# Synchrotron-radiation-induced, selective-area deposition of gold on polyimide from solution<sup>\*</sup>

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#### Introduction

Direct writing of metals on substrates from solutions has been achieved by using laser irradiation [1], a process in which metals contained in a solution are reduced and deposited pyrolytically [2,3], photolytically [4, 5], or even by photoelectrochemical means [6]. The technique may have great potential for microelectronic applications [1, 7]. In this paper, a high-energy synchrotron radiation wet deposition process is described. It is a true electroless process. Since high-energy x-rays penetrate deeply into low-Z materials, the process should be a potential alternative to laser processing when the penetration of the laser light is limited or prohibited. To demonstrate the process, results are shown for gold deposition on polyimide (PI), an important substance for both microelectronics and x-ray optics.

#### **Methods and Materials**

The photoinduced deposition experiments were performed on beamline 2-BM. Either a Cr- or Pt-coated mirror was employed at an angle of incidence of 0.15°, which attenuates photons with energies above 20 keV and 35 keV. respectively. Depending on the mirror used, the incident power can range from 27 watts to 125 watts for 100 mA of storage ring current. The storage ring current decays with time. The beam half-life time was 12 hours when these experiments were performed. For x-ray exposures, a slit system was used to limit the beam size to  $3 \times 20 \text{ mm}^2$ . The stainless steel cell used to contain the solution has an opening on one side that can be O-ring sealed by a 130 µm thick PI window, which also serves as the sample on which the deposition occurs. The flange used to seal the window can hold both a patterning mask and a slit  $(2 \times 20 \text{ mm}^2)$ . The latter defines the exposed area. X-rays transmitted through the PI window induce deposition on the surface facing the solution [4].

Atomic force microscope measurements indicate that the PI (Goodfellow Corp.) surfaces are smooth with a root-meansquare roughness < 3 nm over the terraces of widths from >1 µm to a few microns. Before mounting, the PI sample was dipped into a 5% NaOH solution for 30 seconds to improve adhesion. The metal-containing solution used for deposition is a sodium gold sulfate electroplating solution (Technic, Inc.) with a pH of 6.7. The cell was vertically scanned at 6 mm/s across the beam to produce a uniform exposure. Since the solution precipitates Au nanoparticles under x-ray irradiation, a filtered pumping system was employed to remove the precipitates produced during each scan through an outlet on the cell top and to provide clear solution through an inlet on the cell bottom. We found that continuous pumping resulted in poor quality films. Therefore, an electrical switch was used to momentarily activate the pump after each scan.

#### **Results and Discussion**

Figure 1 shows the scanning electron microscopy (SEM) images of a patterned 60-nm-thick Au deposition on PI (a) and its microstructure (b). The exposure time was 4.7 min. at 71 mA or a dose of 334 mA-min. The microfeatures are well defined. However, a spread of a few microns of Au along the feature edge is detected. This could be due to the pumping operation that may spread a few gold particles onto the nonilluminated areas in the immediate vicinity of the deposition areas. The film consists of uniformly sized grains of a few hundred nanometers; smaller particles of about 20 nm were filtered from the solution after x-ray exposure [8]. A similar morphology has been seen for films deposited on softened polystrene (PS) substrates by physical vapor deposition with the substrate temperature held above the PS glass transition temperature (around 373 K) [9]. Since the x-rays must be transmitted through the growing film, the process is self-limiting. However, Au films of a few microns in thickness should be achievable since significant amounts of high-energy x-rays will penetrate the films. For lighter metals, greater thickness should be obtainable. The process may be useful for producing low-cost test photomasks or microelectronics to fabricate freestanding metal-polyimide circuits [10].

Film thickness values were obtained by atomic force microscope (AFM) measurements. The film growth rate determined from these measurements is about 40 nm/min. It is linear vs. the x-ray dose. Therefore, the film growth rate is not attenuated due to the gold absorption in this thickness regime.

Film growth under other beam and solution conditions was also performed: (1) a Cr mirror was used to attenuate highenergy photons (> 20 keV), (2) a 600  $\mu$ m Al filter was used to attenuate low energy photons (< 5.5 keV), and (3) the concentration was varied. These experiments indicate that the deposition rate is proportional to both photon intensity and solution concentration. It was not possible to determine the x-ray energy dependence of the growth rate, in part because the process is self-limiting such that the x-ray energy composition changes as the film thickness increases.



Figure 1: Scanning electron micrographs of a patterned 60 nm thick Au deposition on (a) Kapton and (b) its microstructure (10,000x).

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