

## Laser induced deposition of tungsten and copper<sup>1</sup>

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### Abstract

We present recent results obtained in our laboratory on the laser processing for deposition of tungsten and copper. Four processes are presented. (1) An Ar<sup>+</sup> laser or a diode laser are used in a direct writing mode to produce W and WSi, lines from WF<sub>6</sub> reduced by H<sub>2</sub> and/or SiH<sub>4</sub>, and deposited on silicon, TiN, SiO<sub>2</sub>, N<sub>2</sub> and polyimide. (2) Pure  $\alpha$ -W films were also deposited on GaAs by KrF excimer laser-induced deposition using a WF<sub>6</sub>:SiH<sub>4</sub>:H<sub>2</sub> gas mixture. (3) Very uniform, shiny metallic copper films, with Cu/C ratios up to 17 were deposited on TiN and fluoropolymer substrates by the KrF excimer laser-assisted decomposition of Cu(hfac)(TMVS). (4) Finally, we have studied the Ar<sup>+</sup> and diode laser direct writing of Pd and Au for the selective activation of the electroless plating of Cu.

*Keywords:* Copper; GaAs; In situ processing; Laser microsurgery; Laser processing; Microelectronics; Packaging; Silicon; Tungsten

### 1. Introduction

Metallization forms a key component on electronic circuits. Indeed, it controls device properties when used as an ohmic or Schottky contact as well as providing interconnections between the devices and the outside world or between the devices themselves [1]. Progress in microelectronic circuits and packaging requires the development of new metallization materials and fabrication techniques. For instance, as the miniaturization of devices and circuits for ULSI is pursued, the commonly used Al and Al-based alloys, which suffer from both electromigration and stress voiding problems, have to be replaced. Depending on the employment of the metals and device structures, W and Cu offer some clear advantages. Copper has a very low resistivity (1.67  $\mu\Omega$  cm), a high electromigration resistance and a high melting point. Tungsten is a low resistivity refractory metal ( $\rho_{\text{bulk}} = 5.6 \mu\Omega$  cm) which either can be used as a

thermally stable interconnect material or can form good Schottky contacts on GaAs.

While these metals can be deposited by various techniques, lasers can be used for selective area processing. Indeed, a laser beam directed onto a surface can be used to locally induce thin film deposition by either pyrolytic or photolytic chemical reactions in the gas phase or on the substrate [2]. In a pyrolytic laser chemical vapor deposition (LCVD) process, lasers are used as the heat source to induce a localized thermal reaction where the beam is focused on the substrate. The movement of the beam on the surface leads to the direct 'writing' of patterns. Micron size metallic lines having low resistivity may be written using visible lasers such as the Ar<sup>+</sup> laser. The applications of laser direct writing are in microsurgery and custom design for both integrated circuits and packaging. However, UV photons with sufficient energy may induce both pyrolytic and photolytic chemical reactions, either in the gas phase or on the surface. Projecting the UV photons from an excimer laser through a mask can lead to thin film deposition with high resolution patterns. This could therefore be compatible with in situ processing.

The objective of this paper is to give a general overview of the development of laser processing tech-

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Table 1  
Laser direct writing of  $WSi_x$  from  $WF_6$

| Laser                          | 488 nm $Ar^+$ (spot size 2 $\mu m$ ) |                   |         | 796 nm diode (spot size 12 $\mu m \times 93 \mu m$ ) |            |
|--------------------------------|--------------------------------------|-------------------|---------|--|------------|
| Substrate                      | Si or $SiO_2/N_x$                    | 0.3 $\mu m$ PI/Si |         | 100 nm TiN on 800 nm $SiO_2/Si$                      |            |
| Gases (sccm)                   |                                      |                   |         |  |            |
| $WF_6$                         | 1                                    | 1                 | 1       | 1  | 1          |
| $H_2$                          | 10                                   | 0                 | 50      | 0  | 0          |
| $SiH_4$                        | 0                                    | 3                 | 3       | 3  | 3          |
| Ar                             | 0                                    | 50                | 0       | 20–150   | 50         |
| Laser power (mW)               | 200–320                              | 80–180            | 140–170 | 30–160   | 200–600    |
| Laser speed ( $\mu m s^{-1}$ ) | 100                                  | 25                | 25      | 100  | 100        |
| Line thickness (nm)            | 200–500                              | 200–480           | 250–700 | 20–180   | 160–860    |
| Line width ( $\mu m$ )         | 3.0–4.2                              | 4–10              | 4–5     | 1.5–11   | 4–12       |
| Growth rate ( $\mu m s^{-1}$ ) | 10–25                                | 2.5–6.0           | 3.1–8.8 | 1.0–9.0  | 0.16–0.86  |
| Composition (W/Si)             | pure W                               | 1.4               | 1.4     | 1.5–1.8  | 1.5–1.8    |
| Resistivity ( $\mu\Omega cm$ ) | 13–25                                | 190–290           | 80–140  | 40–70  | 40–70      |
| Reference                      | [28,31]                              | [37,38]           | [37,38] | [35,36]  | [30,35,36] |

niques for the deposition of W and Cu performed at Ecole Polytechnique de Montréal. Processes covered are the following: (i)  $Ar^+$  and diode laser direct writing of  $WSi_x$  lines on TiN, polyimide and  $SiO_2/N_x$ ; (ii) excimer laser-induced deposition of W and GaAs; (iii) excimer laser-induced deposition of Cu on TiN,  $SiO_2$  and fluoropolymers and (iv)  $Ar^+$  and diode laser-assisted activation of the selective electroless plating of copper.

## 2. Laser induced deposition of W and $WF_6$

Laser induced deposition of W using  $W(CO)_6$  has been extensively studied [3–9] and growth rates were found to be relatively low. Furthermore, the resistivity of the deposits is usually high ( $\sim 200\rho_{bulk}$ ), due to C and O incorporation in the films. In contrast, the use of  $WF_6$  as the precursor usually leads to high purity thin films with low resistivity ( $\sim 2\rho_{bulk}$ ) at relatively high growth rates. Tungsten has been deposited from  $WF_6$  using various types of lasers [10–29]. Most of these studies relied on the reduction of  $WF_6$  by hydrogen, which occurs at relatively high temperatures ( $> 400^\circ C$ ), or by the silicon substrate, which is limited to very thin films [23]. Black and co-workers [25] have recently used silane ( $SiH_4$ ) to reduce  $WF_6$  for the laser deposition of W at temperatures as low as  $\sim 300^\circ C$ . This gas mixture permits one to deposit pure tungsten or tungsten silicide films at relatively low temperatures on thermally sensitive materials at high deposition rates. We have investigated a number of laser processes based on both  $WF_6/H_2$  and  $WF_6/SiH_4$  gas mixtures [27,28,30–38] and we present an overview of the process development of the  $Ar^+$  and diode laser direct writing on TiN, poly-

imide and  $SiO_2/N_x$ , as well as of excimer laser-induced deposition of W on GaAs.

### 2.1. Laser direct writing of $WSi_x$

The laser direct writing system has already been described in detail elsewhere [31,35–37]. Two lasers are available on this system. An  $Ar^+$  laser beam ( $\lambda = 488$  nm, 1.5 W) focused on the substrate to a  $\sim 2 \mu m$  diameter circular spot, using a  $25 \times$  (0.31 NA), long working distance objective, has been used. An AlGaAs diode laser array emitting at  $\lambda = 796$  nm with a maximum power of 1 W has also been used for its compactness and its reliability. The diode laser beam divergence is  $10^\circ$  by  $40^\circ$  in the two directions transverse to the propagation. The beam is first collimated using a 0.5 NA objective, and its ellipticity is reduced by a 4:1 anamorphic prism pair. The collimated and shaped beam is then focused on the substrate using the 0.31 NA objective, yielding an elliptic spot with axes of 12 and 93  $\mu m$ . The clean substrates were placed in a stainless steel reaction chamber closed by a fused silica window and mechanically pumped to a base pressure of  $10^{-2}$  to  $10^{-3}$  Torr. Direct writing was achieved by moving the reaction chamber using computer controlled translation stages having a lateral resolution of 0.1  $\mu m$ . Lines were written at speeds ranging from 2 to 100  $\mu m s^{-1}$  (the maximum velocity of the system) in the direction parallel to the long axis of the diode laser beam, or in any direction using the  $Ar^+$  laser [28,36].

Table 1 summarizes the experimental conditions and the most important results. Very uniform lines have been reproducibly deposited by the two types of lasers on silicon wafers, polyimide (PI) (Dupont PI-2611D), titanium nitride (TiN) and  $SiO_2/N_x$  thin films. The  $WF_6$

flow was fixed at 1 sccm and the reducing gases were  $H_2$  and/or  $SiH_4$ , depending of the substrate or the type of laser. For instance, the low temperature  $SiH_4$  reduction reaction is particularly attractive for the deposition of refractory metals and compounds on thermally sensitive substrates, like polyimide. We limited the  $SiH_4$  flow to 3 sccm to prevent any uncontrolled or explosive conditions. Argon was sometimes used as a buffer gas. The maximum laser power at the surface is limited by the onset of damage formation on the substrate at the speed mentioned in the table. Line thickness and width were measured by using profilometry and optical microscopy, respectively. Average growth rates were deduced using the spot dimension, the writing speed and the line thickness. The growth rates obtained with the diode laser were an order of magnitude smaller than those obtained with the  $Ar^+$  laser, due to the larger laser power densities in the latter case.

The compositions of the deposited lines were determined by Auger electron spectroscopy (AES). Our analysis indicated that no fluorine was incorporated in the bulk of the  $WSi_x$  films within the limits of detection (1 at.%). Aside from some surface contamination, which we attribute to atmospheric exposure between deposition and analysis, no carbon, nitrogen or oxygen was detected in the deposited film. When only  $H_2$  is used, pure W films are produced. For the  $WSi_x$  films, the W/Si ratio was estimated from Si KLL (1620 eV) and W MNN (1736 eV) Auger peak intensities. This ratio was about 1.4 for the lines deposited on polyimide and 1.5 to 1.8 for the lines deposited on TiN. No silicide peaks ( $WSi_2$  and  $W_3Si_5$ ) were detected using Raman spectroscopy, indicating that Si and W were present only in their elemental form in the bulk of the deposits. AES depth profiling measurements indicated, in all  $WSi_x$  films, a silicon depletion at the surface of the deposit over a few tens of nanometers. This tungsten-rich surface is directly related to the nature of the deposition process. According to Lo [39], many competing, temperature-dependent reactions occur between the gaseous species and the deposited material, even at room temperature. In laser direct writing, only a fraction of the substrate is heated at a given time. Room temperature reactions will continue at the surface, even after local deposition. Moreover, the silicon reduction of  $WF_6$  is thermodynamically favorable at and above room temperature, and it consumes silicon to produce tungsten [39]. However, this reaction is limited to a depth of a few tens of nanometers by the diffusion of the silicon atoms through the tungsten layer [23]. This explains the silicon depletion at the surface of the deposits.

The resistivity of the deposits was evaluated using the two-point probe method. The lengths of the lines were measured by optical microscopy, and the cross-sectional areas were determined by SEM. The lowest

resistivity of  $13 \mu\Omega \text{ cm}$  ( $\sim 2\rho_{\text{bulk}}$ ) is obtained when using an  $Ar^+$  laser and  $H_2$  as the reducing gas. Resistivities were approximately one order of magnitude higher when  $SiH_4$  was used, probably due to the presence of Si in the films. The difference in resistivities between the  $WSi_x$  lines deposited on PI and TiN may possibly be attributed to the slightly different Si content in the lines, as observed in thermal CVD from  $WF_6$  and  $SiH_4$  [40].

## 2.2. Excimer laser induced deposition of W on GaAs

The excimer laser direct projection patterning of W Schottky contact metallization on GaAs, to form MES-FETs with self-aligned gates in one step, could prove to be an advantageous process compared to the conventional sputtering, patterning and etching processes presently used in industrial production. This is especially so since GaAs has no stable native oxide and is a relatively fragile substrate [41]. Moreover, a CVD process is preferable to a physical vapor deposition process since it provides better conformal step coverage and less damage to the III-V substrates [42]. This issue has prompted many groups to study the deposition of W on GaAs using a CVD process with  $WF_6$  as the metal precursor gas [32,42–46].

We have developed a UHV system to deposit W from a mixture of  $WF_6$ ,  $SiH_4$ ,  $H_2$  and Ar using a KrF excimer laser incident perpendicularly on the substrate. This system has been described in detail elsewhere [32,47,48]. The laser used is an MPB AQX-150, emitting at 248 nm at a repetition rate up to 60 Hz with a pulse width of 30 ns. The substrates used were  $1 \text{ cm}^2$  samples of (100) oriented undoped and Si-doped ( $10^{17} \text{ cm}^{-3}$ ) liquid encapsulated Czochralski GaAs wafers. They were degreased, dipped in a hot 1:1 HCl: $H_2O$  solution and dried in flowing nitrogen before being introduced into the deposition chamber. We used  $SiH_4$  to lower the required deposition temperature on the thermally sensitive GaAs substrates. Typical operating pressures were of the order of 14 Torr for a mixture of  $WF_6$ ,  $SiH_4$ ,  $H_2$  and Ar gases having flows of 1, 3, 50 and 140 sccm respectively. The Ar flow was used mainly to purge the window to avoid any W deposition on it. A load lock was used to introduce the samples into the chamber and no deposition was attempted before obtaining a base pressure lower than  $5 \times 10^{-6}$  Torr.

Smooth and uniform metallic tungsten was deposited on GaAs at laser fluences between 25 and  $35 \text{ mJ cm}^{-2}$ . No deposition was detected at laser power densities of  $19 \text{ mJ cm}^{-2}$  or less, even after one hour of laser exposure at a repetition rate of 60 Hz. At  $25 \text{ mJ cm}^{-2}$ , we obtained  $0.4 \mu\text{m}$  W films after 340 s at 30 Hz. It is difficult to evaluate the exact deposition rate since we have noted an incubation time, typically 100 s, before

observing the shiny tungsten surface on the samples. On the average, we estimate a deposition rate of  $\sim 1 \text{ nm s}^{-1}$  at 30 Hz with a pulse energy density of  $25 \text{ mJ cm}^{-2}$ . At energy densities  $> 35 \text{ mJ cm}^{-2}$  and a pulse repetition rate of 30 Hz, deposition of W was also detected but the films would usually delaminate very quickly (typically after 1 min) after the onset of the growth, suggesting that the deposited films are under high stress.

AES profiling indicates that almost no As or Ga interdiffusion is detected in the deposit. This is particularly striking when compared to W deposits obtained using  $\text{WF}_6$  and a cw  $\text{Ar}^+$  laser [46]. This is probably because of the very brief heating of the substrate during the 30 ns laser pulse width, which greatly reduced the time during which diffusion of As or Ga into the W layers might take place. Moreover, the substrate stoichiometry was preserved, meaning that very little, if any, degradation of the semiconductor had taken place. In addition, no impurities (such as F, C, O) were detected above the noise level ( $< 1 \text{ at.}\%$ ) in the metal film. Compared to the composition of the films obtained by laser direct writing, the absence of Si was noticeable, suggesting that the  $\text{SiH}_4$  reduction of  $\text{WF}_6$  is complete. This could be explained by the same mechanism which leads to Si surface depletion in the  $\text{Ar}^+$  and diode laser deposited films. Indeed, since the surface cools down during the 30 ms time between two consecutive 30 ns pulses, reaction between  $\text{WF}_6$  and the Si on the surface could produce silicon based volatile compounds, depleting the Si. Therefore, using a pulsed laser in this process presents the advantage of producing pure W.

The crystalline structure of the deposited W was investigated by X-ray diffraction (XRD) and our spectra showed that the pure and stable  $\alpha$ -W was formed. Very little  $\beta$ -W was detected and could probably be eliminated by a post-deposition anneal [43]. The  $\beta$ -W is a metastable phase which can be stabilized by the incorporation of C, F, or O in the deposits [44]. The formation of  $\alpha$ -W is a unique characteristic of this process since at low processing temperatures, granular  $\beta$ -W is usually deposited with a resistivity  $> 100\rho_{\text{bulk}}$  [49]. Preliminary resistivity measurements on the samples, using a 4 point probe, yield resistivity values of  $20 \mu\Omega \text{ cm}$  ( $\sim 4\rho_{\text{bulk}}$ ), which is as expected for low resistivity thin  $\alpha$ -W films.

### 3. Excimer laser-induced deposition of copper

Chemical vapor deposition (CVD) using Cu(I) organometallic precursors has achieved good results, permitting the deposition of thin copper films having near-bulk resistivities [50]. Since Cu is difficult to pattern for ULSI with submicron resolution, a technique

which deposits copper in a selective manner, without any dependence on surface quality, would be quite attractive. Laser-induced CVD is one such technique, where the desired interconnect pattern can be projected on the surface with the appropriate mask and lenses (projection patterning) [51] or written by moving the sample under the focused laser beam (direct writing) [52]. The laser direct writing of Cu, using an  $\text{Ar}^+$  laser, has recently been demonstrated by Han et al. [53] but such a process, even if appropriate for circuit repair, is too slow for circuit production. Furthermore, submicron resolution is difficult to achieve with this technique and excimer laser is a more appropriate tool for obtaining high resolution patterning. We have performed the excimer laser-induced CVD of copper using Copper<sup>1</sup> (hexafluoroacetylacetonate) (trimethylvinylsilane) ( $\text{Cu}(\text{hfac})(\text{TMVS})$ ), and we detail here the deposition and characterization of unpatterned Cu films.

The system for the laser-assisted deposition of copper has been described elsewhere [54–56] and is similar to the one described in Section 2.2, except for the gas distribution system. Since  $\text{Cu}(\text{hfac})(\text{TMVS})$  is a liquid at room temperature, it was placed in a bubbler and heated to  $45^\circ\text{C}$ , giving a vapor pressure of about 0.5 Torr. The rest of the tubing, as well as the reactor, was heated to  $60^\circ\text{C}$  to avoid condensation of the precursor. The substrate temperature could be varied from room temperature to  $200^\circ\text{C}$ , but was always kept below  $120^\circ\text{C}$  during the experiments to avoid thermal deposition. The precursor was carried to the deposition chamber by a flow of  $\text{H}_2$  (20–100 sccm). To avoid any deposition on the window, it was purged with an Ar flow (20 sccm) before and during laser exposure.

Cu was deposited on (80 nm)TiN/Si, and on Teflon<sup>®</sup> PFA fluoropolymer samples with thicknesses of 125 and 250  $\mu\text{m}$ . TiN was used because of its good barrier properties, preventing copper diffusion into Si. Fluoropolymers were used as they are expected to be the low  $\kappa$  dielectrics used in future microelectronic devices. Prior to the deposition, samples were degreased and dried at  $115^\circ\text{C}$  for 30 min. The reaction chamber was evacuated to a base pressure of  $10^{-7}$  Torr. The deposition was carried out at a laser repetition rate of 20 Hz. The KrF excimer laser beam was unfocused, giving energy densities at the substrate ranging from 9 to  $31 \text{ mJ cm}^{-2}$ .

Typical film thicknesses, as measured by profilometry, ranged from 0.1 to 0.5  $\mu\text{m}$  for films deposited with a few thousand laser pulses. This corresponds to growth rates changing from 0.1 to 0.5  $\text{\AA}$  per pulse (2 to  $10 \text{ \AA s}^{-1}$ ). Films grown under various conditions on TiN or fluoropolymer samples appeared as shiny copper mirrors surrounded by a dark, narrow halo. Some of the deposits had regions with matte appearances and sometimes, the entire surface had a matte appearance. In the shiny copper region, the surface was very uniform and

grain size, measured by SEM and AFM, was between 50 and 100 nm. In the matte regions, the surface was much rougher and the grains were larger ( $> 200$  nm). Cu films deposited on either substrate passed the adhesive tape test, but showed some slight removal of the rough grain regions. Thin deposits (less than 50 nm) were invariably shiny, but became matte as thickness increased. We verified on the transparent PFA that all the deposits presented a shiny appearance at the Cu/PFA interface when viewed through the substrate, even the thicker films which are matte at the outer surface. This indicates that two different growth regimes take place, which may perhaps be related to the changes in the optical absorption and the thermal diffusion that occur as the film grows.

Performing an XPS analysis on samples unexposed to air, we found that the binding energy position of the main Cu  $2p_{3/2}$  peak is at 932.6 eV and its width is narrow. This is indicative of metallic copper and we therefore conclude that complete reduction of Cu(hfac)(TMVS) was achieved. No silicon was detected, indicating the absence of TMVS at the surface, probably due to a rapid dissociative desorption of this ligand [57]. Large quantities of carbon, oxygen and fluorine, in several chemical states (e.g.,  $CF_x$ , CO and C), were detected at the surface. However, after cleaning the samples with 2 keV  $Ar^+$  ions, it was found that most of the impurities were removed. For the films deposited on TiN substrates, oxygen was no longer detected, while carbon was substantially reduced and only traces of fluorine could be seen. A Cu concentration of 95 at.%, as measured by XPS, was achieved for substrate temperatures of 100 to 120°C, using a hydrogen flow of 100 sccm and a laser energy density of 20 mJ cm<sup>-2</sup>. For films deposited on the fluoropolymer samples, the F concentration was always greater, even after ion cleaning. AES profiles of a film deposited on a fluoropolymer sample showed that F is present throughout the film. This is due to the laser induced reaction between the depositing Cu and the fluoropolymer substrate, producing low molecular weight fluorinated species which are trapped during the Cu deposition. The maximum Cu content obtained on films deposited on fluoropolymer samples was 80 at.%, using the same deposition parameters used for the deposition on TiN. As hydrogen can not be detected by XPS, elastic recoil detection (ERD) measurements were performed on some samples. Hydrogen, possibly bonded to carbon, was detected at a relative concentration of 7 at.% in films deposited at 60°C on TiN.

Preliminary four-point and two-point probe resistivity measurements were performed on the samples and a minimum resistivity of 41  $\mu\Omega$  cm ( $\sim 25\rho_{bulk}$ ) was obtained. Good conductive contacts were hard to establish and our results probably include high contact resistance effects. However, the possibility of increased

resistivity due to poor morphology or contaminant accumulation at the grain boundary cannot presently be ruled out.

#### 4. Laser-assisted activation of the selective electroless plating of copper

Laser-assisted chemical vapor deposition is also an attractive technique for integrated circuit metallization and for the repair and customization needs of the packaging industry [58]. However, while the high-purity of vacuum processes will definitely be worthwhile for future ULSI applications, the packaging industry could benefit from cutting costs related to vacuum and gas distribution systems. Organometallic films avoid the inherent complexity of gaseous precursors. Several authors have reported the decomposition of Au, Cu and Pd organometallic films [59–66] using  $Ar^+$  laser [59–64], Nd:YAG [65] and a diode laser [66]. However, since it can be difficult to directly produce, from such films, sufficiently thick low resistivity metallic conductors with acceptable morphology, a subsequent step of Cu electroless plating can be used [64,65].


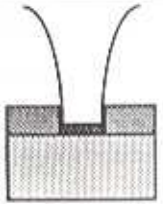
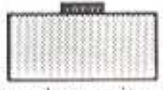

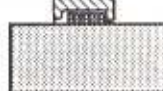
Table 2 summarizes our results for each of the processing steps [67–70]. Solid Pd and Au-containing organometallic films were prepared from commercial solutions on 5  $\mu$ m thick layer of polyimide, a widely used dielectric in packaging applications, and on 0.5  $\mu$ m thick silicon oxynitride. We used the same optical setup described in Section 2.1 to selectively decompose these precursor films by the focused beam of either a  $Ar^+$  laser or a diode laser. After removal of the unreacted precursor in acetone for Pd and trichloroethane for Au, the metallic deposits were dipped into the electroless plating bath. Some deposits needed prior annealing in order to successfully activate the plating.

The  $Ar^+$  laser-induced pyrolysis of Pd-containing organometallic films yielded metallic palladium on polyimide [67]. However, the substrate was affected by the laser, as the Pd deposit was found to be embedded into the polyimide. Although the Pd lines showed a high bulk concentration of carbon ( $[C]/[Pd] = 1.8$ , measured by XPS), the selective plating of copper with a resistivity of 7  $\mu\Omega$  cm ( $\sim 4\rho_{bulk}$ ) was obtained with great reproducibility without the need of a prior annealing.

The pyrolysis of gold-containing film was also performed on  $SiO_xN_x$  with the same laser setup. Unfortunately, the as-deposited gold could not successfully activate the plating. However, a simple and not optimized anneal in air (475°C during 30 min) was used to improve the purity of the deposit to a sufficient level for the plating of copper.

The diode laser-assisted pyrolysis of the Au-containing films was also studied [68–70]. The laser successfully decomposed 80 to 90% of the gold (I) mercapti-

Table 2  
Diode and Ar<sup>+</sup> laser induced pyrolysis of Au and Pd organometallic films for Cu electroless plating

| Step \ Laser  | Ar <sup>+</sup> Laser<br>$\lambda = 488 \text{ nm}$<br>spot size: $2 \mu\text{m}$ |  | Diode Laser<br>$\lambda = 796 \text{ nm}$<br>spot size: $2 \mu\text{m} \times 15 \mu\text{m}$ |   |
|---|---|--|---|---|
| <br>Precursor film           | Pd<br>Engelhard<br>A-2988<br>Resinate   | Au<br>Engelhard<br>Bright<br>Gold NW   | Pd<br>Engelhard<br>A-2988<br>Resinate   | Au<br>Engelhard<br>Bright<br>Gold NW  |
| Substrate   | Polyimide/Si  | SiO <sub>x</sub> N <sub>y</sub>  | Polyimide/Si  | Polyimide/Si  |
| <br>Pyrolysis                | $P_1 = 10 \text{ mW}$<br>$v = 0.025\text{--}0.5 \text{ mm/s}$<br>PI affected      | $P_1 = 15 \text{ mW}$<br>$v = 0.001\text{--}0.1 \text{ mm/s}$<br>PI affected | Pyrolysis not possible  | $P_1 = 30\text{--}40 \text{ mW}$<br>$v = 0.025\text{--}0.5 \text{ mm/s}$<br>PI affected |
| <br>As-deposited metal       | Pd <sup>0</sup> +C  | $\rho = 30 \mu\Omega \cdot \text{cm}$  |   | Au <sup>0</sup> +Au <sup>1</sup> +C<br>$\rho = 30 \mu\Omega \cdot \text{cm}$            |
| <br>Anneal                 | Not necessary   | Necessary, but was not optimized   |   | 300 °C, 10 min  |
| <br>Electroless Cu plating | $\rho = 7 \mu\Omega \cdot \text{cm}$  | Plating observed   |   | $\rho = 8 \mu\Omega \cdot \text{cm}$  |

to the metallic Au<sup>0</sup> state with no apparent damage to the underlying polyimide. The deposits showed fair amounts of carbon (20–30 at.%) and sulfur (10–15 at.%) and once again required annealing at 300°C for 10 min in order to activate the plating of copper. Since this problem also occurred after an Ar<sup>+</sup> laser-assisted pyrolysis, we believe that it is inherent to the precursor itself, not to the choice of the laser. The obvious solution would be to use the Pd-containing films instead of the Au-containing ones. Unfortunately, due to optical considerations, the diode-laser based system could not induce the pyrolysis of the previously described Pd-films. Other Pd precursors such as Pd acetate could be studied for this application.

## 5. Conclusion

Laser CVD from WF<sub>6</sub> and H<sub>2</sub> and/or SiH<sub>4</sub> gave reproducible and high quality W or WSi<sub>x</sub> deposits on various substrates such as SiO<sub>x</sub>N<sub>y</sub>, polyimide, TiN and GaAs. When only H<sub>2</sub> was used, pure W lines with resistivities of  $\sim 13 \mu\Omega \text{ cm}$  were produced by an Ar<sup>+</sup> laser. Using SiH<sub>4</sub> as the reducing gas provoked a low temperature process that could be used on materials with a limited thermal budget, and enabled us to make deposits on fragile substrates such as polyimide and GaAs, or to use a low power density diode laser. WSi<sub>x</sub> lines were deposited by laser direct writing on polyimide and TiN with resistivities of 40–80  $\mu\Omega \text{ cm}$  and W/Si ratios of 1.4–1.8. Excimer laser-induced deposi-

tion on GaAs produced pure  $\alpha$ -W with a resistivity of 20  $\mu\Omega$  cm.

Metallic copper with Cu/C ratios up to 17 was deposited on TiN and fluoropolymer by excimer laser-induced CVD, using Cu(hfac)(TMVS) as the precursor. Although this is still not industrially acceptable for ULSI interconnect applications, the optimization of the deposition parameters is far from complete. Metallic copper with resistivities of 7–8  $\mu\Omega$  cm was also deposited by electroless plating on Au or Pd activation layers produced by Ar<sup>+</sup> or diode laser direct writing on organometallic films.

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