Roll to roll PECVD system for transparent high barrier coating

H.Tamagaki, T.Okimoto, Y.Kurokawa, T.Segawa
Kobe Steel, Ltd.
Outline

- A few words about Kobe Steel
- Introduction
- Description of PECVD Roll Coater
- Barrier Coating by PECVD Roll Coater
- Scaling up to Production System
- Summary
About Kobe Steel

Machinery Business
- Compressor

- Industrial Machinery
  - Tire & Rubber Machinery
  - Plastic Processing Machinery
  - Rolling Mill, HIP, CIP
  - Vacuum Coating System

Vacuum Coating System
- Systems for Hard Coating
  - AIP / UBMS
  - Vacuum Web Coaters
    - Sputter/PECVD/AIP
    - R&D / Production
### Introduction

#### Our Goal: Flexible Electronics
- Flexible Products: Bendable/Rollable
- Roll to roll process

#### Substrate technologies
- Glass-like polymer
- Polymer-like glass

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Glass</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat resistance</td>
<td>◎</td>
<td>× ～△</td>
</tr>
<tr>
<td>Dimensional stability</td>
<td>◎</td>
<td>× ～〇</td>
</tr>
<tr>
<td>Surface roughness</td>
<td>◎</td>
<td>△ ～◎</td>
</tr>
<tr>
<td>Optical Properties</td>
<td>◎</td>
<td>◎ ～◎</td>
</tr>
<tr>
<td>Gas Barrier</td>
<td>◎</td>
<td>×  → Barrier Coating</td>
</tr>
<tr>
<td>Rugged (not brittle)</td>
<td>×</td>
<td>◎</td>
</tr>
<tr>
<td>Flexible</td>
<td>×  →◎ Flexible Glass</td>
<td>◎</td>
</tr>
<tr>
<td>Roll-to-roll processing</td>
<td>×  →◎ Flexible Glass</td>
<td>◎</td>
</tr>
</tbody>
</table>
## Motivations for High Barrier Coating

### Plastic Film: Light • Thin • Rugged

Roll-to-Roll Processing

Use as Substrate for Flexible Displays

<table>
<thead>
<tr>
<th>ADVANTAGE</th>
<th>DISADVANTAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Weight</td>
<td>Poor Heat Resistance</td>
</tr>
<tr>
<td>Density 1~2g/cm³</td>
<td>Normally 100°C</td>
</tr>
<tr>
<td>Flexible</td>
<td>High Grade ~250°C</td>
</tr>
<tr>
<td>Thin • Bendable</td>
<td>Large Thermal Expansion</td>
</tr>
<tr>
<td>Optical Transparency</td>
<td>50 × 10⁻⁶/°C</td>
</tr>
<tr>
<td>&gt;85%</td>
<td>Gas Permeation</td>
</tr>
<tr>
<td>Rugged</td>
<td>Humidity, Oxygen</td>
</tr>
<tr>
<td>Not Brittle</td>
<td>Stability</td>
</tr>
<tr>
<td></td>
<td>UV Degradation</td>
</tr>
</tbody>
</table>
Requirement for Barrier

<table>
<thead>
<tr>
<th>WVTR (g/m²/day)</th>
<th>OTR (cc/m²/day/atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>1000</td>
</tr>
<tr>
<td>0.1</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>100</td>
<td>0.1</td>
</tr>
<tr>
<td>1000</td>
<td>0.01</td>
</tr>
</tbody>
</table>

- Plastic Film
- Food Package
- Industrial Package
- High Barrier
- PV,E-Paper
- OLED
Barrier Coating by Vacuum Deposition

Barrier Coating
- $\text{SiO}_x$: SP, PECVD, Ev
- $\text{SiON}$: SP
- $\text{AlO}_x$: SP, Reactive Ev
- ALD
- DLC: PE-CVD
- Multi-Layer
- Inorganic/Polymer
- Graded-Layer

Sputter, PE-CVD, Evaporation
ALD

10 ~ 1000 nm

10 ~ 200 μm

Plastic Substrate
- PET, PEN, PES, COP
High Barrier Coating  PVD vs PECVD

- Barrier coating from PVD
  - Inorganic layer: Brittle!!
  - Limitation in layer thickness
  - Multilayer with organic layer

- Barrier coating from PECVD
  - Mixture of Organic & Inorganic
  - Flexible coating
  - Thick single layer coating

Barrier Layer Thickness

WVTR・OTR

SP

PECVD

AIMCAL 2013.10.29 ©2013 Kobe Steel, Ltd.
Roll to Roll PE-CVD Barrier Coating

**Advantages**
- High Deposition Rate x10 of Sputtering
- Dense, Clear & Flexible Coating

**Challenges:** Deposition on Counter Electrode
- Particle Formation
- Process Drift
Twin-Roll PECVD Concept

- AC Magnetron Discharge between a Pair of Rollers

Rollers for Plasma Generation

- Process Gas

- Plasma for CVD

Polymer Web

- Vacuum Pump

MF-AC Power Supply
Advantages of Twin-Roll PE-CVD concept

- Deposition Zone between a Pair of Rollers Covered by Substrate
  - No Deposition on Active Electrode (Rollers for Deposition)
  - Process Stability at Long Term Operation
  - No Counter Electrode
  - Effective Use of Source Gas (High Rate)
  - Less Chamber Contamination

- MF-AC Magnetron Plasma
  - Low Pressure (1-5Pa) Operation
  - Ion Bombardment on Film
  - Denser Film

- Scalable
  - Similar to DMS
PECVD Deposition System
Experimental Procedure

Deposition
- Substrate
  - 100um PEN (Q65-FA Teijin DuPont)
  - Width 350mm
- Deposition System
  - W35 R&D Roll Coater
  - Electrode Roller Dia 140mm
  - MF-AC 0.4-1.2kW, 70kHz
- Source Gases
  - HMDSO/O2 Mixture
  - Pressure 1-5 Pa
- Web Speed
  - Adjusted for thickness
  - Typically 0.5-2m/min

Evaluation
- Depo. Rate/Uniformity
  - Step Measurement by Surface Profile meter
- Barrier Measurement
  - 40°C90%RH
  - MOCON Permatran TM (WVTR>0.02g)
  - MOCON Aquatran TM (WVTR<0.02g)
  - Ca Test(WVTR<5E-4g)
- Surface Morphology
  - SEM
Deposition Results

Wide Range of SiOx Properties: depending on process conditions

- **Composition:** SiO2 ～ SiOC(H)
- **Color:** Clear ～ Brownish
- **Barrier:** High Barrier ～ No Barrier
- **Deposition Rate:** Fastest Rate Obtained: 900nm-m/min!

- **Deposition Rate**
  - WVTR
- **Pressure (Pa)**
- **HMDSO Flow (sccm)**
- **Discharge Power (kW)**

- **Transparent Barrier Coating:** 150-200nm-m/min
- **Possible to deposit up to 1000nm**
Dynamic rate & barrier across the web

Dynamic rate across the web

150nm SiOx on 100um PEN

Dynamic rate across the web (nm²/min)

WVTR (g/m²/day)

Position (mm)

±9%

350mm

100mm
Optical properties of SiOx coated PEN

![Image of PEN substrate with 300nm SiOx Coating]

Graph showing transmittance (%) against wavelength (nm) for PEN substrate and PEN substrate with 300nm SiOx Coating.
Barrier properties of SiOx from PECVD

On PEN(Q65FA)
- 1000nm SiOx for $<5 \times 10^{-4} \text{gWVTR}$

On Planarized PEN
- Improved Barrier by x2-5
- 500nm SiOx for $<5 \times 10^{-4} \text{gWVTR}$
  (detection limit of Aquatran™)

![Graph showing WVTR vs Barrier Coating Thickness for PEN and Planarized PEN](image)
Ca test results (40°C 90%RH, 1000Hr)

- SiOx(1000nm) on PEN (Q65FA) (Presented at IDW2010)
  - Ca: 200nm
  - WVTR: $5.5 \times 10^{-5}$ (g/m2/day)

- Optimized SiOx(1000nm) on Planerized PEN
  - Ca: 100nm
  - WVTR: $1.7 \times 10^{-5}$ (g/m2/day)
Up-Scaling of roll-to-roll PECVD system

700mmW  2010

1340mmW × 2zone  2012

350mmW  2008

Thanks to scalable PECVD process
- Plasma Enhancement by Magnetron
- Mid-Frequency AC Power
Summary

A new Roll to Roll PECVD System was developed

Advantages
- Process stability & Low contamination
- Effective use of process gas & High deposition rate
- Scalability of the process

SiOx Coating from HMDSO/O2 source gas demonstrated
- Deposition rate: up to 900 nm-m/min
- Thick coating over 1000nm
- Tradeoff between deposition rate and barrier performance
- Barrier performance strongly depends on the thickness of SiOx
- Barrier performance of WVTR below 5x10^-4 g/m²/day was confirmed
  - By 1000nm SiOx on PEN & By 500nm SiOx on planarized PEN
- The best barrier result was WVTR of 1.7x10^-5 g/m²/day (Ca Test)

Up-scaling from 350mmW to 1.3mW was achieved
- Production system W60-1340C was launched.
Thank you for your kind attention!