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Citation: Applied Physics Letters **47**, 923 (1985); doi: 10.1063/1.95981 View online: http://dx.doi.org/10.1063/1.95981 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/47/9?ver=pdfcov Published by the AIP Publishing

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## Laser-initiated deposition reactions: Microchemistry in organogold polymer films

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(Received 14 January 1985; accepted for publication 14 August 1985)

Micron-sized gold features have been produced by the cw Ar<sup>+</sup> laser-initiated decomposition of thin organogold polymer films. These features may exhibit pronounced periodic structure under a wide variety of experimental conditions, resulting from propagation of the reaction front ahead of the laser by the heat of reaction associated with the chemical transformation. Gold features formed by irradiation of gold chloride-doped polymer films further demonstrate these thermal effects. Thermoanalytical studies provide pertinent data for selection of suitable precursor materials.

Laser direct writing of metal features is attracting much attention as a one-step pattern definition and metal deposition process for very large scale integrated circuit (VLSI) applications.<sup>1,2</sup> Much of the work in this area deals with laser chemical vapor deposition, a photo-initiated thermal process using inorganic and organometallic precursors in the vapor phase.<sup>1-3</sup> These systems require specialized sample chambers and are limited by the small number of sufficiently volatile precursors available. Metal deposition by the laserinduced decomposition of spin-coated organometallic polymer films offers the advantages of increased safety and ease of handling. These films can be exposed in air and are compatible with subsequent processing by current lithographic procedures.<sup>4</sup> More importantly, a wide variety of metals can be incorporated in the synthesis of organometallic polymers, tailoring them to specific applications.

Results for a new approach to laser-induced deposition reactions using a scanning cw Ar<sup>+</sup> laser at 5145 Å and thin films of organogold polymers were presented in a previous paper.<sup>5</sup> Metal features thus formed may exhibit pronounced periodic structure under a wide range of experimental conditions. This structure provides a record of the propagating chemical reaction front driven by an exothermic heat of reaction. Similar structure is observed in the laser-driven explosive crystallization of thin films of amorphous semiconductors.<sup>6–8</sup> In contrast, however, the latter structure results from a physical, rather than a chemical, transformation of the material that is accompanied by the release of a latent heat of crystallization. Control of feature geometry must begin with careful selection of precursor materials. The pertinent data for selection can be derived from thermoanalytical measurements and mechanistic studies. Furthermore, in developing new metallopolymer systems, we note that the metal residues serve as records of the reaction kinetics of these processes.

The 5145 Å output of a cw Ar<sup>+</sup> laser, focused to a typical spot size of 0.8  $\mu$ m FWHM, was used in the direct-writing experiments. Full details of this system have been reported elsewhere.<sup>5</sup>

Engelhard Bright Gold NW screen ink was spin coated on quartz substrates and prebaked to remove excess solvent. After exposure, undeveloped material was removed in a  $CH_2Cl_2$  rinse. Alcohol solutions of ammonium tetrachloroaurate with poly (vinyl alcohol) and nitrocellulose containing 58 and 21 wt. % gold, respectively, were prepared and spin coated on quartz substrates as well. Gold *p*-tert-butyl phenyl mercaptide was synthesized according to a literature procedure.<sup>9</sup> Differential scanning calorimetry and thermogravimetric analysis procedures are described elsewhere.<sup>10</sup> Activation energies were calculated by the Kissinger method.<sup>11</sup>

Examples of the above described periodic structure are shown for the Engelhard gold screen ink in Fig. 1. The screen ink, which absorbs strongly at the laser wavelength of 5145 Å, must exceed a critical threshold temperature for the pyrolytic decomposition to proceed at an appreciable rate. Oxygen must be present in order that the pyrolysis effect complete removal of organic material from the resulting gold feature. The heat of reaction generated by the oxidative pyrolysis drives the reaction front ahead of the scanning laser beam to the point where the temperature falls below the reaction threshold value. As the laser beam approaches unexposed material this sequence is repeated. The magnitude of the period is, therefore, a strong nonlinear function of the laser intensity, scan speed, and film thickness.<sup>5</sup> Periodic structure will develop only when the rate of heat release from



FIG. 1. Optical micrographs of gold features on quartz substrate from Engelhard bright gold NW screen ink as a function of laser power and scan speed. Precursor film thickness, after prebaking, is  $1.6 \,\mu$ m.

the chemical reaction is at least comparable to the rate of energy input from the laser. This energy relationship we refer to as a cooperativity phenomenon.

A comparison of the metal features shown in Fig. 1 demonstrates that as the writing speed is decreased, the lines become more uniform and periodic structure is suppressed. The rate of temperature increase at the forward edge of the irradiated region as the laser proceeds is slower at lower scan speeds. As a result, the energy release from the reaction occurs at lower temperatures. The rate of heat release, which is proportional to the rate of reaction, is therefore lower for slower scan speeds and the reaction is less likely to become self-propagating. At the other end of the scale, at sufficiently rapid scan speeds the laser should outdistance the propagating reaction front, in which case no periodic structure would be observed. On the basis of the thermal analysis data presented below, estimates show that the rate of energy deposition per unit area due to the heat of reaction can be comparable to the rate of energy deposition from the laser under certain experimental conditions.<sup>12</sup> It is in these cases where periodic structure is observed.

The observed self-propagation phenomenon can be understoood in terms of the composition and thermal chemistry of the precursor materials. The rate for a one-step thermal decomposition is given by  $k = A \exp(-E_a/RT)$ . The gold screen ink, however, is a mixture of gold (III) chloride reacted with sulfurized terpenes, resin binders, essential oils, and base metal brightening agents.<sup>13</sup> Differential scanning calorimetry and thermogravimetric analysis in air at heating



FIG. 2. Differential scanning calorimetry (top) and thermogravimetric analysis (bottom) of Engelhard Bright Gold NW screen ink (solid) and gold *p*-tert-butyl phenyl mercaptide (dashed) in air at heating rate of 10 °C/min.

rates of 5 °C/min, shown in Fig. 2, reveal that the gold component decomposes in two endothermic steps at 177-245 and 300–375 °C, with  $\Delta H$  values of 23 cal/g each. Gold ptert-butyl phenyl mercaptide, prepared as a model for the organogold component of the ink, decomposes similarly in two endothermic steps at 173-225 and 263-270 °C, with  $\Delta H$ values of 21 and 18 cal/g, respectively (Fig. 2, dashed line). Although the exact structure of the gold component of the ink is unknown, optical spectra and thermal analysis support its formulation as a gold (I) mercaptide. The ink decomposes further, at 375–455 °C, in an exothermic step ( $\Delta H = -679$ cal/g,  $E_A = 36.9$  kcal/mol) corresponding to pyrolysis of the remaining organic components of the ink. Thus, the overall heat of reaction is highly exothermic. At the rapid heating rates achieved in the laser direct-writing experiments the ink decomposes within a few microseconds of exposure and the three decomposition steps cannot be separated. Reaction rates of this order, namely,  $10^{6}$  s<sup>-1</sup>, require temperatures in excess of 1600 K, based on the above data and assuming Arrhenius-type behavior.

Preliminary Auger analysis indicates that the completeness of the decomposition and resulting carbon contamination in the gold are a strong function of the exposure parameters. The best features contain less than 10 at. % carbon and little, if any, oxygen or sulfur. It should be noted that the decomposition is accompanied by a tenfold decrease in the thickness of the exposed region as the ink ( $\rho = 2.1 \text{ g/cm}^3$ ) is transformed to gold ( $\rho = 19 \text{ g/cm}^3$ ), resulting in a varying vertical profile as a function of the extent of reaction. The feature typically reaches the limiting thickness for bulk density gold in the center, where the laser spot is focused and, therefore, the highest temperatures generated. Preliminary resistivity measurements of gold lines written between gold contact pads on quartz are ten times that of pure gold.

A report on  $CO_2$  laser irradiation of similar screen inks over much larger areas cites feature dimensions smaller than the laser spot size.<sup>14</sup> This is not surprising in view of the much larger volume of material adjacent to the irradiated



FIG. 3. Optical micrographs of gold features on quartz substrate from 1.0- $\mu$ m NH<sub>4</sub>AuCl<sub>4</sub>/poly (vinyl alcohol) film. a: 4.9 mW, 36  $\mu$ m/s; b: 20 mW, 206  $\mu$ m/s.



FIG. 4. Optical micrographs of gold features on quartz substrate from 5.0- $\mu$ m NH<sub>4</sub>AuCl<sub>4</sub>/nitrocellulose film. a: 15 mW, 36  $\mu$ m/s; b: 17 mW, 160  $\mu$ m/s.

region such that quenching of the heat of reaction occurs over a shorter lateral distance. An earlier report similarly deals with large area  $CO_2$  laser irradiation of copper formate-based pastes; however, no data are presented regarding the feature structure and dimensions.<sup>15</sup>

To demonstrate the effect of the heats of reaction on metal deposit geometry, thin films of poly (vinyl alcohol) and nitrocellulose containing ammonium tetrachloroaurate were irradiated. These systems exhibit strikingly different behavior, as shown in Figs. 3 and 4, respectively. Ammonium tetrachloroaurate decomposes endothermically in air at 230-350 °C ( $\Delta H = 96$  cal/g), undergoing a reduction from Au(III) to Au(0). Poly (vinyl alcohol) degrades slowly in air from 275 to 525 °C, whereas nitrocellulose ignites in air at 160 °C.16 The gold salt, in demonstrating the cooperativity phenomenon, also serves to record the thin-film reaction dynamics of the polymer decomposition. In the gold/poly (vinyl alcohol) film, the gold salt begins to decompose prior to pyrolysis of the polymer precluding the appearance of periodic structure under these experimental conditions. It should be noted, however, that in spite of the lack of periodic structure, wider gold features are produced in this system relative to those described above under comparable exposure conditions. In contrast, features in the gold/nitrocellulose film resemble explosive bursts under most conditions, propelled by the rapid rate of nitrocellulose oxidation. Even in such an exothermic system, however, it is possible to alter

the energy balance sufficiently, by decreasing the laser scan speed, to generate more uniform features. It should be noted that nitrocellulose is of interest as a self-developing photoresist in VLSI applications<sup>17</sup> and the gold features deposited during the polymer decomposition provide a method of studying the dynamics of the self-development process.

It has been demonstrated that a knowledge of the reaction exothermicity is an essential first step to understanding the dynamics of laser direct writing in organometallic films. The periodic structure observed in the resulting metal features varies greatly as a function of the balance between the rate of energy input from the laser, determined by the laser scan speed and intensity, and the sign and magnitude of the overall heat of reaction of the metallopolymer. In all the systems described herein the size of the metal features is considerably larger than the size of the laser-irradiated region. In order to achieve spatial confinement of micron-sized metal features, our work would indicate that precursors' heats of reaction should be thermally neutral or endothermic. Alternatively, longer exposure of the film at lower laser powers would serve to contain the reaction zone by slowing the rate at which the heat of reaction is generated. Work is under way to design transition metal/polymer systems from which a variety of metals may be deposited in a controlled fashion based on the above criteria.

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