ICP-RIE of Ultrananocrystalline Diamond

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We haven't even scratched the surfaceSM
Outline

• Motivation

• Preliminary thoughts on direct etching

• Optimization of diamond etching with ICP-RIE

• Discussion of tip etching results

• Conclusions
Ultrananocrystalline diamond (UNCD)

- Smooth: 3-20 nm rms as grown, <1 nm “Horizon”
- Thickness: 40 nm to 20 µm; <5% uniformity
- Tunable electrical and thermal conductivities
- High Young’s modulus (~900 GPa)
- Biocompatibility
- Up to 300 mm wafers
- Most of bulk diamond mechanical properties

- Deposited at 400-900 °C
UNCD micro-manufacturability

- Selective seeding through photoresist or SiO₂ mask
  Rounded edges
  ~1-2 μm resolution

- O₂-RIE through Al mask
  Vertical edges, rough at the nanoscale
  ~ 1-2 μm UNCD
UNCD nano-manufacturability

- E-beam lithography, lift off (Al, Ni), O$_2$-RIE of UNCD, release by KOH (XeF$_2$) etch
- Molding
- Tip-based nanopatterning of seeds and growth
Why is molding not good enough?

It can be spectacular, but...
Why is molding not good enough?

Top look into a V-groove, showing a wedge.

Wedge-shaped tip

Double tip after oxidation-sharpening
Why is molding not good enough?

Statistics

Best median value of wedge size: 13.3 nm
Preliminary thoughts on direct etching

Two ways:

- Isotropic underetching

- Slope amplification by differential etching & sharpening

3-7 μm diamond
UNCD ICP-RIE – needs optimization

Our experience:

- **RIE**: 1 μm in 30 min (33 nm/min)
  \[O_2:CF_4 \text{ (50:2 sccm), 300 W, 20 mTorr}\]

- **ICP-RIE**: 1 μm in 10 min (100 nm/min)
  \[O_2:CF_4 \text{ (50:2 sccm), ICP= 2800 W, RIE=100 W, 20mTorr}\]

Literature:

- **O_2-RIE**: 30-40 nm/min
- **ECR O_2 plasma**, 400 nm/min
Optimization of ICP-RIE, Oxford 100

- Etching rate (nm/min) vs. ICP power (W)
- Etching rate (nm/min) vs. RIE Power (W)
- Etch Rate (nm/min) vs. O₂ Pressure (mTorr)
- Etching rate (nm/min) vs. SF₆ sccm

**Graphs Show:**
- RIE=100 W, O₂=50 sccm, T=20 °C, P=10 mTorr
- ICP=2500 W, O₂=50 sccm, P=10 mTorr, T=20 °C

**Notes:**
- ICP-RIE parameter sweep for optimized etching rates.
- Each graph represents different process conditions and their impact on etching rate.
Thermal oxidation of UNCD in air

- **Diamond etches at > 600 °C in air**
  (but slowly: 25 nm/min)

![Graph showing oxidation in air](image)
ICP-RIE rate with temperature

- Almost no temperature dependence
- Isotropy unlikely in this regime
- Machine tripped above 300 °C (cooling problems)
- Do the isotropic etching by thermal oxidation sequentially
**Investigating isotropy: test mask**

- 100 μm x 100 μm field
- 3.5 μm UNCD/350 nm PECVD SiO₂
- Exposed with Raith 150, (30 keV, 60 um aperture, 1554 pA, dose 400 μC/cm²)
- Resist: ma-N 1405 (MicroChem) @ 2000 rpm, baked at 100°C for 90 sec, thickness 350 nm, developed 30 sec in mD533S
- SiO₂ etched by ICP-RIE (CHF₃-Ar plasma)
- UNCD etched half way for rate measurement, then continued to full removal

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NCCAVS Plasma Applications Group Meeting, San Jose, Febr 10, 2010
Etched structures on 3.5 $\mu$m films
Etched structures: best conditions for isotropy

- No sign of underetching
- No sign of isotropy
- Ultra-sharp “grass” originating from SiO₂ in crevasses (~50 nm) on the surface, generating spikes by differential etching mechanism
- Mostly vertical walls, except the top of structures, where edges are curved by differential etching when the oxide vanishes

Sample etched incompletely at 300°C
ICP=2500W, RIE=50 W, P=50 mTorr, O₂=50 sccm
Thermal oxidation after ICP-RIE

Before

675°C 30 min, air

After

Oxidation proceeds by roughing the surface and generation of cavities.
Boosting differential etching

- 6.5 μm of UNCD
- 350 nm of SiO₂
- ICP= 2800W, RIE= 200 W, P= 9 mTorr
  SF₆= 0.5 sccm, O₂= 50 sccm, T= 20 °C, 12 min

From

Φ = 3 μm circle

R<10 nm
Pleasant surprises: Nanowire ending tips are not that rare! 14%?
• Tips considered: from the 6.5 μm batch, 3 μm circles
• ICP-RIE tips are somewhat worse than the best molded tips
• ICP-RIE tips statistics improved by the NW-ending tips
ICP-RIE: etching of pores*

100-nm-diameter pores     80 nm pores
1 \( \mu \)m low stress UNCD
Same ICP-RIE recipe

*to be presented at EIPBN 2010, O. Makarova et.al.
Conclusions

- Sharp tips can be obtained by ICP-RIE of UNCD, R<10 nm
- Isotropic underetching does not work
- Differential etching and sharpening work
- Post-RIE Oxidation sharpening does not work – roughness
- ICP-RIE was optimized: DRIE of UNCD?
- Maximum rate (674 nm/min) with ICP=2800W, RIE=200W, P = 9 mTorr, O$_2$ = 50 sccm, SF$_6$ = 0.5 sccm, T = 20 °C
- Technique is good for arrays of tips (field emission?), but still inferior to molding for AFM probes
- Some AFM probes may benefit from feathery shape – DPN?
ACKNOWLEDGMENTS

Use of the Center for Nanoscale Materials, Argonne National Laboratory was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357