Laser direct writing of tungsten from WF_6

M. Meunier, R. Izquierdo, P. Desjardins, M. Tabbal, A. Lecours and A. Yelon
Groupe des Couches Minces and Département de Génie Physique, École Polytechnique de Montréal, C.P. 6079, Station A, Montréal, Que H3C 3A7 (Canada)

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Abstract

We present recent results on the development of laser direct writing of tungsten from WF_6 on silicon oxynitride (SiO_xN_y), titanium nitride (TiN) and gallium arsenide (GaAs). Ar^+ laser processing from WF_6 and H_2 on SiO_xN_y produces low resistivity (13 μΩ cm) pure tungsten lines having widths as low as 2.5 μm. Deposition on GaAs using the Ar^+ laser occurs in a very narrow process window and is found to be irreproducible. Surface analysis suggests that a spontaneous reaction between WF_6 and GaAs, producing GaF_3, takes place. This reaction may poison the initiation of the deposition. Finally, in order to develop a compact and inexpensive laser direct writing system, we have also investigated the use of a diode laser as the heat source. Diode laser processing from WF_6 and SiH_4 on TiN yields WSi_x ($x = 0.7$–0.9) lines having widths as low as 4 μm.

1. Introduction

The interest in laser direct writing of conductive materials for circuit microsurgery and custom design in very-large-scale integration applications has increased in recent years [1–4]. Pyrolytic laser chemical vapour deposition (LCVD) uses a laser as a heat source, leading to a localized thermal process where the laser beam is focused on a substrate. Tungsten is particularly interesting as an interconnect material because it is a low resistivity refractory metal. The LCVD of tungsten from $W(CO)_6$ has been extensively studied [5–11], but the tungsten line resistivity is usually high, owing to carbon incorporation in the film. The use of WF_6 as the precursor does not present this problem and usually leads to good quality films. Tungsten has been deposited from WF_6 using excimer [12–14], CO_2 [15, 16] and ion (Ar^+ and Kr^+) [1–4, 17–23] lasers. In most cases, the reducing agent is H_2 while, very recently, SiH_4 has been used to lower the processing temperature [21].

While most previous investigations have been carried out using silicon or employing silicon covered with a native oxide layer of a few ångströms [17, 19], processing in silicon and gallium arsenide (GaAs) microelectronics involves metallic deposition on many other types of substrate. For example, circuit repair or modification requires metallic lines to be deposited over a much thicker (greater than 0.5 μm) passivating layer. Titanium nitride (TiN) is frequently used as an adhesion layer for tungsten metallization on SiO_2 [24, 25] and is an excellent barrier layer [26]. Finally, tungsten is known to form a good Schottky contact on GaAs [27, 28].

In this paper, we present our recent results on the development of laser direct writing of tungsten from WF_6 onto several substrates of interest for silicon and GaAs microelectronics which have not previously been investigated: silicon oxynitride (SiO_xN_y), TiN and GaAs.

Of the various types of laser used in the LCVD of tungsten from WF_6, we chose the Ar^+ laser as the heat source. In addition, as the output characteristics, power and wavelength of diode lasers have improved in the last few years [29, 30], we also investigated the use of a diode laser array for the deposition of tungsten and tungsten silicides from a mixture of WF_6, SiH_4, H_2 and argon for a compact and inexpensive laser direct writing system.

The laser direct writing system is presented in Section 2. Processes using the Ar^+ laser and the diode laser are then discussed in the subsequent two sections. While it is found that Ar^+ deposition of tungsten from WF_6 and H_2 onto SiO_xN_y produces low resistivity (13 μΩ cm) pure tungsten lines having widths as low as 2.5 μm, the deposition on GaAs occurs in a very narrow process window and is not reproducible, probably because of a spontaneous reaction of WF_6 with GaAs, producing GaF_3 which may poison the initiation of the deposition. Diode laser processing from WF_6 and SiH_4 on TiN yields WSi_x lines, with $x = 0.7$–0.9, having widths as low as 4 μm.

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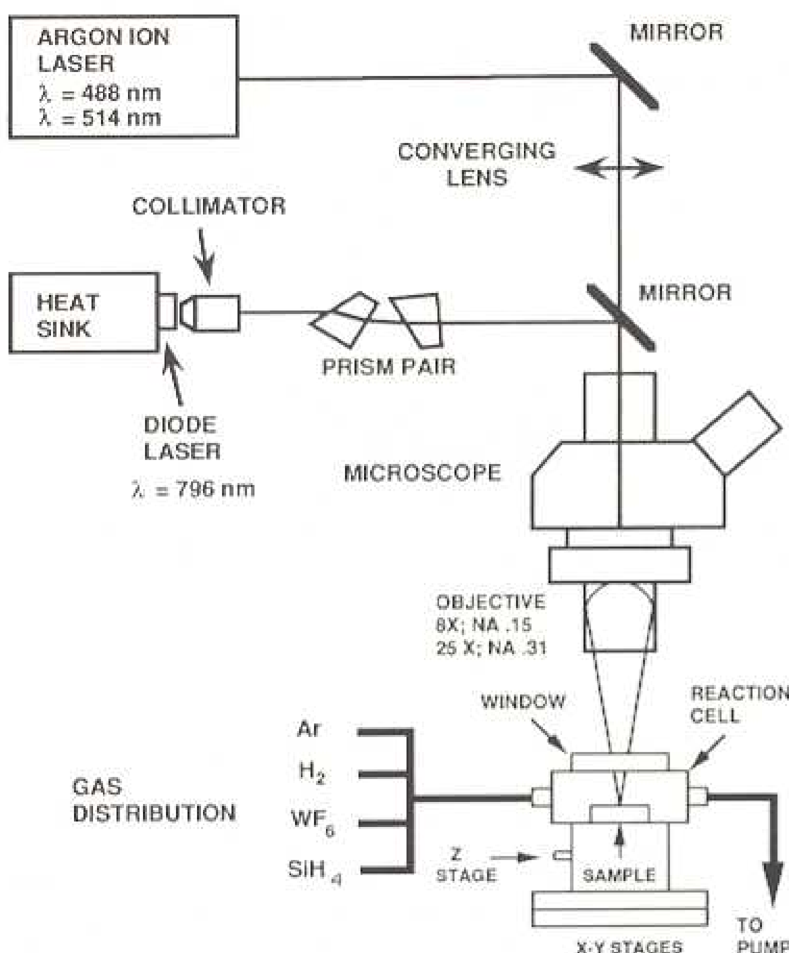

Fig. 1. Schematic diagram of the system for laser direct writing of tungsten from WF_6 using either an Ar^+ laser or a diode laser.

2. Laser direct writing system

The system shown schematically in Fig. 1 consists of a continuous-wave (CW) laser beam focused onto a substrate using long-working-distance microscope objectives with numerical apertures (NAs) of 0.15 or 0.31, depending upon the application. The 5 W Ar^+ laser operates at either the 488 nm line or the 514 nm line. For example, the maximum power at the substrate available using the 514 nm line is 1.3 W. The spot size at e^{-2} in intensity, measured by the scanning knife-edge technique [31], is 3.7 μm when a 0.15 NA objective is used.

In order to develop a compact and inexpensive system, we investigated the use of a diode laser as the heat source. We used a CW $Ga_{1-x}Al_xAs$ diode laser array, emitting at $\lambda = 796$ nm, with a maximum power of 1 W. The beam divergence is 10° (parallel) and 40° (perpendicular) in the two directions transverse to the propagation. The laser beam is collimated with a 0.5 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 25 × (0.31 NA) long-working-distance objective. The efficiency of the optical system is 55%, yielding up to 550 mW at the substrate.

The substrates investigated were (i) silicon oxynitride (SiO_xN_y) 0.6 μm thick deposited by plasma chemical vapour deposition on crystalline silicon (c-Si), with a composition, measured by X-ray photoelectron spectroscopy (XPS), of 30 at.% Si, 65 at.% O and 5 at.% N, (ii) 100 nm of reactively sputtered TiN on 800 nm SiO_2 on c-Si(100), and (iii) liquid-encapsulated Czochralski semi-insulating GaAs. All samples were cleaned in hot trichloroethane, acetone and propanol and rinsed in deionized water. While the SiO_xN_y and TiN samples were then heated to 120 °C for 20–30 min to remove humidity from the IR surface, the GaAs samples were etched in H_3PO_4–H_2O_2–H_2O ($[H_3PO_4]:[H_2O_2]:[H_2O] = 1:1:10$) for 5 s, next rinsed in hot HCl–H_2O ($[HCl]:[H_2O] = 1:1$) for 5 min and in deionized water and then dried in flowing nitrogen.

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}–10^{-3} Torr. The cell was then heated to 80 °C and purged with an argon flow of 100 standard $cm^3 min^{-1}$ for 1 h. Substrates were at room temperature during deposition. Line formation was achieved by moving the reaction chamber, using computer-controlled x–y stages, having 0.1 μm spatial resolution and a maximum velocity of 100 μm s^{-1}. WF_6, H_2 and SiH_4 were used as reactive gases and argon as a buffer gas. The system was used in a static mode, in which the reaction cell is filled to the desired pressure and gas ratio before processing, or in a dynamic mode in which the different gases are kept flowing at an established ratio of flow rates.

3. Ar^+ laser processing

3.1. Processing on SiO_xN_y/Si

LCVD of tungsten is a pyrolytic process in which the deposition takes place when the gas in the reaction chamber is thermally decomposed at the surface of the sample. Since SiO_xN_y is transparent to the wavelength used (488 nm), its surface is heated only as a result of the heat generated by laser light absorption by the silicon substrate. Deposition depends upon the temperature profile at the surface. The characteristics of the deposit also depend upon the reaction kinetics and upon the mass transport to the reaction zone. As a result, the film profile and morphology will be influenced by the power density, writing speed, and gas composition and pressure.

Figure 2 shows the variation of linewidth w and thickness t as a function of incident power P, for the 0.31 NA objective. For all these deposits, we used the maximum available writing speed v_s of 100 μm s^{-1}, and 100 Torr total pressure, with flows f of 1 standard $cm^3 min^{-1}$ for WF_6 and 10 standard $cm^3 min^{-1}$ for H_2.

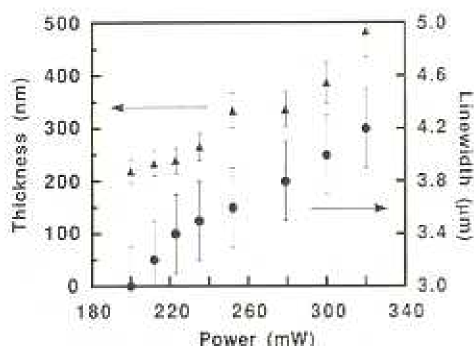

Fig. 2. Line thickness and width of tungsten deposited on SiO_xN_y as a function of laser power (total pressure, 100 Torr; $f(WF_6)$ = 1 standard $cm^3 min^{-1}$; $f(H_2)$ = 100 standard $cm^3 min^{-1}$; v_s = 100 μm s^{-1}; NA, 0.31).

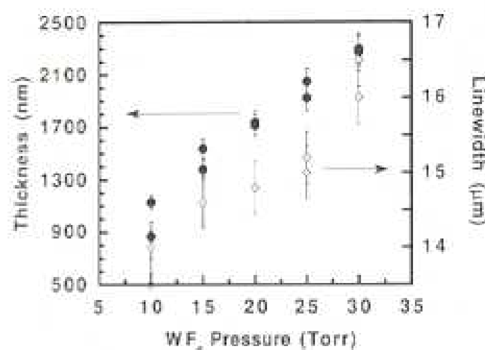

Fig. 3. Line thickness and width of tungsten deposited on SiO_xN_y as a function of WF_6 partial pressure ($P(H_2)$ = 100 Torr; laser power, 0.5 W; v_s = 100 μm s^{-1}; NA, 0.15).

Note that no deposit occurs below a threshold power and that the minimum linewidth in these conditions is 3 μm. Both w and t increase with increasing P, owing to the height and width increase of the temperature profile with increasing laser power. This is what we expect if surface reactions control the growth [32]. The minimum linewidth is particularly important for microsurgery applications. The narrowest lines of 2.5 μm have been achieved in a static reactor with $P(WF_6)$ = 10 Torr and $P(H_2)$ = 100 Torr, all the other conditions being the same as in Fig. 2.

Figure 3 shows w and t variations as a function of the WF_6 partial pressure $P(WF_6)$ when $P(H_2)$, v_s and P are kept constant in a static reactor. The increase in both t and w with increasing $P(WF_6)$ suggests that the growth is rate limited by a surface reaction in this range of total and partial pressures. However, we cannot distinguish between the roles of WF_6 adsorption which should give a linear $P(WF_6)$ dependence [33] and of HF desorption which should give a $P^{1/6}(WF_6)$ dependence [19, 33], since both graphs are linear to within experimental error. More experiments in a wider WF_6 pressure range are required to clarify this point.

The composition of the deposited lines has been measured by Auger electron spectroscopy (AES). Besides tungsten, some contaminants, such as oxygen, nitrogen and carbon are detected on the surface. Their presence is probably due to air exposure before analysis. This contamination can be completely removed by argon sputtering, leaving lines composed of pure tungsten. Note that no fluorine is observed at the surface, nor in the bulk, of these lines at the detection limit of AES (1 at.%).

Resistivity and adhesion are two important features for microelectronic circuit microsurgery. For the laser-deposited tungsten lines, resistivities range from 13 to 25 μΩ cm, which is two to four times the bulk resistivity of tungsten (5.6 μΩ cm). Tungsten is known to exhibit poor adhesion to SiO_2 [34] and little work has been

reported on the adhesion on to SiO_xN_y. We find that the adhesion of the laser-deposited lines is very dependent upon the deposition parameters. However, good adhesion (determined by resistance to the Scotch tape test) to the substrate is obtained for lines deposited under the conditions described above. This process thus seems to be well suited to microsurgery.

3.2. *Processing on GaAs*

Experiments have been performed to deposit tungsten on GaAs using WF_6–H_2 mixtures. To avoid any damage to the substrate, we used laser powers below the damage threshold power reported previously [23]. However, results are very different from those obtained with other substrates such as SiO_xN_y and are very difficult to reproduce. Success in obtaining deposits is found to vary even as different regions on the same sample are scanned [35]. In some cases, tungsten lines are even obtained without any reducing gas, with a WF_6 partial pressure of 10 Torr and writing speed of 25 μm s^{-1}. Figure 4 shows the deposit thickness of successful line formation as a function of the laser power for WF_6–H_2 gas mixtures and for WF_6 alone. The deposit thickness is usually less than 100 nm and decreases with increasing laser power, showing a competition between deposition and etching mechanisms. This leads to deposition in a very narrow process window, about 10 mW wide. The temperature rise corresponding to the lowest power yielding deposition is estimated to about 200 °C [36]. Deposition of tungsten without the use of a reducing gas such as H_2 suggests that GaAs plays a role in the deposition mechanism.

AES analysis shows that all deposits contain only about 30 at.% W [37]. Films also contain oxygen, probably because the sample was exposed to air before surface analysis. Substantial incorporation of arsenic is noted throughout the deposit for the depositions in which no reductant gas was used. This suggests that WF_6 reacts with the GaAs surface, producing arsenic products which could diffuse throughout the growing film. However, when H_2 is used, arsenic incorporation is observed only at the beginning of the deposit, suggesting that H_2 etches arsenic by forming volatile products.

In order to understand this process and the irreproducibility of the tungsten deposition on GaAs, we investigated the interaction of WF_6 with GaAs by XPS. GaAs samples were exposed to WF_6 at 10 Torr as in the conditions for laser direct writing, and were transferred in vacuum to a VG Escalab Mk II XPS spectrometer for analysis. We have found [38] that a primary reaction occurs between WF_6 and the surface oxides (especially As_2O_3). This highly localized surface reaction leads to a loss of arsenic (probably through AsF_3 and AsF_5 compounds) and to the incomplete dissociation of WF_6 into tungsten subfluorides and oxyfluorides. Furthermore, the presence of GaF_3, which is stable and non-volatile at room temperature [39] is detected on the surface of the samples.

While modelling these results and observations needs more investigation, we suggest that these reactions, particularly the formation of GaF_3, will affect the growth of the tungsten film in the LCVD process. Since WF_6 adsorbs on GaAs and is decomposed by laser heating of the substrate to form metallic tungsten, the formation of GaF_3 prior to laser processing might poison the initiation of a deposition process by forming a layer which is inert to WF_6. This layer may inhibit the dissociation of WF_6 into metallic tungsten even in the presence of the laser beam and of a reducing gas, by increasing the activation energy of the tungsten deposition. We were unable to measure this activation energy, owing to the lack of controllability of the process. However, it is interesting to note that the boiling point of GaF_3 is 950 °C, a temperature that is never reached by the substrate in any of the stages of the process. GaF_3 formation seems linked to the presence of As_2O_3 [38] and possibly of other surface oxides, *i.e.* to parameters which may readily vary from one experiment to another and possibly from one region to another on the same sample. These effects are still under investigation.

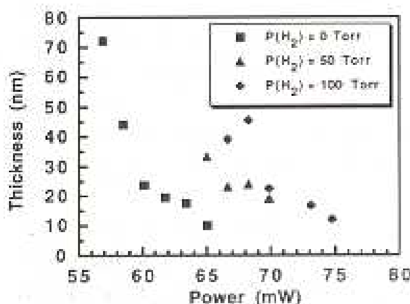

Fig. 4. Line thickness of tungsten deposited on GaAs as a function of laser power for various H_2 partial pressures ($P(WF_6)$ = 10 Torr; v_s = 25 μm s^{-1}; NA, 0.15).

4. Diode laser processing of tungsten on TiN

The use of diode lasers for material processing and device fabrication was first reported by Arjavalingam *et al.* [40] in 1988. They used a 200 mW $Ga_{1-x}Al_xAs$ diode laser array, emitting at 820 nm, to deposit gold from organometallic precursors. The choice of substrates is limited to materials which absorb strongly at the laser wavelength and have a low thermal conductivity. Since many of the materials used in microeletronics do not absorb this wavelength strongly [41], we have chosen TiN for its optical and thermal properties in

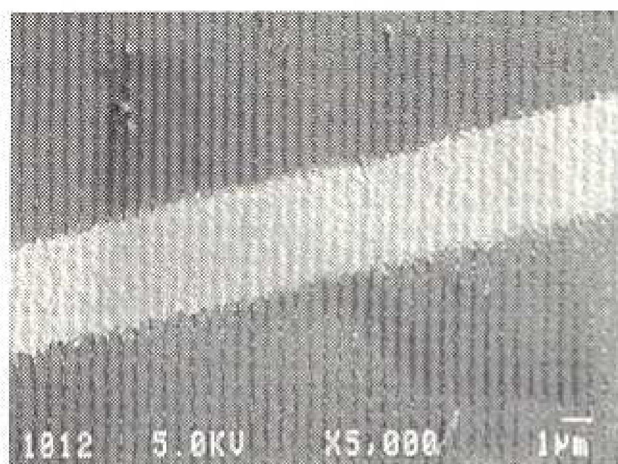

Fig. 5. Scanning electron micrograph of a diode-laser-deposited WSi_x line on TiN ($P(WF_6)$ = 1.0 Torr; $P(SiH_4)$ = 3.0 Torr; laser power, 115 mW; v_s = 5 µm s^{-1}; NA, 0.31).

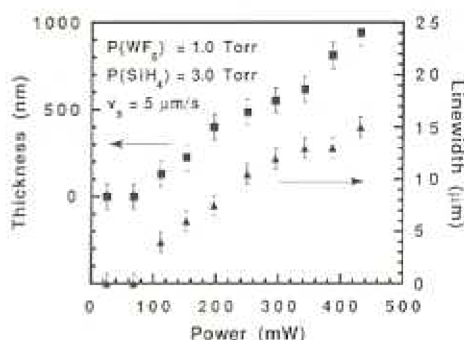

Fig. 6. Thickness and width of WSi_x lines deposited on TiN as a function of diode laser power at the substrate ($P(WF_6)$ = 1.0 Torr; $P(SiH_4)$ = 3.0 Torr; v_s = 5 µm s^{-1}; NA, 0.31).

order to obtain a temperature rise sufficient to induce the WF_6 reduction reaction. As the output characteristics (power and wavelength) of diode lasers are likely to improve in the next few years, it will become possible to extend this process to various types of substrate.

Even on an absorbing substrate such as TiN, the available diode laser power of 1 W is not sufficient to induce hydrogen reduction of WF_6, since that reaction requires a high temperature [20]. It has been reported that SiH_4 can be used to obtain a low temperature reduction of WF_6 [21]. Such a process seems appropriate for deposition with a diode laser. However, the initiation temperature of that reaction depends strongly upon the gas mixture. We present here the diode-laser-induced deposition of WSi_x on TiN from a mixture of WF_6 and SiH_4.

Since tungsten strongly absorbs the diode laser radiation [41], the temperature rise is critical only at the initiation of the reaction, and the reaction is not self-limited. The total pressure of WF_6 and SiH_4 is kept below 15 Torr to avoid uncontrolled reactions and explosive conditions. All experiments are performed in a static reactor with $[WF_6]/[SiH_4]$ ratios varying from 0.2 to 10. In most cases, the writing speed is 5 or 10 µm s^{-1}.

Figure 5 shows a scanning electron micrograph of a typical WSi_x line on TiN, written at 5 µm s^{-1}, using a laser power of 115 mW at the substrate and a gas mixture of WF_6 (1 Torr) and SiH_4 (3 Torr). The 4 µm width line which is deposited is uniform, and the line surface is smoother than that obtained with Ar^+-laser-induced deposition in a WF_6–H_2 atmosphere, discussed in Section 3.1. AES indicates that no fluorine is incorporated in the WSi_x film within the limit of detection [42]. Apart from some surface contamination, which we attribute to atmospheric exposure, no carbon, nitrogen or oxygen is detected in the bulk of the deposited metal. The [W]/[Si] ratio is uniform in the bulk, and estimated to be between 1.1 and 1.4.

Figure 6 shows the line thickness and width as functions of the laser power for lines produced under conditions such as those used for producing the line shown in Fig. 5. The thickness is measured with a stylus profilometer, and the width is evaluated from micrographs. The line width and thickness increase with increasing laser power. For a writing speed of 5 µm s^{-1}, a threshold for deposition at approximately 100 mW is observed. Lines produced at a power higher than 400 mW are irregular and do not adhere well to the TiN substrate. This is due to the high temperature rise of thick deposits, induced by the high absorption of tungsten at the laser wavelength. These temperature rises induce thermal stress, causing cracking of the TiN film.

5. Conclusion

We have investigated the development of laser direct writing of tungsten from WF_6 on SiO_xN_y, GaAs and TiN.

Ar^+ LCVD from WF_6 and H_2 produces tungsten lines with good adhesion on thick (0.6 µm) SiO_xN_y films. Lines of pure tungsten, having linewidths of 2.5–17 µm, line thicknesses of 0.1–2 µm and resistivities from two to four times the bulk resistivity of tungsten are deposited. These deposit characteristics are appropriate for circuit microsurgery.

The deposition by Ar^+ laser from WF_6 and H_2 on GaAs occurs in a very narrow range and can be achieved without using any reductant gas, suggesting that GaAs plays a role in the deposition. The reaction mechanisms seem very complex and more experiments are needed to clarify the role of the GaF_3 and the different oxides in this reaction. Only then can reliable and reproducible results for LCVD of tungsten from WF_6 on GaAs be obtained.

We have demonstrated the use of a diode laser array for laser direct writing of WSi_x on TiN from WF_6 and SiH_4. The low absorption by many electronic materials in the near-IR region has limited this process to specific absorbing substrates. The development of diode lasers with more power at shorter wavelengths will extend the applications of diode-laser-based direct writing systems to various electronic materials.

Acknowledgments

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