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Thermal etching of nanocrystalline diamond films

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ABSTRACT

A dry process for selective etching of nanocrystalline diamond thin films has been developed as an alternative to plasma etching. This process relies on subjecting masked diamond films to a controlled oxygen atmosphere at temperatures of 700–800 °C to controllably etch both vertically through the film and laterally underneath the mask. SiO_2, SiN_x, and Al_2O_3 films constitute viable mask materials for this process, provided that the underlying diamond film is fully outgassed before mask deposition and diamond etching. As expected, etching occurred more rapidly at higher temperatures. The etch rate was higher in the lateral direction than the vertical direction, which has been attributed to accelerated etching along disordered grain boundaries and the underlying nucleation layer. Similar activation energies (136–140 kJ/mol) were obtained for both lateral and vertical etching from 700 to 800 °C. Using the dry etch process developed in this research, diamond films can be removed from exposed features and undercut masked regions at a controlled rate, as indicated by microscopy and Raman spectroscopy.

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1. Introduction

Nanocrystalline diamond (NCD) thin films are currently of great interest for thermal management and passivation of electronic devices due to a high thermal conductivity and high electrical resistivity in undoped films [1,2]. In order to effectively integrate these films into device fabrication processes, selective patterning techniques for creation of NCD features must be developed. At present, two major avenues exist for patterning NCD: selective-area chemical vapor deposition (CVD) or O_2-plasma etching of blanket films. A variety of selective-area deposition processes have been reported; however, the additional processing steps required to generate NCD features while simultaneously avoiding spontaneous nucleation of diamond outside the regions of interest greatly increase process complexity [3–5]. Plasma-based etching processes represent a much simpler alternative to selective-area deposition, and can be used to selectively remove portions of blanket films of NCD [6–8]. However, the energetic nature of these etching processes can create defects in device layers sensitive to O_2-plasma underneath the NCD films during the final stages of etching [9–12]. Plasma etching of diamond is also extremely anisotropic, and an isotropic etch for diamond is not readily available. Development of an isotropic etch would aid in fabrication of diamond films into complex geometries that cannot easily be performed by plasma etching, such as thinning of diamond films on vias and vertical sidewalls, or fabrication of conical diamond structures for electron emitters and atomic force microscope probes [13–15].

In this work, a dry thermal oxidation process for selective etching of NCD films has been developed. A number of studies have examined oxidation processes of diamond crystals and films in oxygen or air atmospheres, wherein the diamond and any graphite or amorphous carbon formed during the growth process are oxidized into volatile CO/CO_2 compounds [16–22]. However, this knowledge has yet to be developed into a selective etching process for NCD films. The process detailed in this work is advantageous for NCD integration into electronic devices, as NCD films can be etched on both lateral and vertical features without plasma-induced damage to the host semiconductor regions.

2. Materials and methods

Samples were fabricated according to the process flow shown schematically in Fig. 1. Nanocrystalline diamond films with thicknesses of 0.9 μm and grain size of approximately 190 nm were prepared on Si substrates by microwave plasma chemical vapor deposition (MW-CVD) [23]. These films were then covered with a blanket mask of SiO_2 (plasma-enhanced (PE) CVD, 100 nm or 1000 nm), SiN_x (PECVD, 100 nm or 1000 nm), or Al_2O_3 (atomic layer deposition (ALD), 50 nm). Prior to patterning, one set of masked samples was heated to 700 °C at a ramp rate of 600 °C/min and held for 15 min under 100 sccm of flowing O_2 in an AnnealSys AS-One rapid thermal annealer (RTA) to assess the integrity of the mask materials under etching conditions. A second set of samples was subjected to a vacuum anneal (pressure below

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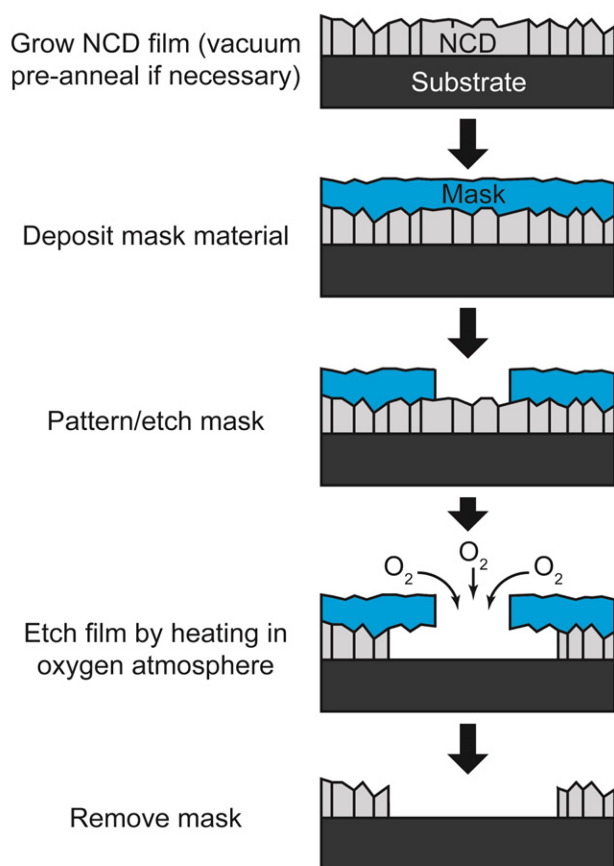

Fig. 1. General process flow for fabrication and etching of masked nanocrystalline diamond films.

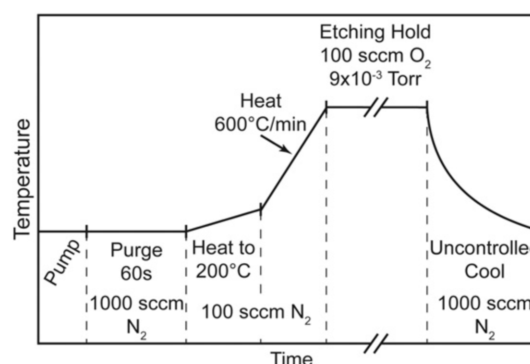

Fig. 2. General process profile for NCD thermal etch rate studies performed in the AnnealSys AS-One RTA. (Etching hold temperature and time were varied between 700–800 °C and 4–20 min, respectively).

1.5×10^{-4} Torr) in the AS-One at 750 °C for 10 min prior to mask deposition in order to remove volatile products from the NCD film that could compromise the mask integrity during etching. These films were observed post-annealing using an Olympus BX51 optical microscope with Nomarski contrast filters and a JEOL JSM-7600F scanning electron microscope to search for etch pits due to pinholes or film delamination.

Masked samples were then patterned using conventional photolithography techniques to selectively expose 1–100 μm features in the NCD films. Features were defined in the SiN_x masks using SF_6 ICP reactive ion etching. SiO_2 and Al_2O_3 masks were patterned using buffered HF wet etching. Initial process demonstration was performed using a Neytech Qex furnace at 650–900 °C with a ramp rate of 50 °C/min under approximately 500 sccm of continuously flowing O_2 at atmospheric pressure, in order to assess suitable etching temperatures and times. These studies indicated that etching at temperatures below 700 °C was too slow for efficient processing, while etching at temperatures above 800 °C occurred so quickly that the etch could not be easily controlled. As such, process temperatures of 700, 750, and 800 °C and times of 4–20 min were selected for more precise determination of the NCD lateral and vertical etching rates. SiO_2 was selected as the mask material, based on the mask integrity results detailed later in this work. The AnnealSys AS-One RTA was employed for the etch rate studies using the process profile shown in Fig. 2, as the RTA allowed better control over the sample temperature and process atmosphere than could be achieved in the Neytech furnace. As the NCD samples exhibited no change during annealing in nitrogen at the selected temperatures, flowing N_2 atmospheres were employed during heating and cooling to prevent unwanted etching and allow precise control over the oxygen etch time. Masked NCD samples were heated to temperature at a ramp rate of 600 °C/min under 100 sccm of flowing N_2 after an initial 1000 sccm flowing N_2 purge at room temperature. A 100 sccm flowing O_2 atmosphere (chamber pressure of 9×10^{-2} Torr) was maintained while at temperature to etch the NCD films, while cooling was performed under a 1000 sccm N_2 purge atmosphere. Following the etching process, lateral etch rates were measured using optical imaging of the mask undercut regions. Vertical etch rates were measured using a Tencor AlphaStep 500 stylus profilometer after stripping the etch mask. Raman spectroscopy and focused ion beam/scanning electron microscopy (FIB/SEM) were used to evaluate NCD decomposition in/near exposed features, using a Thermo Scientific DXR Raman Microscope (4 mW laser at a wavelength of 532 nm, and 100× objective lens with numerical aperture of 0.90 and working distance of 210 μm) and an FEI Nova 600 NanoLab, respectively.

3. Results and discussion

3.1. Mask material comparison

Evaluation of the masks on non-outgassed NCD after annealing at 700 °C for 15 min indicated that thick (1000 nm) PECVD SiO_2 was suitable for use on as-grown NCD films, with minimal pinholes observed (<10 cm^{-2}). However, the thin (100 nm) PECVD SiO_2 developed a large number of pinholes and near-surface blisters (~10^3 cm^{-2}), as shown in Fig. 3a. The ALD Al_2O_3 masks (Fig. 3c) also formed numerous blisters (~10^5 cm^{-2}), while both the thin and thick PECVD SiN_x masks completely delaminated from the as-grown NCD (Fig. 3b).

The mask defects introduced by annealing were suspected to be at least partially due to the release of residual gases trapped in or on the NCD film, possibly hydrogen or residual hydrocarbons from the diamond growth process [24,25]. As such, a second set of NCD films was pre-annealed under vacuum (pressure < 1.5×10^{-4} Torr) at 750 °C for 10 min prior to mask deposition. This outgas pre-anneal corrected the delamination and blistering issues initially observed with the thin SiO_2, thin SiN_x, and Al_2O_3 films, as shown in Fig. 3d–f. However, the thick SiN_x film still completely delaminated; outgassing of the nitride mask itself during heating is suspected to be responsible for the catastrophic mask damage. For the remainder of the study, thick (1000 nm) SiO_2 films were chosen as the mask material, as they could be used on either outgassed or non-outgassed NCD films without defect formation or film delamination. These results also suggest that 100 nm SiO_2, 100 nm SiN_x, and 50 nm ALD Al_2O_3 films were suitable mask materials, provided that the underlying NCD film was annealed in vacuum prior to mask deposition.

3.2. Etch profile evaluation

Upon annealing in an oxygen atmosphere at temperatures of 700 °C and above, the masked NCD films were found to decompose both vertically and laterally, undercutting the mask material. The lateral etching

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