Proton beam writing on polyvinylidene difluoride films for high-aspect-ratio micro-structuring

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Polyvinylidene difluoride [PVDF, -$(CH_2CF_2)_n$-], is a fluorinated polymer with piezoelectricity and pyroelectricity. Microfabrication techniques were reported using either a wet or a dry etching technique for robotics skin sensors. [1] These techniques involve photolithographic processes for an etching mask layer to protect PVDF from etching liquid or gas to obtain microstructures.

In this study, we have proposed a mask-less approach to micro-structuring of PVDF using proton beam writing (PBW), which has been demonstrated as a tool for high-aspect-ratio, micro-structuring.[2] Owing to the high linear energy transfer of MeV protons, we expect that PBW is also applicable to PVDF, as previously reported for polytetrafluoroethylene[3] and polydimethylsiloxane[4].

The PVDF films with a thickness of 100 μm have been used for PBW (beam energy: 1.0 MeV, beam size: 2.0 μm, beam current: ~120 pA). The proton fluence was varied from 0.3 to 4.8 μC/mm^2 in a step of 0.3 μC/mm^2 for PBW. The PVDF surface was measured by a confocal laser microscope (CLMS).

Figure 1 (a) shows the CLMS image obtained for 30-μm square arrays (4 x 4) on PVDF film with varied proton beam fluence. We observed surface patterning with a depth up to ~1.5 μm. An FT-IR ATR analysis shows decreased C-F bonds and formation of carbonyl group. Well-defined features of lines and spaces, and circles on PVDF was written by PBW, as shown in Fig. 1(b).

We then applied wet etching to PVDF after PBW by immersion in a 9.0 mol/L KOH aqueous solution with 0.25 mol/L $KMnO_4$ (80 °C, 1 h). We observed increasing etching depth from ~5 μm in the low fluence (0.3 - 1.2 μC/mm^2) to ~15 μm in the higher fluence regions (3.9 - 4.8 μC/mm^2). The depth of 15 μm is in good agreement with a projected range of 1.0-MeV protons into PVDF.

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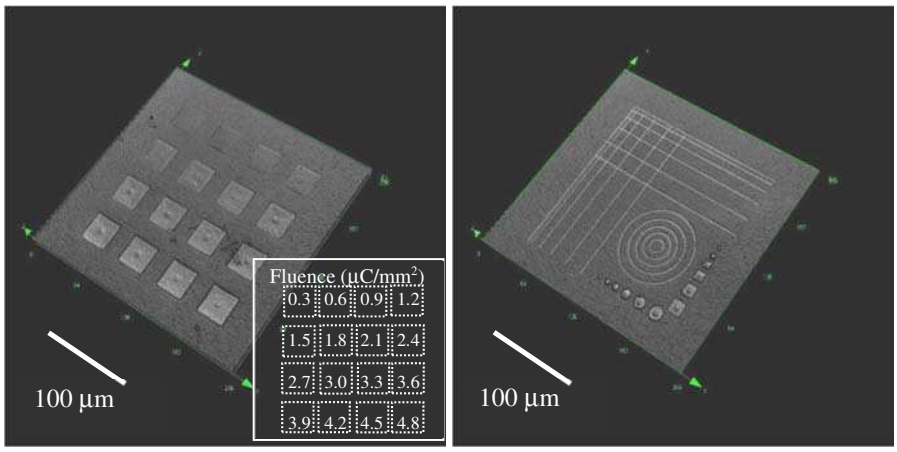

Figure 1: Confocal Laser microscope images of PVDF surface after proton beam writing: The PVDF surface after 1.0-MeV PBW of (a) a square arrays pattern with fluence from 0.3 to 4.8 μC/mm^2 in a step of 0.3 μC/mm^2 (shown in the inset are fluence at each position of the pattern and (b) lines and spaces, and circles by PBW with fluence of 4.8 μC/mm^2.