Laser-Induced Deposition and Etching of Tungsten Microstructures

K. Piglmayer, H. Schieche
Angewandte Physik, Johannes-Kepler-Universität Linz,
A-4040 Linz, Austria

R. Chabicovsky
Institut für Allgemeine Elektrotechnik und Elektronik, TU Wien,
A-1040 Vienna, Austria

Micron-sized deposition and etching of W in $WF_6 + H_2$ atmosphere is investigated by local laser-induced heating of thin tungsten layers on quartz substrates. The process is strongly dependent on the partial pressures of the two gases. A process with high amount of hydrogen permits deposition of W, whereas etching of W occurs if the working gas does not contain hydrogen.

1. Introduction

Tungsten is an attractive material for use in microelectronics, because of its refractory nature, relatively low resistivity, high melting point, low thermal expansion coefficient, and high chemical inertness. Both blanket and selective deposition of W is applied in the VLSI technology [1], [2]. Micron sized structures of tungsten can be generated with focused ion beams [3]. But also lithographic patterning of W using RIE is widely implemented for submicron manufacturing [4], [5].

Laser chemical processing is a method for fast single-step modification and patterning of solid surfaces with dimensions down into the submicrometer range. Laser-induced chemical vapor deposition (LCVD) allows localized growth and direct writing of structures with specified materials [6]. The process can be employed for fast 3D processing of non-planar substrates and for fabrication of free standing 3D micron sized devices [7].

For tungsten deposition, WF_6 is a standard precursor. The frequently used Si reduction process allows selective deposition, whereas hydrogen reduction of WF_6 provides high deposition rates [1]. This latter thermal process shows a number of interesting phenomena which can be visualized on SiO_2 substrates covered with a thin W layer of well defined thickness.

2. Experimental

2.1. Production of Tungsten Films

Tungsten films have been fabricated by using the Perkin Elmer 4400 sputtering system at the *Institut für Allgemeine Elektrotechnik und Elektronik*, Technical University of Vienna. The most important technical details are as follows: 8” magnetron cathode; purity of the target material (tungsten) 99,97%; rf-sputtering with 13.57 Megahertz;

sputter power 800W; substrate palette rotation mode; substrate bias 20V; deposition without using a substrate heater; quartz substrates freely lying on a glass support; substrates ultrasonically cleaned with propanol and further cleaned in the sputtering chamber by sputter etching (300 W, 15 min) immediately prior to the deposition of a tungsten film; purity of the sputter gas (argon) 99.9999%; argon pressure 5×10^{-3} Torr (6.7×10^{-3} mbar), film thickness 850 Ångström, sputter time 16 minutes; waiting time prior to taking out the substrates of the vacuum chamber 30 minutes.

Film thickness measurements have been carried out with a Tencor Alpha Step 200 instrument. The film steps necessary for these measurements have been fabricated on test substrates by applying the well known photoresist float-off technique. These test samples are placed quite close to the quartz substrates during film deposition.

Mechanical stress in the film has been controlled by detecting the curvature of very thin glass plates (24 x 24 x 0.15 mm) which are also coated simultaneously with the quartz substrates. The sputter parameters have been carefully chosen in such a way that the internal mechanical stress is minimized (very small compressive stress, definitely no tensile stress).

2.2. Deposition/Etching Experiments

The experimental setup employed is similar to that described in [8], [9]. The high reactivity of WF_6 requires the reaction chamber and feed pipes to be fabricated out of stainless steel. Only a few Viton seals have been used. The system was flooded with argon and heated out to temperatures between 150°C and 400°C. The W-covered SiO_2 substrates were rinsed in aqueous KOH, acetone and methanol, and baked out before mounting.

The WF_6 gas employed (Fluka-Chemie) had a purity of 99.56% with tungsten oxyfluorides (< 0.4%), CF_4 (< 0.025%), HF (< 0.01%) and SF_6 (< 0.01%) as main contaminants. The flow rate (15 sccm) of gases was controlled by needle valves and flowmeters.

The Ar^+-laser beam was focused onto the substrate at perpendicular incidence ($\lambda \approx$ 515 nm, $2w_0$ (1/e) $\approx$ 2.1μm). Laser pulses with variable duration were generated by means of a Pockels cell.

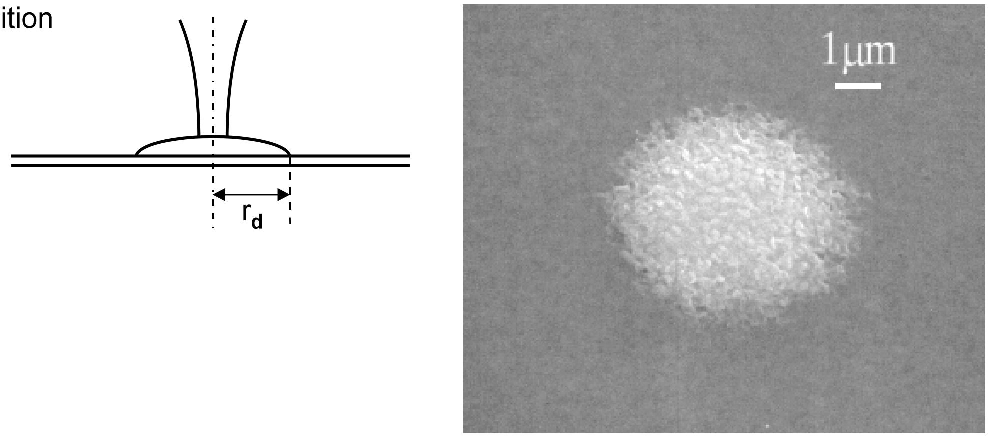
Patterning was performed by moving the substrate with respect to the laser beam. The whole process was observed via a TV camera in combination with a lens system. The geometry and morphology of patterns were investigated by a scanning electron microscope (SEM).

3. Results and discussion

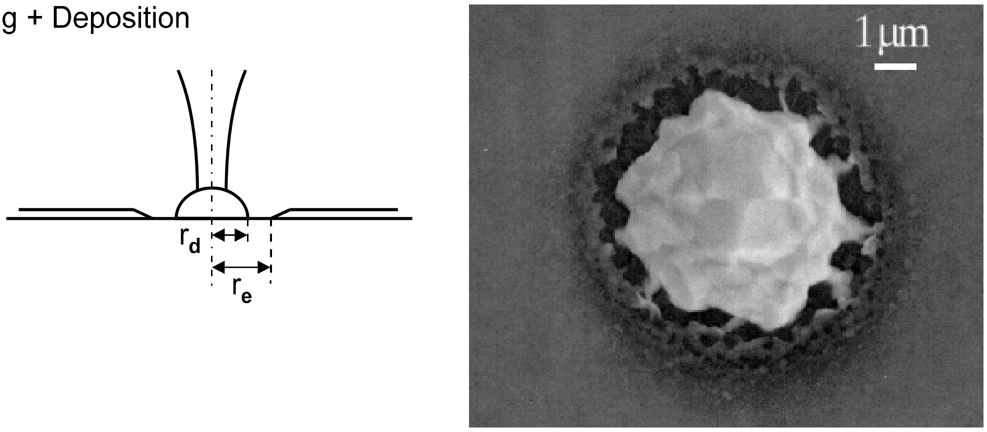
3.1. Single Dots

With both the substrate and the laser beam fixed, the deposition/etch pattern has circular symmetry. Figure 1 shows SEM pictures and corresponding sketches of patterns observed with various partial pressures of gases.

a. Deposition



b. Etching + Deposition



c. Etching

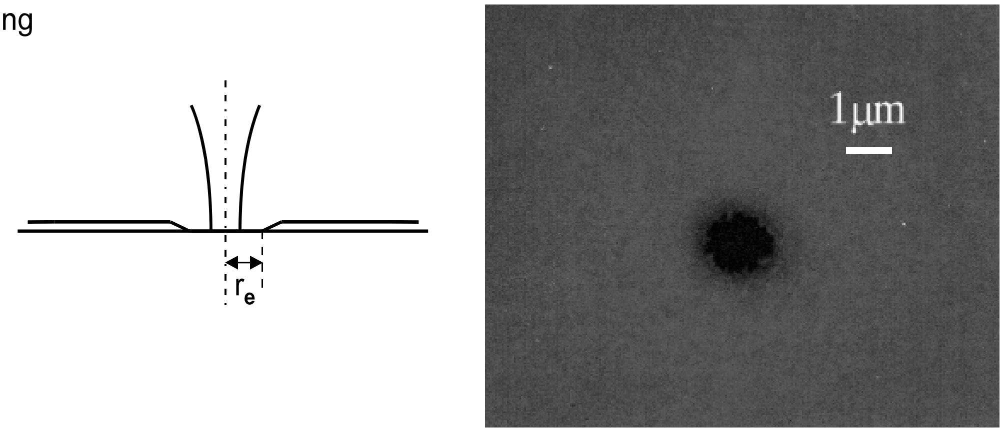


Fig. 1: Schematic illustrations and SEM pictures of the different types of processes occurring with different values of Γ_P. a) $p_{WF_6} = 1$ mbar, $\Gamma_P = 5$, incident laser power $P_{inc} = 160$ mW, b) $p_{WF_6} = 2$ mbar $\Gamma_P = 0.25$, $P_{inc} = 160$ mW, c) $p_{WF_6} =$ 2 mbar, $\Gamma_P = 0$, $P_{inc} = 96$ mW.

With pressure ratios $\Gamma_P \equiv p_{H_2}/p_{WF_6} \geq 1$ we observe deposition without any indication for etching (in standard CVD [1] pressure ratios $\Gamma_P >> 1$ are employed). Figure 1a shows W dots deposited with $p_{H_2} = 5$ mbar and $p_{WF_6} = 1$ mbar. Here the overall deposition reaction is

$$WF_6 + 3\,H_2 \rightarrow W(s) + 6\,HF. \qquad (1)$$

The morphology of deposits is similar to that described in [6].

The situation changes significantly with decreasing Γ_P. Figure 1b shows the pattern observed with p_{H_2} = 0.5 mbar and p_{WF_6} = 2 mbar. The deposit within the center is now surrounded by a circular ring of (outer) radius r_e . Within this ring, i.e. within the area $r_d \leq r \leq r_e$, the W film is etched. The process can be described by [8], [9], [10]

$$W(s) + 5\ WF_6 \rightleftarrows 6\ WF_5\ . \tag{2}$$

With decreasing Γ_P, the diameter of both the deposit and etched ring decreases. In the absence of hydrogen ($\Gamma_P = 0$), only etching is observed (Fig. 1c).

At the laser wavelength used both the deposition and the etching process are thermally activated, i.e. they obey to Arrhenius laws with certain activation energies ΔE_d and ΔE_e, respectively. Due to the nonlinearity of both the deposition and the etching process structures with lateral dimensions less than the focal width of the laser beam are possible. The nonlinear characteristics of the process provide also the possibility to etch through the W layer totally, i.e. with no metal remaining within the etch hole. This is possible because if $r_e < w_0$, enough laser radiation will be absorbed at the borders of the etch hole even when the hole is etched through, and thereby the temperature is kept high enough to maintain the etching process. It should be noted here that the etching process proceeds efficiently even at very moderate temperatures, i.e. at p_{WF_6} = 2 mbar and T ≈ 500 K the etch rate is ≈ 100 Å/s. At high process temperatures additional removal of the SiO_2 substrate is observed. Because high temperatures are localized to a narrow area around the laser-beam center, this possible “etching” effect is of small lateral size [10].

The overall process has been analyzed in detail by thermodynamic calculations and by modeling of etching/growth based on the accurate calculation of laser-induced temperature distributions [11].

3.2. Direct writing

Deposition of tungsten lines by direct writing has been widely investigated [6]. Nevertheless, the possibility of writing W lines on optically transparent SiO_2 substrates should be mentioned. Starting the deposition on an absorbing medium, when passing onto SiO_2, the thermally activated deposition process is maintained due to the fact that the laser radiation is partly absorbed by the already deposited stripe. Similar as in the case of etching, this absorbed power keeps the temperature high enough for further deposition to occur. But continuous and homogeneous patterns are only possible in narrow parameter regimes. Figure 2 shows SEM pictures of a stripe written on SiO_2.

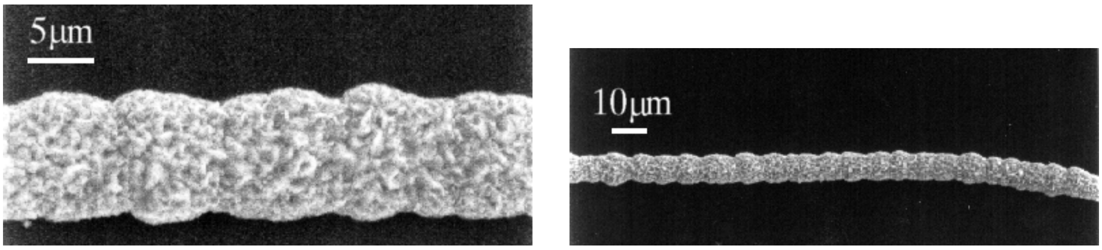


Fig. 2: SEM pictures with different magnifications showing a W-line “written” on SiO_2 (thermal induction by self-absorption of laser radiation), p_{WF_6} = 1 mbar, Γ_P = 2, P_{inc} =140 mW. Scanning velocity v_S = 10 μm/s.

With $\Gamma_P = 0$ the direct writing of etch patterns in the thin W-layer is possible. Figure 3 shows SEM pictures of lines etched at two different scanning velocities v_s.

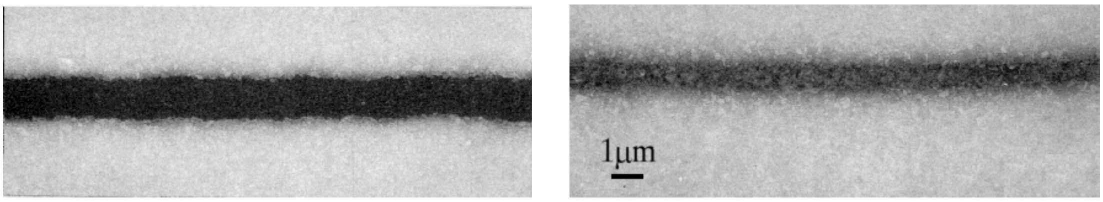


Fig. 3: SEM pictures showing etch lines directly “written” within the W-layer at different scanning velocities. $p_{WF_6} = 2$ mbar, $P_{inc} = 96$ mW.
Left: $v_S = 4.2$ µm/s, right: $v_S = 42$ µm/s.

With increasing scan speed the complete etching is possible due to an increase in processing temperature. The necessary increase in absorbed laser power occurs due to the flattening of the front groove angle of the etch line [12]. Total etching of the layer is possible below a parameter dependent value of v_S.

4. Conclusion

Laser-induced deposition/etching of W in $WF_6 + H_2$ atmosphere has been investigated. With pressure ratios $\Gamma_P = p_{H_2}/p_{WF_6} > 1$ we observe only deposition, while with $\Gamma_P \leq 1$ deposition *and* etching takes place simultaneously. With $\Gamma_P = 0$ the net reaction results in pure etching.

Concerning the conditions $\Gamma_P > 1$ and $\Gamma_P = 0$ an application as a single step writing/ erasing tool of W structures by adding/removing of H_2 in a defined passivated system is possible.

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