# Diode laser-induced pyrolytic decomposition of spin-coated organometallic thin films

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## ABSTRACT

We have developed a compact and reliable diode laser-based system for the direct writing of metals from thin organometallic films deposited onto polyimide and $SiO_2$ substrates. This system uses an AlGaAs diode laser array, emitting at $\lambda = 796$ nm with a maximum power of 1 W.

A commercially available gold ink was spin-coated onto the substrate to form the precursor film. Direct writing was achieved by focusing the laser beam onto the film and by moving the substrate at speeds ranging from 10 to 15 000 µm/s. We deposited gold lines 2-12 µm wide onto $SiO_2$ and 13-17 µm wide onto polyimide; a thickness of 0.1 µm was evaluated by profilometry. Conductive deposits with resistivities of 30 µΩ·cm were obtained on polyimide with good reproducibility at high writing speeds. The selective electroless plating of copper was achieved onto the gold lines deposited on $SiO_2$. However, prior annealing was necessary to obtain reproducible plating.

Copper was also directly deposited from copper formate films. The formate was dissolved in water with glycerol and a commercial surfactant also added. Drops of the solution were deposited on the substrate and dried at 85 °C for 5 min. The pyrolysis of the resulting films produced deposits with thicknesses ranging from 2 to 5 µm and widths ranging from 10 to 35 µm.

## 1. INTRODUCTION

The laser-assisted deposition of metals offers interesting possibilities for mask and circuit repair and for the fabrication of interconnections in packaging applications. Laser-assisted chemical vapor deposition (LCVD) is already making its way into commercial applications[1]. The use of spin-coated organometallic films instead of a gas precursor would increase the appeal of laser-assisted repair by reducing the costs related to expensive vacuum and gas distribution systems. Furthermore, processing in air offers a certain advantage for the large substrates that are commonly found in the flat panel display industry and in LCD interconnection applications. The laser-assisted pyrolytic decomposition of thin organometallic films using $Ar^+$ [2-7], Nd:YAG[8,9] and excimer[10] lasers has been studied extensively for several metals such as Au[2,3,11], Pd[3,4,10], Ir[5] and Cu[5,9].

A compact and reliable diode laser-based system would make this simple process even more economical. Indeed, semiconductor lasers are small and competitively priced. They require no maintenance and are easy to operate. The potential use of such diode lasers for materials processing and device fabrication was first reported by Arjavalingam *et al* [11]. We have already developed such a diode laser-assisted direct writing system for the deposition of $WSi_x$ from a gas mixture of $WF_6$ and $SiH_4$[12].

Because of its low resistivity, copper is widely used in packaging applications. Gold is also considered for this industry's repair and customization needs[1]. In this paper, we present the development of a diode laser-based system for the local pyrolytic decomposition of thin Au and Cu organometallic films. Preliminary results on the electroless plating of copper onto the Au deposits is also reported.

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## 2. DIODE LASER-ASSISTED DIRECT WRITING SYSTEM

The direct writing system is schematically shown in Fig. 1. The light source consists of a continuous wave AlGaAs diode laser array (Spectra Diode Labs, SDL-2462-P1) emitting at $\lambda$ = 796 nm with a maximum power of 1W. The beam divergence is 10° by 40° in the two directions transverse to the propagation. The laser beam is collimated with a 0.5 numerical aperture (NA) objective and the ellipticity is reduced with a 4:1 anamorphic prism pair. The collimated beam is directed into a microscope and focused with a 50X (0.55 NA) objective. The efficiency of the optical system is 19 %, yielding up to 190 mW at the substrate. The dimensions of the elliptical laser spot have been measured using the scanning knife-edge technique. The smallest illuminated area was obtained when the two axis of the elliptic beam measured 2 and 15 µm, respectively, at 1/e of the intensity.

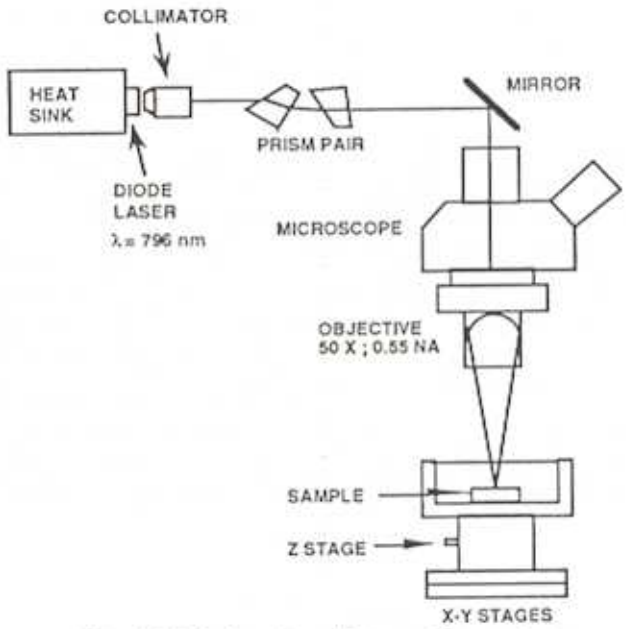


Fig. 1. Diode laser-based direct writing system

Once the substrate was covered with a thin precursor film, direct writing was achieved using computer-controlled XY stages (Aerotech Unidex 12) with a resolution of 0.1 µm. Lines were written at speeds ranging from 10 to 15 000 µm/s.

## 3. DIRECT WRITING OF GOLD

Gold lines were produced by the diode laser-assisted pyrolysis of thin organogold films. These films were deposited by diluting and spin-coating a commercially available ink (Engelhard Liquid Bright Gold NW) that contains 18% by weight of gold. This ink was reported to contain gold (I) mercaptides and various organic and inorganic additives[13].

### 3.1. Characterization of the precursor films

Thermogravimetric analysis performed in air on the undiluted ink showed reaction peaks at 175-260 °C and at 325-380 °C at a temperature ramp of 10 °C/min. Another peak was also observed at 380-450 °C. This last peak was not seen when the experiments were conducted in a nitrogen atmosphere. Our results are in good agreement with those of Gross *et al* [13]. They showed that the organogold component of the ink undergoes two endothermic reactions at 177-245 °C and at 300-375 °C. They also showed that the ink further decomposes at 375-455 °C in a highly exothermic reaction corresponding to the pyrolysis of the remaining organic components of the ink. The absence of this third reaction in an $N_2$ ambient indicates the necessity of oxygen for complete pyrolysis.

The precursor films were prepared by diluting 1 volume of ink in 1 volume of toluene, spin-coating the solution at 3000 rpm for 30 s. and drying at 120 °C for 30 min. After local pyrolysis, the unreacted material was easily removed with trichloroethane. This process produced organogold films ~ 1 µm thick on both $SiO_2$ and polyimide substrates

X-Ray photoelectron spectroscopy (XPS) was performed on unreacted films and on films heated at 475 °C in vacuum or in air for 1 hr. Polyimide was the substrate used for these experiments. The composition of the films was studied by recording the area of the $C_{1s}$, $O_{1s}$, $S_{2p}$, $Au_{4f}$ and $Bi_{4f}$ peaks after 5 min. of $Ar^+$ sputtering at a rate of 100 Å/min, calibrated on Al. These results are shown in Table 1. The C/Au ratio was 9.9 for the unreacted film; it decreased to only 3.7 for the film heated in vacuum but reached 0.3 for the film heated in air. However, since the sputtering yield is about 6 times greater for gold than for carbon[14], these C/Au ratios are probably an overestimation of the actual C content of the films. XPS analysis also revealed the presence of O, S and Bi. While S is part of the gold (I) mercaptide molecule, the presence of Bi was explained by the use of base metal resinates in the ink to promote the adhesion of the gold deposits. These results supported our previous conclusion: although the gold mercaptide component of the ink was partly reacted in vacuum, an absence of oxygen prevented the complete pyrolysis of the film and led to deposits containing high amount of C and S.

| | Unreacted film (at. %) | Pyrolysis in vacuum (at. %) | Pyrolysis in air (at. %) |
|---|---|---|---|
| Au | 7.9 | 20.6 | 73.2 |
| C | 78.5 | 75.3 | 22.4 |
| O | 8.3 | 1.3 | 0.8 |
| S | 5.3 | 2.7 | < 0.1 |
| Bi | < 0.1 | 0.1 | 3.6 |

Table 1. XPS analysis of unreacted precursor film, precursor film heated in vacuum at 475 °C for 1 h and precursor film heated in air at 475 °C for 1h. Films are spun onto polyimide substrates. $Ar^+$ sputtering of 500 Å (calibrated on Al) was performed on the films prior to the analysis.

3.2 Deposition of gold on $SiO_2$

Precursor films were deposited using the method described in section 3.1 on 7000 Å thick $SiO_2$ layers grown on Si by plasma enhanced chemical vapor deposition (PECVD). The diode laser-assisted pyrolysis of these films produced gold lines 2-10 µm wide (measured by optical microscopy) depending on laser power and writing speed (Fig. 2). The deposited lines had a thickness of 0.1 µm (measured by profilometry). No significant variation of thickness was observed, leading us to believe that the pyrolysis reaction occurred throughout the thin precursor film. Two-probe resistivity measurements showed that these gold lines were not conducting. This was explained with scanning electron microscopy (SEM) which revealed a highly granular structure and several discontinuities in the lines.

Auger electron spectroscopy (AES) showed significant C and S incorporation in the as-deposited lines. An incomplete pyrolysis of the precursor film due to an insufficient temperature rise during reaction is the most probable cause of their presence. However, because the unreacted precursor can be stripped in a trichloroethane bath without removing the as-deposited lines, it was possible to complete the pyrolysis of these deposits with an anneal in air at 475 °C for 1 hr. AES analysis of the annealed lines showed only carbon from atmospheric contamination: no C or S within the 1 % precision limit is recorded after 50 s of $Ar^+$ sputtering (sputter rate of 100 Å/min, calibrated on Si). The difference between this result and our XPS analysis of the precursor film heated in air is not surprising when considering the major differences between the two pyrolysis processes.

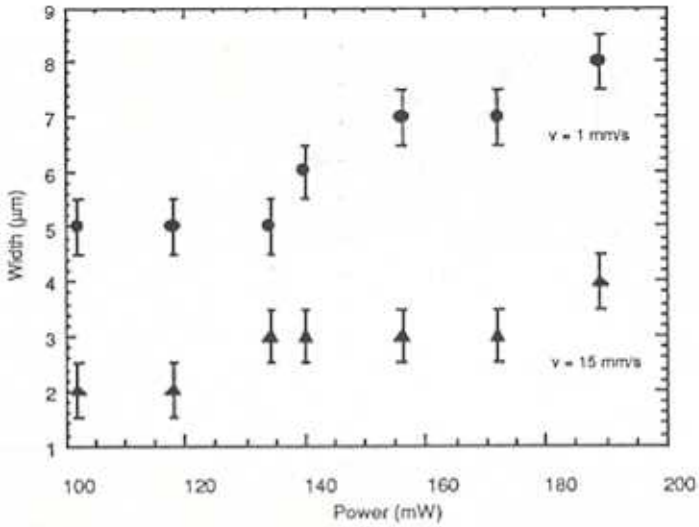


Fig. 2. Gold lines deposited onto $SiO_2$ by the diode-laser assisted pyrolysis of precursor films. Linewidth vs. laser power for two writing speeds (v). No thickness variation was observed with laser power or writing speed.

The electroless plating of copper on these gold deposits was investigated by dipping the substrates in a McDermid Metex 9027 bath for 5 min. at room temperature. For these experiments, lines were written using a 25 X (0.31 NA) focusing objective instead of the 50 X objective. No plating was observed on the as-deposited lines. The laser-assisted pyrolysis may have produced deposits that are insufficiently decomposed to activate the electroless reaction. When an anneal was performed on the deposits before the plating attempt, copper deposition was observed in all cases. We evaluated that a maximum thickness of 0.2 µm was deposited after 5 min. of plating. However, the poor morphology of the activation layer was not significantly improved by the process. Attempting to improve morphology with longer plating times decreased the adherence of the deposits.

3.3. Deposition of gold on polyimide

Diode laser-assisted direct writing of gold was also achieved on 5 µm thick DuPont PI-2611 polyimide (PI) films spin-coated on $Al_2O_3$. However, the process was found to be much more delicate on this substrate. Even though this polymer is known to withstand high temperatures, its chemical and dielectric properties will be permanently altered when exceeding 620 °C[15]. This gives a narrow process window when considering the temperature needed to achieve the pyrolysis of the gold containing film. For instance, while no gold deposition was achieved at a laser power under 30 mW for a writing speed of 1000 µm/s, pyrolysis of the underlying polyimide was observed for a power exceeding 40 mW. Furthermore, the process window was dependent of focusing and writing speed.

SEM revealed that lines 13-17 µm wide could be deposited on polyimide with minimal effects to the substrate (Fig. 3) when a laser power of 34-38 mW was used at writing speeds higher than 1 mm/s. Accurate thickness measurements were difficult using profilometry, due to partial embedding in the substrate. This embedding was due to a slight alteration of the polyimide surface around the deposited gold. However, profilometric analysis revealed that the precursor films had roughly the same thickness on $SiO_2$ as on PI. Assuming that the pyrolysis occurred again throughout the precursor film, a thickness of ~ 0.1 µm was evaluated for the gold deposited on PI.

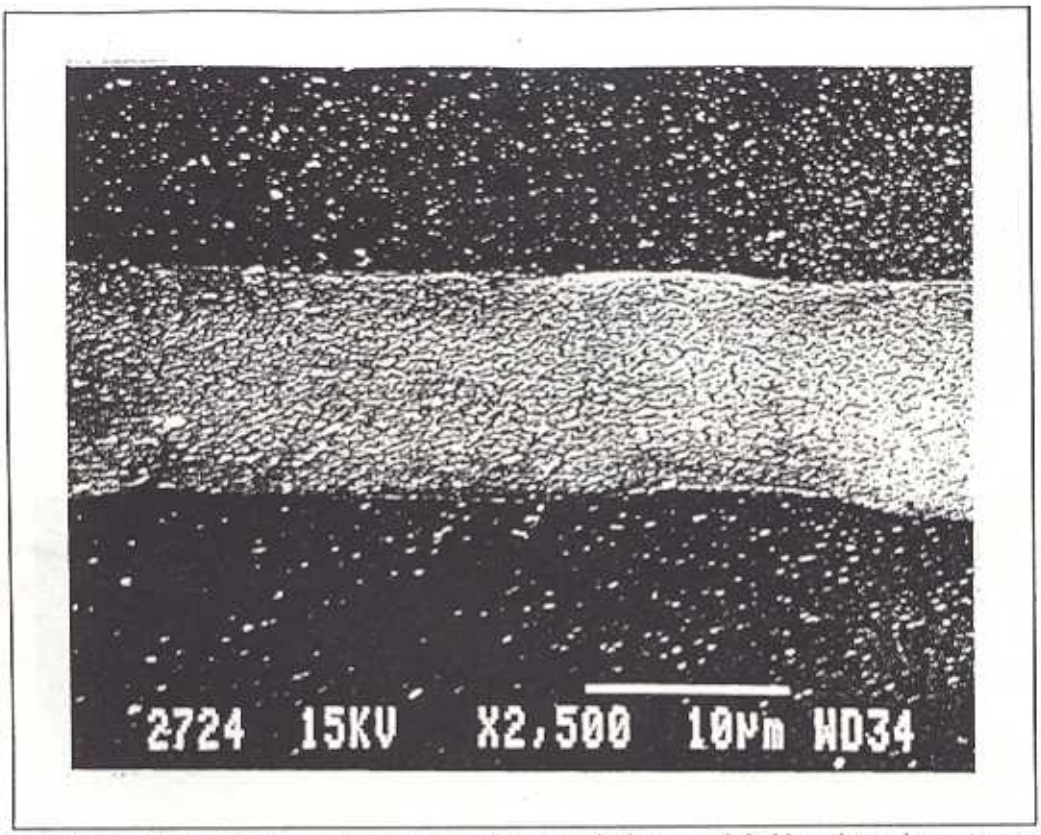


Fig. 3. SEM micrograph of a conducting gold line deposited onto polyimide using a laser power of 36 mW and a writing speed of 15 mm/s. The gold line smoothly follows the topology of the underlying substrate. Damage to the polyimide is minimal.

SEM observations also showed the presence of periodic structures in the lines. Similar structures were studied by Gross *et al.*[13] and were explained by considering the highly exothermic reactions occurring during the pyrolysis. The heat released by the pyrolysis pushes the reaction front ahead of the laser beam until the temperature rise is insufficient to pursue this propagation. The cycle will start again when the laser beam catches up with the unreacted film. A reaction front velocity of 30-50 cm/s was measured by Gross *et al.* using laser pump-probe experiments[16]. Scanning speeds higher than this reaction front velocity should prevent the formation of periodic structures. In Fig. 4 we can observe the evolution of the line morphology with the writing speed. As expected, the periodic structures fade out with increasing speed. These structures were found to affect the electrical properties of the lines. Indeed, two-probe measurements revealed a correlation between resistivity and writing speed. While lower speeds produced lines with several opens, conductive lines with a resistivity of 30 $\mu\Omega$·cm were obtained with good reproducibility using a writing speed of 15 000 µm/s .

The insulating properties of the polyimide caused severe charging problems and prevented a quantitative AES analysis. However, C and S were detected in the as-deposited lines, revealing again an incomplete pyrolysis.

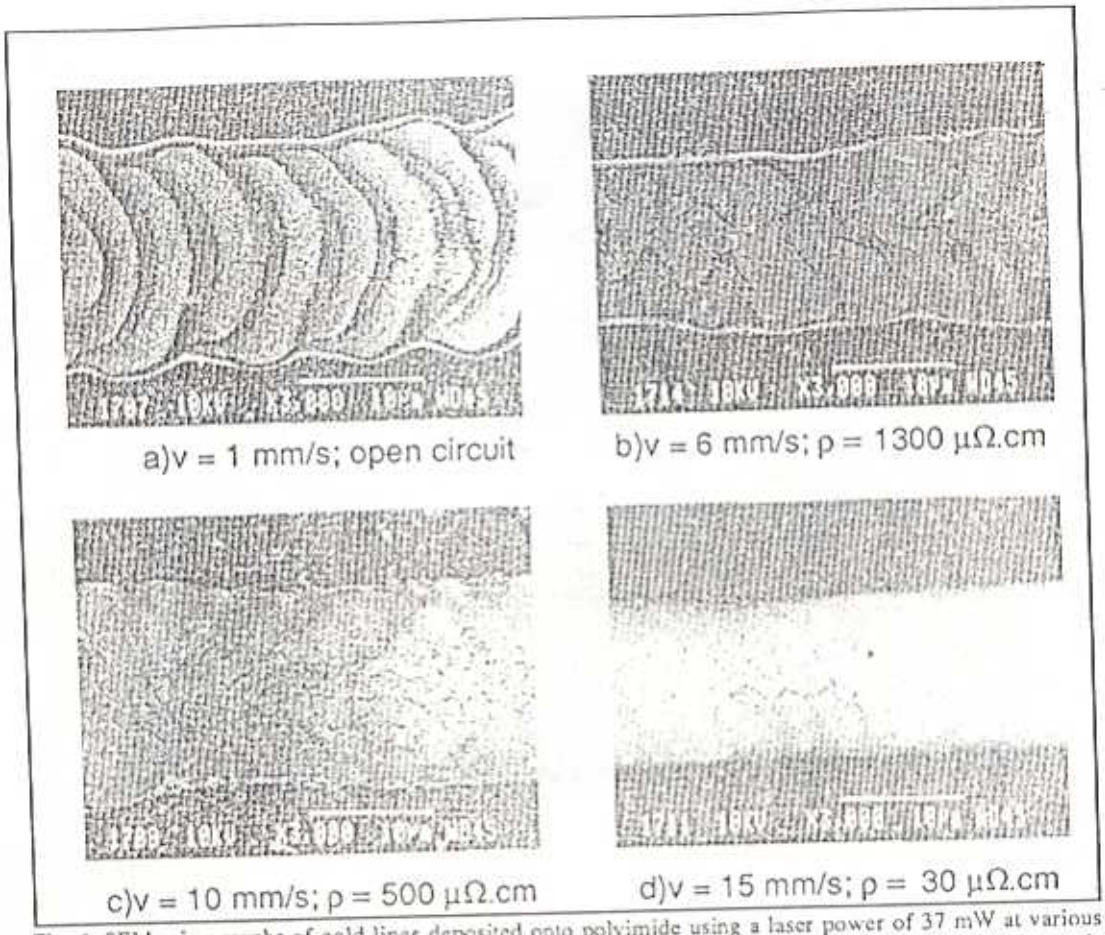


Fig. 4. SEM micrographs of gold lines deposited onto polyimide using a laser power of 37 mW at various writing speeds. Scanning direction is from left to right. The periodic structures fade out at higher speeds and the resistivity drops sharply.

## 4. DIODE LASER PROCESSING FOR COPPER DEPOSITION

For the direct writing of copper, a precursor solution was obtained by dissolving copper (I) formate hydrate in an appropriate solvent. Water would be preferred for its high polarity and capacity to dissolve a large amount of formate powder. However, high polarity implies higher surface tension, poorer wettability and causes problems for the reproducible deposition of precursor films. The addition of glycerol and of a commercial surfactant to the solution was reported to improve the morphology of the dried films and reduce the wettability problems[8]. Copper formate films were reported to decompose into copper at temperatures of 190-210 °C[7].

A solution of water, 1 % glycerol and 0.1 % Triton X-100, a commercially available surfactant was saturated with copper formate. Drops of the solution were deposited onto the PI/$Al_2O_3$ surface and dried at 85 °C for 5 min. Circular films with a diameter of ~ 1 cm were obtained. The center region of these films showed adequate uniformity over several square millimeters. The diode laser-assisted pyrolysis produced deposits 10-35 μm wide and 2-5 μm thick (Fig. 5) when laser powers of 25-50 mW were used at writing speeds of 10-100 μm/s. The thickness of the deposits varied with the initial thickness of the precursor film.

Other solvents are currently under investigation in an attempt to reach a compromise between wettability and copper formate solubility. These solvents include methanol, n-methyl pyrrolidone, formamide, ethylene glycol and chloroform.

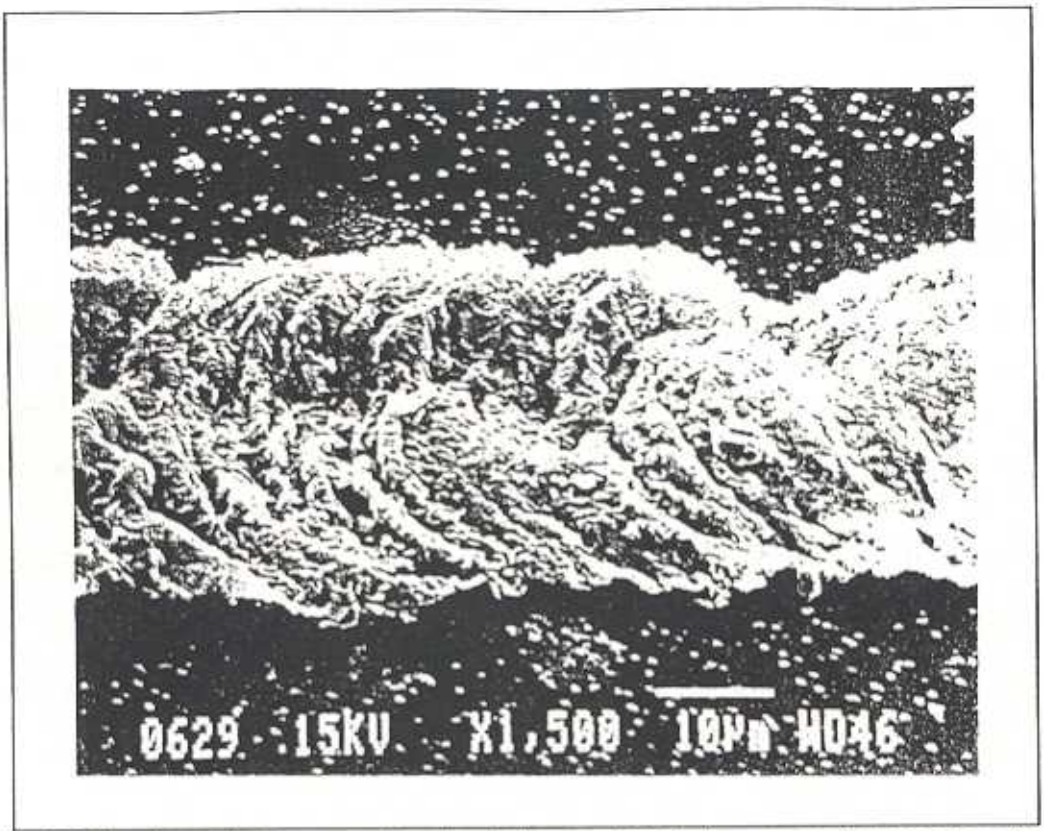


Fig. 5: SEM micrograph of a copper line deposited onto polyimide from copper formate using a laser power of 42 mW and a writing speed of 10 µm/s

## 5. CONCLUSION

Diode laser-assisted pyrolysis of organogold films produced deposits with poor morphology on $SiO_2$. The presence of C and S in the as-deposited lines indicated that the precursor film was only partially pyrolyzed. A post-deposition anneal completed the decomposition and permitted the electroless plating of copper. However, the plating of copper did not improve the morphology.

We observed a significant improvement of the morphology when we deposited gold onto PI. However, periodic structures and incomplete decomposition limited the conductivity of these lines. The first problem was solved using higher writing speeds. Conducting lines ($\rho$ = 30 µΩ·cm) were produced at 15 000 µm/s. A post-deposition annealing process is currently being studied to complete the pyrolysis on PI and obtain deposits with lower resistivities and sufficient decomposition to activate the electroless plating of copper.

Copper was also directly deposited from the pyrolysis of copper formate films. These films were deposited from an aqueous solution of the formate. Other solvents are currently being investigated to solve surface tension problems.

## 6. ACKNOWLEDGMENTS

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