POLYMER NANOCOMPOSITES/ CERAMICS SYSTEMS

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Beytepe, Aralık 2011
MEHMET ÇOPUROĞLU

- BSc: Chemistry, Hacettepe University
- MSc: Chemistry, Hacettepe University; Supervisor: Asst. Prof. Murat Şen
  - Ageing characteristics of ethylene-vinyl acetate copolymer and ethylene-vinyl acetate/carbon black mixture
- PhD: Microelectronic Engineering, Tyndall National Institute at National University of Ireland, Cork (aka UCC); Supervisors: Prof. Gabriel Crean, Dr. Shane O’Brien
  - Development of polymer/nanocomposite thin films
- Post-doc: Tyndall National Institute at UCC
  - Development of lead-magnesium-niobium titanate-based material systems for ultra-high-value capacitor applications
Developed two material systems
- Inorganic-organic hybrids for potential short-range photonic interconnect/optical waveguiding applications
- Ceramics for transparent conducting oxide (TCO) applications
- Sol-gel synthesis
- Thin-film deposition and processing
- Characterisation
THE SOL-GEL METHOD

➢ Production of materials
  • ceramics
  • inorganic/organic hybrid materials (e.g. organically modified silicates (ORMOSILs or CERAMERs))
THE SOL-GEL METHOD-ADVANTAGES

- Low cost
- Relatively low-temperature synthesis
- Precise control over microstructure and material properties
- Ease of doping
- No need for sophisticated instrumentation
THE SOL-GEL METHOD

Involves

• preparation of a colloidal dispersion system (sol)
• gelation of the sol
• removal of the solvent

The sol may

• be produced from inorganic or organic precursors (e.g. alkoxides, acetates, nitrates)
• consist of dense oxide particles of polymeric clusters
THE SOL- GEL METHOD

Metal Alkoxides:

\[ M(OR)_4 + 4H_2O \rightarrow M(OH)_4 + 4ROH, \]
\[ mM(OH)_4 \rightarrow (MO_2)_m + 2mH_2O. \]
THE SOL-GEL METHOD

- Many parameters:
  - $\text{H}_2\text{O}:\text{Si}$ ratio
  - Other precursor/s and/or metal/s
  - type and concentration of the catalyst
  - alcohol
  - temperature

- Acid-catalyzed
  - yield primarily linear or randomly branched polymer

- Base-catalyzed
  - yield highly branched clusters
ORMOSILs

Functional groups based on type IV

Heteroatoms in inorganic structures based on type II

Inorganic silica network based on type I

Organic crosslinking based on type III

Structural elements of ORMOSILs.
Combining desired properties of the individual constituents.

Invaluable for various interdisciplinary applications
- optoelectronics-waveguides
- coating industry-protective coating
- biotechnology-dental restorative materials

Various requirements simultaneously met
- thermal/mechanical stability
- transparency
- biocompatibility, etc.
Materials

Inorganic/organic hybrid

ORMOSIL with transition metal
ORMOSIL with aryl groups

Ceramic

Zinc oxide-undoped
Zinc oxide-doped
STUDY

- Investigated parameters:
  - refractive index modifier, Zr
  - UV light
  - sol ageing

- Characterised properties:
  - structural
  - morphological
  - optical
  - spectroscopical
  - thermal
  - reliability
Skeletal formulae of the chemicals used, and outline of the synthesis. GDPTMS: (3-glycidyloxypropyl)trimethoxysilane; DMDMOS: dimethyldimethoxysilane; Zr(OPr\textsuperscript{n})\textsubscript{4}: zirconium(IV) \textit{n}-propoxide; MAA: methacrylic acid; IPA: isopropanol.
Outline of the film preparation and processing, and waveguide fabrication.

1. Sol-gel mixture
2. Filtration
3. Spin-coating @ 800 rpm for 30 s
4. Heating @ 75 °C for 30 min
5. UV irradiation
6. Heating @ 75 °C for 30 min
Cross-sectional *scanning electron microscopy* (SEM) image (a) of the films; *optical microscopy* (OM) image of the waveguide structures (b); and *near-field* (NF) image (c) of the guided light output from the waveguide.
Representative UV/vis (a) and IR spectra (b) of the films.
 Modes

A prism coupling curve.
Variation of refractive index (633 nm) and Δn with Zr content. (Un: Unexposed, Ex: UV-exposed)

Variation of thickness with Zr content.
Dynamic thermograms of the unexposed (a) and the UV-exposed (b) materials in air, and their 1st derivative curves ((c) and (d), respectively).

Variation of refractive index (at 633 nm) (a) and thickness (b) with sol ageing, for the system with 11 mol % Zr content.
Dynamic thermograms of the unexposed (a) and the UV-exposed (b) materials in air, and their 1\textsuperscript{st} derivative curves ((c) and (d), respectively).
**OPTICAL LOSS MEASUREMENT**

Insertion loss

\[ \text{InsertionLoss} = -10 \log \frac{P}{P_0} \]

Optical microscopy image

Near-field image

Optical waveguides
**OPTICAL LOSS MEASUREMENT**

![Graph showing insertion loss vs. waveguide length](image)

**Insertion Loss**

\[
\text{InsertionLoss} = -10\log\frac{P}{P_0}
\]

Optical waveguides
RELIABILITY ANALYSIS

OM images of the waveguide structures ((a)-(c)), and NF images of the guided light output from the waveguides ((d)-(f)) with no Zr, subjected to a temperature cycling treatment between: none (a) and (d); 4 and 38 °C (b) and (e); -40 and 65 °C (c) and (f) (100 cycles in both cases).

<table>
<thead>
<tr>
<th>Temperature Range (°C)</th>
<th>Optical Propagation Loss (dB cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.8</td>
</tr>
<tr>
<td>4-38</td>
<td>2.4</td>
</tr>
<tr>
<td>-40-65</td>
<td>5.2</td>
</tr>
</tbody>
</table>
Materials

Inorganic/organic hybrid

- ORMOSIL with transition metal
- ORMOSIL with aryl groups

Ceramic

- Zinc oxide-undoped
- Zinc oxide-doped
Investigated parameters:
  • refractive index modifier, DPDMS
  • UV light
  • sol ageing

Characterised properties:
  • structural
  • morphological
  • optical
  • spectroscopical
  • thermal
  • reliability
Skeletal formulae of the chemicals used, and outline of the synthesis. DPDMS: diphenyldimethoxysilane.
Outline of the film preparation and processing:

- **Sol-gel mixture**
- **Filtration**
- **Spin-coating @ 800 rpm for 30 s**
- **Heating @ 95 °C for 30 min**
- **UV irradiation**
- **Heating @ 95 °C for 2 h**
Representative cross-sectional SEM image (a) and IR spectrum (b) of the UV-exposed films.
EFFECT OF DPDMS AND UV LIGHT

Variation of refractive index (at 633 nm) and thickness with DPDMS content.

Dynamic thermograms of the unexposed (a) and the UV-exposed (b) materials in air, and their 1\textsuperscript{st} derivative curves ((c) and (d), respectively).

Dynamic thermograms of the unexposed (a) and the UV-exposed (b) materials in air, and their 1st derivative curves ((c) and (d), respectively).
CONCLUSIONS-ORMOSILS

- Two novel ORMOSIL systems synthesised by the sol-gel method, and their thin-films deposited by the spin-coating technique
- Comparative effects of refractive index modifiers, UV light and sol ageing on microstructure and functional properties, and their tunability detailed for the first time
- Planar optical waveguide structures with reasonable optical propagation loss and reliability obtained for the Zr-doped system, at its low concentrations

Materials

Inorganic/organic hybrid
- ORMOSIL with transition metal
- ORMOSIL with aryl groups

Ceramic
- Zinc oxide-undoped
- Zinc oxide-doped
STUDY

- Investigated parameters:
  - single-/multi-step coating
  - Al-doping

- Characterised properties:
  - structural
  - morphological
  - optical
  - spectroscopical
  - thermal
  - reproducibility
  - reliability
Skeletal formulae of the chemicals used, and outline of the synthesis. MEA: 2-aminoethanol.


Outline of the film preparation and processing.

Top-view ((a) and (b)), and cross-sectional SEM images ((c) and (d)) of the single- ((a) and (c)), and multi-layer ((b) and (d)) films.
UV/vis spectra (a), and their 1st derivatives (b) of the single- and multi-layer films. The table shows the data obtained from these spectra.
X-ray diffraction patterns of the undoped single- (a) and multi-layer (b) films. The table shows the data obtained from these patterns.

<table>
<thead>
<tr>
<th>Film Type</th>
<th>Relative Intensity of (002)</th>
<th>Crystal Orientation</th>
<th>Average Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-layer</td>
<td>0.62</td>
<td></td>
<td>37</td>
</tr>
<tr>
<td>Multi-layer</td>
<td>0.94</td>
<td></td>
<td>46</td>
</tr>
</tbody>
</table>
Scherrer’s equation:

\[ t = \frac{0.9\lambda}{B \cos \theta_B} \]

- \( t \): thickness of the crystal,
- \( B \): actual full width at half maximum of the peak centred at \( 2\theta_B \).
- \( \lambda \): wavelength of the incident light (X-ray)
ELECTRICAL CHARACTERISATION

Current-voltage plots of the single-layer film before and after FGP. The table shows the data obtained from these plots.

<table>
<thead>
<tr>
<th>Measurement Stage</th>
<th>Minimum Electrical Resistivity (Ω m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before FGP</td>
<td>4.5</td>
</tr>
<tr>
<td>After FGP</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The table above shows the electrical resistivity of the single-layer film before and after FGP. The plots illustrate the current-voltage relationship, measured by a 4-point probe method.
SEM images of the single- (1st and 3rd row) and multi-layer (2nd and 4th row) films. (From left to right: Day-1 to Day-5; the width of the scale bars corresponds to 500 nm)

UV/vis spectra of the single- (a) and multi-layer (b) films and their first derivatives ((c) and (d), respectively).
X-ray diffraction patterns of the single- (a) and multi-layer (b) films.
Current-voltage plots of the single-layer film before and after FGP. (From (a) to (b): Day-1 to Day-5)

Average Electrical Resistivity ($\Omega \text{ m}$)

<table>
<thead>
<tr>
<th>Before FGP</th>
<th>After FGP</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>18</td>
</tr>
<tr>
<td>1.5</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Materials

Inorganic/organic hybrid
- ORMOSIL with transition metal
- ORMOSIL with aryl groups

Ceramic
- Zinc oxide-undoped
- Zinc oxide-doped
X-ray diffraction patterns of the single- (a) and multi-layer (b) films. The table shows the data obtained from these patterns.

Top-view ((a) and (b)) and cross-sectional ((c) and (d)) SEM images of the Al-doped single- ((a) and (c)) and multi-layer ((b) and (d)) films.
UV/vis spectra of the single- (a) and multi-layer (b) films, and their first derivatives ((c) and (d), respectively).
ELECTRICAL CHARACTERISATION

Current-voltage plots of the undoped and the Al-doped single-layer films.

<table>
<thead>
<tr>
<th>Measurement Stage</th>
<th>Minimum Electrical Resistivity (Ω m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>4.5</td>
</tr>
<tr>
<td>Al-doped</td>
<td>0.34</td>
</tr>
</tbody>
</table>
Top-view ((a), (b) and (e)) and cross-sectional ((c), (d) and (f)) SEM images of the undoped single- ((a) and (c)) and multi-layer ((b) and (d)), and the Al-doped multi-layer ((e) and (f)) films after the temperature cycling test (-40-65 °C) (100 cycles).
CONCLUSIONS-ZINC OXIDE

➤ Both undoped and Al-doped ZnO systems synthesised by the sol-gel method

➤ Thin-films deposited by the spin-coating technique

➤ Reproducible desired properties obtained

➤ Electrical conductivity improved by Al-doping

➤ High degree of reliability demonstrated
Development of perovskite-type lead-magnesium-niobium titanate (PMNT)-based material systems for monolithic above-IC ultra-high-value capacitors for mobile and wireless communication systems.

Involves

- sol-gel synthesis under controlled environment (atmosphere, temperature, etc.)
- nanoparticle seeding
- various thin-film processing techniques including rapid thermal annealing (RTA), UV-irradiation, and laser-activation
- characterisation
Flowchart of synthesis. (2ME: 2-Methoxyethanol)

Outline of film preparation and processing, and RTA time-temperature profile and conditions.

Planar (a) and cross-sectional (b) SEM images of two representative films annealed at 750 (unexposed) and 550 (UV-exposed) °C, respectively.
**FILM CHARACTERISATION - THICKNESS EVALN.**

Thickness profiles of the films.

(a) Thickness profiles for Annealing temperature (°C)/No of layer/Annealing atmosphere:
- 750/1/O2
- 750/2/O2
- 750/3/O2
- 750/4/O2

(b) Thickness profiles for Annealing temperature (°C)/No of layer/Annealing atmosphere:
- 550/4/O2
- 650/4/O2
- 700/4/O2
- 750/4/O2
- 750/4/N2
Thickness values of the films.

FILM CHARACTERISATION - XRD

XRD patterns of the unexposed (a) and the UV-exposed (b) films that were annealed at various temperatures.

% perovskite phase = 97 (750 °C)

% perovskite phase = 61 (750 °C)
FILM CHARACTERISATION-ELECTRICAL MEAS.

DC bias dependence of $k$ and $\tan \delta$ of the films composed of 4-layer, and annealed at 750°C in $O_2$ (a) and (c), and $N_2$ (b) atmosphere. (a) and (b) unexposed, (c) UV-exposed.
FILM CHARACTERISATION-ELECTRICAL MEAS.

Remnant polarisation = 7 μC cm\(^{-2}\)   Coercive field = 35.8 kV cm\(^{-1}\)

Polarisation (P) hysteresis loops of the film composed of 4-layer, and annealed at 750°C in O\(_2\) atmosphere.
## LASER PROCESSING

<table>
<thead>
<tr>
<th>Rows</th>
<th>mJ/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>57</td>
</tr>
<tr>
<td>2</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Columns</th>
<th>No of shots</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
</tr>
</tbody>
</table>

- Delamination upon Cr/Au electrode deposition (by sputtering)
- Observed even if cleaning step (H₂O₂/NH₃ aq. soln.) skipped
CONCLUSION

- Crack-free films with tunable thickness obtained
- Unexposed film annealed at 750 °C in O₂ atm (4-layer) exhibited a considerably high k value (1425)
- Use of gentle-UV-irradiation could facilitate the lattice formation-initiation at lower temperatures, and play a role in modifying the microstructure
- This PMNT thin film system appeared potentially suitable for ultrahigh-value capacitor applications
Synthesis and preparation:

- Avail of
  - sol-gel method-based approaches
  - polymerisation/crosslinking regimes

- Employ combinations of precursors
  - polyfunctional silicon and/or metal alkoxides
  - optionally containing polymerisable/crosslinkable functional moieties
  - other oligomers/polymers

- Make use of various techniques
  - thermal processing
  - photon-assisted processing

- Tailor desired properties
Skeletal formulae of the chemicals used, and outline of the synthesis. GDPTMS: (3-glycidyloxypropyl)trimethoxysilane; DMDEOS: dimethyldiethoxysilane; Ti(OPr\(^n\))\(_4\): titanium(IV) isopropoxide; MAA: methacrylic acid.
**Diş Dolgu Malzemeleri İçin Yeni Polimer Nanokompozitlerin Geliştirilmesi** (Akronim: “DİP”)

1. GDPTMS + DMDEOS + TEOS
2. Ti:MAA
3. 15 dakika oda sıcaklığında karıştırma
4. IPA
5. 5 dakika oda sıcaklığında karıştırma
6. (damla damla) H₂O/H₃O⁺
7. 2.5 saat oda sıcaklığında karıştırma
8. Foto-baslatici
9. 1 saat oda sıcaklığında karıştırma
10. Sol yaslanması

Takip edilen sentez rotasının şeması.
Diş dolgu malzemeleri için yeni Polímer nanokompozitlerin geliştirilmesi (akronim: “DİP”)

Sol-jel karisimi

Kaliplama

60 ºC'de 30 dakika kurutma

UV-kür işlemi

Takip edilen işlem rotasının şeması.
**Dış Dolgu Malzemeleri İçin Yeni Polimer Nanokompozitlerin Geliştirilmesi (Akronim: “DİP”)**

<table>
<thead>
<tr>
<th>Kod</th>
<th>Ti bileşimi (mol %)</th>
<th>Sol yaşlanma süresi</th>
<th>Kür süresi (dakika)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti0</td>
<td>0</td>
<td>0 saat</td>
<td>0</td>
</tr>
<tr>
<td>Ti1</td>
<td>5</td>
<td>1 saat</td>
<td>1</td>
</tr>
<tr>
<td>Ti2</td>
<td>10</td>
<td>3 saat</td>
<td>2</td>
</tr>
<tr>
<td>Ti3</td>
<td>15</td>
<td>6 saat</td>
<td>5</td>
</tr>
<tr>
<td>Ti4</td>
<td>20</td>
<td>12 saat</td>
<td>10</td>
</tr>
<tr>
<td>Ti5</td>
<td>25</td>
<td>1 gün</td>
<td>20</td>
</tr>
<tr>
<td>Ti6</td>
<td>30</td>
<td>2 gün</td>
<td>30</td>
</tr>
<tr>
<td>Ti7</td>
<td>40</td>
<td>3 gün</td>
<td>60</td>
</tr>
<tr>
<td>Ti8</td>
<td>50</td>
<td>6 gün</td>
<td>120</td>
</tr>
<tr>
<td>Ti9</td>
<td>75</td>
<td>10 gün</td>
<td>300</td>
</tr>
</tbody>
</table>

Örneklerin isimlendirilmesinde kullanılan kodlama sistemi.
Molce % 0 (a) ve 25 (b) Ti başlangıç maddesi içeren örnekler için sol yaşlanma süresi FT-IR profili.
Molce % 0 (a) ve 25 (b) Ti başlangıç maddesi içeren örnekler için UV kür süresi FT-IR profili.
DIŞ DOLGU MALZEMELERİ İÇİN YENİ POLİMER NANOKOMPOZİTLERİN GELİŞTİRİLMESİ (AKRONİM: “DİP”)

Molce % 0 (a) ve 25 (b) Ti başlangıç maddesi içeren örnekler için UV kür süresi TGA profili.
Polimer nanokompozitler ve potansiyel uygulamaları. (Sertlik testi ve hesaplamaları)
Shore-A hardness & elastic modulus:

<table>
<thead>
<tr>
<th>Sample</th>
<th>0 mol % Ti UV-irrad. 10 min.</th>
<th>0 mol % Ti UV-irrad. 60 min.</th>
<th>25 mol % Ti UV-irrad. 10 min.</th>
<th>25 mol % Ti UV-irrad. 60 min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore-A hardness</td>
<td>46</td>
<td>70</td>
<td>71</td>
<td>81</td>
</tr>
<tr>
<td>E (MPa)</td>
<td>~ 0</td>
<td>0.5</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>

Shore-A hardness and elastic (Young’s) modulus (E) values for particular samples.
Polimer nanokompozitler ve potansiyel uygulamaları (adesiv). (Mekanik test)