

Science and Technology of Ultrananocrystalline Diamond (UNCD) Thin Films for Multifunctional Devices

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SCIENCE AND TECHNOLOGY OF ULTRANANOCRYSTALLINE DIAMOND (UNCD) THIN FILMS FOR MULTIFUNCTIONAL DEVICES

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Abstract

MEMS devices are currently fabricated primarily in silicon because of the available surface machining technology. However, Si has poor mechanical and tribological properties[1,2], and practical MEMS devices are currently limited primarily to applications involving only bending and flexural motion, such as cantilever accelerometers and vibration sensors. However, because of the poor flexural strength and fracture toughness of Si, and the tendency of Si to adhere to hydrophilic surfaces, even these simple devices have limited dynamic range. Future MEMS applications that involve significant rolling or sliding contact will require the use of new materials with significantly improved mechanical and tribological properties, and the ability to perform well in harsh environments.

Diamond is a superhard material of high mechanical strength, exceptional chemical inertness, and outstanding thermal stability. The brittle fracture strength is 23 times that of Si, and the projected wear life of diamond MEMS moving mechanical assemblies (MEMS-MMAs) is 10,000 times greater than that of Si MMAs. However, as the hardest known material, diamond is notoriously difficult to fabricate. Conventional CVD thin film deposition methods offer an approach to the fabrication of ultra-small diamond structures, but the films have large grain size, high internal stress, poor intergranular adhesion, and very rough surfaces, and are consequently ill-suited for MEMS-MMA applications. A thin film deposition process has been developed that produces phase-pure nanocrystalline diamond with morphological and mechanical properties that are ideally suited for MEMS applications in general, and MMA use in particular. We have developed lithographic techniques for the fabrication of diamond microstructures including cantilevers and multi-level devices, acting as precursors to micro-bearings and gears, making nanocrystalline diamond a promising material for the development of high performance MEMS devices.

1. INTRODUCTION

1.1 Si as a MEMS material

The development of methods for the production of miniaturized mechanical components and devices in Si is a natural outgrowth of the Si surface machining methods that have been developed for the production of microcircuits. Complex shapes, such as levers, gears and pinwheels [3, 2] have been produced using standard lithographic patterning and etch methods, and fully assembled devices such as micromotors and geartrains have been produced using multiple masks and multilayer deposition and etching techniques [3]. Unfortunately, Si has poor mechanical and tribological properties, and practical MEMS devices typically must be designed to circumvent these limitations. In particular, it is common practice to avoid extensive sliding and rolling contact, and to minimize the flexural stress required of torsion bars and cantilevers. The poor brittle fracture strength of Si and the tendency of Si to adhere to surfaces with which it makes contact limit the degree of flex that a Si cantilever can undergo, and also rules out the use of motion limit structures to prevent cantilever breakage under high load conditions. Consequently, cantilever acceleration sensors used as automotive airbag actuators are designed as limited range threshold detectors, rather than wide-range measuring devices. Rotating devices such as pinwheels [2] and microturbines [4] have been fabricated, but are frequently subject to stiction problems that prevent startup [3], or wear-related failure after a few minutes of operation [2]. In order to be able to realize the full potential of MEMS technology, it will be necessary to produce MEMS devices that survive under conditions of significant rolling and sliding contact under extreme environmental conditions. SiC has been proposed as an alternative material, especially for MEMS applications that involve high temperature oxidizing environments [4], but the fabrication methods are limited [5-7].

1.2 Diamond as a MEMS material

Diamond is an ultrahard material with high mechanical strength, exceptional chemical inertness, and outstanding thermal stability. Relevant mechanical properties of Si, SiC and diamond are shown in Table I. The friction coefficient of diamond is exceptionally low (~ 0.1 - 0.01), and the projected wear life is 10,000 times greater than that of Si [8, 9], making diamond, in principle, an ideal tribomaterial for MEMS components.

TABLE I. Selected Mechanical Properties of Si, SiC, and Diamond

Property	Silicon	Silicon Carbide	Diamond
Cohesive Energy (eV)	4.64	6.34	7.36
Young's Modulus (GPa)	130	450	1200
Shear Modulus (GPa)	80	149	577
Hardness (kg/mm ²)	1,000	3,500	10,000
Fracture Toughness	1	5.2	5.3
Flexural Strength (MPa)	127.6	670	2944

Lubrication poses a major limitation on the design of MEMS devices since the usual methods of delivering lubricant to the interface between contacting parts are very difficult to implement. Additionally, the viscosity of liquid lubricants is sufficient to prevent motion of MEMS components. Diamond is naturally hydrogen or oxygen-terminated, and the passivated surface provides a natural lubricant.

For high temperature exposure to oxidizing atmospheres, one would expect Si or SiC to be the superior material, since they form a refractory oxide, whereas diamond burns in oxygen. For relatively low oxygen partial pressures however, diamond exhibits friction and wear coefficients that are considerably lower than those of Si and SiC, even at temperatures in excess of 900 °C. Pin-on-disk tribometer measurements of the coefficients of friction (COF) of Si, SiC and mechanically polished polycrystalline diamond (PCD) rubbing against like counterface materials are shown in Fig. 1 during a temperature ramp to 900-950 °C in an oxygen atmosphere of 3.4 Torr.

The COF of Si has a relatively high and constant value of ~0.6 throughout the temperature range, whereas the COF of diamond starts at ~0.05 at room temperature and drops to 0.01-0.02 as the temperature increases. This behavior has been tentatively ascribed [9, 10] to the formation of a stable adsorbed oxygen moiety on the diamond surface that saturates the diamond dangling bonds and therefore minimizes bonding between contacting diamond surfaces. SiC exhibits a behavior that is intermediate between that of Si and diamond in that the friction coefficient is high (0.5) at room temperature, and then drops to a value of ~0.2 as the temperature exceeds 200 °C. This behavior is consistent with a linear superposition of the friction of separate Si and carbon surface phases.

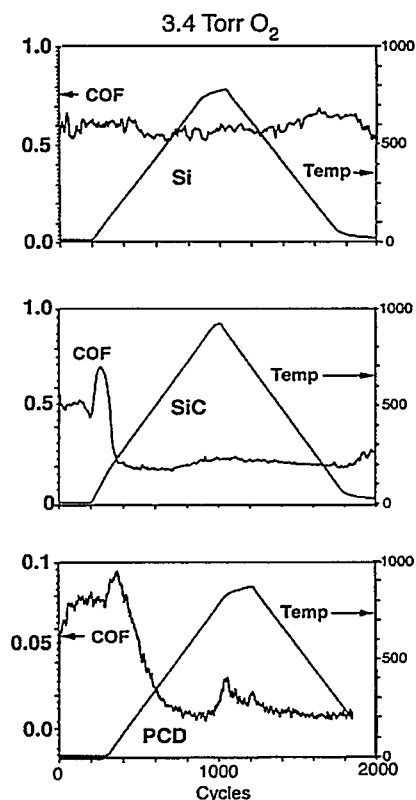


Figure 1. Friction coefficient of Si, SiC and PCD during heating in an oxygen atmosphere of 3.4 Torr.

Table II shows that the wear rates at 900-950 °C, for PCD in low partial pressures of oxygen is lower than that of both Si and SiC. The wear rate of PCD shows a much smaller increase than that of Si and SiC as the oxygen partial pressure increases, and at 3.4 Torr, it is an order of magnitude lower than that of SiC, and three orders of magnitude lower than that of Si.

TABLE II Friction and wear coefficients of Si, SiC and polished diamond in oxygen atmospheres at temperatures up to 950 °C.

	Wear Rate (mm ³ /N-m)		Friction Coefficient	
	0.2 Torr O ₂	3.4 Torr O ₂	0.2 Torr O ₂	3.4 Torr O ₂
Si	8.8x10 ⁻⁴	7.4x10 ⁻⁴	.045	0.6
SiC	1.8x10 ⁻⁶	1.1x10 ⁻⁵	.06-.08	0.2
PCD	6.1x10 ⁻⁷	8.6x10 ⁻⁷	0.35	0.01-0.02

It should be noted that it is difficult to integrate a mechanical lapping step with MEMS fabrication methods. The data presented here are intended to illustrate the potential tribological properties of diamond, and we do not intend to suggest the use of mechanically polished diamond films as a practical MEMS material.

2. DIAMOND FILM GROWTH AND MORPHOLOGY

As the hardest known material, it is difficult to fabricate diamond into net shape for both macroscopic and MEMS components. The most obvious means of producing MEMS components is via modification of Si thin film surface machining methods. It has been demonstrated that oxygen plasma etching through a hard resist can be used to produce 2D thin film patterned diamond structures [11, 12]. However, in order to evaluate the suitability of such methods for MEMS device applications, we will first consider the morphology and mechanical properties of diamond thin films.

2.1 Methyl radical growth processes for micro- and nanocrystalline diamond films

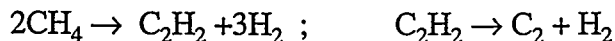
In order to grow diamond, which in the bulk is thermodynamically less stable than graphite, CVD methods have been developed [13, 14] that require a volatile hydrocarbon, an energy source, and an abundant source of atomic hydrogen [15, 16]. The growth species is CH₃*, typically produced by a methane-containing plasma. Atomic hydrogen drives the hydrogen abstraction reactions that (1) prepare the CH₃* adsorption site by removing a hydrogen atom from the hydrogen-terminated diamond surface, and (2) remove the hydrogen atoms from the adsorbed CH₃*, thereby permitting the carbon atom to move into the position corresponding to an extension of the diamond lattice. Additionally, atomic hydrogen preferentially regasifies the graphitic phase. By using a plasma containing 98-99% H₂, it is possible to grow diamond films that are largely free of non-diamond secondary phases. However, atomic hydrogen also etches the diamond phase, resulting in the formation of intergranular voids and a columnar morphology with grain size and rms surface roughness typically ~10% of the film thickness. The grain morphology is therefore not suited for the fabrication of components requiring resolution on the order of several microns.

The grain size can be reduced to 50-100 nm by increasing the CH₄/H₂ ratio in the plasma, and the film roughness is correspondingly reduced, but intergranular non-diamond carbon phases are introduced. Consequently, the brittle fracture strength is limited by intergranular failure, and the mechanical properties of single crystal diamond are not realized [17].

2.2 Carbon Dimer Growth Process for ultrananocrystalline diamond (UNCD) films

In the above-described process, the methyl radical is sterically hindered by the attached hydrogen atoms from entering a diamond lattice site, thereby necessitating large quantities of atomic hydrogen to drive the abstraction reactions. The atomic hydrogen leads to an undesirable film morphology for MEMS applications. A process has been developed [18-21] that uses the gas

phase carbon dimer, derived either from collisionally-induced fragmentation of gas phase C_{60} in an Ar plasma or from methane via the reactions



in atmospheres containing very small quantities of hydrogen. The film morphologies and tribological properties have been found to be largely independent of the carbon dimer precursor species. Typical deposition conditions for a 2.56 GHz microwave CVD reactor would be: 1sccm CH_4 /99 sccm Ar at a total flow rate of 100 sccm at a pressure of 100 Torr, and a substrate temperature ranging from 350-800 °C [22, 23]. As a result of the limited amount of atomic hydrogen in the plasma, a very high renucleation rate ($\sim 10^{11} \text{ cm}^{-2} \text{ sec}^{-1}$) is maintained, grain coarsening does not occur. The resulting film consists of equiaxed grains with a diameter of 2-5 nm [24] as shown in Fig. 2. The relative lack of atomic hydrogen in this process also minimizes regasification of these very small grains, thereby achieving a reasonably high linear growth rate and the formation of continuous films at very low thickness. Because of the small grain size, diamond is the thermodynamically stable phase of carbon [25], and there is no need to suppress the formation of non-diamond phases.

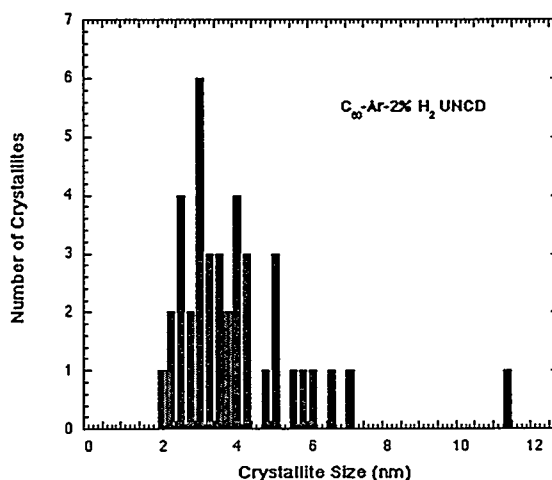


Figure 2. Grain size distribution of UNCD film. The distribution is approximately Gaussian, with a mean crystallite size of approximately 3 nm.

The grain boundaries of diamond films grown via direct insertion of the gas phase carbon dimer have been shown via TEM investigations [26] to be atomically abrupt and devoid of non-diamond secondary phases, although UV Raman spectroscopy [27] shows the presence of a few percent sp^2 bonding. A tight binding pseudopotential calculation [28] based on the assumption of randomly oriented nanometer-sized diamond grains predicts that the boundary is 3.56 Å wide, consisting of two opposing half-atomic layers from the two adjoining grains. The electronic bonding of the grain boundary is $\sim 80\%$ sp^2 in character, and because of the small grain size, there are sufficiently many atoms at the grain boundaries to account for the observed Raman data, even though there is no non-diamond phase formed. The grain boundaries are predominantly high energy boundaries with $\Sigma 29$ or $\Sigma 13$ character. Consequently, it is predicted that the brittle fracture strength is equal to or greater than that of single crystal diamond.

Although the material grown by the direct insertion of gas phase carbon dimers into the lattice is a form of nanocrystalline diamond, its properties are different from those of the conventionally grown nanocrystalline diamond described in the previous section. We have

therefore coined the term “ultrananocrystalline diamond” (UNCD) to distinguish this material from microcrystalline diamond (MCD) [29], nanocrystalline diamond (NCD) [30], ultrananocrystalline diamond (UNCD) [11] and stress-relieved diamond-like carbon (DLC) which have [31] been used as materials to fabricate MEMS-scale components. Table III shows a comparison.

TABLE III. Characteristics of Diamond and Diamond-Like Carbon (DLC) Films

	Microcrystall. diam.(MCD)	Nanocrystalline diamond(NCD)	Ultrananocrystal diam.(UNCD)	Diamond-Like Carbon	
				ta-C	ta-H:C
Growth Species	CH_3^* (H°)	CH_3^* (H°)	C_2	C	C
Crystallinity	Columnar	Mixed diamond/non-	Equiaxed diamond	Mixed diam/amorp	Amorphous
Grain Size	$\sim 0.5\text{-}10\ \mu\text{m}$	50-100 nm	2-5 nm	variable	---
Surf. Rough.	400 nm-1 μm	50-100 nm	20-40 nm	5-100 nm	1-30 nm
Electronic Bonding	sp^3	up to 50% sp^2 (second phase)	2-5% sp^2 (grain boundary)	up to 80% sp^3	up to $\sim 40\%$ sp^3
H Content	<1%	<1%	<1%	<1%	15-60%

3. TRIBOLOGICAL PROPERTIES OF CVD DIAMOND FILMS

The previous discussion of the tribological behavior of diamond is based on the properties of bulk samples with near-atomically smooth surfaces. The morphology of thin diamond films often results in significantly different tribological behavior from that of cleaved bulk specimens. Wear is typically the result of intergranular fracture, resulting in small particles of loose diamond grit at the interface, with correspondingly high wear of the counterface material. Friction is primarily the result of the interlocking of surface asperities and mechanical ploughing [32], rather than the result of chemical forces between the sliding surfaces. Figure 3 shows atomic force microscopy (AFM) data for microcrystalline and ultrananocrystalline diamond films grown in a microwave plasma. It can be readily seen from these images that the nature of the sliding contact is very different for these two materials.

Figure 4 shows hardness vs elastic modulus nanoindenter data for MCD and UNCD films. Because of the high surface roughness, the MCD film exhibits a wide spread in values, whereas the UNCD film exhibits a relatively small spread in either the hardness or the modulus values. The average hardness value of 88 GPa for the UNCD film is close to that of bulk diamond. The measured hardness is found to be independent of indentation depth, indicating that the measured values are reliable.

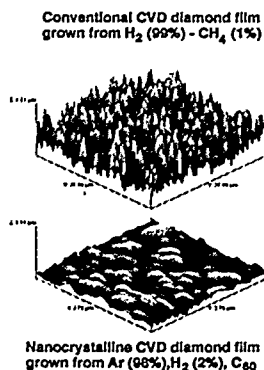


Figure 3. AFM comparison of the surfaces of MCD and UNCD thin films.

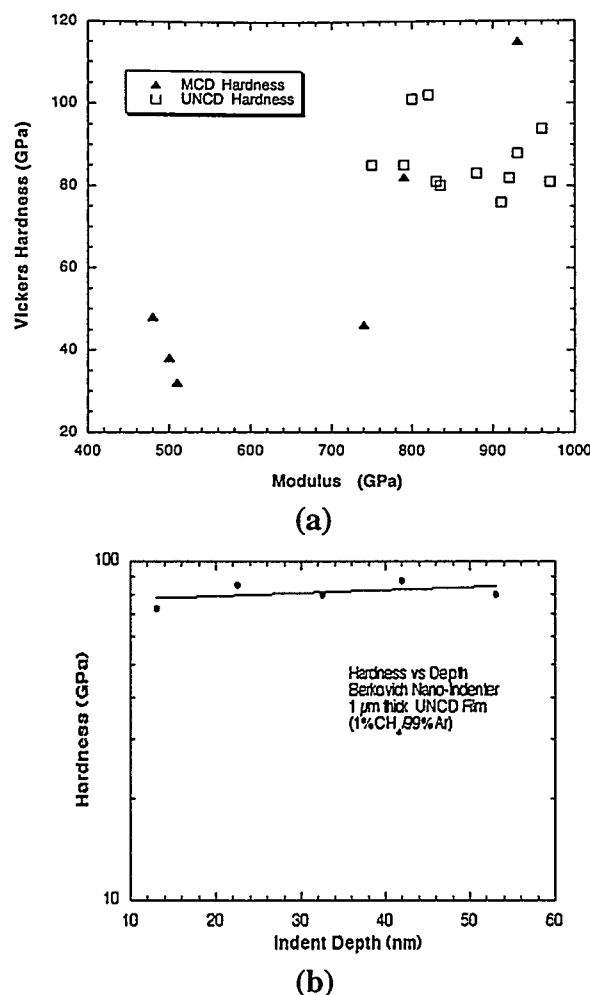


Figure 4. (a) Nanoindenter data (Berkovich indenter) for MCD (▲) and UNCD (□) films (b) Measure hardness vs indentation depth.

Pin-on-disk tribometer measurements have been carried out on UNCD and MCD films using a SiC pin [32], and it has been found that for MCD, the film roughness increases by approximately a factor of four (95-376 nm) as the film thickness increases from 2 to 10 microns, and the pin wear rate increases from 0.48 to 55.0 (10^{-6} mm³/N-m). For the 10 μ m thick film, the wear rate was $\sim 1 \times 10^{-6}$ mm³/N-m. For UNCD films grown with either C₆₀ or CH₄ as the carbon precursor, and 2% H₂ added to the Ar plasma, the wear coefficient of the SiC pin ranged from ~ 0.1 for short runs (8000 cycles) to 0.01 for a long run (2.2×10^6 cycles). A wear rate of 0.018×10^{-6} mm³ was measured for a 6.0 μ m thick UNCD film grown from a C₆₀-carbon precursor. Consequently, we find that the as-grown UNCD films have wear coefficients roughly two orders of magnitude lower than those of MCD films of comparable thickness. The wear rate of an SiC pin rubbing against UNCD film is ~ 4000 times lower than that of an SiC pin rubbing against an as-deposited MCD film.

4. FABRICABILITY OF DIAMOND MEMS COMPONENTS AND DEVICES

There are a number of ways in which diamond components can be fabricated for MEMS applications using thin film deposition methods. Some of these are analogous to Si surface machining methods, and others have no counterpart in Si fabrication technology.

4.1 Conformal Diamond Coating

One of the more obvious methods of obtaining the tribological benefits of diamond while exploiting the availability of Si fabrication technology is to produce Si components to near-net shape and then provide a thin, low wear, low friction diamond coating. [33-40] This approach only works if the diamond film can be produced as a thin, continuous, conformal coating on the Si component. Conventional diamond CVD deposition methods result in discontinuous films with a low density of large grains and poor ability to form thin conformal coatings on Si microstructures such as the Si field emission microwhisker array shown in Fig. 5(a) [41]. In Figure 5(b), all but one whisker of an uncoated array have been broken off in the SEM, leaving a single Si microwhisker. In Figure 5(c), the whisker has been conformally coated with a 300 nm thick film of UNCD, and the top of the whisker has been broken off, leaving a UNCD-coated Si structure. In Figure 5(d), the Si core of the structure in Figure 5 (c) has been removed by etching in HF/HNO_3 , leaving a hollow 3D UNCD hexagonal prism 5 μm from flat-to-flat, with uniform 300 nm thick walls.

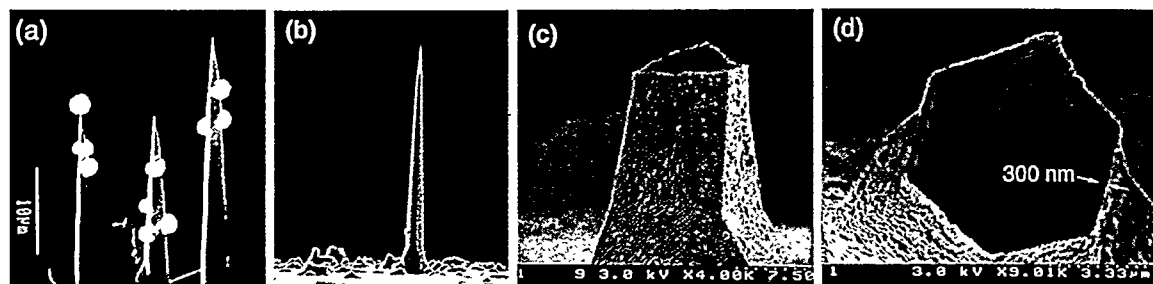


Figure 5. (a) Si microwhisker array (b) Single Si microwhisker (c) Base of fractured UNCD-coated Si microwhisker (d) hollow UNCD 3D hexagonal prism.

This fabrication method is comparable in some respects with the LIGA method, and permits fabrication of complex 3D shapes as opposed to the 2D or layered 2D structures produced by Si microfabrication methods. Similar Si microwhiskers have been conformally coated up to 2.4 μm thick as shown in Figure 6.

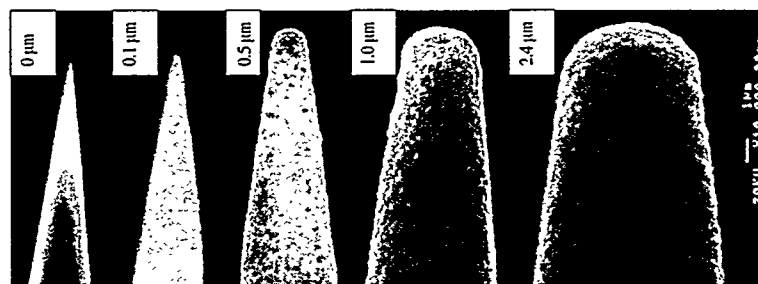


Figure 6. A series of SEM images of a 25 nm diameter Si tip emitter coated with a UNCD diamond film with incremental coating thickness. The tip on the left is uncoated and successive images represent coatings ranging from 100 nm to 2.4 μm in thickness.

4.2 Selective Deposition

Selective deposition represents a second method that may be used for the production of UNCD microstructures but has no analog in Si microfabrication technology. All diamond films, including UNCD require a nucleation layer, usually achieved by exposing the substrate to a suspension of fine diamond particles. It is possible to seed a selected portion of the substrate by (a) using photoresist to prevent exposure of selected areas to the diamond powder, (b) using diamond-

loaded photoresist to produce a patterned nucleation layer, or (c) seeding the substrate uniformly and then selectively etching portions of the surface to remove diamond-seeded areas. Alternatively [42, 43, 17] it is possible to use SiO_2 as a mask since diamond films grown from $\text{CH}_4\text{-H}_2$ plasmas are normally unable to form on SiO_2 substrates. The feature resolution that can be achieved by this method is limited by the grain size [42]. A UNCD structure formed by selective removal of the seed layer on Si is shown in Figure 7 (a) and 7 (b), exhibiting submicron edge detail.

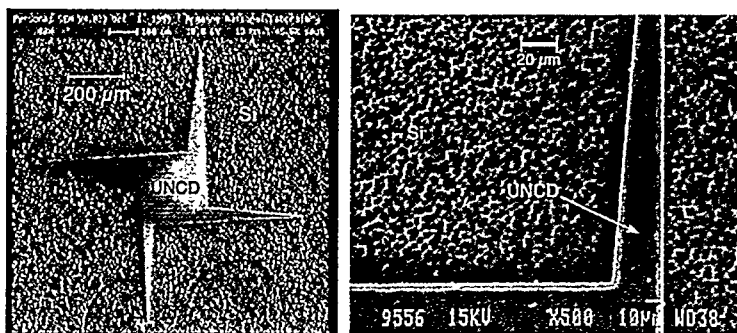


Figure 7. Two-dimensional UNCD patterned films on Si (100).

Si (100) can be anisotropically etched in a KOH solution. It is therefore possible to undercut a patterned diamond thin film structure such as that of Figure 7, leaving a set of $1\text{ }\mu\text{m}$ thick diamond “propellers” supported from below by a slender ($100\text{ }\mu\text{m}$ high) Si pedestal as shown in Figure 8.

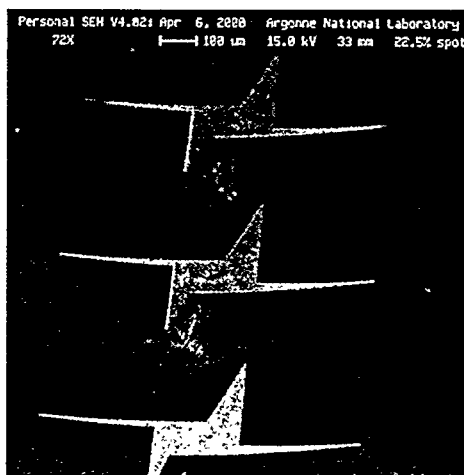
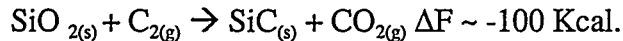


Figure 8. Free-standing $1\text{ }\mu\text{m}$ thick UNCD “propellers” grown by selective deposition followed by KOH etching of $100\text{ }\mu\text{m}$ tall Si posts.

The long arms extending from the corners remain flat, proving that the UNCD film is nearly stress-free, unlike conventional diamond films that exhibit significant out-of-plane stress and consequent warping upon release from the substrate.

4.3 Lithographic Patterning

In order to produce diamond multilayer structures, it is necessary to deposit a thin diamond film on a sacrificial release layer such as SiO₂. Methods have been reported [43, 29] to force the growth of conventional CVD diamond on SiO₂, typically by damaging the SiO₂ surface by ultrasonic abrasion in a diamond powder suspension. Continuous diamond films have been achieved using this method for film thickness in the range 15-20 μm although there are gaps between the film and the substrate, and the films are extremely rough [29]. Diamond films grown from CH₄-Ar plasmas are able to form directly on SiO₂ substrates without the need for damaging the SiO₂ layer since the gas phase carbon dimer growth species in the UNCD process forms an intermediate SiC nucleation layer via the reaction



It is therefore possible to use SiO₂ as a sacrificial substrate layer for multilayer UNCD devices. As shown in Figure 9 (a), a UNCD layer is deposited on a thermal SiO₂ layer, followed by a second SiO₂ layer deposited by CVD. Photoresist (b) is then used to pattern the hard SiO₂ mask using RIE with a CF₄/CHF₃ (2:1) plasma (c). An oxygen plasma is then used to etch the UNCD film through the hard SiO₂ mask. Finally (d) an HF wet and/or gas etch is used to remove the sacrificial oxide layer, leaving the diamond film suspended above the Si substrate.

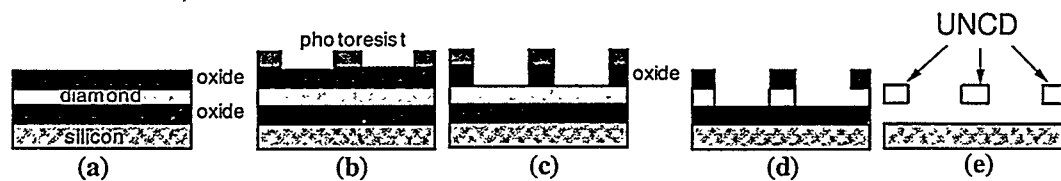


Figure 9. Lithography and etching scheme for producing a free-standing UNCD film.

Figure 10 shows a cantilever system produced by the method of Figure 9. The opposed ends of the two cantilevers constitute a vernier readout system for a cantilever strain gauge with 100 nm feature resolution. The UNCD film is 3.3 μm thick, and it is separated from the substrate by 2 μm.

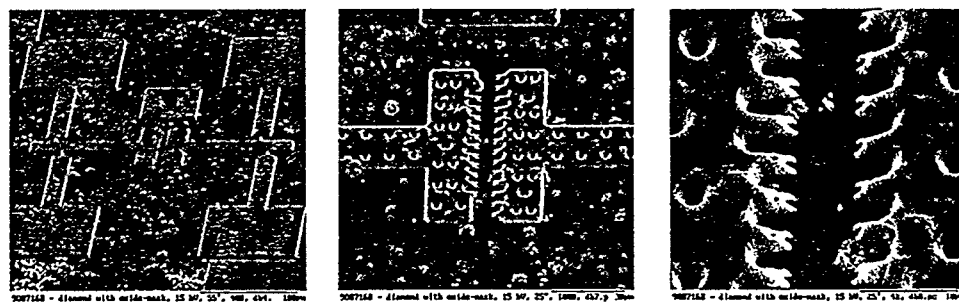


Figure 10. A UNCD MEMS cantilever strain gauge produced by blanket film deposition and etching through a hard oxide mask.

4.4 Combined methods

By combining selective deposition and lithographic etching of blanket UNCD films, it is possible to fabricate multilevel diamond devices using methods that are not feasible or require a larger number of steps in Si. A scheme for fabricating a captive rotor using combined methods is

shown in Figure 11. A blanket UNCD film is deposited on a Si substrate, followed by deposition of photoresist to yield the structure shown in figure 11 (a). An SiO_2 layer is then deposited and used as a hard mask in combination with an oxygen plasma etch to produce the structure shown in Figure 11 (b). A conformal SiO_2 layer is then deposited, and the trenches are selectively seeded using one of the methods described in the preceding section (Figure 11 (c)). The seeded trenches are filled with UNCD, and the SiO_2 layer is then removed by HF etch, leaving the wheel free within the retaining trench of the stator (Figure 11 (d)). Further NCD growth results in both an increase in height and a lateral spread of the stator components, which act to capture the rotor within the track, as shown in Figure 11(e).

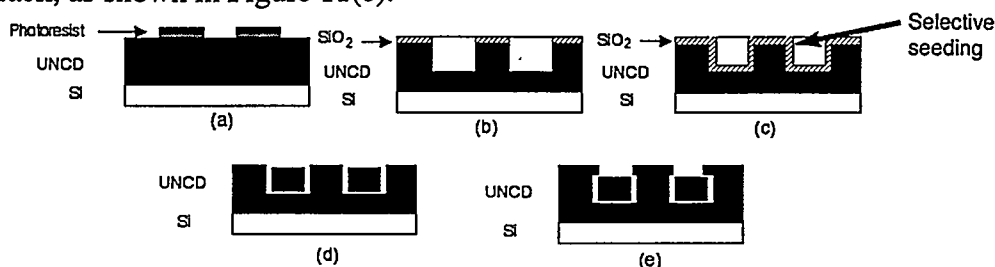


Figure 11 Combined lithographic patterning and selective deposition methods.

5. SUMMARY

The tribological and mechanical properties of diamond make it in principle an ideal material for MEMS applications, particularly in harsh environments. However, the high intrinsic stress, rough surface, and inappropriate grain morphology associated with conventional CVD deposition makes most diamond films unsuitable for use as a MEMS material. A process has been developed for the growth of phase-pure nanocrystalline diamond films with mechanical and tribological properties that seem well-matched for MEMS applications. Fabrication methods, some of them related to those of Si fabrication technology and others unique to diamond have been demonstrated in the fabrication of UNCD MEMS components.

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THIN FILMS FOR MULTIFUNCTIONAL DEVICES**

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