DLC coatings deposited by magnetron sputtering on insulating substrates with high hardness and enhanced adhesion properties

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Plasma sputtering
Instrumentation
Power supplies
Diamond-like Carbon (DLC) is a metastable form of amorphous carbon with significant sp$^3$ bonding. DLC coatings are of interest in a wide variety of applications to provide low friction and high hardness and wear resistance.

Applications
- Glass: anti-scratch.
- Molds: prevent plastic transfer
- Engine parts: low friction (a-C).
- Space parts: low friction (a-C:H).
- Cutting tools: lubricated and dry conditions.
- Oil & gas: super lubricity in pipes.
- ....
DLC: State of the art

<table>
<thead>
<tr>
<th>Material</th>
<th>Preparation technique</th>
<th>Density, (\text{g m}^{-2})</th>
<th>% sp(^2)</th>
<th>Hardness, (GPa)</th>
<th>Young’s modulus, (GPa)</th>
<th>Friction coefficient against metals*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>Naturally occurring</td>
<td>3.52</td>
<td>100</td>
<td>100</td>
<td>1.050</td>
<td>0.02–0.10</td>
</tr>
<tr>
<td>DLC</td>
<td>Sputtering</td>
<td>1.9–2.4</td>
<td>2–5</td>
<td>11–24</td>
<td>140</td>
<td>0.20–1.20</td>
</tr>
<tr>
<td>Me doped H:DLC</td>
<td>Reactive sputtering</td>
<td>–</td>
<td>–</td>
<td>10–20</td>
<td>100–200</td>
<td>0.10–0.20</td>
</tr>
<tr>
<td>H:DLC</td>
<td>r.f plasma</td>
<td>1.57–1.69</td>
<td>–</td>
<td>16–40</td>
<td>145</td>
<td>0.02–0.47</td>
</tr>
<tr>
<td>H:DLC, DLC</td>
<td>Ion beam</td>
<td>1.8–3.5</td>
<td>–</td>
<td>32–75</td>
<td>–</td>
<td>0.06–0.19</td>
</tr>
<tr>
<td>ta-DLC</td>
<td>Vacuum arc</td>
<td>2.8–3.0</td>
<td>85–95</td>
<td>40–100</td>
<td>500</td>
<td>0.04–0.14</td>
</tr>
<tr>
<td>ta-DLC</td>
<td>PLD</td>
<td>2.4</td>
<td>70–95</td>
<td>30–60</td>
<td>200–500</td>
<td>0.03–0.12</td>
</tr>
</tbody>
</table>

Ion assistance required ~ 100eV

DLC hard coating magnetron deposition

Anode to extend the plasma

Magnetically linked magnetrons

Set of Pumps
Anode Supply (+ 200 V / 100 A)

Watercooled Steel Chamber
( DC Pulser )

HIPIMS

Satellite

Substrates

UBM ( 30 kW )

Turntable

Etch/Impantation Substrates
(- 1200 V/5 A ) - 300 V/50 A )
DLC hard coating magnetron deposition

55GPa Micro hardness, comparable to filtered arc

Bias required

Glass? Plastics?
Drawbacks with current technologies

- High level of electron bombardment
- Bias requirements
- Low deposition rates
- Very narrow process window

SOLUTION?
Ion assisted deposition on insulators

Magnetron magnetic design (electron filter)  Modified asymmetric bipolar pulsed PS

Proprietary technology: Patent application number GB1605162.5 (March 2016)
Ion assisted deposition on insulators

Proprietary technology: Patent application number GB1605162.5 (March 2016)

- Positive ion bombardment
- No electron bombardment
- Reduced thermal load?
Ion assisted deposition on insulators

Modified asymmetric bipolar pulsed PS

Floating Potential in substrate

Magnetron Voltage

Plasma ON OFF

Hardness > 30GPa
Modified DC-Pulsed PS

Hardness < 12GPa
Commercial DC-Pulsed PS

Proprietary technology: Patent application number GB1605162.5 (March 2016)
Ion assisted deposition on insulators

Evidence of high energetic ions

The distribution of ion energies at the substrate in an asymmetric bi-polar pulsed DC magnetron discharge

3 energy regimes are measured
Magnetron magnetic design (electron filter)

Magnetron size 400x100mm² (industrially relevant) – WC, Graphite targets
Optimized magnetic field configuration to enhance positive ion assisted deposition
Ion assisted deposition on insulators

Magnetron magnetic design (electron filter)

Magnetron size 400x100mm² (industrially relevant) – WC, Graphite targets
Optimized magnetic field configuration to enhance positive ion assisted deposition
The hiP-V power supply
Adhesion

Surface preparation

DLC coating
Buffer layer (WC)
Bonding layer (Cr/Ti)
PREP/pret

Substrate
Bias pre-treatment

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Low accumulated stress @ high hardness

Biased process: high DLC coating stress

N4E process: low DLC coating stress

No charge build-up in sharped edges
DLC coating on Glass

Reactive Oxygen Ion Etching

Substrate can be pre-treated by ion etching with reactive gases such as oxygen

Current to floating potential (10mV/A)
DLC coating on Glass

Reactive Oxygen Ion Etching

Untreated glass substrate

RMS roughness: 2.6 nm

Oxygen treated glass substrate

RMS roughness: 1.4 nm
# DLC coating on Glass

## Reactive Oxygen Ion Etching test results

<table>
<thead>
<tr>
<th>DLC Coating description</th>
<th>Total light transmission</th>
<th>Taber test result</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 min O2 plasma cleaning + 60 sec DLC (aprox. 6nm)</td>
<td>89.2</td>
<td>≤20 times NG</td>
</tr>
<tr>
<td>30 min O2 plasma cleaning + 30 sec DLC (aprox. 3nm)</td>
<td>89</td>
<td>≤20 times NG</td>
</tr>
<tr>
<td>5 min O2 plasma cleaning + 30 sec DLC (aprox. 3nm)</td>
<td>91.2</td>
<td>≤10 times NG</td>
</tr>
</tbody>
</table>
DLC coating on Glass

24N scratch test

DLC coated

Uncoated

GG3

GG4

Soda Lime

Tape to hold broken glass together
DLC coating on Glass

Haze test

DLC coated

Uncoated
DLC coating on Glass

High level of light transmission
DLC coating on Glass

nano-scratch tests

Film thickness 10nm

500mN critical load – 5 micron tip radius
DLC coating on Glass

Coating Hardness: above 30 GPa on insulating substrate

Hysitron TI950 Triboindenter
Berkovich tip indenter BKL4

Hardness = 32 GPa
Young modulus = 220 GPa
500nm thick DLC
Si substrate
SEM image: Dense DLC film

SEM cross section of WC/DLC coating
DLC hard coating magnetron deposition

15GPa Microhardness with -75V Bias!

Bias required
Conclusions

By optimizing the magnetic configuration and tailor the power delivery we have proven that:

• DLC deposited by magnetron sputtering can reach very high hardness levels without using Bias

• The thermal load of the substrate can be greatly reduced enabling deposition on temperature sensitive substrates
Conclusions

By optimizing the magnetic configuration and tailor the power delivery we have proven that:

- The process window as well as the deposition rate is increased, enabling less sensitive industrial production with higher production rates
Thank you for your attention!

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