Glass (SiO₂) CMP using an innovative chamber type polishing machine with high-pressure gasses and manganese oxide slurries

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   1) Basic processing characteristics of glass substrates by ceria slurry
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   3) Polishing characteristics of glass substrates in a radical environment, which is an atmosphere-controlled, closed Bell-jar CMP machine
4. Conclusions (Closing remarks)

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Motivation of the research

High functional glasses: - applied to display FPD, memory HDD, exposure photo mask, optical fiber, etc.,

High quality, high accuracy and high efficiency finishing

Polishing of glasses and quartz substrates, etc.,

A lot of cerium oxide (CeO₂, ceria) is used as slurries

Planarization CMP of oxide films for LSI devices
Application of slurry with ultra-fine ceria abrasives

Cerium (Ce) & cerium oxide (CeO₂)

One of the rare metals, and applied massively to advanced technological fields.

- Depletion of cerium has become a controversial issue worldwide
- Development of resource saving slurry has become essential and urged for the good of this earth

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Objectives of this research

1) Understanding polishing characteristics of glasses by ceria slurry → reduction of slurry consumption

2) Discussions on the mechanism of glass polishing
→ Search for other abrasives with oxidation actions as ceria abrasives
   Focused attention on manganese oxide particles
   Comparison with polishing characteristics between ceria and manganese oxide slurry

3) Introduction of an atmosphere-controlled, closed type CMP machine
→ creating radical environment in the polishing area
   ① Conditions to reduce ceria slurry
   ② Effective polishing methods and conditions of manganese oxide slurry as an alternative for ceria

4) Proposal of the effective processing conditions for glass substrates

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Experimental Machines & Polishing Conditions

<table>
<thead>
<tr>
<th>Workpiece</th>
<th>Glass substrates (soda lime glass), φ 2” x t1.8mm</th>
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<tr>
<td>Polishing Machine</td>
<td>&quot;Conventional machine&quot;: Ring type polishing machine (Lapmaster Co., LM-15)</td>
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<td>&quot;Bell-jar machine&quot;: Closed atmosphere controlled Bell-Jar shaped CMP machine (Prototype)</td>
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<td>Pressure inside the Bell-Jar: -100 ~ +500 kPa (Gauge pressure)</td>
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<td>MnO₂, Mn₃O₄-(a), Mn₃O₄-(b), Mn₃O₄ slurry (prototype, p.s:0.2 - 0.4 μ)</td>
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The processing atmospheres and their pressures should have large influence on the removal rates.
Construction drawing of the bell-jar shaped CMP machine
(Moving-mechanism inside the Bell-jar)

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Workpiece
Glass substrates (soda lime glass), φ 2” x t1.8mm

Polishing Machine
- Ring type polishing machine (Lapmaster Co., LM-15)
- Bell-jar machine: Closed atmosphere controlled Bell-Jar shaped polishing machine (Prototype)

Pressure inside the Bell-Jar: -100 ~ +500 kPa (Gauge pressure)
Gas: Air, Oxygen, Nitrogen, or in vacuum

Slurry
- CeO₂ slurry (Showa Denko K.K, Shorox-V2104, p.s:0.35 μm)
- MnO₂, Mn₃O₄-(a), Mn₃O₄-(b), Mn₄O₄ slurries (prototype, p.s:0.2 - 0.4 μm)

Pad
Foamed polyurethane (φ 320mm) (Nitta-Haas Co., MH-N15A)

Experimental Machines & Polishing Conditions

- Commercially available ceria slurry
- Four different type of manganese oxide slurries

CeO₂
prototype manganese oxide

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Change of valence of manganese oxide abrasive with annealing temperature

- $\text{MnO}_2$ to $\text{Mn}_2\text{O}_3$ at 600℃
- $\text{Mn}_2\text{O}_3$ to $\text{Mn}_3\text{O}_4$ at 1050℃

Possibility of oxide manganese abrasives to be applied to glass polishing

Ceria particles: having oxidizing actions

Preparing four different types of manganese oxide abrasives

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Basic polishing characteristics of glass substrates with ceria slurry by a conventional CMP machine

- A tendency to become saturated when concentration goes 5 wt%.
- Slurry is consumed uselessly without contributing to the polishing.

Relations between the removal rates and abrasive concentrations by manganese oxide slurries with a conventional CMP machine.

- MnO2 (a): Same removal rate as CeO2 was obtained in the region below 2.0 wt%.

Polishing pressure [kPa]
Pad revolution [min⁻¹]
Ablation rate [μm/rev]
Removal rates and glass surface roughness by type of slurry at 2wt% abrasives by a conventional machine

Manganese oxide abrasive; Promising candidates to replace ceria slurry for the glass polishing.

Polished with CeO₂ Slurry
Ra 1.002[nm]
Rz 18.717[nm]

Polished with Mn₂O₃-(b) Slurry
Ra 0.823[nm]
Rz 23.143[nm]

Surfaces roughness of glass substrate polished (AFM)

Pressure & 2Pa
Revolution speed 90min⁻¹
Abrasive concentration 2.0 wt%

Removal rates and glass surface roughness by type of slurry at 2wt% abrasives by a conventional machine

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Comparison of the increasing ratio of the removal rates with various slurries and gases using a Bell-jar machine

Abrasives having strong oxidization actions are not always good for glass polishing.

It is necessary to tailor the radical environment for each property of the slurry.

Mn$_2$O$_3$(b) was found not so sensitive to the radical environment inside the Bell-jar.

Conventional polishing

Relation between the removal rates of glass substrate and pressures inside Bell-jar using ceria slurry

Polishing characteristics by applying “Bell-jar CMP machine”

Pressure = 7.7 kPa
Revolution speed = 60 min$^{-1}$
Abrasive concentration = 2.0 wt%
Conclusions

We aimed to reduce the consumption of ceria slurry, and found that manganese oxide slurries give better performance to that of ceria for glass polishing with the conventional CMP machine.

When a new, closed-atmosphere controlled, Bell-jar CMP machine was applied, more effective polishing results were obtained.

“Bell-jar shaped CMP machine for a next generation polishing technology”

Suggestions for effective processing conditions of glass substrates

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<th>Ceria slurry</th>
<th>Abrasive concentration of 5 wt%</th>
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<tr>
<td>Manganese oxide slurry</td>
<td>Mn_2O_3(b) slurry at 5wt%</td>
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<tr>
<td></td>
<td>→ Alternative for ceria slurry</td>
</tr>
<tr>
<td></td>
<td>Removal rate: equal to or better than ceria slurry</td>
</tr>
<tr>
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<td>Surface roughness: better roughness than ceria slurry</td>
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Effective conditions for atmosphere-controlled, closed type CMP machine:

Polishing by ceria slurry:

- high pressure air atmosphere

MnO_2 slurry: high pressure N_2 atmosphere
(However, removal rate is low)
Mn_2O_3 slurry: high pressure N_2 atmosphere
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OH-  H2O  H+  OH-

OH-  H2O  H+  OH-

≡Ce-OH + OH-Si≡  ⇒  ≡Ce-O-Si≡ + H2O

(1) H+, OH- in water unite the surface of the CeO2 abrasive with glass substrate.

(2) Chemical reactions occur between CeO2 and glass surfaces.

(3) Siloxane bonds, which are hydration reaction products, are broken.

(4) Glass surface unites with the CeO2 surface via O2, which promotes material removal.

Processing mechanism of glass polishing

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