrosion resistance. BaTiO$_3$ thin films showed low impedance and less reflectivity in comparison with pure steel samples. More efforts are needed in future search to prepare high quality film.

5. References
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