

Photopatterning 3-amino-propyl-triethoxy-silane (APTES) self-assembled molecular layers on alumina

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Molecular patterning has broad applications for micro- and nano-scale devices used in electronics, biological and chemical sensing, and other areas requiring precise control of surface properties. In addition, we have recently implemented patterned self-assembled monolayers (SAMs) as fiducial grids for low-voltage spatial-phase locked electron-beam lithography (SPLEBL).^{1,2} Alkanethiol SAMs on Au or Ag are the most widely investigated systems,³ and these SAMs can be photopatterned by irradiation with various wavelengths of ultraviolet light. In this case, irradiation yields alkylsulfonates that are subsequently displaced by a second alkanethiol SAM. However, it is often necessary to form SAMs on oxide, rather than metal, surfaces and various organosilanes have been used for this purpose. With the exception of photocatalytic patterning of fluorosilanes on TiO₂⁴ and photo-modification of functional groups on more complex SAMs,^{5,6} direct lithographic patterning of simple organosilane SAMs has been limited to electron-beam⁷ or vacuum-ultraviolet (VUV)^{8,9} techniques.

Here we report the first direct patterning of organosilane molecular layers using deep-UV (266-nm) light. Specifically, 3-amino-propyl-triethoxy-silane (APTES) layers were formed on partially oxidized aluminum films (~ 5 nm thick). These films were supported by silicon substrates coated with ~ 50 nm of PMMA. This geometry was chosen for its relevance to low-voltage (SPLEBL).¹ A deep-UV, 266-nm wavelength laser (Azure, Coherent Inc.) was used to expose the APTES through a TEM grid with 12.5 μm pitch. Typical exposures were carried out over a 1 cm² area for 15 minutes at a power of 50mW. The irradiated samples were immersed in a toluene solution containing a second organosilane molecule, e.g. n-butyltrichlorosilane (BTS) or n-octadecyltrimethoxysilane (ODS), that displaced the exposed SAM. Figure 1 shows the final sample geometry. We also prepared a control sample without a second SAM. In all cases, we imaged the sample using SEM (2 to 10keV) and compared secondary electron (SE) signals from the different regions. As shown in Figure 2, all of the patterns demonstrate clear SE contrast. We found that BTS/APTES patterns exhibited contrast reversal compared to ODS/APTES structures. Direct patterning of organosilane films using deep-UV (rather than VUV or e-beam) exposure allows the use of coherent and continuous wave sources and also prevents exposure of underlying e-beam resist layers in SPLEBL configurations. In addition, exposures are conducted under ambient conditions with reduced environmental influence.

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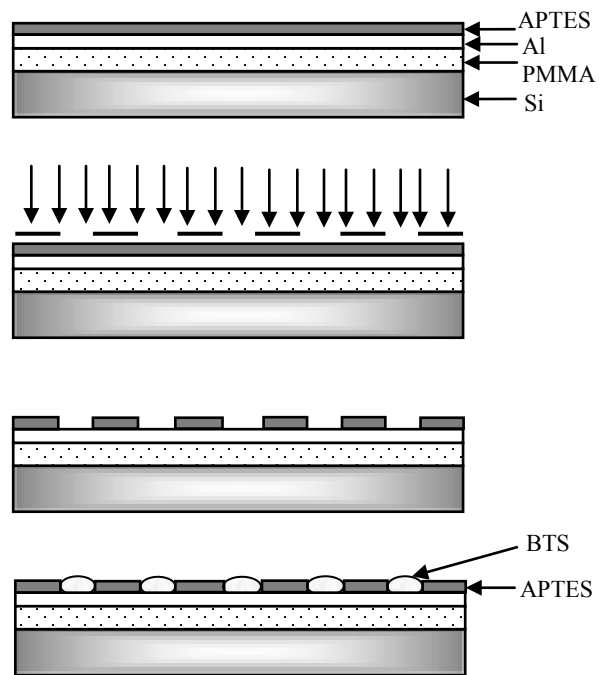


Figure 1. Photopatterning process for 3-amino-propyl-triethoxy-silane (APTES) on partially oxidized aluminum.

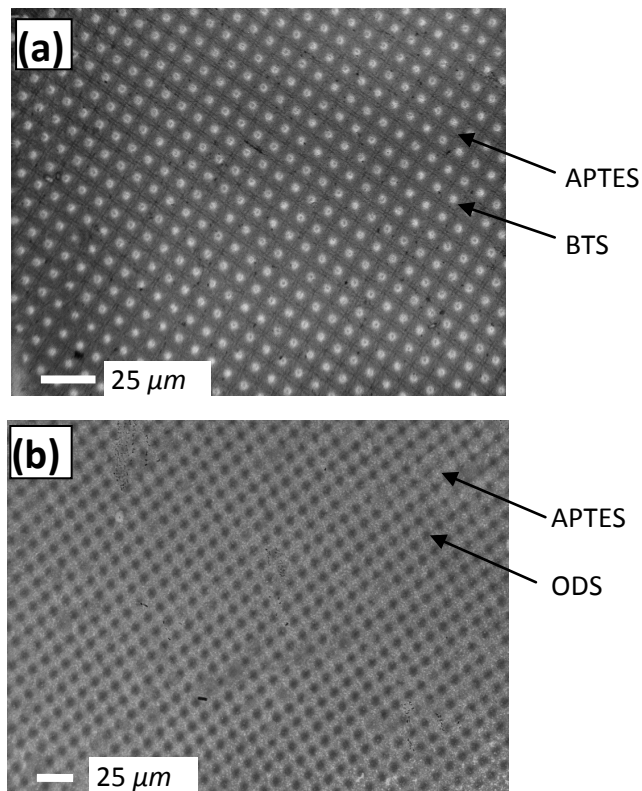


Figure 2. (a) SEM images for n-butyltrichlorosilane (BTS) activated and (b) octadecyltrimethoxysilane (ODS) activated APTES on $\text{Al}_2\text{O}_3/\text{Al}/\text{PMMA}/\text{Si}$ photo patterns using 266 nm laser sources (50 mW) for 15 mins, taken at 2 keV.