Conductive Copper Patterns by an Additive, Solventless, Contact Printing Technique

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Introduction

As the drive for low-cost electronics intensifies, the ability to directly pattern copper by a straightforward, low-cost means is increasingly desired. One of the more promising direct patterning techniques currently under development is ink-jet printing [1]. This process uses copper precursors dispersed in organic solvents that are subsequently annealed and sintered at high temperatures to generate continuous copper patterns. In this paper, we report an alternative copper patterning technique – nanotransfer printing [2] – that is purely additive, solventless, and can be carried out at ambient conditions.

Experimental

Nanotransfer (nTP) printing has been previously described for patterning gold [2]. Briefly, poly(dimethylsiloxane), PDMS, prepolymer (Dow Corning Sylgard 184) is cast and cured against a silicon wafer patterned with photoresist to produce an elastomeric stamp with relief features of the desired geometry. Deposition of copper onto the raised and recessed regions of the PDMS stamp occurs by e-beam evaporation. Simultaneously, 1,8-octanedithol ($HS(CH_2)_8SH$) is deposited onto a freshly-etched GaAs substrate from a 10mM ethanolic solution resulting in covalent bonds between the GaAs substrate and one of the thiol (-SH) endgroups. We believe that the dithiol molecules are generally oriented with the free thiol functionality away from the substrate, thereby creating a molecular brush that is available for further reaction. Contacting the PDMS stamp, freshly evaporated with copper, against the treated GaAs substrate results in intimate molecular contact between the raised regions of the stamp and the substrate. An instantaneous reaction between the unreacted thiol endgroups of octanedithiol and copper occurs at the interface resulting in permanent copper attachment to the GaAs substrate. Pattern transfer is completed upon stamp removal; this process occurs at ambient conditions with contact times less than 30 seconds. Since the copper patterns are covalently bound to the substrate through a molecular layer of octanedithiol, these patterns always pass Scotch Tape adhesion tests. Currently, this technique permits large-area patterning with feature sizes ranging from 1 to 500 microns [3].

X-ray photoelectron spectroscopy (XPS) measurements were conducted with a Physical Electronics ESCA 5700 spectrophotometer equipped with a monochromatic Al Kα X-ray source, a hemispherical electron analyzer and a low energy electron flood gun for charge compensation of insulating samples. All Samples were analyzed at a takeoff angle of 45°C and a pass energy of 11eV. For depth profiling, an argon ion beam was used to etch the samples. The etch rate was linear (0.3 nm/sec) and can be controlled by the sample current. Atomic force microscopy (AFM) was carried out with a Digital Instruments Dimension 3100 with Nanoscope IV controller. Images were collected in tapping mode. Current-voltage characterization was completed with an Agilent 4156C Precision Semiconductor Parameter Analyzer.

Results and Discussion

Although printing copper is procedurally similar to printing gold, there is a marked difference in the conductivity of the resulting patterns. Gold features printed with as-cast PDMS stamps are always conductive [2] with resitivities comparable to those of evaporated gold films of the same thicknesses. In contrast, copper features (varying in thickness from 15-75nm) printed with as-cast PDMS stamps are never conductive. To determine the discrepancy between gold and copper printing, we performed XPS depth profiling experiments on printed gold and copper patterns, looking specifically at the metal (Cu 2p at 925-970eV and Cu Auger LMM lines at 600-640eV or Au 4f at 80-95eV), oxygen (O 1s at 525-540eV) and silicon (Si 2p at 90-110eV) peaks [4].

Since copper readily oxidizes to form Cu(I)O and Cu(II)O at ambient conditions, we hypothesized that the formation of copper oxide may be the origin of the insulating nature of these patterns. XPS analysis along the depth of the copper patterns, however, eliminated copper oxidation as the cause of non-conductivity. Specifically, Cu 2p and Cu LMM spectra from the interior of the copper pattern indicate that metallic copper, and not oxidized copper, comprises the majority of the pattern.

Because the printed surface was previously in direct contact with the PDMS stamp, we also speculated that contamination from the stamp could cause the printed patterns to be non-conductive. Monitoring the O 1s region, we observed a peak associated with the oxygen-silicon linkage in PDMS (532.2eV) on both printed gold and copper surfaces, which is consistent with previous studies reporting PDMS surface contamination [5]. There is, however, a significant difference between the contamination on gold and copper patterns: XPS indicates that while this contamination is limited to the surface of the gold patterns, it is observed throughout the thickness of the copper patterns. This trend is also observed with the Si 2p peak associated with the silicon-oxygen bond in PDMS (102.1eV); both the O 1s and Si 2p peaks persist throughout the entire thickness of a 72nm printed copper pattern. While we fully expect PDMS contamination on the printed surface (since this was the PDMS stamp/copper interface prior to printing), we were surprised that PDMS can in fact permeate the copper patterns. The origin of this phenomenon remains unclear; we attribute it to morphological differences in the gold and copper patterns. Preliminary AFM scans of the printed metal surfaces indicate that PDMS oligomers may be able to permeate between individual copper grains thereby disrupting the percolative pathway of conduction. Detailed AFM studies to confirm this hypothesis are currently underway.

Removing residual oligomers from the PDMS stamps allows conductive copper features to be printed via nTP. This is accomplished by leaching the stamps in hot toluene for 48-72 hours prior to printing. Copper features printed with leached stamps exhibit an average resistivity of 31micro-ohms-cm. Although XPS still indicates a minute amount of PDMS oligomer contamination in these patterns, the presence of these oligomers does not significantly alter the electrical properties of printed copper.

References

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