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Original Research Paper

Investigation on the dielectric properties of titanium-loaded ionic liquid-based nano-organosilica as a novel material

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ABSTRACT

Titanium-loaded ionic liquid based nano-organosilica (Ti@IL-NOS) as a novel material was synthesized and characterized using low-angle XRD, diffuse reflectance spectroscopy (DRS), Fourier transformed infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and EDS mapping. Dielectric constant, band gap and breakdown field of Ti@IL-NOS were obtained to be 21.9, 3.5 eV and 0.91 V/nm, respectively. In addition, the thermal stability of this material was investigated and found to be reasonably good. However, further investigation and optimization is required to suggest such metal-loaded ionic liquid-based nano-organosilica as possible low leakage transistor gate material for the fabrication of low-dimension electronic devices. Furthermore, metals such as Zr and Hf may be suggested as metal constituent of such nano-organosilica.

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1. Introduction

Gate leakage increases to a level, which is unacceptable where the thickness of conventional gate dielectric film used in complementary metal oxide semiconductor (CMOS) devices approaches one nanometer [1]. Therefore, it is necessary to resolve such leakage problems by fabricating new gate dielectrics with less leakage [2]. A group of high- k dielectrics based on oxides has shown to be applicable as gate in metal-oxide semiconductor field-effect transistor (MOSFETs) [3]. Moreover, the stability at interface with substrate is an important challenging factor. To this date, ZrO_2 , HfO_2 , TiO_2 , Al_2O_3 , Y_2O_3 and Si_3N_4 are/can potentially be most applicable materials [4,5]. The barrier height and direct tunneling leakage of materials are affected by parameters such as dielectric constant, band gap and the breakdown electric field [6–8]. Therefore, these key parameters should be studied for new materials.

The creation of ordered mesoporous organosilica (OMO) materials with tunable physicochemical properties was a valuable

achievement in the last decade [9,10]. These are prepared *via* both sol-gel and grafting approaches in the presence of surfactant template under acidic and/or basic conditions [9,10]. Among different kinds of OMOs, periodic mesoporous organosilicas (PMOs) containing organic functional groups in mesoporous wall are of more interest due to advantages such as high thermal and mechanical stability, excellent loading of organic groups, high specific surface area and their potential applications in the fields of catalysis, chromatography, adsorption, *etc* [9–14]. Especially, the management and tuning the physicochemical properties of PMOs, *via* selecting suitable organic functional group precursors, make them as applicable candidate in designing electronic devices [15]. In fact, the integration of electroactive organic moieties such as electroactive dye molecules into the pore walls of ordered PMO materials is an important method for developing a new class of porous silica hybrid material for current and future electronic applications [16,17]. Recently, Inagaki group have prepared a three-arm bridged PMO film containing phenylenevinylene units with long-range hole transport properties [18]. The hole mobility of organosilica films has been experimentally shown to be $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. It has also been shown that it is possible to prepare electrically conductive PMOs by introducing a large conjugated π -system into the framework. More recently, Elhamifar et al. also developed a new strategy for the preparation of novel ionic liquid-based PMOs (PMO-ILs) containing alkyl imidazolium moieties in their

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framework [11–14]. These materials were successfully applied as powerful support for the immobilization of several metal and organo-catalysts in a number of organic transformations [11–14], which may make them electrically active in nature due to the presence of imidazolium rings in the backbone of PMO-ILs. Accordingly, herein for the first time we have developed a method for preparing a novel titanium-loaded ionic liquid-based nano-organosilica (Ti@IL-NOS) with high loading of alkyl-imidazolium moieties followed by studying its dielectric properties. This nano-material was characterized using low-angle XRD, DRS, FTIR, TGA, FESEM, EDS, and EDS mapping. The band gap, dielectric constant and breakdown field of Ti@IL-NOS were studied in details, which satisfactorily showed some of desired electronic properties. However, further investigation is required to suggest such metal-loaded ionic liquid-based nano-organosilica as possible transistor gate material for the fabrication of low-dimension electronic devices. Furthermore, metals such as Zr and Hf may be suggested to be included in such nano-organosilica to achieve most desired nanomaterials.

2. Experimental and methods

2.1. Materials and instruments

All chemicals such as ethanol, toluene, THF, dichloromethane, HCl, sodium imidazolidine, 3-chloropropyl-trimethoxysilane, pluronic P123 surfactant and Ti(O^tBu)₄ were purchased from Merck and Fluka companies.

This nanomaterial was characterized using low-angle XRD over 2θ range of 1–10° by X'pert Pro (Philips, Netherland) using Cu Kα radiation (40 kV and 40 mA). TGA was carried out by NETZSCH instrument model STA 449F3 over the temperature range of 25–1000 °C with a rate of 10 °C/min. The morphology, elemental analysis and mapping of sample were performed by field emission scanning electron microscopy (FESEM: Sigma, Zeiss). Diffuse reflectance spectroscopy (DRS) was applied for the band gap measurement by using an Avante's spectrophotometer (Avaspec-2048-TEC). Fourier transform infrared (FTIR) spectrum was recorded by RX-IFTIR spectrometer (Perkin Elmer-Spectrum) in the range of 400–4000 cm⁻¹.

2.2. Synthesis of 1,3-bis(trimethoxysilylpropyl)imidazolium chloride

This ionic liquid was prepared according to our recent reported procedure with a slight modification [11–14]. Typically, 15 mmol of sodium imidazolidine and 15 mmol of 3-chloropropyl-trimethoxysilane were added to a well-dried flask containing super dry THF (50 mL) with stirring and refluxing under argon atmosphere for 24 h. After that, the stirring was stopped and the system was cooled to room temperature. After removing the solvent under reduced pressure, the residue was transferred in another flask containing 15 mmol of 3-chloropropyl-trimethoxysilane in super dry toluene (50 mL). The obtained mixture was stirred and refluxed for 48 h under argon atmosphere. After cooling the reaction mixture to room temperature, it was washed thoroughly with toluene to remove unreacted reactants. Next, super dry CH₂Cl₂ was added to precipitate NaCl. Finally, the solvent was removed and a yellow viscous ionic liquid called 1,3-bis(trimethoxysilylpropyl)imidazolium chloride was obtained.

2.3. Synthesis of Ti@IL-NOS

According the following procedure, the Ti@IL-NOS was synthesized. 1 g of pluronic P123 was added to 15 mL of ethanol under stirring at room temperature followed by the addition of 0.8 mL

of HCl (12 M). After achieving a homogeneous solution, a pre-prepared mixture of 0.6 g of ionic liquid and 0.3 g of Ti(O^tBu)₄ were added to the reaction vessel under argon flow and stirred at room temperature for 6 h. Then, 2 mL of distilled water was added and the reaction mixture was stirred at 60 °C for 48 h. The material was used as filling material (dielectric) of capacitor designed for the measurement of dielectric constant. 100 mL of ethanol and 3 mL of concentrated HCl were used twice in a Soxhlet apparatus during 24 h to extract the surfactant. The obtained material was finally dried in an oven at 70 °C and denoted as Ti@IL-NOS (Scheme 1).

3. Results and discussion

3.1. Characterization of Ti@IL-NOS

XRD pattern of the Ti@IL-NOS was taken at low angle over the 2θ range of 1–10°. The sharp peak appeared at 2θ below 2° confirms that the Ti@IL-NOS is a periodic mesoporous material (See Fig. 1).

FTIR spectrum of Ti@IL-NOS is shown in Fig. 2. It shows well incorporation of ionic liquid units in organosilica framework and proves their stability. The symmetric and asymmetric stretching vibrations of Si–O–Si bonds are observed at 1037 and 910 cm⁻¹, respectively [11–14]. Stretching vibration of unsaturated C–H is

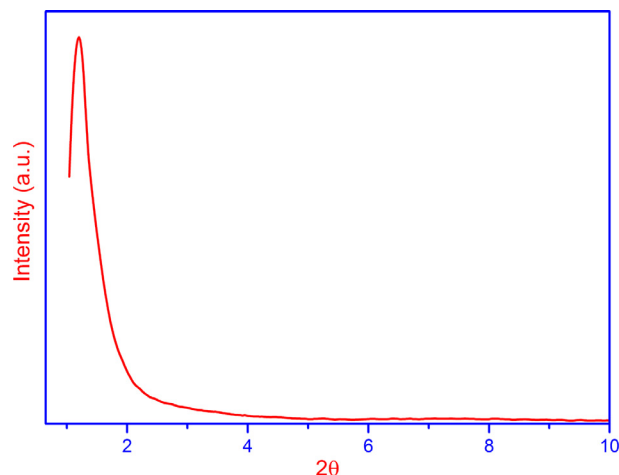
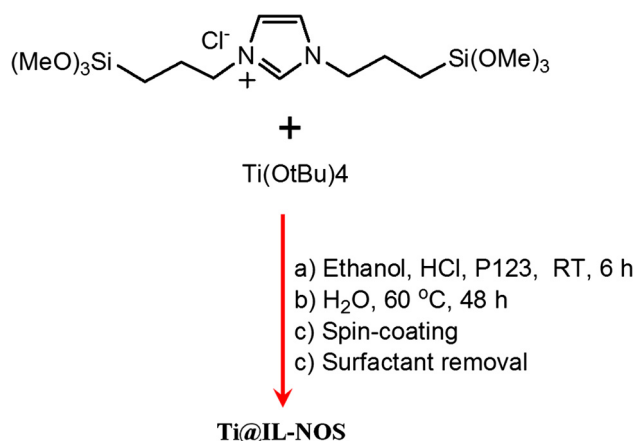


Fig. 1. Low-angle XRD pattern of Ti@IL-NOS.



Scheme 1. Preparation of titanium-loaded ionic liquid-based nano-organosilica (Ti@IL-NOS).

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