Annealing PEDOT Thin Films to Generate a Selectively Deposited Etching Hard Mask Layer

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As feature sizes in contemporary device architectures aggressively shrink, enhanced understanding of area-selective deposition (ASD) is critical to support advanced patterning and feature alignment. In recent years, new strategies have been developed for ASD of poly(3,4-ethylenedioxythiophene) (PEDOT) conjugated polymer by molecular layer deposition (MLD) and chemical vapor deposition (CVD) on SiO_2 vs. Si-H,[1] orthogonal ASD of W and PEDOT,[2] and inverted "dual-tone" ASD of PEDOT on Si-OH vs. SiO_2-TMS.[3]

Hard masks for etching are a key application for ASD materials. However, conjugated polymers are expected to etch quickly during plasma exposure. In this work, we describe the effect of post-deposition annealing on the etch rate of PEDOT during O_2 plasma and demonstrate means to "reactivate" the film to convert it from non-etching to etching. In their as-deposited form, the materials etch readily, as expected. As shown in Figure 1(a), the etch rate decreases by 50% upon annealing at 250 °C and decreases to near zero after heating to 350 °C. XPS analysis in Figure 1(b) shows an increase in the concentration of the Sb oxidant after annealing. Also, Figure 1(c-e) shows HAADF STEM images and an EDS elemental map of a film after annealing 350 °C. The EDS indicates that upon annealing, Sb segregates to the film surface. We hypothesize that this Sb layer contributes to the observed reduction in etch rate. This is consistent with XPS after etching in Figure 1(f) showing Sb present in the film.

Interestingly, we find that after treating the annealed PEDOT in deionized liquid H_2O at 80 °C for 10 minutes, the films readily etch in O_2 plasma, as indicated by XPS in Figure 1(g). The ability to enable plasma etching resistance for a selectively deposited conjugated polymer film opens innovative avenues and strategies for protecting surfaces during plasma deposition or selective etching steps. These findings bolster the significance and versatility of ASD for modern manufacturing methodologies.

[1] J.-S. Kim et al., *Chem. Mater.* **33**, 23 (2021).
[2] H. Oh et al., *Chem. Mater.* **35**, 11 (2023).
[3] N. Carroll et al., *Chem. Mater.* **36**, 8 (2024).

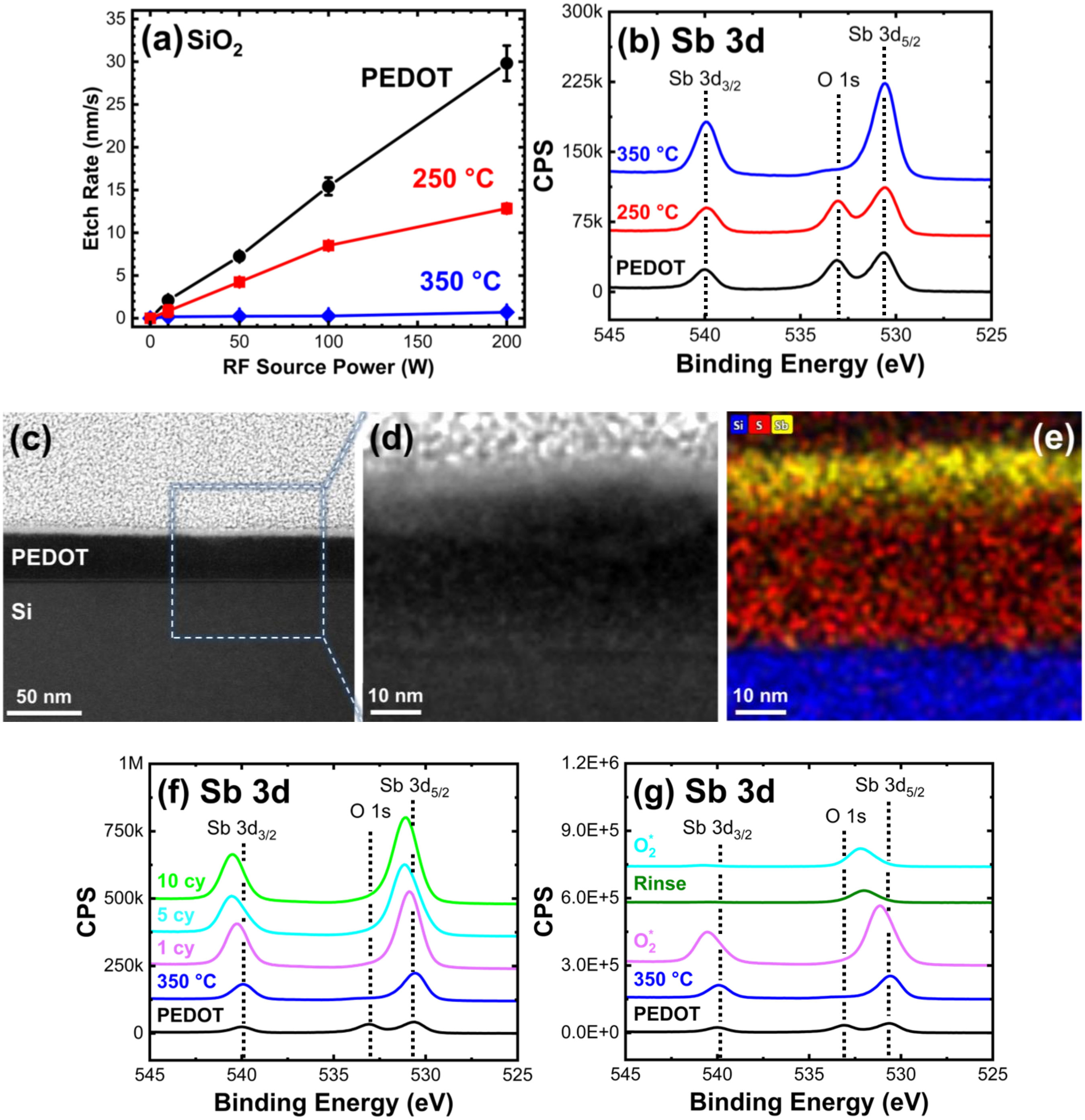

Figure 1. (a) PEDOT etch rate at varying O_2 plasma RF source power levels for different annealing temperatures. (b) X-ray photoelectron spectroscopy (XPS) data in the Sb 3d region for PEDOT films annealed at different temperatures. (c) HAADF STEM image of PEDOT after annealing at 350 °C. (d) Zoomed in image from the region in (c). (e) STEM-EDS scan of (d) showing Si, S, and Sb signals, where S is a characteristic indicator of PEDOT. (e) XPS scan after continued cycles of O_2 plasma exposure after annealing at 350 °C. (f) XPS scan showing the removal of Sb content via liquid deionized H_2O treatment followed by O_2 plasma etching.