

Medusa 84 SiH - A novel high Selectivity Electron Beam Resist for Diamond Quantum Technologies

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Abstract

We investigate the novel electron beam resist Medusa 84 SiH by Allresist GmbH (Germany) for nanostructuring of single crystal diamond and its effects on the spin properties of nitrogen vacancy (NV) centers in nanopillars as prototypes for photonic structures. We find contrast curves comparable to previously employed resists (Hydrogensilsequioxane FOx). We present a selectivity for diamond etching of 11 to 12. Using an adhesion-promoting silicon interlayer potentially enables fabrication yields of up to 96%. We measure T_2 times of up to $\sim 25 \mu\text{s}$ before and after processing, demonstrating that the manufactured structures are usable for diamond-based quantum sensing.

Keywords: diamond, lithography (deposition), reactive ion etching, scanning electron microscopy (SEM), electron beam resist

1 Supplementary Materials

1.1 Nanofabrication

Table 1 provides a comprehensive summary of all process steps in sequential order, detailing the majority of the process parameters specifically related to the electronic grade diamond. For diamonds of lower purity utilized in process development, the stress relief etch, ion implantation and high vacuum annealing steps were omitted. Moreover, the silicon samples used for contrast curve analysis did not undergo Tri-Acid or KOH treatments, and procedures such as electron beam evaporation, deposition of a conductive layer, and proximity correction were also excluded.

Table 2 summarizes the parameters used to establish the ICP-RIE plasmas used to conduct stress relief etches on an Oxford Instruments Plasmalab 100 or to structure diamond with the proposed fabrication process using a Sentech PTSA-ICP Plasma Etcher SI 500. We point out that using different ICP system for the different steps does not have scientific background, but the Oxford Instruments Plasmalab 100 was not available anymore for the final steps of the study. We assume both ICP-RIE devices can realize all described processes with individual parameter sets.

Table 1 Medusa 84 SiH Nanofabrication Process

Process Step	Process Parameters
Substrate Characteristics	Single crystalline, electronic grade, (100)-oriented CVD diamond Surface Roughness: $0.6 \text{ nm} \pm 0.5 \text{ nm}$ Size: $4 \text{ mm} \times 2 \text{ mm} \times (0.047 \text{ mm} \pm 0.002 \text{ mm})$ Wedge Dimensions: Long Side: $2.6 \text{ } \mu\text{m} \pm 0.6 \text{ } \mu\text{m}$, Short Side: $2.2 \text{ } \mu\text{m} \pm 0.7 \text{ } \mu\text{m}$ Impurity Levels: $[\text{N}]_s < 5 \text{ ppb}$, $[\text{B}] < 1 \text{ ppb}$ ^{13}C Proportion: 1.109% Suppliers: Synthesis: Element Six, Polish: Delaware Diamond Knives
Tri-Acid	65% HNO_3 , 70% HClO_4 , 96% H_2SO_4 - 1:1:1 at $500 \text{ }^\circ\text{C}$ for 1 h
Ultrasonic Bath	ACE $\Rightarrow$ IPA, 6 min at room temperature
Stress Relief Etch	Deep Etch: $3.66 \text{ } \mu\text{m}$, Biased Etch: 100 nm, 0V Bias Etch: 4 nm See Table 2 for plasma parameters
Ion Implantation	$2 \times 10^{11} \text{ cm}^{-2} \text{ N}^+$ at 6 keV with angle of 7° , $9.3 \text{ nm} \pm 3.6 \text{ nm}$
High Vacuum Annealing	Heating at $800 \text{ }^\circ\text{C}$ for 2 h starting below $7.8 \times 10^{-7} \text{ mbar}$
Substrate Preparations	Tri-Acid and Ultrasonic Bath, see the preceding text
Electron Beam Evaporation	25 nm Silicon deposited at $4.5 \text{ } \text{\AA}/\text{s}$ under $3.0 \times 10^{-6} \text{ mbar}$
Moisture Removal	$100 \text{ }^\circ\text{C}$ for 6 min
Spin Coating of Resist Layer	Step #1: 1500 rpm for 6 s, Acc.: 500 rpm/s Step #2: 4000 rpm for 30 s, Acc.: 1000 rpm/s Resist: SX AR-N 8400 (Medusa 84 SiH) Thickness: 150 nm, Soft Bake: $100 \text{ }^\circ\text{C}$ for 2 min
Application of conductive Layer	Resist: ES spacer 300Z, 4000 rpm for 30 s, Acc.: 1000 rpm/s Layer Thickness: 20 nm, Soft Bake: $80 \text{ }^\circ\text{C}$ for 90 s Resist: Electra 92, 2000 rpm for 60 s, Acc.: 1000 rpm/s Layer Thickness: 60 nm, Soft Bake: $90 \text{ }^\circ\text{C}$ for 120 s
Proximity Correction	$\frac{1}{\pi(1+\eta+\nu_1+\nu_2)} \left(\frac{1}{\alpha^2} e^{-\frac{x^2}{\alpha^2}} + \frac{\eta}{\beta^2} e^{-\frac{x^2}{\beta^2}} + \frac{\nu_1}{2\gamma_1^2} e^{-\frac{x}{\gamma_1}} + \frac{\nu_2}{\gamma_2^2} e^{-\frac{x^2}{\gamma_2^2}} \right)$ $\alpha = 4 \text{ nm}$, $\beta = 8816 \text{ nm}$, $\gamma_1 = 126 \text{ nm}$, $\gamma_2 = 237 \text{ nm}$ $\eta = 23.393483$, $\nu_1 = 1.56053$, $\nu_2 = 1.015$
Electron Beam Lithography	Acceleration Voltage: 30 kV, Aperture: $30 \text{ } \mu\text{m}$ Working Distance: 6.107 mm, Step Size: 12.8 nm Dose Array: $160 \text{ } \mu\text{C}/\text{cm}^2$ - $430 \text{ } \mu\text{C}/\text{cm}^2$ Working Distance Correction: Focus
Development	AR 300-44 (2.38% TMAH) for 90 s Rinse: Ultrapure water for 30 s, Cleaning: Isopropanol for 30 s
Structuring	Biased SF_6 : 21 nm, Pillar Etch: 432 nm See Table 2 for plasma parameters
Mask Removal	Buffered Oxide Etch 12.5% for 20 minutes at room temperature
Adhesion Layer Removal	3 M Potassium Hydroxide at $80 \text{ }^\circ\text{C}$ for 30 min
Final Cleaning	Tri-Acid, see the preceding text Stir for 30 s in ACE $\Rightarrow$ IPA at room temperature

Table 2 ICP-RIE Etch Recipes

	Gas Composition [sccm]			Power [W]				
Stress Relief ¹	O ₂	Ar	SF ₆	RF	ICP	DC Bias	Pressure	Etch Rate ³
Deep Etch	22.5	15	7.5	100	700	300 V	12 mTorr	61 nm/min
Biased O ₂ Etch	50	0	0	165	500	450 V	11 mTorr	98 nm/min
0V DC Bias Etch	50	0	0	0	550	0 V	11 mTorr	8 nm/min
Structuring ²	O ₂	Ar	SF ₆	RF	ICP	DC Bias	Pressure	Etch Rate ³
Biased SF ₆ Etch	0	0	50	60	500	-160 V	1 Pa	2.647 $\mu\text{m}/\text{min}$ ⁴
Pillar Etch	30	25	0	100	450	-167 V	1 Pa	108 nm/min

¹Were performed on Oxford Instruments Plasmalab 100.

²Were performed on Sentech PTSA-ICP Plasma Etcher SI 500.

³Were determined via surface profilometry using a Bruker Dektak XT.

⁴Etch rate for silicon.