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A Surface Micromachining: HNA Etchant for Stiction-free Release of Micro/Nanomechanical Structures

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ABSTRACT

We report a simple and efficient silicon wet etchant HNA (Hydrofluoric acid, Nitric acid, Acetic acid) for the stiction free release of silicon nitride/metal micro/nanomechanical structures. The HNA concentration was varied with the aim of developing a slow etch rate, which could be utilized to suspend the micron and sub-micron cantilever and fixed beam structures. The etch rate was found to decrease with decrease in HF and increase in HNO_3 concentrations. Smooth surface and high selectivity are obtained in case of high HNO_3 content. The obtained etchant with a slow etch rate of 440 nm/minute was successfully utilized for the release of silicon nitride cantilevers and fixed beam structures of 500 nm, 2 μm and 5 μm widths with varying lengths. The resonance frequency of suspended cantilevers characterized by Laser Doppler Vibrometer is in close agreement with the COMSOL simulated resonating frequencies proving that the etching process has been precise without changes to cantilever dimensions. In addition, the generated etchant was successfully used in releasing chrome/gold nanobeams as well without any damage to the metal layers.

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1. Introduction

Micro and nano electro mechanical systems (MEMS and NEMS) are of great interest due to their versatile application in atomic force microscopy [1], various sensors [2,3], actuators [4] and infrared detectors [5]. Especially the silicon nitride microcantilevers are extensively used as scanning probes in single-molecule force spectroscopy (SMFS) [6], mass sensors [7], and gas sensors [8,9]. The integration ability of these cantilevers as array systems for multiplexed detection makes them attractive in sensor applications. The change in displacement and resonating frequencies are quantifiable when these microcantilevers are subjected to a mechanical deformation. The theoretical calculation of resonance frequency for a given cantilever with thickness 't', length 'L' is given by the Euler–Bernoulli equation (1) [4],

$$f_n = \frac{\propto_n^2}{2\pi\sqrt{12}}\frac{t}{L^2}\sqrt{\frac{E}{\rho}} \tag{1}$$

where, E is Youngs modulus, ρ is mass density and ∝ has the mode-dependent values of 1.875 and 4.694 for n = 1 (first mode of vibration) and 2 (second mode of vibration) respectively.

The fabrication of these microstructures is mainly carried out by surface micromachine and bulk micromachine techniques *via* dry or wet etch methods [10]. The main advantage of dry etch is its simplicity and stiction-free release while wet etch techniques suffer from stiction problems [11]. The main drawback of the dry etch process is the harsh plasma treatment that can induce stress and cause surface and bulk damages to the film during etching process and the unavailability of such an expensive set up at all research places [12]. On the other hand, the vast application of wet etch is still limited by the critical dimensions of the feature due to isotropic nature of the etchant and an additional drying technique such as critical point dryer (CPD) making the process more tedious. Down scaling of such release processes in wet etch technique intensifies the practical challenges and the stiction problems. Though, these uncertain stiction problems persist, wet etch is still widely used due to the ease of process, cost effectiveness, batch process, absence of stress effects and minimal or zero surface damage on released structures.

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The most widely used wet etchants to release the Si microstructures are alkaline solutions such as TMAH (Tetra methyl ammonium hydroxide) and KOH (Potassium hydroxide). Another well-known Si wet etchant containing acidic mixtures of hydrofluoric acid, nitric acid and acetic acid (HNA) is less explored in the field of surface micromachining due to its high and uncontrollable reaction rates and poor selectivity to SiN/metal films. By careful selection of the etchant concentration in HNA, it is possible to release the submicron structures without any stiction problems. The main objective of this study is to develop an efficient alternative isotropic wet etchant to the dry etch techniques. The presented mild HNA (Hydrofluoric acid, Nitric acid, Acetic acid) etchant suspended the submicron and micron (0.5 μm and 2, 5 μm) sized SiN cantilever and fixed beam structures without the utilisation of any conventional drying processes such as CPD (Critical Point Dryer) with an extended application in releasing the Cr/Au nano beams as well.

2. Experimental

An *n*-type silicon (1 0 0) wafers with 1–10 Ω.cm resistivity were used as substrates for our experiment. 250 nm of silicon nitride was deposited using Low Pressure Chemical Vapor Deposition (LPCVD, First Nano Furnace) on Si substrate after standard RCA cleaning procedure. The thickness of the deposited layer was measured using ellipsometer (M-2000, J.A. Woollam) with ±2 nm accuracy. The stress of the deposited nitride film was ~1.1 GPa measured using kSA MOS UltraScan tool. The experiments were divided into two sections, one is the development of slow silicon etch rate HNA by varying the HF and HNO_3 concentrations at room temperature (Scheme 1A). The other one is the application of the developed HNA etchant to release the SiN cantilever and fixed beams (Scheme 1B).

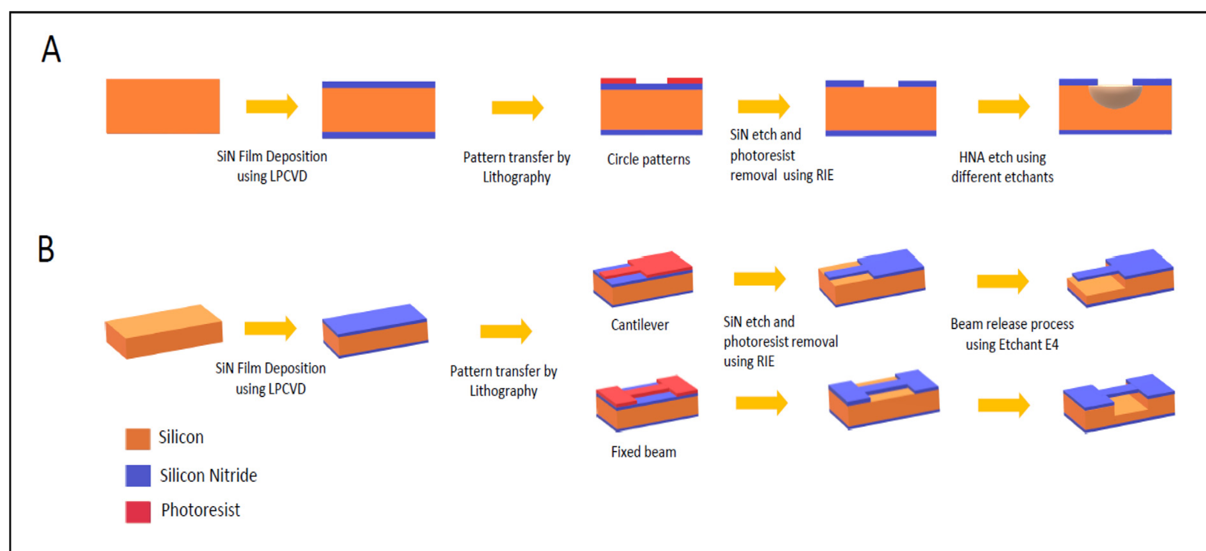
2.1. Development of HNA etchant highly selective to silicon nitride film with slow lateral and vertical Si etch rates

Initially, the circle patterns of 50 μm diameter were used as a test structure for the slow etch rate HNA etchant development. Optical lithography technique using Az5214E photoresist was employed to generate the circle patterns followed by SiN etching by Reactive Ion Etching-fluorine (RIE-Fluorine) chemistry. The photoresist was removed by oxygen plasma etch using the same RIE tool. The patterned substrates were used to etch silicon using HNA etchant at room temperature. The HNO_3 and HF concentrations were varied in the etchant solution as shown in Table 1 and the resultant cross-sectional etched profiles were characterized using Field Emission Scanning Electron Microscopy (FE-SEM, Karl Zeiss ULTRA 55) as shown in Figs. 2 and 3. Scheme 1A depicts the cross- sectional view of the fabrication process carried out.

2.2. Release of Micro/Nanomechanical structures using HNA etchant

The developed etchant from the previous section was used to release the micro and nanostructures. Scheme 1B shows the graphical representation of fabrication steps followed. The cantilever and fixed beam patterns of width 2 and 5 μm with varying lengths from 10 to 30 μm were patterned using Az5214E photoresist by optical lithography. Fixed beam patterns with 500 nm width were obtained using PMMA (Poly(methyl methacrylate)) photoresist by *e*-beam lithography (Raith *e*-line) technique. These patterns were transferred on to the silicon nitride film by RIE using fluorine chemistry. The wet release process of the nitride beams was achieved using initially developed etchant E4. After the wet release process, the acid residues were removed using sufficient amount of deionised water. Further, the substrates were transferred into the isopropyl alcohol and dried by allowing alcohol to evaporate spontaneously. The substrates were not exposed to the atmosphere while transferring from water to isopropyl alcohol to avoid the stiction of released beams. The successful release process was confirmed by Scanning Electron Microscopy (SEM). The resonance frequency was measured by Polytec MSA-500 Laser Doppler Vibrometer (LDV) by using piezoelectric actuators (Fig. 1). COMSOL software was used to simulate the resonance frequency of the desired microstructures for comparison.

In addition, to test the selectivity of the etchant E4 to metal films, fixed beams with 500 nm and 2 μm width were patterned on PMMA (*e*-beam lithography) and on Az5214E (optical lithography) respectively. Cr/Au film (thickness ca. 20/100 nm) was deposited on patterned Si substrate using TECPORT *e*-beam evaporator at room temperature and base pressure of $3x10^{-6}$ Torr. After metallisation, the substrates were dipped in acetone for lift off process. During lift off process, the metal film coated on photoresist will be lifted off as soon as the photoresist dissolution occurs in acetone



Scheme 1. Graphical representation of fabrication steps for (A) Wet etch of silicon using different etchants (E1-E7) depicted as cross-sectional view and (B) Release of cantilever and fixed beam structures using etchant E4.

Table 1
HNA etching with varying etchant concentrations.

Sl No	Etchant	Ratio of HF : HNO_3 : CH_3COOH	Etch Rate of SiN Film (~nm/min)	Vertical Etch Rate (~μm/min)	Lateral Etch Rate (~μm/min)	Anisotropy (Vertical : Lateral)
1	E-1	15:35:0	43	17.54	14.53	1:0.82
2	E-2	10:35:5	31.1	10.64	7.04	1:0.66
3	E-3	5:35:10	12.5	6.24	4.00	1:0.64
4	**E-4**	**1:35:14**	**1.05**	**0.42**	**0.44**	**1:1.04**
5	E-5	1:25:24	0.5	0.16	0.14	1:0.87
6	E-6	1:15:34	–	–	–	–
7	E-7	2:35:13	7	0.77	0.58	1:0.75

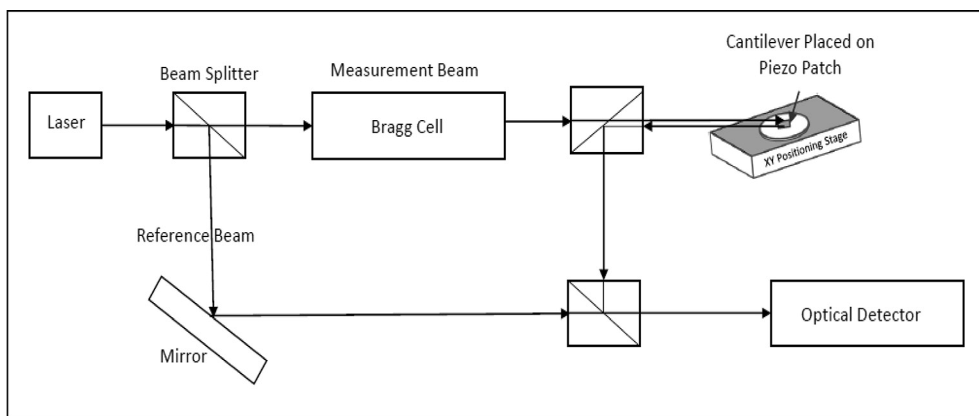


Fig. 1. Line diagram of Laser Doppler Vibrometer measurement of cantilevers.

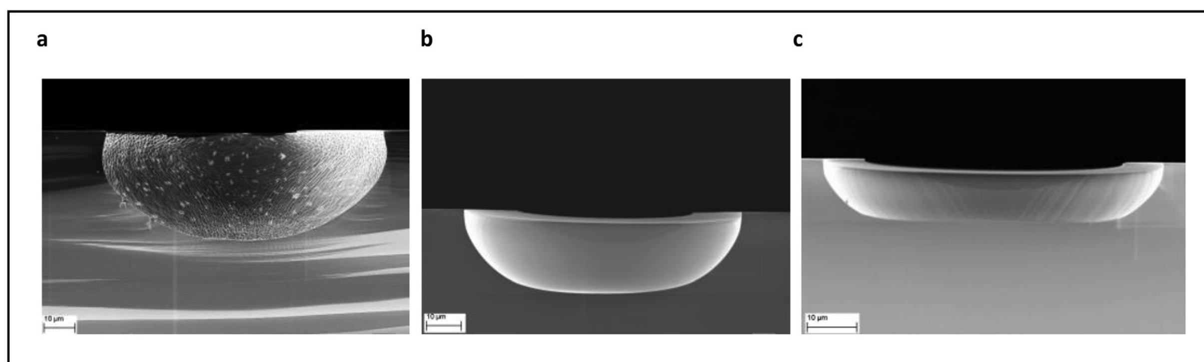


Fig. 2. Cross sectional SEM images of the HNA etching (a) E-1, (b) E-2 and (c) E-3 for 2 min.

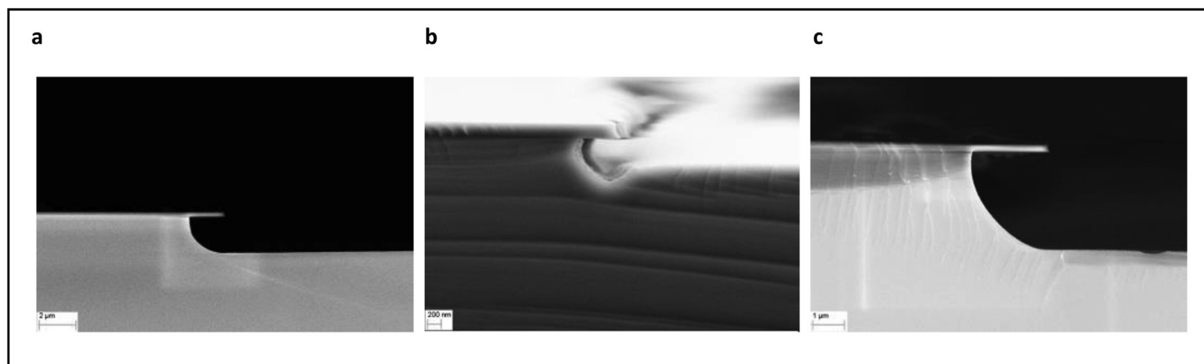


Fig. 3. Cross sectional SEM images for the HNA etchant (a) E-4, (b) E-5 and (c) E-7 for 4 min.

Table 2
Release of microcantilevers of varying width and length.

Sl No	Cantilever width (μm)	Cantilever length (μm)	Resonance Frequency (kHz)		Q-factor
			COMSOL Simulated Value	Experimental Value	
1	5	**25**	**478**	**432**	**50.8**
2		30	331	314	21.89
3	2	15	1.32 MHz	1.26 MHz	248.6
4		**20**	**745.5**	**730.5**	**102.8**
5		25	477.15	422.2	144

whereas the metal film in direct contact with Si surface will be intact. Further, the obtained mechanical structures were suspended using etchant E4. The Scanning Electron Microscopy (SEM) was used to image the suspended structures.

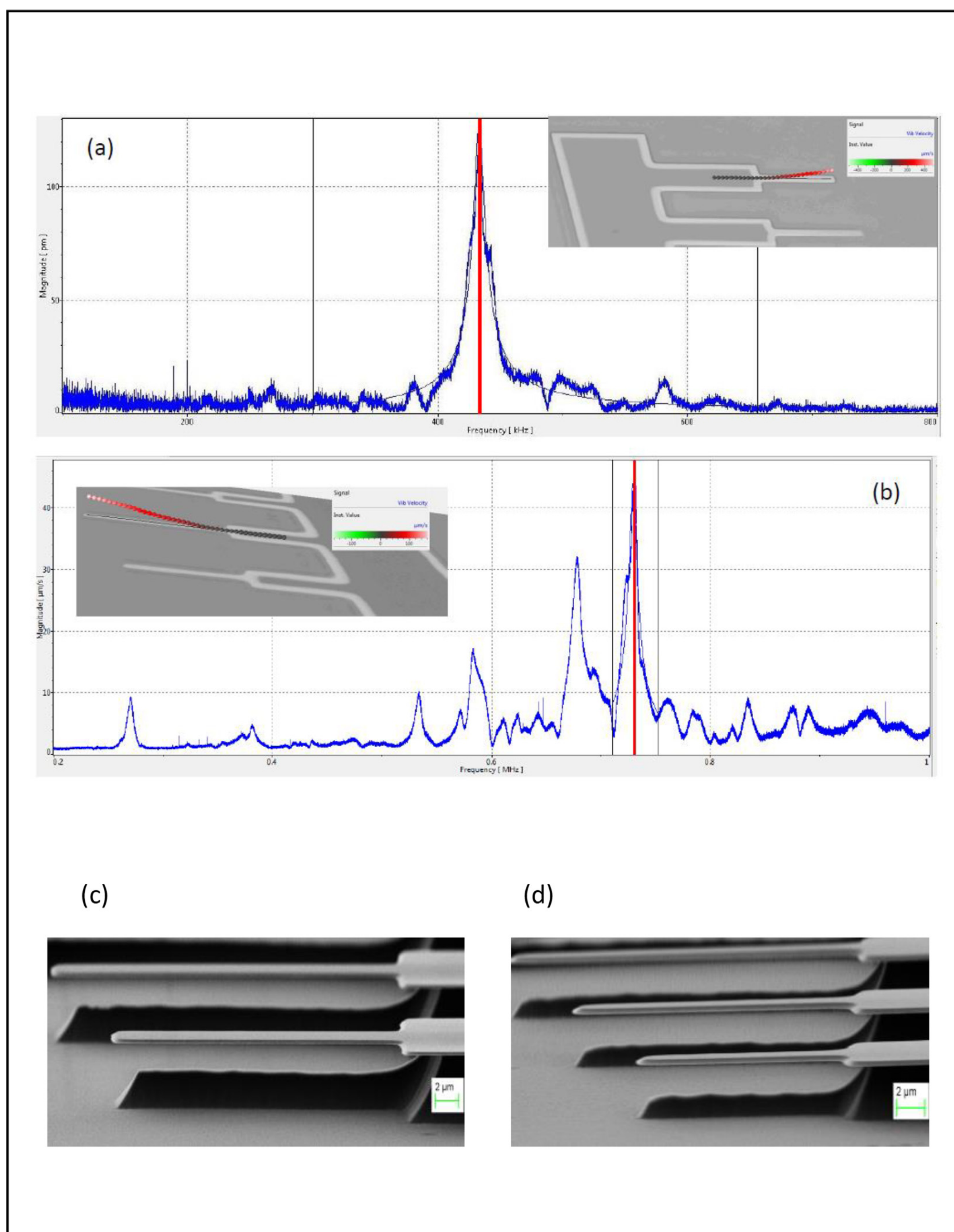


Fig. 4. The resonance frequency by LDV for cantilevers released using E4 with width × length of (a) 5 × 25 μm, (b) 2 × 20 μm and cross sectional SEM images of (c) 5 × 25, 30 μm and (d) 2 × 15, 20, 25 μm.

3. Result and discussion

3.1. Development of HNA etchant highly selective to silicon nitride film with slow lateral and vertical Si etch rates

HNA is a well-known isotropic wet etchant for silicon substrate. Three prime factors are considered here in the release process of submicron beams using HNA. They are, the attainable etch rates, selectivity and the etched Si surface morphology. The high etch rates due to the exothermic reaction of HNA with Si and poor selectivity to the SiN and metal films confines its application for NEMS/MEMS release process. Hence, the concentrations of HF and HNO_3 in HNA has to be precisely tuned in order to obtain the slowest possible etch rates with high etch selectivity to silicon nitride and Cr/Au films. From the various experiments conducted as per the Table 1, it was observed that both HF and HNO_3 has profound effect in controlling the aforementioned etch properties.

In the beginning, the etching was performed with high HF concentration with gradual decrease from E-1 (HF: HNO_3:CH_3-COOH::15:35:0) to E-3 (HF:HNO_3:CH_3COOH::5:35:10). High vertical and lateral etch rates of 17.54 and 14.53 μm/min respectively were obtained for etchant E-1 with an anisotropy of 1: 0.82 and highly rugged surface (Fig. 2a) as compared to E-2 and E-3. This isotropic nature and the surface roughness are due to the faster dissolution of SiO_2 in presence of copious amount of HF as compared to the oxidation of Si by HNO_3. Again, the decrease in HF concentration in E-2 and E-3 gave lower etch rates with increase in the anisotropy to 1:0.66 and 1:0.64 respectively (Fig. 2b & c and Table 1). The smooth etch profile in both the cases is due to the lower HF and higher HNO_3 concentration which offers controlled oxidation followed by oxide layer dissolution in presence of sufficient amount of HF [13]. In all the etchants from E-1 to E-3, silicon nitride film also etched with considerable etch rate due to high HF concentration (Table 1) lead to the poor selectivity of the etchants.

Further, to reduce the Si etch rates with high selectivity to SiN, the HF concentration was decreased in E-4 (HF: HNO_3:CH_3-COOH::1:35:14) while maintaining HNO_3 volume ratio same as before anticipating to get controlled etch rates. As expected, the vertical and lateral etch rates were decreased drastically to 0.42 and 0.44 μm/min respectively with even surface profile (Fig. 3a) as perceived for E-2 and E-3. A sharp decrease in silicon nitride etch rate to ~1.05 nm/min was obtained as compared to the previous etchants (E-1 to E-3). A further lowering of HNO_3 concentration resulted in lowered etch rates of ~0.16 and 0.14 μm/min for vertical and lateral directions respectively for E-5 and surface polishing without considerable etching for E-6. However, the limited oxide dissolution reaction caused by insufficient amount of HF in the etchant, lead the reaction to occur just below the silicon nitride mask in E-5 and resulted in an uneven etch profile (Fig. 3b). Hence, it was decided to increase HF ratio in E-7 (HF:HNO_3:CH_3COOH:: 2:35:13) to examine the etch profile change. As expected, the vertical and lateral etch rates were increased to 0.77 and 0.58 μm/min with good etch profile as shown in Fig. 3c and Table 1. From all the experiments conducted E-4 and E-7 offered much lower etch rates with even surface profile and higher etch selectivity. Finally, the etchant E-4 with lowest etch rate, highest selectivity to SiN and 1:1.04 anisotropy was selected for further release process of nano/micro structures.

3.2. Release of micro and nanomechanical structures using HNA etchant

The isotropic wet etchant HNA with controlled etch rate developed in the previous section, E-4, was used to release the microstructures. The microcantilevers with varying lengths and widths with their resonance frequency and Q-factor are tabulated in Table 2. The simulated frequencies were obtained using COMSOL software were also tabulated for comparison. In the beginning of release process, the cantilevers with 5 μm width and 25 and 30 μm lengths were released using E-4 etchant. The SEM results and LDV characterization confirmed the successful release of cantilevers (Fig. 4a and c). The resonance frequency (f_n) of the suspended structures was found to have 432 kHz & 314 kHz respectively. These frequencies are in close agreement with the COMSOL simulated frequencies of 478 and 331 kHz respectively (Table 2). The slight deviation in the simulated and experimental results could be attributed to the undercut during releasing process [7].

Further, the cantilevers with 2 μm width and 15, 20 and 25 μm length were also successfully released using same etchant E-4 was confirmed by SEM and LDV characterization (Fig. 4b and d). Again, the resonance frequency obtained using LDV measurement were in close agreement with the simulated results as shown in Table 2. Further, to check the practical applicability of the etchant developed, the cantilever (width 500 nm and length 15, 18, 20 and 22 μm) and fixed beam (width 500 nm and length 35 μm) release process was also tested in etchant E4. Interestingly, these structures were also successfully suspended without any stiction problems (which usually persist with wet etch release processes for submicron structures) as shown in Fig. 5a and b. The LDV measurement was unable to complete as the width of the cantilever (500 nm) was limited by the laser spot size of the objective lens

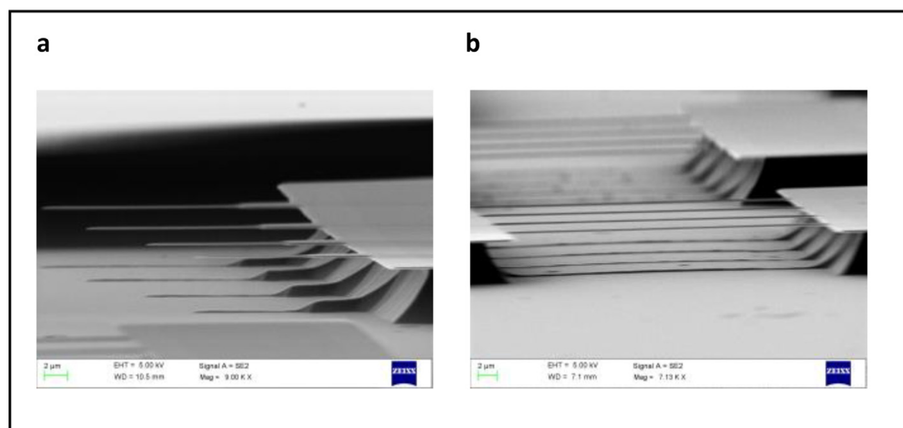


Fig. 5. SEM images of released SiN structures with respective w × l of (a) cantilever, 500 nm × 15, 18, 20 and 22 μm and (b) fixed beam, 500 nm × 35 μm.

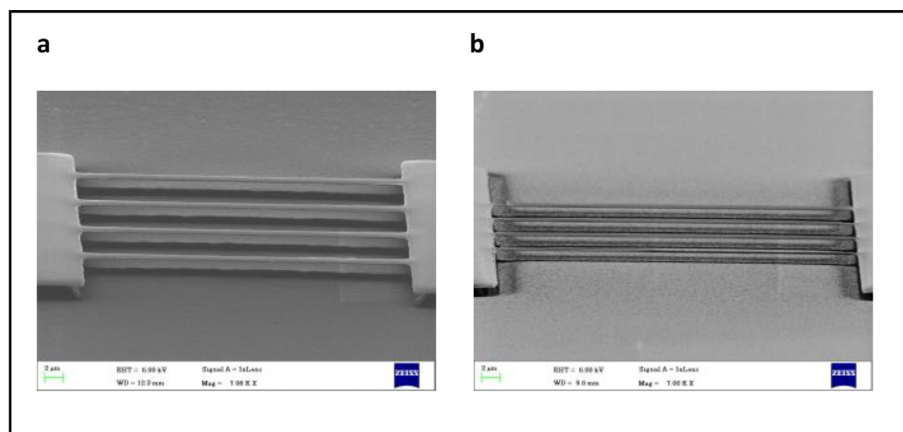


Fig. 6. SEM images of released Cr/Au fixed beams with respective w × l of (a) 2 μm × 35, and (b) 500 nm × 35 μm.

used in our vibrometer setup. However, the success of the release process was evident in the SEM micrographs.

In addition, to extend the developed etchant selectivity to the metal (Cr/Au of 20/100 nm thickness) films, the etchant E4 was used to suspend the Cr/Au nano and micro beams of 500 nm and 2 μm width with 35 μm length. It can be noticed that the nano and micro beams were released successfully using E4 without damaging to the metal films and no reduction in the dimensions is noticed as shown in Fig. 6a and b. In all the experiments conducted the CPD was not used as an additional drying process, which is an added advantage of the current methodology developed. This method opens up a pathway for successful utilization of wet etch method in the field of NEMS/MEMS device fabrication that demands surface micromachining.

4. Conclusion

A silicon etchant with well controlled lateral and vertical etch rates with smooth surface morphology and ~1:1 anisotropy was successfully developed by varying the HNA concentrations. Low etch rates and smooth etched profiles were obtained for the etchant with low HF and high HNO_3 concentration. Among various etchants tested the etchant E4 had the lowest etch rate of 0.42 μm and 0.44 μm along vertical and lateral direction respectively. The developed etchant was successfully used to release the nano/micro structures without using conventional CPD drying process. The cantilever and fixed beam structures of SiN and Cr/Au with width of 500 nm, 2 and 5 μm and varying lengths were successfully suspended using etchant E4. The resonance frequency of the released cantilevers as determined using LDV were similar to COMSOL simulated values. The developed etchant is highly selective to Cr/Au metal films as well and hence offers an easy integration of these SiN/Metal NEMS/MEMS structures in the field of various sensors which demands surface micromachining.

CRediT authorship contribution statement

Bagur R. Deepu: Methodology, Validation, Formal analysis, Investigation, Writing - original draft. **Ponnusubramaniyam Venkatachalam:** Investigation, Writing - review & editing. **Fakirappa N. Mirji:** Investigation, Writing - review & editing. **Varghese Littin:** Investigation, Writing - review & editing. **Hebbal Naveen:** Investigation, Writing - review & editing. **Purakkat Savitha:** Conceptualization, Methodology, Validation, Supervision, Writing - review & editing. **Yeriyur B. Basavaraju:** Conceptualization, Methodology, Validation, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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