Materials Science in Semiconductor Processing 38 (2015) 306–313

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

The influence of solvents on sol–gel derived calcium aluminate

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ARTICLE INFO

Available online 27 January 2015

Keywords:
Calcium aluminate
Sol–gel
Chelation
Solvents
Morphology

ABSTRACT

High purity calcium aluminate (CA) samples were derived by a sol–gel method using aluminium-sec-butoxide (ASB) and calcium nitrate tetrahydrate (CN). In order to facilitate the controllable synthesis process an ethyl acetoacetate (EAA) was used as a chelating agent for ASB (EAA:ASB=3:2). Synthesis was performed using different solvents: ethanol (EtOH), 2-propanol (PrOH), and 2-butanol (BuOH) in order to influence the early stage of CA sol–gel synthesis. The gels were examined using Fourier transform infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy. Al was found to be highly prone to change of coordination states as a consequence of different synthesis parameters and thus various processes occurring; oligomerisation, hydrolysis, condensation, and chelation.

The derived gels were dried and thermally treated to form CA. The thermal evolution, crystallisation behaviour and final microstructure of dried gels were monitored by means of Differential Thermal and Thermogravimetric Analysis (DTA/TG), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) with Energy dispersive X-ray spectroscopy (EDS), particle size distribution and N_2 adsorption/desorption isotherms. It was determined that solvents influence gel composition, structure and particularly the morphology of CA precursor powders. The influence of solvents on the properties of sols and gels also reflects in the properties of calcined CA powders like phase composition, crystallisation parameters and the morphology.

EtOH based sample is characterised with emphasised condensation stage on behalf of which gel thermal stability is enhanced. Thereby final CA microstructure may differ upon calcination. EtOH based sample yields Scherrer crystallite size of 150 Å and bimodal particle size distribution with size between 5 and 20 μm while specific surface area was 5 $m^2 g^{-1}$, differing to samples where other solvents were used.

It was shown that better utilisation of the CA sol–gel synthesis process can be achieved by simple modification of synthesis parameters.

1. Introduction

Calcium aluminate, CA, is the main crystal phase of aluminate cement [1] and constituent of various high-performance ceramic-based composite materials and refractories. Recent applications (minute IR transmissions scattering, photoelectrical sensitivity, biocompatibility and hosting capabilities) utilise CA as a promising, optical, electrical and semiconducting material candidate [2–6]. However general requirement for all of the mentioned advanced application is high purity of CA. Traditional solid-state preparation methods can hardly meet the high purity standards, whereas various wet chemical approaches offer a better success rate. One of the leading synthesis methods, the sol–

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http://dx.doi.org/10.1016/j.mssp.2015.01.004

gel process, was proven to ensure more homogeneous, finer and thus more reactive product under lower thermal processing requirements. Some of the reported sol–gel derived CA gels were based on polymer assisted Ca and Al salts mixture [7]. On the other hand, sol–gel syntheses more commonly repose on distinct alkoxides like aluminium isopropoxide [8] and aluminium sec-butoxide [9], not only as a source to achieve desired elemental stoichiometry, but also as essential reactants for sol–gel polymerisation. While Al alkoxides enable the gelation process, Ca atoms are purely entrapped in the –O–Al–O– based gel network.

In such manner, through alkoxide hydrolysis and polycondensation reactions, an amorphous precursor gel is obtained. Following thermal treatment brings about gel crystallisation into ceramic product.

Common Al alkoxides, like aluminium-sec-butoxide, ASB, were found impracticable for sol–gel synthesis due to their high water affinity and therefore rapid hydrolysis even when exposed to air humidity. In order to surpass the hydrolysis rate-controlling difficulties, a complexation agents like β-ketoester Ethyl acetoacetate, EAA, were introduced. In the presence of ASB the EAA molecules readily replace the reactive alkoxy groups of the ASB molecule, thus forming more stable ASB–EAA chelates. Such chelates, with respect to the EAA ratio used, are far less prone to hydrolysis, enabling controllable synthesis, as often reported concerning aluminium alkoxide-chelates formation and hydrolysis [10–16]. Alkoxides chelated with β-ketoesters and β-diketones such as ethyl acetoacetate and acetyl acetone have been successfully applied to produce a wide range of Al-based products like: mullite [17] and cordierite [18] ceramic, alumina nano-powders [19], thin films [12], fibres [20] and aerogels [21].

In order to acquire advanced CA product, good control over synthesis parameters is required. In this case, the final CA properties are determined by the precursor gel structure, whereas the gel structure is affected by chelation and hydrolysis conditions and structure of the alkoxide chelates. One can say that most of the properties are defined in the early stages of synthesis when elements have set their coordinating number in the modified compounds. There is only limited controlled influence one can have in the following processing stages (hydrolysis, drying, thermal treatment, etc.). Thereby the upgrade of early-stage synthesis-chemistry is imposed as a key in the process, especially knowing that the chemical equilibrium can quite easily be manipulated in wet systems.

Since the sol–gel processes are known to be highly condition-sensitive, one often has to avoid complex modifications (pH, surfactants, temperature, etc.) possibly leading to the long-term process-optimisation with unpredictable outcome. Sol–gel synthesis can be performed with a wide range of different solvents where they could also influence the early stage chemical equilibrium. Different solvent molecules, having different molar masses, chain lengths, dipole moments and dielectric constants, can modulate complexation reactions, condensation process and affect the extent of gel interpenetration. The solvents also, through viscosity, could influence the migration capabilities of the species. Finally, the solvents could behave as true chemical reagents, and as such react with the precursors and thus change them at the molecular level, altering the whole sol–gel process [22]. If shown favourable, such optimisation can easily be feasible in various systems.

For these reasons, CA powders were derived using calcium and aluminium based chemicals, chelated with EAA in the presence of several solvents: ethyl, propyl and butyl alcohol. The influence of the solvents on the alkoxide chemical modification, oligomerisation and chelation processes, as well as on structural and thermal evolution to final CA powder has been investigated.

2. Experimental

2.1. Gel synthesis

In order to prepare samples the following laboratory grade chemical were used; aluminium-sec-butoxide ($Al(OsC_4O_9)_3$, ASB, 97%, Aldrich, Great Britain), Calcium nitrate tetrahydrate (($Ca(NO_3)_2 \cdot 4H_2O$, CN, 99.8%, Kemika, Croatia) as Al and Ca source, Ethyl acetoacetate ($C_6H_{10}O_3$, EAA, 99%, Fluka, Germany) as a complexation agent and ethyl alcohol (C_2H_5OH, EtOH, 99.8%, Kemika, Croatia), 2-propyl alcohol (C_3H_7OH, PrOH, 99.8%, Fluka, Germany) and 2-butyl alcohol (C_4H_9OH, BuOH, 99.5%, Fluka, Germany) as solvents. All chemicals were used as received. Stoichiometric CA sols were prepared. The EAA and CN were dissolved in solvents separately. ASB was slowly added to the EAA solution using syringe to minimise contact with air humidity. Both solutions were stirred for 1 h before the CN solution was slowly added to the ASB/EAA solution under vigorous stirring. The mixture was then stirred in a closed reactor at room temperature for 24 h, thereafter yielding clear sol. The sol was hydrolysed by means of exposure to air humidity to form gel and then dried (14 days). Overall chemical molar ratios were held at ASB:CN:EAA:solvent=2:1:3:30.

The synthesis procedure was previously optimised with respect to the solvent amount, synthesis duration and temperature, water addition, complexation level, in order to define most beneficial synthesis conditions to achieve gel homogeneity and CA phase purity [23]. Derived gel samples differing only in used solvent were denominated accordingly; CAE (with EtOH), CAP (with PrOH) and CAB (with BuOH). For the purpose of spectroscopy measurements, sampling of the gels was performed 14 days after mixing of precursors. Following the drying process the gels were ground to fine precursor powders then calcined to CA in box furnace in static air with heating rate of 10 °C min^{-1} and unassisted cooling.

2.2. Characterisation techniques

^{1}H, ^{13}C and ^{27}Al NMR spectra of the gel samples were acquired using a high-resolution NMR Spectrometer Bruker Avance 600, operating at 600.13, 150.92 and 156.38 MHz for ^{1}H, ^{13}C and ^{27}Al resonance, respectively. The samples were dissolved in $CDCl_3$ and measured in 5 mm NMR tubes. The ^{1}H, ^{13}C and ^{27}Al NMR chemical shift values (δ) are expressed in ppm referred to internal standards (tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR and aluminium nitrate nonahydrate (ANN) for ^{27}Al NMR).