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A direct-write, resistless hard mask for rapid nanoscale patterning of diamond

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ABSTRACT

We introduce a simple, resist-free dry etch mask for producing patterns in diamond, both bulk and thin deposited films. Direct gallium ion beam exposure of the native diamond surface to doses as low as 10^{16} cm^{-2} forms a top surface hard mask resistant to both oxygen plasma chemical dry etching and, unexpectedly, argon plasma physical dry etching. Gallium implant hard masks of nominal 50 nm thickness demonstrate oxygen plasma etch resistance to over 450 nm depth, or 9:1 selectivity. The process offers significant advantages over direct ion milling of diamond including increased throughput due to separation of patterning and material removal steps, allowing both nanoscale patterning resolution as well as rapid masking of areas approaching millimeter scales. Retention of diamond properties in nanostructures formed by the technique is demonstrated by fabrication of specially shaped nanoindenter tips that can perform imprint pattern transfer at over 14 GPa pressure into gold and silicon surfaces. This resistless technique can be applied to curved and non-planar surfaces for a variety of potential applications requiring high resolution structuring of diamond coatings.

1. Introduction

Diamond nanostructures have been produced that exploit some of the material's superlative properties including, for example, its high mechanical rigidity and strength for MEMS [1,2] and nanoimprint templates [3–5], its high thermal conductivity for optoelectronic thermal management systems [6,7] and power electronics [8], and its chemical inertness for electrochemical [9] and biocompatible devices [10,11]. Patterning of these structures can be achieved by well-established resist mask-and-etch techniques or subtractive ion beam milling. In this letter we introduce a new, robust mask for efficient patterning of diamond. A low dose exposure of the native surface by an energetic gallium ion beam forms a barrier of high selectivity to subsequent plasma etching. At low aspect ratio we demonstrate dense 25 nm line features, while at intermediate (1:1) aspect ratio, 400 nm features are demonstrated with sharp corners and smooth sidewalls.

The diamond hard masking effect is related to ion top surface imaging, a recently demonstrated nanoscale patterning technique for silicon where direct exposure to an ion beam modifies an “imaging” layer at the sample surface. For silicon, the imaging layer can be formed at a specialized, ultrathin resist layer or, simply, at the native surface itself. In the former case the imaging layer is used to process an intermediate conventional thick resist etch barrier [12], while in the latter, a high performance barrier is formed for certain deep reactive ion etch conditions [13]. Our diamond hard mask is a resist-free top surface image, which functions against both reactive (oxygen) and purely physical (argon) plasma etch conditions. It offers significant advantages over direct ion milling of diamond including increased throughput and potentially better resolution and sidewall angle control due to separation of patterning and material removal steps. Limitations of resist-based processing of diamond, including planar substrate requirements and overall process complexity, are further ameliorated by the direct write, direct masking approach.

2. Experimental

To illustrate the technique, panels A and B of Fig. 1(A and B) show the two steps involved in the formation of a truncated conical flat punch diamond nanostructure in boron doped (10^{21} cm^{-3}), synthetic high-temperature high-pressure (hthp) diamond crystal used for nanoindentation. First, a focused ion beam (FIB, FEI Strata 240) was used to implant a region of the native diamond surface with 30 kV Ga^+ ions below the threshold for milling, in this case to a dose of 7.5×10^{15} cm^{-2}. Then, in step 2, the sample was transferred to a dry etch tool and the surface exposed to an energetic plasma. This reveals the latent image of the FIB exposure by selective removal of diamond material below unexposed (unmasked) regions. The plateau of the structure is a flat circular surface 400 nm in diameter created by a radial FIB exposure to form the hard mask. Feature relief of 450 nm was achieved by etching the sample for 35 min using a Diener “Pico” plasma etcher in pure O_2 atmosphere at 150 mTorr pressure operating at 40 kHz, 160 W power. Note the smooth etch walls, sharp corners, and lack of mask undercut in the etched structure. High resolution line features of 25 nm at 65 nm pitch are demonstrated in Fig. 1C. We have applied the technique to

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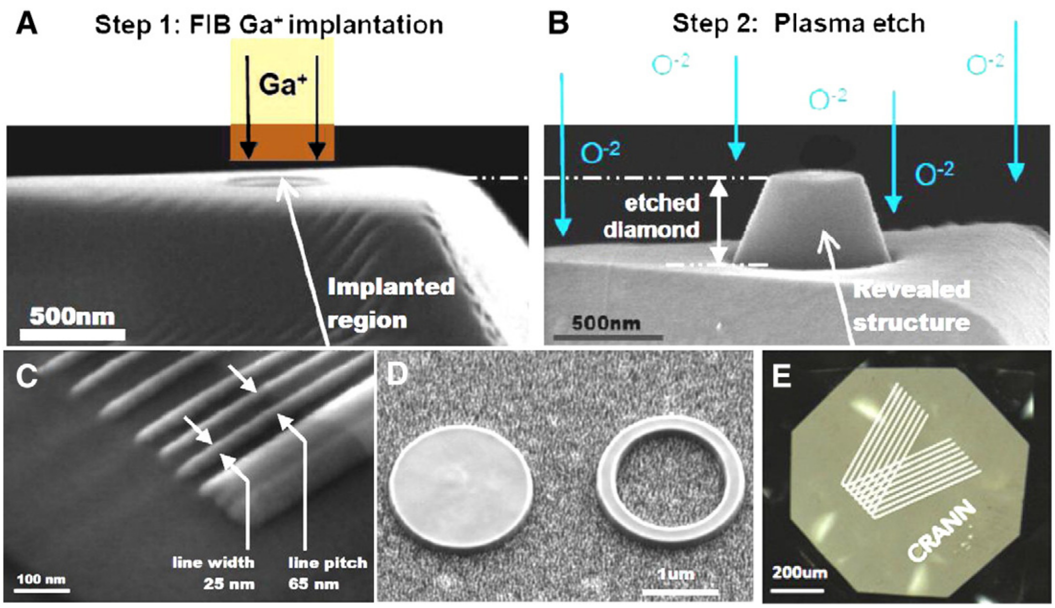

Fig. 1. Process summary and features of gallium implant diamond masking. A boron doped, single crystal synthetic diamond is implanted by gallium ions (A) forming a direct-write, negative tone mask for oxygen plasma dry etching (B) which reveals a truncated conical flat punch indenter nanostructure. Lines to 25 nm width, 65 nm pitch are fabricated (C) in singe crystal diamond. In D, larger area features are etched into a nanocrystalline diamond on silicon (DOS) film, while in E a large ~1 mm^2 area pattern is etched in positive relief on a facet of a natural diamond gemstone. Images A and B are oriented near perpendicular, and C and D oriented at 52° to the normal of the patterned surfaces.

diamond-on-silicon thin films (Fig. 1D), as well as over large areas (1 mm) on natural gemstones as shown in Fig. 1E.

3. Results and discussion

Unlike standard FIB processing, the production of vertical relief here is independent of the total area and complexity of patterns. We have achieved etching rates of the masked diamond of up to several 100 nm per minute, thus the throughput of this simple two-step, low ion dose process should be comparable to standard electron beam lithography processing of resists, which is limited by patterning time.

To characterize the masking process, we have analyzed a cross section of a patterned structure by scanning transmission electron microscope (STEM) imaging using a high annular angle dark field (HAADF) signal, selected area electron diffraction (SAED), and energy dispersive X-ray (EDX) spectral analysis. Cross sectional STEM samples were prepared using a FIB-based in-situ lift-out technique, including a 3 kV Ga^+ beam final polishing step, using a Zeiss NVision 40 CrossBeam facility. STEM images (Fig. 2) were obtained using a custom built aberration-corrected, cold field emission VG STEM (SuperSTEM 1, SuperSTEM Laboratories, Daresbury UK) operating at 80 kV. SAED images (insets in Fig. 2A) were obtained using a JEOL 3000F field emission TEM operating at 300 kV.

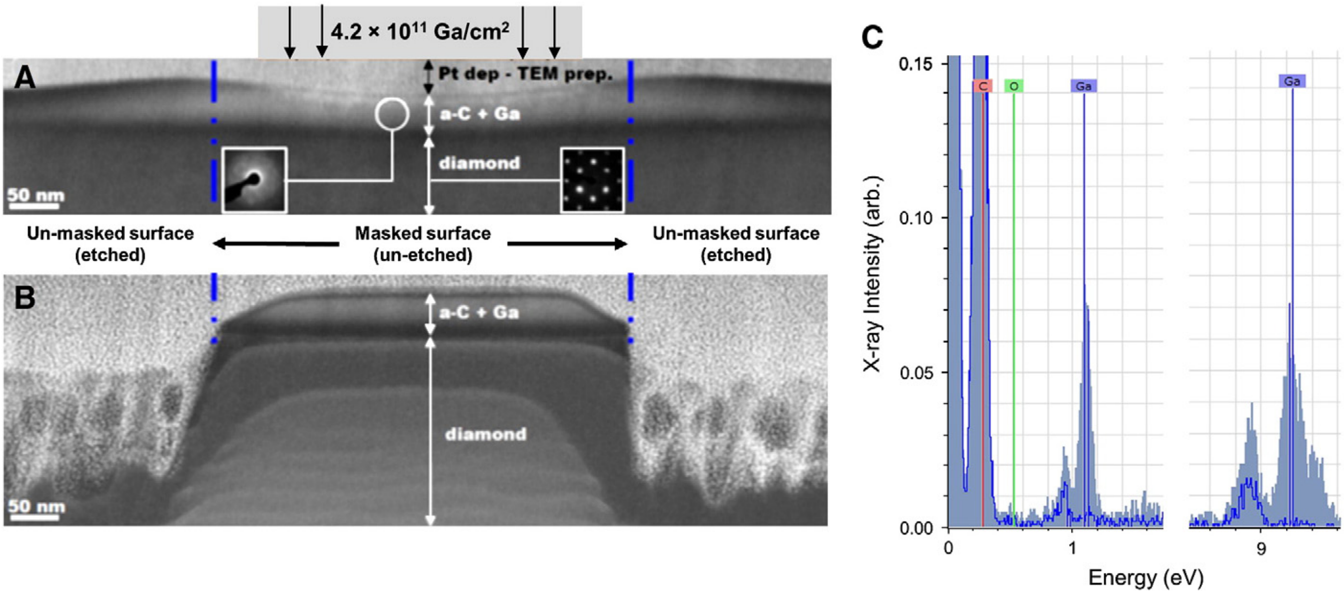

Fig. 2. High annular angle dark field scanning transmission electron microscopy images from cross sections of processed single crystal diamond samples: (A) Immediately after Ga^+ ion implantation over the nominal surface indicated. Selected area electron diffraction (SAED) patterns of the underlying diamond and implanted surface layer are shown as insets. (B) Following oxygen plasma etch of a sample implanted identically to A. (C) Energy dispersive X-ray spectra taken by TEM of the same areas defined for the SAED patterns in A: Implanted a-C + Ga (light blue solid spectra) regions confirm the presence of gallium, while the underlying diamond (dark blue line spectra) shows absence of Ga.