Laser direct writing of tungsten from WF₆

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Abstract

We present recent results on the development of laser direct writing of tungsten from WF₆ on silicon oxyxnitride (SiOₓNₓ), titanium nitride (TiN) and gallium arsenide (GaAs). Ar⁺ laser processing from WF₆ and H₂ on SiOₓNₓ 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 reproducible. Surface analysis suggests that a spontaneous reaction between WF₆ and GaAs, producing GaF₃, 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 WF₆ and SiH₄ on TiN yields WSiₓ (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 WF₆ as the precursor does not present this problem and usually leads to good quality films. Tungsten has been deposited from WF₆ using excimer [12–14], CO₂ [15, 16] and ion (Ar⁺ and Kr⁺) [1–4, 17–23] lasers. In most cases, the reducing agent is H₂ while, very recently, SiH₄ 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 SiO₂ [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 WF₆ onto several substrates of interest for silicon and GaAs microelectronics which have not previously been investigated: silicon oxyxnitride (SiOₓNₓ), TiN and GaAs.

Of the various types of laser used in the LCVD of tungsten from WF₆, 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 nitrides from a mixture of WF₆, SiH₄, H₂ 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 WF₆ and H₂ onto SiOₓNₓ 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 WF₆ with GaAs, producing GaF₃ which may poison the initiation of the deposition. Diode laser processing from WF₆ and SiH₄ on TiN yields WSiₓ lines, with x = 0.7–0.9, having widths as low as 4 μm.
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_{x}As diode laser array, emitting at λ = 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 x (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_{2}N_{x}) 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_{2} N_{x} 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_{3}PO_{4}:H_{2}O: H_{2}O (1:1:10) for 5 s, next rinsed in hot HCl–H_{2}O (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 $10^{-2}$ to $10^{-3}$ Torr. The cell was then heated to 89°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$_2$, N$_2$, 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$_2$, N$_2$, 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 $v_w$ 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$_2$.

Note that no deposit occurs below a threshold power and that the minimum linewidth in these conditions is 5 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$_2$), $v_w$ and $P$ are kept constant in a static reactor. The increase in both $w$ and $t$ with increasing $P$(WF$_6$) suggests that the growth is 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 $P^{1/2}$(WF$_6$) dependence [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$_2$, N$_2$. 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$_2$, N$_2$, 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$_2$O$_3$). 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$_2$O$_3$ [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.

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$_x$As 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 microelectronics do not absorb this wavelength strongly [41], we have chosen TiN for its optical and thermal properties in
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$_x$ 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$_4$ (2 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 adherence 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$_2$, N$_2$, GaAs and TiN.

Ar$^+$ LCVD from WF$_6$ and H$_2$ produces tungsten lines with good adhesion on thick (0.6 μm) SiO$_2$, N$_2$ 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, on TiN from WF₆ and SiH₄. 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.

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